

OpenGRID

EXPLORING BEYOND BOUNDARIES

Compilation of

Open Access Publishing at BARC, Trombay
One DAE One Subscription (ODOS)



भाभा परमाणु अनुसंधान केंद्र
BHABHA ATOMIC RESEARCH CENTRE

WILEY
SPRINGER NATURE

JULY - DECEMBER 2025

CONTENTS

Preface	vii
---------	-----

WILEY

1	Biogenic Silver Nanoparticles Exhibit Antifungal and Antibiofilm Activity Against <i>Candida albicans</i> via Intracellular ROS Production	1
	Nidhi Chandrakar, Sudhir K. Shukla, Dugeshwar Karley, Namrata Upadhyay, Y. V. Nancharaiah	
2	Delineation of the reaction mechanism of Ti₂AlC MAX-phase formation during spark plasma sintering synthesis	3
	Mohammad Yunus, Bikas Maji	
3	Effect of low dose gamma radiation on inactivation of <i>Salmonella</i> and physical properties of fresh betel leaves	5
	Indu Pant, Vanshika Adiani, Shashidhar Ravindranath	
4	Estimation of Flexural Crack Width in Reinforced Concrete Beams Using International Codes: A Parametric Analysis	7
	Saha Dauji, Kapilesh Bhargava, Deeksha Gupta	
5	Heptapleurum assamicum (Araliaceae): A New Species From Assam, India	9
	Santanu Dey, Hussain A. Barbhuiya, Jayanta Das, Deepak Kumar Baruah	
6	High Valent Mercury Hydrides	11
	Thankan Jayasekharan	
7	Multi-Modal Luminescence from LaAlO₃:Eu³⁺ via Trap Modulation for High-Temperature Applications	13
	Abdulelah Alolayan, Nimai Pathak, Kawsar Ali, Yuanbing Mao	
8	Subgigawatt Level X-Band BWO Using Adiabatically Tapered SWS at Low Magnetic Field	15
	Chitaranjan Jadab, Romesh Chandra, Sandeep Singh, Amitava Roy	
9	Synthesis and Characterization of Gum Kondagogu Stabilized Zinc Oxide Nanoparticles and Its Application as an Antibacterial Agent Against Wastewaterborne Bacteria	17
	Aruna Jyothi Kora, Venkata Balarama Krishna Mullapudi	
10	Synthesis of BODIPY-Linked N-Heterocyclic Carbene Metal Complexes for Cancer Chemotheranostics and Catalysis Applications	19
	Shraddha SP Yadav, Ananda Guha Majumdar, Manish Ramesh Shingole, Seemita Banerjee, Mahesh Subramanian, Rohit Singh Chauhan, Soumyaditya Mula	
11	Unveiling Calcium-Decorated Psi-Graphene as a High-Capacity Hydrogen Storage Material: A First-Principles Investigation	21
	Sruthi Thulaseedharan Jayasree, Afsal S. Shajahan, Nandakumar Kalarikkal, Brahmananda Chakraborty	
12	Tannic Acid Intercalated Tb Doped Graphene Oxide Layer: A Multifunctional Hybrid Photothermal Structure for Solar Energy Driven Water Purification, Power Generation, and Disinfection	23
	Subhash Sarkar, Hirakendu Basu, Amarnath Marimuthu, Sudeshna Saha, Rishu Bhati, Pallavi Chandwadkar, Celin Acharya, Sangita D. Kumar, Chandra Nath Patra	
13	Effect of Halide Variations on Cation Dynamics in MAPbX₃ (X = Cl, Br, and I)	25
	Veerendra K. Sharma, Ashutosh Mohanty, Victoria García Sakai, Madhusudan Tyagi, D. D. Sarma	
14	Garcinia kusumae (Clusiaceae): A New Species From Assam, India	27
	Jatindra Sarma, Hussain A. Barbhuiya	

15	Efficient and Fast Microplastic Separation From Aqueous Media by Electron Beam Assisted Developed Superhydrophobic Jute Fabric	29
	Atanu Jha, Amol Thite, Subhendu Ray Chowdhury	
16	Development of Water-Dispersible CuS Nanoparticles for Chemo–Photothermal Therapy and Photoacoustic Application	31
	Sonali Gupta, Bijaideep Dutta, Subhadip Paul, Ratan K. Saha, Kanhu C. Barick, Puthusserickal A. Hassan	
17	Multifocal Medullary and Papillary Thyroid Carcinoma Occurring as a Collision Tumor: A Case Report	33
	Sayali Gadre, Raji T. Naidu, Prachi R. Gaddam, Neha Mittal, Susan Cherian	

SPRINGER NATURE

18(1)	A coincidence ion beam analysis methodology for high resolution depth profiling of nickel using a resonance in the $^{58}\text{Ni}(p, \gamma)^{59}\text{Cu}$ reaction	37
	A. A. Sukumar, D. V. Lakshmipathy, Y. Sunitha, Sk Jayabun, J. V. Ramana, G. L. N. Reddy	
19(2)	A comprehensive study on the impact of He ion irradiation on the microstructure and mechanical properties of a Ni-Cr-Mo alloy	39
	Sanjay Saini, Ranjini Menon, S. K. Sharma, P. Y. Nabhiraj, Suman Neogy, A. P. Srivastava	
20(3)	A persistent radon anomaly signal preceding the destructive 7.7 Mw earthquake in Myanmar on March 28, 2025	41
	B. K. Sahoo, B. K. Sapra, Arshad Khan, M. P. Ratheesh, D. H. Kumbhar, J. J. Gaware, S. D. Kanse, Sumitra Phanjoubam, D. K. Aswal	
21(4)	Adsorption Behaviour of Sarin on $\text{Zn}_{12}\text{O}_{12}$ and $\text{Cu}_{12}\text{O}_{12}$ Nanoclusters: A Theoretical Study Based on DFT Approach	43
	P. Sharma, C. Rajesh, C. Majumder	
22(5)	Agronomic improvement using gamma ray induced mutagenesis is associated with changes in phytochemical and phytohormonal profiles in functional rice variety ‘Gathuwan’	45
	Anjali Chauhan, Rahul Checker, Parmeshwar K. Sahu, Raviraj Singh Patel, Samrath Baghel, Deepak Sharma, Deepak Sharma, Bikram K. Das	
23(6)	Assessment of TFWT and OBT in terrestrial plants at Tarapur, a tropical NPP Site in India, and a comparative analysis with model-computed concentrations	47
	A. Baburajan, R. H. Gaikwad, V. K. Varakhedkar, I. V. Saradhi, A. Vinod Kumar	
24(7)	Calorimetric investigation of ternary oxides in the $\text{CuO-V}_2\text{O}_5$ system	49
	P. M. Aiswarya, S. Narang, Rimpi Dawar, P. D. Babu, R. Mishra	
25(8)	Cardio-renal protection and mechanisms of the antihypertensive activity of Alcalase-derived moth bean hydrolysate in DOCA-salt induced hypertensive Wistar rats	51
	Nancy Goyal, Jitesh Singh Rathee, Sachin N. Hajare, S. Gautam	
26(9)	Comparative study on sugars for high doses measurements using diffuse reflectance spectrometry	53
	S. H. Shinde, Sandip Mondal, Sneha Chandrasekhar, Probal Chaudhury	
27(10)	Comparison of electrochemical properties of bismuth oxide/sulfide core@shell and heterostructure composites as anode material for lithium-ion batteries	55
	Akhilesh C. Joshi, Dimple P. Dutta, B. Vishwanadh	
28(11)	Development of a High-Performance chemiresistive H_2S sensor based on sandwich type SnO_2: CuO film realized using hybrid PVD approach	57
	Damu V. Rupnar, Deepak Goyal, P. Sarawade, Niranjana S. Ramgir	

29(12)	Distribution and Leaching Behavior of Trace Elements and Radionuclide in Waste Rocks of a Uranium Mine: Implications for Environmental Risk Assessment and Mitigation	59
	Samim Molla, Aditi Chakrabarty Patra, Ranjit Kumar, V. S. Srivastava, S. K. Jha	
30(13)	Dosimetry studies on amino acids using diffuse reflectance measurements for high doses	61
	Sandip Mondal, S. H. Shinde, Sneha Chandrasekhar, Probal Chaudhury	
31(14)	Effect of borosilicate glass environment on creep behaviour of alloy 690 at temperatures over 800–1000 °C	63
	M. Karri, A. Verma, J. B. Singh, C. V. Singh	
32(15)	Effect of Ni addition on dehydrogenation behavior of MgH₂	65
	Bhaskar Paul, Pankaj Shrivastava, Shubham Kumar, Jugal Kishor, Sanjay Kumar, Sanjib Majumdar	
33(16)	Effect of Solutionization Temperature on the Interfacial Microstructure of a Hot Roll Bonded Alloy 690/Carbon Steel Clad Steel Plate	67
	Laxya Gupta, Nachiket Keskar, Bikas C. Maji	
34(17)	Effect of Trigger Material on the Uranium Metal Produced by Deterministic Triggering of Magnesiothermic Reduction of UF₄	69
	Pasupuleti Kalpana, Sonal Gupta, U. R. Thakkar, S. K. Satpati, Rishi Verma	
35(18)	Evaluation of gross α and gross β activities in air particulate matter at Trombay, Mumbai	71
	V. B. Yadav, V. M. Joshi, Vandana A. Pulhani, A. Vinod Kumar	
36(19)	Evaluation of vacuum distillation column performance using radiotracers	73
	Sunil Goswami, U. K. Sahoo, V. K. Sharma, Rajesh Kumar	
37(20)	Experimental and theoretical insight into the complexation of tetra secondary butyl diglycolamide (TSBDGA) with trivalent f cations into ionic liquid	75
	Adityamani Nagar, Anuj Shukla, A. Srivastava, Arijit Sengupta, Dipita Karmakar, Sk. Musharaf Ali, Willem Verboom, Prasanta K. Mohapatra	
38(21)	Exploring Anisotropy in Zr-2.5%Nb Pressure Tube Material through Hardness Measurements: Role of Microstructure and Hydrogen Concentration	77
	Arnomitra Chatterjee, R. N. Singh	
39(22)	Exploring Manual Laser Oscillation Welding of Stainless Steel in Different Joint Configurations	79
	Aniruddha Kumar	
40(23)	First evidence of coexistence of Pseudo Pelger Huet anomaly and balanced translocation in a two decades retrospectively exposed human subject	81
	Rajesh Kumar Chaurasia, Ranjana S. Pathak, Anjana Goel, Kapil B. Shirsath, Nagesh N. Bhat, Arshad Khan, Balvinder K. Sapra	
41(24)	Fission product mass distribution studies in ³⁵Cl + ¹⁷⁶Yb and ³⁵Cl + ¹⁶⁵Ho reactions	83
	S. Kumar, R. Tripathi, S. Patra, A. Mhatre, A. Kumar, K. Ramachandran, T. N. Nag, S. Santra	
42(25)	From minerals to the electrodes of lithium-ion battery: facile and precise determination of lithium by ⁷Li(p,α)⁴He nuclear reaction	85
	Yerroju Sunitha, D. V. Lakshminpathy, Sk Jayabun, G. L. N. Reddy	
43(26)	Hypoxia-drives reversible cell cycle arrest in lung cancer cells via modulation of cellular redox and gene expression	87
	Dharmendra Kumar Maurya, Varshita Mehta, Babita Singh	
44(27)	Identification of known and novel genetic variants in sensorineural hearing loss: insights from whole exome sequencing in Indian families	89
	Kurva Jagannath, Nalini Bhat, Anu Ghosh, Harshada Tawade, Susan Cherian, Suresh Shettigar	

45(28)	Improving power factor of multiwalled carbon nanotube films through dual doping and sequential energy filtering of charge carriers	91
	Suman K. Mishra, Meetu Bharti, Bhanu Partap Singh, S. Bhattacharya, S. Samanta, P. Jha, Vinod S. Rawat, Ajay Singh	
46(29)	Influence of phantom material on the depth-dose profile and radiation quality factor of 126 MeV antiprotons – a FLUKA Monte Carlo study	93
	Arghya Chattaraj, T. Palani Selvam	
47(30)	Influence of ultrasonic vibration at different tensile deformation stages on the ductile fracture morphology of aluminum alloy	95
	Arpan Das	
48(31)	Investigation of microstructural and magnetic property evolution in mechanically milled Co–Zr metallic ribbon	97
	Sanjay Saini, A. P. Srivastava, P. S. Ghosh, Archana Sagdeo, A. Ghosh, D. Arvindha Babu, S. V. Madge, S. Neogy	
49(32)	Is heptelidic (koningic) acid a microbial hormone that regulates secondary metabolism in the biocontrol fungus <i>Trichoderma virens</i>?	99
	Ravindra Bansal, Sunil Kumar Sethy, Vitthal T. Barvkar, Prasun Kumar Mukherjee, Suwendu Mondal	
50(33)	Leveraging the Aswal Model to Understand and Amplify the Impact of India’s National Education Policy	101
	Dinesh K. Aswal, Anirudh Chandra	
51(34)	Machine learning based predictive model to enhance human reliability analysis for risk assessment of nuclear reactors	103
	Vipul Garg, Gopika Vinod, Vivek Kant	
52(35)	Microscopic structure of lead-silicate glass and its correlation with thermal, mechanical, and radiation shielding properties	105
	Pooja Sahu, Musharaf Ali Sheikh	
53(36)	Minimally Invasive Management of a Cesarean Scar Pregnancy: A Case Report and Review	107
	Shruti Rane, Anurag Bhate, Fariza Shaikh	
54(37)	Monte Carlo calculation of correction factors for determining the operational quantity	109
	Vandana Shrivastava, T. Palani Selvam, S. M. Pradhan	
55(38)	Monte Carlo-based dosimetric comparison of indigenous and commercial ¹⁰⁶Ru/¹⁰⁶Rh eye plaques using a mathematical eye phantom	111
	Vandana Shrivastava, Arghya Chattaraj, T. Palani Selvam, M. S. Pathan, Rajesh Kumar, B. K. Sapra	
56(39)	Numerical hydrodynamic modeling of free surface flow by solving shallow water equations	113
	Manish Chopra, R. B. Oza	
57(40)	Oxidative transformation of Ti₃C₂T MXene on gamma radiation exposure in aqueous media	115
	Pragati Patil, Arijit Ghoshal, Nitin Gumber, Raj Kumar Mondal, Gotluru Kedarnath, Kumar Abhinav Dubey, Y. K. Bhardwaj	
58(41)	Phenotypic Characterization of Null Mutants of ΔcbpA and ΔcbpB in <i>S. enterica</i> Serovar Typhimurium	117
	Indu Pant, Shashidhar Ravindranath	
59(42)	Plant Gum Synthesized Phytogenic Silver and Palladium Nanoparticles Towards Decolourization of Rhodamine B and Methylene Blue Dyes	119
	Aruna Jyothi Kora	
60(43)	Plasma copolymerized oxazoline and fluoro monomer based amphiphilic coatings for antibacterial and antifouling applications	121
	Nilanjali Misra, Swarnima Rawat, Sweetie R. Kanatt, Shubhangi A. Shelkar, Anitta Thomas, Ankita Pathak, Sanjay Kumar, Manish Singh, Virendra Kumar	

61(44)	Rapid screening of mutations for second-line-drug-resistant genes in <i>Mycobacterium tuberculosis</i> culture isolates by in-house developed DNA bio-chip	123
	Bharti Jain, Savita Kulkarni, Nawab Singh Baghel	
62(45)	Realistic simulation of molecular emission spectra: an advancement in direct calibration-free isotopic analysis	125
	Anandhu Mohan, Anannya Banerjee, Rajesh V. Pai, Arnab Sarkar	
63(46)	Redox investigation of L-A9 peptide and evaluation of its binding with double stranded DNA	127
	Preeti Dwivedi, Sudipa Manna, Drishty Satpati, Amit Das, Suresh Shendage, Ashis Kumar Satpati	
64(47)	Residence time distribution studies in rotating packed bed (RPB) reactor for improving its hydrodynamics and design validation using radiotracer	129
	Sunil Goswami, Jayashree Biswal, J. S. Samantray, Vijay K. Sharma	
65(48)	Structural and functional insights into Ubl domain-mediated regulation of SARS-CoV-2 PLpro	131
	Rimanshee Arya, Janani Ganesh, Vishal Prashar, Mukesh Kumar	
66(49)	Structural and thermal stability studies on irradiated magnesium potassium phosphates for back end nuclear fuel cycle applications	133
	Rumu H. Banerjee, Naina Raje, Kulwant Singh, Pranesh Sengupta	
67(50)	Structure, thermal stability and thermodynamics investigations on Na_2MnF_5	135
	S. Narang, P. M. Aiswarya, Rimpi Dawar, Akanksha Samanta, R. Mishra	
68(51)	The effect of composition and electron beam irradiation on the free volume and crystallinity of linear low-density polyethylene (LLDPE)/ethylene-octene copolymer (EOC) blends: a positron annihilation lifetime spectroscopic study	137
	Manjeet Singh, Rohini Agarwal, Dhanadeep Dutta, Subhendu Ray Chowdhury	
69(52)	Thermal study of bombyx mori silk fibroin film obtained through degumming process for biomaterial application	139
	Sanasam Yaiphabi, Sanjenbam Kabita, Sorokhaibam Jibankumar Singh, Shamjetshabam Babeeta Chanu, Langlen Meinam, Thota Manoj Kumar, R. Mishra, Senjam Sunil Singh, Laishram Rupachandra Singh, Sanjenbam Kunjeshwori Devi, Raghumani Singh Ningthoujam	
70(53)	Twin formation through repeated dislocation impingement on phase boundary in Ni-based superalloys using atomistic simulations	141
	Sagar Chandra, Mahendra K. Samal, Vivek M. Chavan	
71(54)	Utility of low specific activity ^{90}Y produced in a medium flux research reactor in the preparation of radioactive patch for the treatment of skin ailments	143
	K. V. Vimalnath, A. Rajeswari, Sai Kishore, Nandini Pandit, Sudipta Chakraborty	
72(55)	Whole genome sequencing reveals transcriptional and translational elements potentially regulating biotic and abiotic stress responses in cowpea	145
	Dhanasekar Punniyamoorthy, Souframanien Jegadeesan	
	Open Access Journal	147
	BARC Divisions	149
	BARC Authors	150

मनोज सिंह
MANOJ SINGH



अध्यक्ष, वैज्ञानिक सूचना संसाधन प्रभाग
भाभा परमाणु अनुसंधान केंद्र
Head, Scientific Information Resource Division
Bhabha Atomic Research Centre

PREFACE

In May 2024, the Department of Atomic Energy (DAE) took a significant step towards strengthening the culture of Open Access (OA) publishing by entering into Transformative Agreements (Read and Publish) with M/s Springer Nature Group and M/s Wiley India Private Limited under the banner of One DAE One Subscription (ODOS). The initiative continued into 2025, further facilitating wider and more equitable dissemination of scientific research emanating from DAE institutions.

It gives me immense pleasure to present the fourth compilation of OpenGRID – Exploring Beyond Boundaries, covering the period July–December 2025. This edition brings together 72 Open Access articles published by researchers of BARC comprising 55 articles in Springer Nature journals and 17 in Wiley journals. Of these, 17 articles were published in fully OA journals, while the remaining articles appeared as Hybrid Open Access publications under this framework.

During this period, authors and co-authors from 45 Divisions/Sections of BARC contributed to these publications, with 12 Divisions/Sections publishing through both publishers. Such wide participation demonstrates the increasing acceptance of OA as an integral component of scholarly communication across diverse scientific and technical disciplines at BARC.

This compilation has been designed for the convenient to scientific knowledge. Hyperlinks and QR codes have been provided for direct access to the full text of all 72 OA articles. The publication also presents the list of journals, along with their Impact Factors, preferred by BARC authors for OA publishing under ODOS. In addition, the participating Groups, Divisions and Sections are listed to provide an institutional perspective of this endeavour. An alphabetical list of all 307 authors associated with these Open Access publications is also included.

I take this opportunity to congratulate and acknowledge my colleagues in SIRD who have contributed to this initiative by providing the necessary OA infrastructure, facilitating authors through the publishing process, coordinating with publishers, and compiling this edition of OpenGRID.

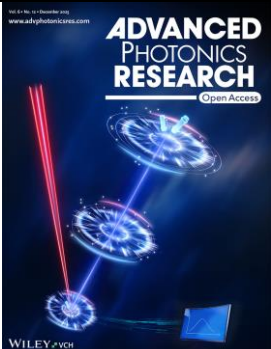
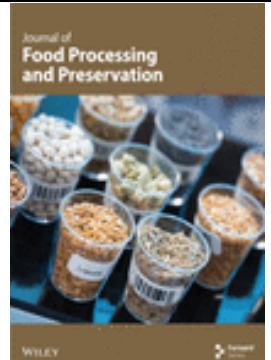
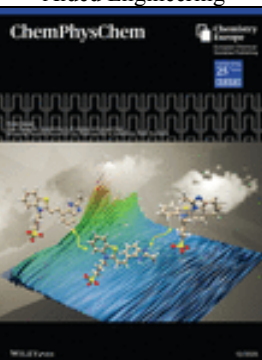
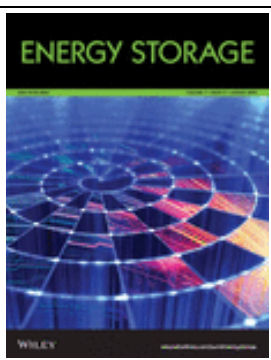
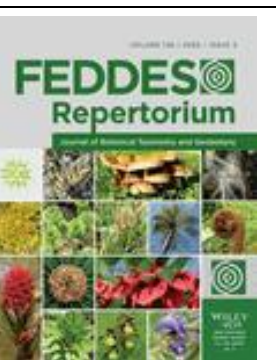
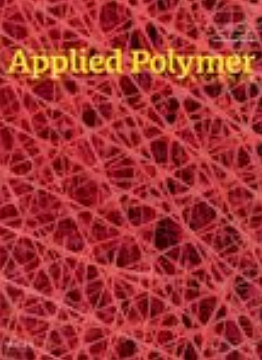
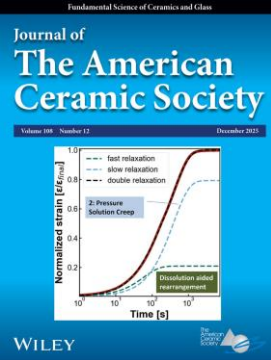
With this edition, we look forward with enthusiasm to 2026 for expanding the reach of BARC's scientific contributions, and continuing our endeavour to make research more accessible, discoverable and impactful.

Manoj Singh
(Manoj Singh)



भाभा परमाणु अनुसंधान केंद्र, ए-01, सेंट्रल कॉम्प्लेक्स, ट्रॉम्बे, मुंबई - 400 085, भारत
Bhabha Atomic Research Centre, A-01, Central Complex, Trombay, Mumbai 400 085, India
दूरभाष / Tel.: (91-22) 2559 0820 / 3685 / 2073 • फैक्स / Fax: (91-22) 2551 9613 / 2550 5151
आवास / Res.: +91-22-96195 16929 • ई-मेल / E-mail: smanoj@barc.gov.in, headsird@barc.gov.in

WILEY

			
Advanced Energy & Sustainability Research	Advanced Photonics Research	Advances in Civil Engineering	Case Reports in Pathology
			
International Journal of RF and Microwave Computer-Aided Engineering	Journal of Food Processing and Preservation	APMIS	Chemistry - An Asian Journal
			
ChemPhysChem	Energy Storage	Feddes Repertorium	International Journal of Quantum Chemistry
			
Journal of Applied Polymer Science	Journal of the American Ceramic Society	Small	



Journal of Pathology, Microbiology and Immunology

SPECIAL ISSUE BBC 2024: Recent Developments in Biofilms and Biofouling Control

PMI
PATHOLOGY
MICROBIOLOGY
IMMUNOLOGY

ORIGINAL ARTICLE **OPEN ACCESS**

Biogenic Silver Nanoparticles Exhibit Antifungal and Antibiofilm Activity Against *Candida albicans* via Intracellular ROS Production

Nidhi Chandrakar^{1,2} | Sudhir K. Shukla^{2,3} | Dugeshwar Karley¹ | Namrata Upadhyay⁴ | Y. V. Nancharaiiah^{2,3}

¹Amity Institute of Biotechnology, Amity University Chhattisgarh, Raipur, Raipur, Chhattisgarh, India | ²Biofouling and Biofilm Processes Section, Water and Steam Chemistry Division, Bhabha Atomic Research Centre, Kalpakkam, India | ³Homi Bhabha National Institute, Mumbai, India | ⁴Corrosion Science and Technology Division, Indira Gandhi Centre for Atomic Research, Kalpakkam, India

Correspondence: Sudhir K. Shukla (skshukla@igcar.gov.in) | Dugeshwar Karley (dkarley@rpr.amity.edu)

Received: 9 April 2025 | **Revised:** 27 June 2025 | **Accepted:** 4 August 2025

Funding: The authors received no specific funding for this work.

Keywords: antifungal resistance | biofilm inhibition | biogenic silver nanoparticles | *Candida albicans* | oxidative stress | reactive oxygen species | yeast-to-hyphal transition

ABSTRACT

The emergence of antifungal resistance in *Candida albicans* necessitates the development of novel therapeutic strategies. This study evaluates the antifungal and antibiofilm activity of biogenic silver nanoparticles (bAgNPs) synthesized using *Staphylococcus saprophyticus* bacterial supernatant. UV-Visible spectroscopy confirmed the formation of bAgNPs, with a distinct absorbance peak at 418 nm. Minimum inhibitory concentration (MIC) testing determined that 50 µg/mL effectively inhibited fungal growth. bAgNPs significantly reduced biofilm biomass, with an 80 µg/mL concentration resulting in over a 70% reduction, as demonstrated by crystal violet staining and fluorescence microscopy. Mechanistic studies revealed that bAgNPs induced reactive oxygen species (ROS) production, with fluorescence intensity peaking at 80 µg/mL, leading to oxidative stress-mediated cell death. The yeast-to-hyphal transition, a key virulence mechanism, was inhibited, impeding the fungal invasiveness. Furthermore, the disruption of cell membrane integrity was confirmed by SYTO 9/propidium iodide staining, where over 60% of cells displayed compromised membranes at MIC. MTT assay results demonstrated that bAgNPs impaired mitochondrial function by reducing metabolic activity by 75% at MIC. These findings suggest that bAgNPs target multiple critical pathways, including ROS-mediated oxidative damage, membrane disruption, and metabolic impairment, thereby exerting a potent antifungal effect; thus, they present a promising approach for treating biofilm-associated *C. albicans* infections.

1 | Introduction

Fungal infections, particularly those caused by *Candida albicans*, have emerged as a major global health concern, especially among immunocompromised individuals and those with chronic illnesses [1]. *C. albicans*, a dimorphic fungus, is capable of switching between yeast and hyphal forms, a critical factor in its ability to colonize and invade host tissues. This morphological transition, coupled with its ability to form biofilms, makes

C. albicans a formidable pathogen [2]. Biofilms are structured communities of microbial cells encased in a self-produced extracellular matrix, which confers resistance to conventional antifungal therapies [3]. The rise of drug-resistant fungal strains has further complicated the treatment of candidiasis, necessitating the development of novel therapeutic strategies [4].

Fungal biofilms are particularly problematic in clinical settings, as they are associated with persistent infections on medical

This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial](https://creativecommons.org/licenses/by-nc/4.0/) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

© 2025 The Author(s). *APMIS* published by John Wiley & Sons Ltd on behalf of APMIS - Journal of Pathology, Microbiology and Immunology.

devices such as catheters, prosthetics, and implants [5]. The extracellular matrix of biofilms acts as a barrier, limiting the penetration of antifungal agents and protecting the embedded cells from immune responses [6]. This resistance is exacerbated by the ability of biofilm-associated cells to upregulate efflux pumps and exhibit phenotypic plasticity, further reducing the efficacy of antifungal drugs [7]. As a result, there is an urgent need for alternative approaches to combat biofilm-associated infections.

In recent years, nanotechnology has emerged as a highly promising approach for developing novel antifungal agents. Among these, silver nanoparticles (AgNPs) have garnered significant attention due to their broad-spectrum antimicrobial activity, including potent antifungal properties [8–11]. Traditionally, AgNPs are synthesized using chemical methods, which often involve toxic reducing agents and generate harmful byproducts [12–14]. To address these environmental and health concerns, researchers have turned to “green” or biogenic synthesis methods, which utilize biological entities such as plants, fungi, bacteria, and algae [15]. Biogenic AgNPs offer several advantages, including eco-friendliness, cost-effectiveness, and scalability [16].

Recent studies have demonstrated the efficacy of biogenic AgNPs against fungal biofilms. For instance, AgNPs synthesized using plant extracts have shown significant antibiofilm activity against *C. albicans* by disrupting the extracellular matrix and inhibiting cell adhesion [17]. Similarly, bacterial-mediated synthesis of AgNPs has been reported to enhance their stability and antimicrobial properties [18, 19]. These biogenic AgNPs have been shown to exert their antifungal effects through multiple mechanisms, including the generation of reactive oxygen species (ROS), disruption of cell membrane integrity, and inhibition of biofilm formation [20–22]. The ability of biogenic AgNPs to target multiple pathways makes them a promising candidate for combating drug-resistant fungal infections. While this study provides foundations for the prospective use of bAgNPs to treat *Candida albicans* infections, further research must focus on determining their safety and efficacy in vitro and in animal models. Successful pre-clinical results would pave the path for future clinical trials to determine their medicinal potential.

This study focuses on the biogenic synthesis of silver nanoparticles using bacterial supernatant and evaluates its antifungal activity against *C. albicans*. We investigate the antifungal, antibiofilm, and mechanistic effects of these nanoparticles, with a particular emphasis on their ability to inhibit biofilm formation, disrupt cell membrane integrity, and induce oxidative stress. Our findings contribute to the growing body of research on biogenic AgNPs and their potential applications in antifungal therapy.

2 | Materials and Methods

2.1 | Cultivation and Growth of Microorganism

Candida albicans ATCC 10231 (Microbiologics, USA) was used as the reference strain. Strains were grown on potato dextrose agar (PDA) plates (HiMedia, India) at 37°C and subcultured at

regular intervals. A single colony was inoculated into potato dextrose broth (PDB) and incubated at 37°C for 12h, stirring at 120rpm. Commercially available Yeast Extract-Peptone-Dextrose (YPD) media (HiMedia, India) was prepared according to the manufacturer's instructions, filter-sterilized, and kept at 4°C. Overnight cultures of *C. albicans* grown in PDB were centrifuged and resuspended in YPD at the stipulated cell density for growth and biofilm experiments.

2.2 | Nanoparticle Synthesis and Characterization

The biogenic production of silver nanoparticles (bAgNPs) was done using *Staphylococcus saprophyticus* bacterial supernatant, which was chosen for its ability to produce stabilizing extracellular polymeric substances (EPS) as a reducing and stabilizing agent [23, 24]. To produce cell-free culture supernatant, overnight-grown *Staphylococcus saprophyticus* was heat-treated at 60°C for 30min before filtration through a 0.22µm syringe filter. The heat treatment ensured protein denaturation and eliminated potential residual metabolic activity, thus improving the safety and consistency of the supernatant utilized for nanoparticle formation. The use of cell-free supernatant reduces pathogenicity risks, making this a safe method of nanoparticle production [25]. First, a 1mM silver nitrate (AgNO₃) solution was prepared and mixed with the cell-free bacterial supernatant of *S. saprophyticus* in a 1:1. To obtain cell-free culture supernatant, overnight-grown *S. saprophyticus* was filtered with 0.22µm syringe filters. The reaction mixture was incubated at 60°C at pH10.0 for 5 days in dark conditions in a hot air oven. The synthesis of silver nanoparticles was indicated by a color change in the suspension from light yellow to dark brown.

The formation of bAgNPs was confirmed using UV-Visible spectroscopy in the wavelength range of 300–700nm. The morphology and size of the synthesized bAgNPs were observed using Scanning Electron Microscopy (Zeiss Sigma 300 SEM). A drop of the bAgNP solution (in 10% DMSO) was placed on a carbon-coated copper grid and allowed to dry at room temperature. The grid was then examined under the SEM at an accelerating voltage of 20kV.

The hydrodynamic size and polydispersity index (PDI) of the silver nanoparticles were determined using dynamic light scattering (DLS). The nanoparticles were dispersed in dimethyl sulfoxide (DMSO) and diluted in water (dilution factor, DF=80) prior to analysis. Measurements were performed in triplicate, and the results are reported as the Z-average size standard deviation.

2.3 | Planktonic Growth Kinetics Studies

Candida albicans growth kinetics were examined using a modified methodology [26]. An overnight *C. albicans* culture was adjusted to an optical density (OD) of 0.05 at 600nm in fresh YPD broth. The broth microdilution method was used to assess the minimum inhibitory concentration (MIC) of biogenic silver nanoparticles (bAgNPs) against *C. albicans* [27]. This assay was carried out in 96-well plates. Overnight cultures of *C. albicans* were adjusted to a specified optical density and then treated





Received: 2 May 2025 | Revised: 20 June 2025 | Accepted: 2 July 2025

DOI: 10.1111/jace.70130

Journal
of The American Ceramic Society

RESEARCH ARTICLE

Delineation of the reaction mechanism of Ti_2AlC MAX-phase formation during spark plasma sintering synthesis

Mohammad Yunus | Bikas C. Maji

Mechanical Metallurgy Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India

Correspondence

Bikas C. Maji, Mechanical Metallurgy Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India.
Email: bikchan@barc.gov.in

Funding information

BARC, Grant/Award Number: RBA4012

Abstract

Despite several attempts to synthesize Ti_2AlC MAX-phase using different processes and input materials, a comprehensive understanding of its formation mechanism is still lacking. This study reports, for the first time, a novel reaction mechanism of Ti_2AlC MAX-phase formation, based on extensive microstructural characterizations and density functional theory (DFT)-based ab initio calculations. A systematic investigation was carried out up to 1400°C temperature to understand the phase transformation behavior in stoichiometric $2\text{Ti}:\text{Al}:\text{C}$ elemental powder mixture during spark plasma synthesis of Ti_2AlC MAX-phase. An integrated approach was adopted to establish correlations between results obtained through differential scanning calorimetry, x-ray diffraction, scanning electron microscopy–energy-dispersive spectroscopy–electron backscattered diffraction characterizations, and DFT calculations. Microstructural examination revealed that the formation of Ti_2AlC MAX-phase was preceded by successive transformation of Ti powder particles via a series of transient Ti–Al intermetallic formation between 660 and 1200°C , until the Ti particles get transformed into a core–shell structure of Ti_2Al surrounded by TiAl intermetallic. The formation of Ti_2AlC MAX-phase was observed to occur via two different reactions. Initially, the peripheral TiAl intermetallic reacts with TiC to form Ti_2AlC MAX-phase in the temperature range of 1000 – 1200°C . At a later stage, the inner Ti_2Al phase transforms to Ti_2AlC MAX-phase through inward carbon diffusion till 1350°C .

KEYWORDS

density functional theory, differential scanning calorimetry, reaction mechanism, spark plasma sintering, Ti_2AlC MAX-phase

This is an open access article under the terms of the [Creative Commons Attribution License](https://creativecommons.org/licenses/by/4.0/), which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2025 The Author(s). *Journal of the American Ceramic Society* published by Wiley Periodicals LLC on behalf of American Ceramic Society.

1 | INTRODUCTION

MAX-phases represent a well-known family of layered compounds usually characterized by their distinct compositions with a general formula $M_{n+1}AX_n$, where M represents an early transition metal, A denotes an A-group element primarily from the group 13 or 14 of the periodic table, and X can be either carbon or nitrogen.¹ Although the discovery of MAX-phase was first reported in 1960s, over the years, more than 300 MAX phases have been discovered. A recent review by Dahlgqvist et al.² has summarized the drastic progress made in the field of MAX-phase research and showed that the number of MAX-phases discovered in the last 6 years has doubled. These nano-layered MAX-phase compounds usually possess hexagonal crystal structure with $P6_3/mmc$ (194) space group.^{1–4} Remarkably, MAX-phases exhibit a blend of properties from ceramic as well as metallic materials, encompassing from high-temperature stability, resistance to oxidation, lightweight, irradiation resilience, high hardness, and low thermal expansion coefficient along with commendable thermal and electrical conductivities, thermal shock resistance, and excellent machinability.^{1–16}

Within the diverse MAX-phase family, aluminum (Al)-containing MAX-phases, such as Ti₂AlC, Ti₃AlC₂, and Cr₂AlC, demonstrate exceptional high-temperature oxidation resistance,^{17,18} owing to their capability to form a thin protective adherent dense layer of Al₂O₃ especially beyond 1000°C temperature, coupled with self-healing capability.^{14,15,18–20} These inherent properties position Al-containing MAX-phases as highly desirable materials for numerous engineering applications such as coating for Zr-based accident-tolerant fuel clad,^{21,22} bond coat materials for thermal barrier coatings,^{23,24} thermal shock-resistant heating elements,²⁵ lightweight armor materials,^{26,27} in-core nuclear components^{28,29} and other functional applications such as electrical contacts and nano-wires.^{30–34} Among Al-containing MAX-phases, the Ti-based Ti₂AlC MAX-phase has been observed to possess superior oxidation resistance as compared to higher order Ti₃AlC₂ MAX-phase, essentially due to the availability of higher Al concentration.¹⁸

Worldwide numerous efforts on the synthesis of high-purity Ti₂AlC MAX-phase, employing diverse input materials and processing methods, have been comprehensively summarized recently by Badie et al.³⁵ These authors have revealed that the purity of the Ti₂AlC MAX-phase is predominantly constrained by the presence of secondary phases such as TiAl, TiC, and Ti₃AlC₂ in the final product.^{35,36–39} The commercial-grade Ti₂AlC MAX-phase powders exhibit a maximum purity of 67–85 vol.% only, depending on the proprietary synthesis route employed.^{40–42} The remaining secondary phases mostly

comprise TiC, TiAl, and Ti₃AlC₂ phases. Hence, it is quite evident that optimized processing parameters for synthesizing high-purity Ti₂AlC MAX-phase are still lacking in published literature. Therefore, understanding the factors that affect the purity of MAX-phase in bulk quantities is absolutely necessary.

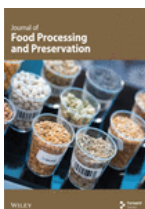
Among various techniques so far employed to synthesize MAX-phase, spark plasma sintering (SPS) stands out to be the most useful technique.⁴³ This technique offers several advantages over others, due to its unique ability to rapidly heat input materials (sometimes up to 1000°C/min) to a desired sintering temperature under pressure, hold it for a specific time period, and follow it with subsequent rapid cooling (>150°C/min). The fast cooling in SPS is especially useful in freezing the microstructure at any instance while heating and enables one to study the microstructural evolution through various characterization tools. Therefore, SPS can provide enough insight into the formation mechanism while synthesizing various MAX-phases from different starting materials and can be utilized effectively for optimization of processing parameters.

In our earlier studies, we have comprehensively studied the microstructural evolution during Ti₃AlC₂ MAX-phase formation using 3Ti:Al:2C elemental powder mixture through SPS synthesis route and were able to delineate the reaction mechanism governing the Ti₃AlC₂ MAX-phase formation.^{44,45} Our study revealed the formation of Ti₃AlC transient carbide at a temperature of 1200°C and above, principally due to the presence of Ti:Al in 3:1 ratio in the starting powder mixture that led to Ti₃Al formation, which further transformed to Ti₃AlC due to carbon diffusion. This transient Ti₃AlC phase starts decomposing into Ti₂AlC MAX-phase and TiC mixture beyond 1300°C temperature and finally resulted in the formation of Ti₃AlC₂ MAX-phase through a recombination reaction. In this study, our objective was to understand the mechanism of Ti₂AlC MAX-phase formation from elemental 2Ti:Al:1C powder mixture through SPS synthesis route. As the starting material (2Ti:Al:C powder mixture) used for this work contains Ti:Al in 2:1 ratio, it will be interesting to explore whether this will lead to the formation of transient Ti₃AlC carbide or not and its impact on the phase transformation and microstructural evolution.

An integrated approach was adopted to establish correlations among results obtained from differential scanning calorimetry (DSC), x-ray diffraction (XRD), scanning electron microscopy–energy-dispersive spectroscopy (SEM–EDS), and electron backscattered diffraction (EBSD) characterizations and density functional theory (DFT)-based ab initio calculations to delineate the reaction mechanism of Ti₂AlC MAX-phase formation. The comprehensive microstructural investigation has also resulted in the



Scan the QR Code or Click for full text



Wiley
Journal of Food Processing and Preservation
Volume 2025, Article ID 3133331, 9 pages
<https://doi.org/10.1155/jfpp/3133331>

3

WILEY

Research Article

Effect of Low-Dose Gamma Radiation on Inactivation of *Salmonella* and Physical Properties of Fresh Betel Leaves

Indu Pant,¹ Vanshika Adiani,¹ and Shashidhar Ravindranath²

¹Food Technology Division, Bhabha Atomic Research Centre, Mumbai, India

²Life Sciences, Homi Bhabha National Institute (DAE-Deemed University), Mumbai, India

Correspondence should be addressed to Shashidhar Ravindranath; shashi@barc.gov.in

Received 25 February 2025; Revised 20 July 2025; Accepted 25 July 2025

Academic Editor: Efstathios Giaouris

Copyright © 2025 Indu Pant et al. Journal of Food Processing and Preservation published by John Wiley & Sons Ltd. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Betel leaves (*Piper betle* L.), integral to Indian culture and traditional medicine, are prone to microbial contamination, particularly by *Salmonella* Typhimurium. About 10%–20% of the world's population—roughly 600 million people—regularly chew betel quid wrapped in betel leaf, making it one of the most widely used psychoactive substances globally. *Salmonella* has been detected in as many as 77% of betel leaf samples, and they can also internalize in the tissue, making standard surface washing often insufficient to eliminate contamination. Therefore, this study investigated the efficacy of gamma irradiation to enhance the microbial safety of betel leaves. Initial microbial assessments revealed bacterial counts between 2 and 3 log CFU/g and yeast and mold counts around 1.8 log CFU/g. The D_{10} value, indicating the radiation dose required for a 90% reduction of *S. Typhimurium*, was determined to be 240 Gy 0.015 Gy on betel leaves. An optimal irradiation dose of 1 kGy effectively reduced *Salmonella* by 3 log CFU/g, aligning with typical surface contamination levels. After irradiation, the betel leaves were stored at 6°C for 8 days in order to minimize moisture loss and extend shelf life. Texture analysis indicated a significant decrease of 22%–40%, while color parameters (L^* , a^* , b^* , chroma C^* , and hue angle h) showed no significant alterations. The volatile compound profiles, assessed via gas chromatography–mass spectrometry (GC-MS) revealed that the storage period has a significant influence on the volatile profile of the betel leaves. Sensory evaluations on Day 0 demonstrated negligible differences between nonirradiated and 1 kGy-treated samples, with scores ranging from 7.0 to 6.5 and 7.0 to 6.6, respectively. After 8 days, irradiated samples exhibited a slight decline in sensory scores (6.66–5.85) but remained within acceptable limits of the hedonic scale. Notably, antioxidant activity increased 2.5-fold during storage. These findings suggest that gamma irradiation at 1 kGy is effective in reducing microbial load without compromising their sensory and physicochemical qualities.

Keywords: betel leaf; gamma radiation technology; GC-MS; irradiation; *Salmonella*; texture

1. Introduction

Betel leaves are known as paan leaves in Hindi. These are heart-shaped leaves and belong to the Piperaceae family. These are cultivated in the hotter and damper regions in India [1]. It is also grown in Malaysia, Bangladesh, Indonesia, and East Africa [2]. The shelf life of betel leaf is 3–5 days [3]. India is home to 40 different varieties of betel vine, whereas in total 100 varieties of betel vine exist in the world [3]. It serves as traditional ready-to-eat food for Asians. Its

role as a curative agent of various ailments is described in Indian Ayurveda since ancient times [4].

The betel leaf industry holds significant economic and social importance in India. It is estimated that the sector contributes approximately ₹900–₹1000 crore annually to the national economy. Moreover, the industry provides direct or indirect employment to around 20 million people across various activities, including cultivation, processing, transportation, and marketing [3]. The export of betel leaves to countries like the United Kingdom further adds benefits

to the Indian economy as these are consumed by Asians [5]. The Asian population settled in foreign countries likes to have betel leaves along with filling as a breath freshener.

In the past, there have been multiple reports on the contamination of betel leaves with *Salmonella* spp. The presence of foodborne pathogens like *Salmonella* has been reported previously in India and Bangladesh [6–9]. Furthermore, it has been noted that several people who consumed *Salmonella*-contaminated betel leaves suffered from typhoid fever in India as well as in Cambodia [9, 10]. The association of multidrug-resistant *Salmonella* on betel leaves further adds to the problem.

After this, exportation of betel leaves was reduced to EU. In India, there have been reports of betel leaves acquiring *Salmonella* spp. from the water, which is used to soak betel leaves. Good agricultural practices and effective postharvest processing and packing are essential to ensure safety. The quality attributes such as texture and color are affected by cold and heat treatment. The use of chemical fumigants is also not advisable, as chemicals like methyl bromide and ethylene dibromide lead to residual toxic residues in the food, causing health issues in humans [11].

One of the best food preservation techniques for leafy vegetables is gamma ray treatment. In earlier studies, gamma ray has been shown to eliminate food-borne pathogens from various fruits and vegetables.

Therefore, in the current study, our aim is to use gamma radiation for the elimination of *Salmonella* from betel leaves so they can be made safe to be used as ready-to-eat product. To the best of our knowledge, this is the first report to use gamma radiation to enhance the microbiological safety of betel leaves.

2. Materials and Methods

2.1. Sample Preparation. Betel leaves were purchased from the local market in Vashi, Mumbai. Bangla betel leaves were chosen for our experiments. These fresh leaves were washed in water and then air dried and packed into low-density polyethylene (LDPE) bags for further experiments.

2.2. Microbiological Media. Media used were from Hi-Media Laboratories Pvt. Ltd., Mumbai, India.

2.3. Bacterial Strain. The *Salmonella* Typhimurium LT2 (MTCC 98), the representative of *Salmonella* species, was obtained from MTCC (Chandigarh, India). The culture was maintained in the glycerol stock at -80°C .

2.4. Assessment of the Bioburden on Betel Leaves. The bioburden on the betel leaves was evaluated as described. The betel leaves (30 g) were aseptically shredded and immersed in 100 mL of sterile 0.85% saline solution. This mixture was agitated at 37°C for 10 min to facilitate the release of surface-associated microorganisms into the solution. Following agitation, 100 μL of the resulting suspension was subjected to serial dilution using 0.85% saline to prepare samples for microbial enumeration.

For bacterial count estimation, plating was done on plate count agar. The plates were incubated overnight at 37°C for bacterial growth.

The mold count estimation was done by plating on potato dextrose agar. The plates for mold growth were incubated at 28°C for 48 h.

2.4.1. Gamma Radiation. The irradiation of betel leaves and *Salmonella* Typhimurium was carried out using a Gamma Chamber 5000 (Board of Radioisotope and Technology, Mumbai, India) at a dose rate of 0.083 kGy/min. This dose rate was determined using a Fricke reference standard dosimeter as per the ASTM Standard E1026 (Standard Practice for Using the Fricke Reference Standard Dosimetry System, 2014) [12]. The GC-5000 is a Category I type of irradiation facility. The irradiation chamber is cylindrical with an approximate volume of 4 L. Dose calibration was carried out at the center of the irradiation chamber by placing a Fricke dosimeter and the dose rate of 0.083 kGy/min was determined at the body center. All the experimental samples were irradiated at identical positions (body center) to ensure precise exposure. Based on the measured dose rate, the experimental sample was exposed to deliver the desired radiation doses. In case of the samples exposed to deliver more than 400 Gy, ceric cerous sulfate (3 mM) dosimeter (dose range: 500–5000 Gy) was also used to measure the real dose received by the samples.

2.4.2. Determination of the D_{10} Value for *Salmonella* Typhimurium. *Salmonella* Typhimurium was cultured overnight in Luria Broth at 37°C with agitation at 150 rpm. The resulting culture, with a concentration of approximately 10^9 CFU/mL, was diluted to 10^7 CFU/mL using a 0.85% saline solution. Six aliquots of this diluted suspension were prepared and then subjected to gamma irradiation at doses of 100, 150, 200, 250, and 300 Gy using a Gamma Chamber 5000, with samples kept on ice during exposure. Each irradiation condition was tested in triplicate to ensure reproducibility. A similar experiment was repeated to evaluate the D_{10} value for *S. Typhimurium* on betel leaves. The radiation doses used to determine the D_{10} value fall within the range of the Fricke Reference Standard Dosimetry System [12]. Since the D_{10} value is crucial for optimizing the radiation dose in food irradiation, it is essential to ensure the accuracy of the delivered dose. To achieve this, vials containing *Salmonella* Typhimurium and a Fricke dosimeter were irradiated together in triplicate at the body center of the irradiation chamber to measure the actual dose received by the samples while minimizing uncertainty.

Postirradiation, surviving bacteria were enumerated using the spread plate method. Plates were incubated at 37°C for 24 h, after which colony-forming units (CFU) were counted. The CFU/milliliter was calculated using the formula: $\text{CFU/mL} = (\text{Number of colonies} \times \text{Dilution factor}) / \text{Volume of the dilution plated}$.

To determine the D_{10} value, a survival curve was plotted between the logarithm of CFU/ milliliter and the corresponding radiation doses. Linear regression analysis was performed using Microsoft Excel 2007 to calculate the slope



Scan the QR Code or Click for full text



Wiley
Advances in Civil Engineering
Volume 2025, Article ID 9961763, 25 pages
<https://doi.org/10.1155/adce/9961763>

4

WILEY

Research Article

Estimation of Flexural Crack Width in Reinforced Concrete Beams Using International Codes: A Parametric Analysis

Saha Dauji ^{1,2}, Kapilesh Bhargava ^{2,3} and Deeksha Gupta ⁴

¹Civil Design Division, Nuclear Recycle Board, Bhabha Atomic Research Centre, Mumbai 400 094, Maharashtra, India

²Department of Engineering Sciences, Homi Bhabha National Institute, Mumbai 400 094, Maharashtra, India

³Engineering Services Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, Maharashtra, India

⁴Human Resource Development Division, Bhabha Atomic Research Centre, Mumbai 400 094, Maharashtra, India

Correspondence should be addressed to Kapilesh Bhargava; kapil_66@barc.gov.in; kapilesh_66@yahoo.co.uk

Received 28 October 2024; Accepted 16 May 2025

Academic Editor: Fabrizio Scozzese

Copyright © 2025 Saha Dauji et al. Advances in Civil Engineering published by John Wiley & Sons Ltd. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Crack width is an important parameter for concrete design, particularly from serviceability and durability considerations. This study focused on a critical comparison of the 12 formulations for estimation of maximum flexural crack, available in 13 international codes from 10 countries/geographic regions. Four common factors are: tensile stress in reinforcement, clear cover, spacing, and diameter of reinforcement; whereas the other factors were employed selectively. Using an extensive synthetic database representing a 10-dimensional hyperspace of possible beam sections, crack widths were estimated and were subsequently analyzed to evaluate the contributions from the major factors. Up to M50, higher grade of concrete caused higher stresses and resulted in larger crack widths; this reduced thereafter, possibly due to the enhanced tensile capacity of concrete. The descriptive crack width statistics (CWS) increased monotonically for all the international codes with the increase in: cover to reinforcement; stress in the tensile steel; spacing between reinforcing bars—indicating these as very important factors. For higher diameter of reinforcement up to 28 mm diameter, CWS were higher; possibly due to the higher stress contribution from larger diameter bars. Beyond 28 mm and up to 40 mm, the higher area of reinforcement might have resulted in lower steel stress, thereby indirectly lowering CWS. The insights obtained from this critical comparative study would be invaluable in design and control of crack width flexural members through reinforcement detailing and other methods.

Keywords: crack control; crack width; flexural member; international codes; reinforced concrete

1. Introduction

Concrete is one of the most widely adopted materials of construction for infrastructure across the world [1–3]. The present design methodology of many countries involve limit state philosophy [4]. The broad categories of the limit state design may include the limit states of: strength, serviceability, durability, and stability. Concrete structures may have constraints on the allowable maximum crack width arising from the limit state of serviceability, that is, functional requirements (example: water tank) [5, 6] or from the limit state of durability, that is, maintaining the concrete integrity and prevention of corrosion of the reinforcement (all reinforced concrete (RC) structures) [4].

The formation of cracks on the concrete surfaces may accelerate the degradation of the material (concrete), enhance corrosion of the reinforcement [7, 8], and eventually lead to the spall of the concrete cover [9]. Concrete cover would, therefore, call for appropriate measures for preventing such occurrences during the service life of RC structures [9]. Partial loss of concrete section due to the spall may result in compromising the limit state of strength as well. Therefore, the aspect of crack width is an important consideration for the design of RC structures.

Corrosion of the reinforcement is one of the main contributors for the formation of cracks in the RC structures. From this consideration, the use of high-performance concrete could be beneficial over ordinary concrete [10], though the denser

concrete matrix may lead to explosive spalling in case of fire exposure [9]. Another approach to control the corrosion cracks in RC members is using stainless steel as reinforcement, and research for the large-scale practical implementation of this approach is gathering momentum in recent years [11–14]. For important concrete infrastructure, such as bridges, monitoring of the cracks using image processing techniques is implemented employing artificial intelligence tools [15–19]. The measured crack widths can be used to update the surface deterioration assessment of the bridges, based on the probability-based models [20]. Another construction challenge is the control of cracking during casting of the mass concrete, especially when there are interruptions [21] and the reduction of crack widths has been attempted for such cases based on the predicted temperature regimes across dams [22].

The duration and the frequency of loading affect the formation of cracks in RC structures. The effect of the load duration on the concrete cracking was studied by Bazant and Xiang [23]. They inferred that the initial stage of crack opening was dominated by creep, whereas the final stage of crack opening was controlled by time-dependent crack growth. Repeated loading resulted in higher strains and higher cracking in the tension zone of the beams, indicating that the tension stiffening effect according to some codes (Eurocode 2) could be overestimated and this would result in inaccuracy of the estimated crack widths [24]. Both numerical models and experimental studies have been reported for the prediction of the cracking in RC structures under sustained loading [25–27]. The use of steel or polypropylene fibers in the concrete has become popular for controlling the long-term serviceability (cracking) in RC sections [28], but this has not been integrated in many concrete codes. Machine learning models have been developed based on synthetic data to predict the crack width in fiber-RC [29]. The effects of the degree of cracking and the restrained boundary conditions on the crack widths have been recently investigated and the results indicated underestimation of the crack widths for higher strains when European codes were adopted [30]. It is indicated from the aforementioned discussion that the formulas for estimating the cracks under the serviceability checks recommended by the various codes could often be inaccurate due to the typical cracking behavior under sustained and/or repeated loading.

There are two broad approaches of controlling the crack width in the concrete structures advocated by the various design codes/standards (e.g., [4]). The first one is to limit the tensile stress in concrete such that the tensile capacity of concrete is not exceeded. This is generally implemented by limiting the tensile stress allowed in the reinforcement during the design of the section for the limit state of strength. Alternately, this can be implemented by controlling the diameter and the spacing of the reinforcement in the RC section. The second approach to design for crack width is to estimate the crack width in the RC section due to the imposed load and to compare this estimated crack width with the allowable maximum value (from durability and/or serviceability) to verify the safety margin (or lack thereof) in the design of the RC section.

For adopting the second approach, an estimation of the maximum crack width becomes necessary for the RC design.

There are different formulations for calculating the crack width in the RC sections, both in the international codes/standards and the research articles, and these will be discussed in some more detail in a subsequent section. The maximum width of the flexural crack in a RC beam, for example, would depend on, and would be affected by, multiple factors. The formulations available in the various international codes consider some of or all these factors, and consequently, there are possible limitations in the accuracy that can be achieved by any formula.

There have been scattered studies encompassing a few of the international codes regarding the comparison of the estimated crack widths or the accuracy of the same with respect to experimental or field data. For example, Eurocode [31]; Eurocode, ACI code, Egyptian code, and British code [32, 33]; Eurocode, Egyptian code, ACI code, British code, and Indian code [34]; Polish code, Eurocode, and ACI code [35]; Eurocode, Egyptian code, ACI code, British code, Singapore code, and Japanese code [36]; Indian code, Eurocode, Egyptian code, and ACI code [37]; Eurocode, Model Code, and ACI code [38]; ACI code, Eurocode, and Chinese code [39]; Eurocode (two versions), Model Code (two versions), and German guideline [40]. However, a comprehensive review of such formulations is scarce in the literature. Moreover, many of the aforementioned studies were limited by their choice of sections (laboratory/actual structure) that were employed for evaluating the accuracy of the formulas. More specifically, a study comparing the formulas from the major international codes in a sound statistical framework, considering a wide array of RC beam sections, is largely missing from the literature. This article is motivated to bridge this gap and provide a systematic evaluation of the different formulas in international codes considering a wide array of synthetic RC beam sections. The study focused on a critical comparison of the 12 formulations in 13 international codes (two codes, ACI 224.1R-07 [41] and ACI 318-1995/ACI 318R-1995 [42] prescribe the same formula—so the number of formulas is 12) from 10 countries/geographic regions. Similar comparison of the different approaches for estimating other properties of concrete are available in the literature, for example, the shear capacity [43].

1.1. Novelty of Study. This article first presents the formulas for estimating the widths of the flexural cracks in the RC flexural sections from the major international codes and this is followed by a critical comparison of these formulas. The insights obtained from this exercise, into the respective strengths and limitations of different formulas, would be beneficial for considering any future revision(s). This comprehensive and critical review of the provisions from the major international codes is the first novel contribution of this article.

Though the accuracy of any individual formula(s) may be determined by comparing with the actual test data, the evaluation would be limited by the number of data, and nature of the specimens used during the experiments. Therefore, a wide array of possible beam sections is synthetically generated in this study employing appropriate statistical sampling techniques. As compared to the hundreds of RC sections reported for such evaluations in the literature employing actual test/field data (discussed above), this study employs a larger number



Scan the QR Code or Click for full text



Feddes Repertorium

5

RESEARCH ARTICLE OPEN ACCESS

Heptapleurum assamicum (Araliaceae): A New Species From Assam, India

Santanu Dey¹ | Hussain A. Barbhuiya² | Jayanta Das³ | Deepak Kumar Baruah⁴

¹Guwahati, Assam, India | ²Landscape and Cosmetic Maintenance Section, Architectural and Structural Engineering Division, Bhabha Atomic Research Centre, Mumbai, Maharashtra, India | ³AFRY India Pvt. Ltd., Noida, Uttar Pradesh, India | ⁴Assam Power Generation Corporation Limited, Guwahati, Assam, India

Correspondence: Hussain A. Barbhuiya (hahmed@barc.gov.in)

Received: 4 June 2025 | **Revised:** 19 July 2025 | **Accepted:** 22 July 2025

Funding: The authors received no specific funding for this work.

Keywords: Araliaceae | Assam | *Heptapleurum* | new species | Northeast India

ABSTRACT

A new species, *Heptapleurum assamicum* (Araliaceae), is described and illustrated from Assam, India. It was discovered during floristic documentation conducted in the Kopili River basin, in the Dima Hasao and West Karbi Anglong districts. The species is distinguished by a unique combination of morphological characters. Detailed comparisons with morphologically similar species are provided to support its recognition as a distinct species.

1 | Introduction

The genus *Heptapleurum* Gaertn., recently reinstated from the formerly broad and polyphyletic genus *Schefflera* J.R.Forst. & G.Forst. (Lowry II and Plunkett 2020), has emerged as a taxonomically dynamic group within the family Araliaceae, comprising over 320 currently accepted species (POWO 2025). The genus exhibits remarkable morphological diversity across tropical and subtropical Asia and the western Pacific (Plunkett et al. 2020). In India, the genus is represented by 23 species (Karthikeyan et al. 2009). Despite increasing interest in its taxonomy and systematics, *Heptapleurum* remains underexplored in several parts of northeastern India, a region known for its high biodiversity and endemism.

As part of ongoing botanical investigations in the Kopili River basin, a field survey in the Dima Hasao and West Karbi Anglong districts of Assam led to the discovery of a previously undocumented taxon of *Heptapleurum*. The plant was observed in a unique microhabitat along the river Kopili, Diyung, and Amring, where it exhibited morphological traits that deviated notably from known species within the genus.

This paper presents the formal description of a new taxon, *Heptapleurum assamicum*, endemic to Assam. Detailed morphological analyses and comparisons with allied taxa are provided, highlighting the characters that support its novelty and taxonomic placement within the genus. The discovery not only contributes to the growing diversity of *Heptapleurum* but also underscores the value of intensive floristic studies in botanically rich yet underexplored regions such as Northeast India.

2 | Materials and Methods

While documenting the flora around the Kopili River basin, Assam, India, the authors encountered an undescribed taxon exhibiting distinct morphological characteristics not attributable to any known species. Specimens were collected following standard herbarium practices, including pressing, drying, and preservation (Jain and Rao 1977).

Morphological observations and measurements were conducted using a stereo zoom microscope and digital calipers. Comparative analysis was carried out with the aid of relevant

This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial-NoDerivs](https://creativecommons.org/licenses/by-nc-nd/4.0/) License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

© 2025 The Author(s). *Feddes Repertorium* published by Wiley-VCH GmbH.

literature, including regional floras, taxonomic revisions, and original species descriptions (Kanjilal et al. 1938; Grierson 1991; Xiang and Lowry 2007; Esser and Jebb 2019). Digital images of type material of closely related species were examined from the herbaria viz. A, BM, E, G, K, LE, P, and PE (Thiers 2025), accessed through online databases.

The new species is described here in accordance with the guidelines of the International Code of Nomenclature for algae, fungi, and plants (Turland et al. 2018). The holotype and isotype are deposited at HBARC and CAL (Thiers l.c.) for future reference. Photographic documentation was undertaken both in situ and under controlled conditions to capture diagnostic features.



FIGURE 1 | *Heptapleurum assamicum* S. Dey & Barbhuiya. (A) Plants in natural habitat, (B) lenticellate exposed roots growing over rocks, (C) portion of stem showing bark, leaf scars, and lenticels, (D) leafy crown with inflorescence, (E) arrangement of leaves on stem, (F) secondary axes of inflorescence, (G) portion of inflorescence showing umbels and stellate axis, (H) opened flower with six stamens, (I) petals falling off from flower, (J) leafy crown with infructescence, (K) portion of infructescence showing developing fruits, (L) infructescence showing ripe and unripe fruits. Photos by S. Dey, based on living material.





RESEARCH ARTICLE OPEN ACCESS

High Valent Mercury Hydrides

Thankan Jayasekharan

Atomic and Molecular Physics Division, Physics Group, Bhabha Atomic Research Centre, Mumbai, India

Correspondence: Thankan Jayasekharan (jsekhar@barc.gov.in)

Received: 30 January 2025 | **Revised:** 26 May 2025 | **Accepted:** 10 June 2025

Funding: The author received no specific funding for this work.

Keywords: CCSD(T) | DFT | highvalent mercury hydrides

ABSTRACT

High valent mercury hydrides ($\text{HgH}_{n=1-8}^{0+}$) are studied using DFT-B3LYP/PBE0 and CCSD(T) methods to analyze their structure, stability, bonding, electronic properties, and electrical characteristics. Molecular orbital calculations reveal a high HOMO–LUMO energy gap of ≈ 7 eV for HgH_2 , HgH_4 , and HgH_6 , while HgH_8 shows a lower energy gap of ≈ 3 eV. The Hg–H bond capacitance ($\xi^{(AB)}$) values are 1.84, 2.03, 2.09, and 1.52 for HgH_2 , HgH_4 , HgH_6 , and HgH_8 , at the PBE0 level. These values are comparable to the C=C bond capacitance range ($\xi^{(AB)} = 1.84–2.07$), providing evidence for stable high-valent HgH_n with oxidation states ranging from I to VIII. Furthermore, they show a linear response to an external static electric field up to 0.1 a.u., with a gradual decline for higher fields. These observations indicate their possible future detection through molecular beam deflection or the matter-wave interferometry technique.

1 | Introduction

The relativistic mass of the electron in the Dirac-Hamiltonian perturbs the orbital energy levels of atoms through mass–velocity contraction, spin-orbit coupling, and Darwin's contract term [1–10]. Consequently, the 6s and 5d atomic orbitals in the mercury (Hg) atom undergo contraction and expansion respectively [11]. Various theoretical methods predicted the participation of 5d¹⁰ shell electrons in chemical bonding with highly electronegative atoms, such as fluorine (F) [12–17]. The involvement of 5d electrons in chemical bonding was recently confirmed in HgF_n^{0+} through vibrational spectroscopy [18] and mass spectrometry [19].

The interaction between the Hg and the hydrogen (H) atom offers a unique opportunity to explore the effects of the special theory of relativity on Hg through “sd” hybridization. Quantum chemical calculations predicted the possibility of HgH_4 and HgH_6 with Hg in +IV and VI oxidation states (OS) [20].

However, other molecules in the HgH_n series like HgH_3 , HgH_5 , HgH_7 , and HgH_8 and their corresponding ions remain unexplored. We have systematically investigated $\text{HgH}_{n=1-8}^{0+}$ for bonding, stability, electronic properties, and electrical characteristics by quantum chemical methods to support their possible detection through molecular beam deflection or matter-wave interferometry technique.

2 | Computational Methods

The molecular structure of $\text{HgH}_{n=1-8}^{0+}$ is optimized using the density functional theory (DFT) based method at B3LYP/PBE0 hybrid electron exchange-correlation functional [21–24] and wave functional theory-based coupled cluster-single-double and perturbative triple [CCSD(T)] level [25]. Atomic natural orbital with relativistic core corrections and quadrupole- ζ plus polarization (ANO-RCC-VQZP) basis set with the following primitive/contracted sets: 25s22p16d12f4g2h/9s8p6d4f2g1h and

This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial-NoDerivs License](#), which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

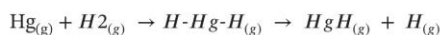
© 2025 The Author(s). *International Journal of Quantum Chemistry* published by Wiley Periodicals LLC.

14s9p4d3f2g/5s4p3d2f1g is used for Hg [26] and H [27]. The scalar relativistic effects are included through one-electron integrals in ANO basis sets using the X2C (exact two-component) method [28–31]. The spin-orbit coupling (SOC) corrections are not calculated due to their negligible contribution to similar systems, HgX_n ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) [32], although SO splitting of 5d orbitals in Hg is 2.052 eV at the Dirac-Fock level [4]. The resolution identity (RI) decomposed two-electron repulsion integrals are stored in Cholesky decomposition (CD) style to reduce the computation time [33, 34]. The vibrational frequency analysis is also carried out within harmonic approximation to identify the nature of minima on the potential energy surface (PES). The stability of HgH_n is determined using the atomization energy, transition state, and the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The isotropic polarizability and bond capacitance are computed for a range of electric field strengths using the LoProp method. All the calculations are performed using MOL-CAS 8.0 [35] and CFOUR 2.1 software [36].

3 | Results and Discussion

3.1 | Structure of HgH_n

Mercury has a closed shell electronic configuration $[\text{Xe}] 4f^{14} 5d^{10} 6s^2$ ($^1\text{S}_0$) and it does not react with molecular hydrogen (H_2 ; $^1\Sigma_g^+$) in their ground state. The reaction $\text{Hg}_{(\text{g})} + \text{H}_{2(\text{g})} \rightarrow \text{HgH}_{2(\text{g})}$ is predicted to be endothermic with a high activation energy barrier. However, HgH_2 can form via spin-orbit coupling with a triplet state that correlates to the $\text{Hg}(^3\text{P}_1) + \text{H}_2$ asymptote, resulting in an exothermic reaction. Accordingly, by exciting Hg in its first excited electronic state, HgH and HgH_2 are produced through electronic-to-vibrational (E-V) energy transfer processes in a supersonic molecular beam [37–40]. The reaction proceeds through the following sequence:



A stable $\text{HgH}_2/\text{HgD}_2$ has also been prepared by the reaction between excited Hg and H_2 gas in H_2/D_2 , H_2/Ar , and H_2/N_2 matrices. The product molecules formed are detected and characterized using IR spectroscopy supported by quantum chemical calculations. Moreover, by annealing processes, $(\text{HgH}_2)_2$, $(\text{HgH}_2)_3$, and solid HgH_2 were observed in solid hydrogen in a low-temperature matrix isolation technique [40–43]. The stability of $(\text{HgH}_2)_n$ is attributed to the closed shell $\text{Hg}^{2+}-\text{Hg}^{2+}$ mercuriophilic interaction that arises from the relativistic effects and other noncovalent dispersive forces [44, 45]. Additionally, gaseous $\text{HgH}_2/\text{HgD}_2$ is prepared through the direct gas phase reaction of Hg vapor with H_2/D_2 in an electrical discharge. High-resolution infrared emission spectra reveal a linear covalent $\text{H}-\text{Hg}-\text{H}$ molecule with a $\text{Hg}-\text{H}$ bond length of 1.646543 Å and Hg in a typical +II oxidation state [46, 47]. Theoretical calculations predicted a bond length of 1.615–1.713 Å with real frequency values [48–55]. In the past, HgH_4 and HgH_6 have been investigated computationally for high OS by employing DFT-B3LYP, MP2, and CCSD(T) methods [20]. However, structural and spectroscopic data for other members in the HgH_n family and their corresponding ions have not yet been reported. Table 1 lists the computed structural data, symmetry,

IR frequency, ionization potential (IP), and electron affinity (EA) of $\text{HgH}_{n=1-8}^0$ at the DFT-B3LYP/PBE0 and CCSD(T) levels.

3.1.1 | HgH

HgH is a linear molecule with $C_{\infty v}$ symmetry and shows an equilibrium bond length (r_e) of 1.776/1.742/1.686 Å at B3LYP/PBE0/CCSD(T) levels. The r_e value calculated at the B3LYP level agrees with the experimental value (1.776 Å) [37] and earlier reported theoretical values (1.790, 1.796 Å) at the same level of theory [38, 44]. The HgH^+ ion shows shortened r_e of 1.607/1.600/1.560 Å and agrees with the experimental value (1.594 Å) [42] and also the reported theoretical values (1.610/1.579/1.607 Å) [20] at the B3LYP/MP2/CCSD(T) levels with an IP of 8.164/8.022/7.978 eV. While its negative ion (HgH^-) shows elongated r_e of 2.107/1.981/1.890 Å with a positive EA value of 1.093/0.904/0.873 eV, indicating that the anion is more stable than neutral. The molecule shows a frequency of 1041/1346/1606 cm^{-1} with intensity of 94/113/107 km mol^{-1} . The computed zero-point vibrational energy (ZPVE) is 520/673/803 cm^{-1} . The molecule and the ions show real frequency values, indicating they are stable species.

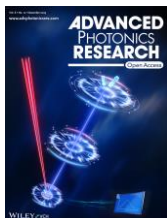
3.1.2 | HgH_2

HgH_2 is a linear molecule with $D_{\infty h}$ symmetry and shows r_e of 1.654/1.647/1.604 Å at B3LYP/PBE0/CCSD(T) levels and is in agreement with the earlier reported values at different levels of theory viz., 1.656/1.617/1.641 Å at B3LYP/MP2/(CCSD(T)) levels [20, 42–46]. The cation shows a bend geometry with C_{2v} symmetry and slightly elongated r_e of 1.713/1.704/1.667 Å and $\angle \text{H}-\text{Hg}-\text{H} = 148.23/145.92^\circ$ at B3LYP/PBE0 level while (CCSD(T)) shows linear structure with an angle of 180° . The anion also shows a linear structure with r_e of 1.658/1.652/1.609 Å. The linear HgH_2 shows 3N–5° of freedom and shows 4 normal modes of vibration with A_1 , B_1 , B_2 , and A_1 irreducible notation. All the modes show real frequency and are IR active except $1A_1$. Among the three IR active modes, B_2 shows a high IR frequency of 1964/1954/2099 cm^{-1} with an intensity of 434/411/373 km mol^{-1} and ZPVE of 2829/2427/2608 cm^{-1} . The HgH_2^0 systems show real frequency values indicating they are stable on the PES. The molecules show an IP of 10.589/10.533/10.795 eV and an EA of –0.448/–0.491/–0.603 eV. The negative EA value indicates that the anion is less stable than the neutral molecule.

3.1.3 | HgH_3

HgH_3 exhibits T-shaped trigonal planar geometry with C_{2v} symmetry and shows two distinct types of bonds with r_e of 1.657, 1.886/1.650, 1.868 Å along with $\angle \text{H}_1-\text{Hg}-\text{H}_2 = 174.67/174.82^\circ$ and $\angle \text{H}_2-\text{Hg}-\text{H}_3 = 92.66/92.59^\circ$ at the B3LYP/PBE0 level. In contrast, the CCSD(T) method shows an equal bond length of 1.671 Å with $\angle \text{H}-\text{Hg}-\text{H} = 120^\circ$. The cation shows a short $\text{Hg}-\text{H}$ of r_e 1.593/1.587 Å and a long $\text{Hg}-\text{H}$ of r_e of, 2.075/2.025 Å along with reduced bond angles at B3LYP/PBE0 level and it exists as HgH^+ and H_2 . The CCSD(T) method shows elongated r_e of 1.734 Å and $\angle \text{H}-\text{Hg}-\text{H} = 120^\circ$ and





RESEARCH ARTICLE

ADVANCED
PHOTONICS
RESEARCH

www.adpr-journal.com

Multimodal Luminescence from $\text{LaAlO}_3:\text{Eu}^{3+}$ via Trap Modulation for High-Temperature Applications

Abdullelah Alolayan, Nimai Pathak,* Kawsar Ali, and Yuanbing Mao*

Persistent phosphors with high charge storage capacity are promising for a wide range of applications, mostly demonstrated at room temperature. Designing such long-persistent phosphor (LPP) applicable at higher temperature is largely unexplored and challenging. To prevent spontaneous charge release and ensure long-term data retention, high-temperature LPPs must feature multilevel traps with sufficient activation energies. In this report, $\text{LaAlO}_3:\text{Eu}^{3+}$ (LAO:E) phosphor is investigated with multiple traps and four integrated luminescent emissions: down-conversion photoluminescence and radioluminescence, thermally stimulated luminescence, persistent luminescence (PersL), and optically stimulated luminescence (OSL). Unlike earlier optical storage phosphors, our LAO:E phosphor possesses charge carriers that are released from these traps, ranging from shallow trap 1 to deep trap 4, across various temperatures. The potential for the long-term storage of charge carriers at both room and elevated temperatures is also examined. Supported by experimental data and density functional theory calculations, we establish a correlation between the various traps and the desired PersL and OSL properties of the LAO:E phosphor. Additionally, a comprehensive trapping–detrapping mechanism for charge carriers is developed. The studies here are expected to pave the way for designing advanced multimode phosphors for a wide range of applications at high temperatures.

1. Introduction

There is an urgent need of storage media with ultrahigh capacity to manage the rapidly growing amount of data in today's digital world where data generated in major sectors such as education, health, and business is doubling every year.^[1] Optical data storage is one of potential technologies with multiple advantages, including high storage capacity, efficient writing and reading processes, high information security, and low power consumption.^[2–5] Compared to traditional magnetic storage, which has limitations related to 2D spatial resolution, the information capacity in optical data storage systems can be greatly enhanced through information multiplexing techniques, such as multiplexing by intensity, wavelength, polarization, and time gate.^[6–10] The greatest advantages of optical storage over other storage types, such as magnetic tape, hard disk drives (HDDs), or solid-state drives (SSDs), are its durability and resistance to degradation over time. Furthermore, when a mechanical hard drive is exposed to temperatures exceeding its threshold range, (5–60 °C), there is a high risk that the magnetic material in the HDD's platters will lose its magnetic properties as the temperature surpasses its “Curie temperature” to data loss. Therefore, for data storage in high-temperature environments, such as space exploration missions, deep-well drilling, and combustion engines, optical data storage device may be a more suitable choice than HDD.

Persistent phosphors are highly promising candidates for optical storage applications due to their unique properties of trapping charge carriers (electrons and holes) under specific excitation conditions, preserving these charge carriers in various traps, and releasing them under different stimulation conditions as thermally stimulated luminescence (TSL) and optically stimulated luminescence (OSL).^[5,11–17] In long-persistent phosphor (LPPs), electrons can be easily captured into defect-related traps under short-wavelength irradiation (write-in process) and subsequently released (read-out process) by thermal stimulation or long-wavelength irradiation. Due to their ability to store charge carriers and emit light for extended periods in the absence of excitation sources, LPPs have found widespread applications in glow-in-the-dark materials,^[18,19] bioimaging,^[20–26] alternating current light-emitting diodes (AC-LEDs),^[27–29] anticounterfeiting,^[30,31] and information storage technology.^[11–17] Additionally, LPPs that exhibit multimode luminescence in response to various excitations (down-conversion and

A. Alolayan, N. Pathak, Y. Mao
Department of Chemistry
Illinois Institute of Technology
Chicago, IL 60616, USA
E-mail: nimai@barc.gov.in; ymao17@iit.edu

N. Pathak
Radiochemistry Division
Bhabha Atomic Research Centre
Mumbai 400085, India

N. Pathak
Chemical Sciences
Homi Bhabha National Institute
Mumbai 400094, India

K. Ali
Glass and Advanced Materials Division
Bhabha Atomic Research Centre
Mumbai 400085, India

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adpr.202500092>.

© 2025 The Author(s). Advanced Photonics Research published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/adpr.202500092

up-conversion) or stimuli (TSL and OSL) hold potential for use in anticounterfeiting and encryption technologies.^[32] Therefore, LPPs with multimode luminescence characteristics offer versatile applications.

The nature of the traps plays a crucial role in determining the applications of LPPs. For instance, LPPs with a large number of shallow traps are well-suited for room-temperature applications such as night-vision security signs, AC-LEDs, and in vivo bioimaging due to their normal detrapping processes occurring at room temperature. In contrast, LPPs with deep traps exhibit slower detrapping processes and are not ideal for these applications at room temperature because they require additional stimulation. However, if the temporary photons stored at room temperature are used for data encoding and photon emission for data decoding under additional stimulation, LPPs with deep traps can be effectively applied in the information storage field. To prevent the spontaneous release of stored charges by thermal stimulation and retain the recorded information at room temperature for a sufficiently long duration, the trap depth should be significantly deeper, typically in the range of 0.8–1.6 eV.^[33–35] Additionally, traps with large trap depths can store memory even at high temperatures because greater energy is required to release the stored charge carriers. Therefore, trap engineering modulated by defects is critical, especially for developing phosphors for optical storage.^[13,36,37] Currently, the number of reported LPPs with deep traps is limited, and optimizing the trap depth of LPPs will be key to developing efficient optical storage phosphors capable of operating at higher temperatures.

To date, the most commercially successful optical storage phosphors are based on halides and sulfides, such as BaFBr:Eu^{2+} , $\text{SrS:Eu}^{2+}, \text{Sm}^{3+}$, and $\text{CaS:Eu}^{2+}, \text{Sm}^{3+}$, which exhibit strong OSL intensity and storage capacity.^[38–40] These materials have been extensively used in imaging plates for computed radiography. However, their poor chemical and thermal stabilities remain a concern. Alternative hosts, such as oxides, oxynitrides, and silicates, which offer better chemical and thermal stability, have been explored. Examples of LPPs include $\text{Sr}_3\text{SiO}_5\text{:Eu}^{2+}, \text{Dy}^{3+}$, $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}, \text{Dy}^{3+}$, and $\text{SrSi}_2\text{O}_2\text{N}_2\text{:Eu}^{2+}, \text{Dy}^{3+}$.^[13,41,42] Since the notable report of “afterglow” from $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}, \text{Dy}^{3+}$ by Matsuzawa et al. came out in 1996,^[18] aluminate-based host materials have garnered increasing attention from researchers worldwide for developing efficient LPPs. However, the traps in aluminate-based hosts (e.g., $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}, \text{Dy}^{3+}$) are not deep enough, which leads to information loss and limits their practical applications.

Lanthanum aluminate (LaAlO_3) is a perovskite material with a cubic crystal structure and space group $Pm\bar{3}m$. While there have been some reports on the persistent luminescence (PersL) and OSL properties of rare earth-doped LaAlO_3 (LAO) phosphors, the PersL typically lasts only for a few seconds or minutes.^[35,43] In this study, we explored Eu^{3+} -doped LAO (LAO:E) phosphors as efficient optical storage materials and investigated their storage capabilities at high temperatures. More specifically, in contrast to previously reported optical storage phosphors,^[5,11–17] our work here focuses on examining the PersL properties of our LAO:E phosphors generated by the release of charge carriers from various shallow and deep traps at different temperatures, ranging from room temperature up to 240 °C. We systematically

analyzed the release of charge carriers from these traps, spanning from shallow trap 1 to deep trap 4, across different temperatures. This temperature range corresponds to the external stimulus energy required to depopulate the various traps. This study provides valuable insights into the design of multilevel traps in optical storage phosphors, helping us understand trap populations and their behavior under high-energy light irradiation, and thus enabling data storage over a wide temperature range.

Moreover, unlike previous studies on rare earth-doped LAO,^[35,43] we observed a significant improvement in the PersL properties, specifically a long-lasting red-PersL lasting for 17 h, in our LAO:E phosphors synthesized using a molten-salt-assisted coprecipitation method. Additionally, here we observed intense TSL and OSL signals from the LAO:E samples even 35 days after UV irradiation, confirming their suitability for long-term optical storage applications. We further integrated four types of luminescence in our LAO:E samples: down-conversion photoluminescence (PL) and radioluminescence (RL), TSL, PersL, and OSL. This integrated multimode luminescence from our LAO:E samples makes them a promising candidate for anticounterfeiting and optical storage applications. To enable practical applications of the LAO:E phosphors, we fabricated phosphor films using an in-house prepared ink of the LAO:E phosphors. The write-in process involved UV light exposure, followed by reading out the stored information via thermal stimulation or 980 nm light.

Since these traps in our LAO:E phosphors are created by various lattice and impurity defects, which contribute to the multimode luminescence, we performed density functional theory (DFT) calculations to understand the range of traps modulated by potential defects within the LAO bandgap. This study helps us understand and establish a correlation between the different traps and the desired PersL and OSL properties of the LAO:E phosphors. Based on both experimental and theoretical findings, we developed a comprehensive trapping–detrapping mechanism for charge carriers, explaining the PersL and OSL properties of our LAO:E samples. We believe this detailed investigation will pave the way for the design of advanced multimode luminescent materials for a wide range of applications.

2. Results and Discussion

2.1. Phase Purity and Crystal Structure

X-ray diffraction (XRD) patterns of the prepared LAO:E samples with various Eu^{3+} doping levels (Figure 1a) are consistent with the standard ICDD card no. 01-078-2861, confirming the formation of pure phase products. A zoomed-in view of the XRD patterns at $2\theta \approx 33.7^\circ$ is provided in the supporting information (see Figure S1, Supporting Information), which shows a shift of the XRD peaks toward higher 2θ values. This shift can be explained by the relative size difference between the La^{3+} and Eu^{3+} ions. Since the Eu^{3+} ion has a smaller ionic radius than the La^{3+} ion, the unit cell volume is expected to decrease. According to Bragg's diffraction principles, this results in the XRD peaks shifting toward higher 2θ values. To further investigate the structure of the LAO:E phosphors, we performed Rietveld refinement on the LAO:0.5 E sample (Figure 1b).





Wiley
International Journal of RF and Microwave Computer-Aided Engineering
Volume 2025, Article ID 9618627, 10 pages
<https://doi.org/10.1155/mmce/9618627>

8

WILEY

Research Article

Subgigawatt Level X-Band BWO Using Adiabatically Tapered SWS at Low Magnetic Field

Chitaranjan Jadab^{1,2}, Romesh Chandra^{1,2}, Sandeep Singh^{1,2} and Amitava Roy^{1,2}

¹Physical Sciences, Homi Bhabha National Institute, Mumbai, Maharashtra, India

²Accelerator & Pulse Power Division, Bhabha Atomic Research Centre, Mumbai, Maharashtra, India

Correspondence should be addressed to Chitaranjan Jadab; jadabc@barc.gov.in

Received 24 April 2025; Revised 23 June 2025; Accepted 9 July 2025

Academic Editor: Piotr Gas

Copyright © 2025 Chitaranjan Jadab et al. International Journal of RF and Microwave Computer-Aided Engineering published by John Wiley & Sons Ltd. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Improving the efficiency of backward wave oscillators (BWOs) operating in a low magnetic field regime remains a significant research challenge. In this field regime, increased transverse motion of electrons leads to variable interaction impedance. Consequently, the beam wave synchronization with the desired mode is disrupted, resulting in reduced efficiency. To partially overcome this challenge, an adiabatically varying nonuniform slow wave structure (SWS) with a circular ridged wall profile is proposed. The SWS helps in maintaining the synchronization of the beam bunch with the desired normal mode throughout the interaction length. The circular SWS increases the field breakdown limit of the electrodynamic structure. This, in turn, results in an average output power of 810 MW at 9.8 GHz with a power increment of 50% compared to the uniform SWS, guided by a 0.6 T magnetic field. The low magnetic field operation helps in the implementation of a permanent magnet, which results in a repetitive microwave system. The novelty of this work lies in the use of an adiabatically tapered, nonuniform SWS geometry to ensure continuous synchronism at low magnetic fields, which is rarely addressed in conventional BWO designs. This method offers practical significance in reducing system size, weight, and cost by eliminating bulky electromagnets. Further efficiency enhancement is limited by overbunching, which induces Coulomb instability and leads to back-streaming of electrons, as observed in particle-in-cell simulation conducted using CST Microwave Studio.

Keywords: backward wave oscillator; interaction impedance; slow wave structure

1. Introduction

Microwave devices have broad applications in many scientific and engineering fields, like plasma heating, material processing, high-resolution RADARs, and many other strategic applications [1–3]. BWO is a device used to efficiently convert the electron kinetic energy into electromagnetic radiation at microwave frequencies [4] and is preferred among all microwave devices due to its wide range of frequency scalability and high spectral purity.

A strong guiding magnetic field usually generated by electromagnets or superconducting magnets is used for guiding the intense relativistic electron beam inside the SWS. To reduce the refrigeration cost and energy consumption by the above magnets, it is very important to reduce the magnetic field to the levels attainable by permanent mag-

nets. Additionally, permanent magnets help in enhancing the pulse repetition frequency of the entire microwave system, thereby increasing the average output power [5–7].

The electron beam interacts with the desired normal mode of SWS, whose phase velocity is slightly greater than the beam velocity. This synchronism commonly referred as the Cerenkov synchronism and has been extensively studied in the context of beam-wave interaction. The mechanism of achieving the Cerenkov synchronism using SWS in microwave devices is well explained in literature [1, 2, 4, 8]. Building upon this, Schamiloglu and Figotin [9] provided a detailed explanation on coherent Cerenkov radiation generation in TWTs, using classical field theory. Interaction between electron beam and electric field inside the SWS is an iterative process, in which beam alters the field's direction and amplitude, leading to further beam modulation.

Modulated electron beam, in turn, continues to influence the field, creating a continuous feedback loop. This interaction leads to certain instabilities that facilitate microwave amplification. In BWO, this instability type is absolute, whereas in TWT, it is of convective type [10]. The distinction has been thoroughly explained based on the first principle of Lagrangian field theory in [9].

Previously, several BWOs have been designed using nonuniform SWSs, demonstrating improved efficiency compared to the uniform ones in both high and low magnetic field regimes. In the high magnetic field domain, Ref. [11] reports a 33% increase in efficiency by varying the ripple amplitude of the SWS. Similarly, Ref. [12] achieves the same improvement by modifying the average radius toward the end of the SWS, while Ref. [13] demonstrates a 23% increment through variation in corrugation depth.

In low magnetic field regime, radial oscillations of electrons become significant [14] and electrons hit the inner wall of SWS. To suppress this, Ref. [15] introduces nonuniformity in SWS by increasing the inner radius toward the output end, resulting in a 20% efficiency enhancement. Furthermore, Ref. [16] presents a dual-mode operation with nonuniform SWS, achieving 44% efficiency. In another approach, Ref. [17] demonstrates that by increasing the transverse dimension at diode region suppresses radial oscillations and maximum efficiency of 44% is attained.

Despite these notable enhancements, none of the existing studies explain how a single electron beam line can synchronously interact with different normal modes across multiple sections of nonuniform SWS, that is, how multiple interaction points (Ps) appear on the dispersion curve due to geometry variations, leading to a single operating frequency. The mechanism is thoroughly explained in Section 4.

Our design uniquely addresses this gap by demonstrating the interaction point preservation across SWS sections by simultaneously varying both the period and ripple amplitude of the SWS. This provides a systematic way to control beam-wave synchronism and enables efficient energy transfer in nonuniform BWOs.

This article is aimed at analyzing the impact of adiabatically tapered nonuniform SWS on the output power, efficiency, and axial electric field of the BWO, compared to a uniform one (only having Section “A” type unit cells). In the latter case, the bunched electron beam always encounters lower magnitude of decelerating electric field towards the end, which inherently limits power transfer. However, by introducing nonuniformity into the structure, the beam experience progressively higher decelerating field magnitudes after traversing each uniform section of the SWS, thereby enhancing the power conversion [18].

The proposed SWS consists of three distinct sections (A, B, and C), each comprising two unit cells as illustrated in Figure 1. The period and corrugation depths of the unit cells vary by almost 2% from one section to another, with the specific dimensions listed in Table 1. To avoid the abrupt change in operating frequency, desired mode of operation or mode conversion, wave reflections, and significant impedance change of the resonant SWS, adiabatically tapering is implemented in the design. This variation does not alter

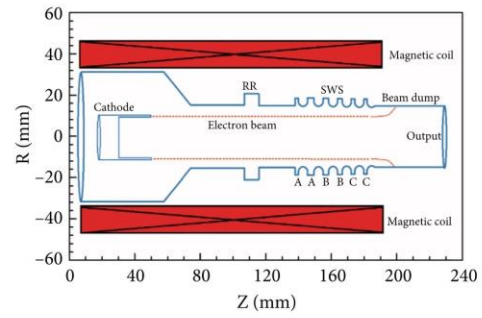


FIGURE 1: Schematic of X-band overmoded BWO.

TABLE 1: Dimensions of different sections of nonuniform SWS.

Section type	Period (z_0)	Corrugation depth ($r_{\max} - r_{\min}$)
A	12.00 mm	$\lambda_0/6$
B	11.75 mm	$\lambda_0/6 + 0.25$ mm
C	11.50 mm	$\lambda_0/6 + 0.5$ mm

the key operating parameters such as the dispersion curve and other cold parameters to a large extent; while significantly changing the output power of the device by 50%.

Briefly, two approaches have been implemented for efficiency enhancement. The first is the adiabatic tapering, and the second is by employing a smooth semicircular wall to increase the electric field breakdown limit of the electrodynamic structure. By incorporating the ideas, the beam-wave conversion efficiency changed to 27% from 18%. Additionally, the paper used CSTMS [19] to assess the difficulties encountered during PIC simulation. Operational challenges with low magnetic field, such as beam divergence and cyclotron absorption, were also observed in PIC simulation and will be explained through phase space plots in upcoming sections.

2. Model Description

The schematic of the overmoded X-band BWO is shown in Figure 1. The average diameter of SWS, $D \approx 1.6\lambda_0$, where λ_0 is the free space wavelength of the generated microwave. The electron beam is emitted from an annular cathode of outer diameter, $D_c \approx \lambda_0/1.5$, and is faintly modulated at RR. The radius (r_r) and length (L_r) of the cavity RR are calculated with reference to [9]. Here, RR acts both as a reflector for the backward wave and as a premodulation cavity for the electron beam.

The period of uniform SWS is 12.00 mm with average radius of 24.00 mm. Both uniform and nonuniform SWSs have 6-unit cells each and number of unit cells are determined by taking into account the device's starting current approximation [20]. TM_{01} dispersion diagram of three different types of SWS is shown in Figure 2, with beam line intersection. The curves are almost overlapping with each other. Hence, the cold parameters of the SWS do not change



Scan the QR Code or Click for full text



Journal of Pathology, Microbiology and Immunology

PMI
PATHOLOGY
MICROBIOLOGY
IMMUNOLOGY

ORIGINAL ARTICLE OPEN ACCESS

Synthesis and Characterization of Gum Kondagogu Stabilized Zinc Oxide Nanoparticles and Its Application as an Antibacterial Agent Against Wastewaterborne Bacteria

Aruna Jyothi Kora^{1,2} | Venkata Balarama Krishna Mullapudi¹

¹National Centre for Compositional Characterisation of Materials (NCCCM), Bhabha Atomic Research Centre (BARC), Hyderabad, India | ²Homi Bhabha National Institute (HBNI), Mumbai, India

Correspondence: Aruna Jyothi Kora (koramaganti@gmail.com)

Received: 2 April 2025 | **Revised:** 2 June 2025 | **Accepted:** 17 June 2025

Funding: The authors received no specific funding for this work.

Keywords: antibacterial | tree gum | water disinfection | zinc oxide nanoparticles

ABSTRACT

Wastewater recycling is one of the viable options for attaining sustainable water management. In this scenario, gum stabilized zinc oxide nanoparticles (ZnO NP) were synthesized employing the alkaline precipitation method with gum kondagogu stabilizer. Synthesized NP were characterized using UV-vis, DLS, zeta potential, XRD, FTIR, and TEM. ZnO NP exhibited an absorption peak at 351 nm in UV-vis, a zeta potential value of -35 mV, and a z-average value of 254 nm in DLS. XRD pattern showed a characteristic hexagonal wurtzite crystal structure and FTIR data indicated the capping of NP by various gum functional groups. The size of spherical NP varied from 12.4 to 35.7 nm, and the mean particle size was 24.8 ± 5.1 nm. The in vitro antibacterial activity of ZnO NP against wastewaterborne bacteria, *Escherichia coli* (Gram-negative) and *Bacillus subtilis* (Gram-positive) was studied with the resazurin broth assay. MIC values of 900 µg/mL and 900 µg/mL and MBC values of 1800 µg/mL and 900 µg/mL of ZnO NP were recorded towards *E. coli* and *B. subtilis*. Notably, ZnO NP exhibited superior bactericidal activity against *B. subtilis* compared to previous studies. Thus, the current study on ZnO NP mediated bacterial disinfection has wide applications in wastewater treatment and remediation of microbially contaminated effluents.

1 | Introduction

The material zinc oxide (ZnO) is classified as generally recognized as safe (GRAS) by the Food and Drug Administration (FDA) agency. The GRAS is a chemical or substance added to food that is considered safe for its intended use based on scientific procedures or experience of common usage. It gained momentum as a food additive for cereal fortification, food can lining material, filler in dental cement, toothpaste, etc. because of its abundance, low price, superior durability, heat resistance, biocompatibility, and antimicrobial properties [1–6]. The nanoparticles of ZnO are of current importance due to their smaller particle size, high surface-to-volume ratio, chemical

stability, broad antibacterial spectrum, and minimal human toxicity [2, 6, 7].

Previous studies suggest that the antibacterial activity of ZnO NP operates through multiple mechanisms, including abrasiveness arising from surface defects, surface oxygen species of ZnO NP [8] and the release of hydrogen peroxide [4, 9–11], all of which contribute to their biocidal effect. The chain of events occurring during the interaction of ZnO NP with bacteria includes attachment, transport, and internalization of NP facilitated by the electrostatic interaction of positive zinc ions with the negatively charged membrane, membrane pore-mediated diffusion, endocytosis; binding of zinc to proteins and lipids; generation

This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial-NoDerivs](https://creativecommons.org/licenses/by-nc-nd/4.0/) License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

© 2025 The Author(s). *APMIS* published by John Wiley & Sons Ltd on behalf of APMIS - Journal of Pathology, Microbiology and Immunology.

of reactive oxygen species (ROS), initiation of cell wall damage, membrane permeabilization, and oxidative stress; release of intracellular contents (proteins, DNA, RNA, phosphate ion), enzyme inhibition, leading to damage to proteins, nucleic acids, and lipids; interruption of metabolic pathways, and ultimate bacterial cell death [2–10, 12–15].

Many natural polymers such as starch [16], gum acacia [1], gum ghatti [17], gum kondagogu [18], gum tragacanth [19], xanthan gum [20] etc. are widely utilized for the synthesis and stabilization of metal [18, 21] and metal oxide [17, 22] nanoparticles. Gum kondagogu (*Cochlospermum gossypium*) is an exudate tree gum and is composed of carbohydrates, proteins, fatty acids, fiber, minerals, etc. The carbohydrate compositional analysis of the gum indicated the presence of uronic acids such as glucuronic acid (16.2 mol%) and galacturonic acid (10.5 mol%) and sugars such as galactose (19.5 mol%), rhamnose 15.8 (mol %), glucose (7.8 mol%) and arabinose (1.8 mol%). The structural assignment for this acidic polysaccharide is (1 → 2) β -D-Gal p, (1 → 6) β -D-Gal p, (1 → 4) β -D-Glc p A, 4-O-Me- α -D-Glc p A, (1 → 2) α -L-Rha, and (1 → 4) α -D-Gal p A. It is classified as rhamnogalacturonan type of gum, and the molecular weight ranges from 8.2×10^5 to 7.2×10^6 g/mol. The amino acid composition of the gum includes aspartic acid (72.8 μ g/g), methionine (44.2 μ g/g), proline (42.4 μ g/g), glutamic acid (34.2 μ g/g), tyrosine (32.8 μ g/g), alanine (32.2 μ g/g), threonine (30.2 μ g/g), tryptophan (10.8 μ g/g), valine (7.2 μ g/g), glycine (5.0 μ g/g) and leucine (3.8 μ g/g). The tree gum carbohydrate polymer is abundant in various functional groups such as acetyl, hydroxyl, carbonyl, and carboxylic acids and functions as a hydrogel due to the presence of acetyl groups (10 wt %) [21–23].

Wastewater is a rich source of pathogenic microbes (heterotrophic bacteria, total coliforms, *Escherichia coli*, fungi, viruses), protozoans, helminths, etc. and the main reason for many waterborne diseases and disease outbreaks in humans and animals [24–27]. In addition, the wastewater is a reservoir of antibiotic-resistant bacteria, and its release into drinking water sources can lead to and contribute toward antimicrobial resistance [26, 27]. Also, tremendous pressure is exerted on the efficient utilization of limited freshwater resources and effective water management essential for ensuring global food security in the current scenario of climate change and unpredictable weather patterns [24]. Wastewater disinfection and recycling is therefore a viable option for achieving sustainable water management and meeting the global demand for clean water [27, 28]. The most commonly used technologies for disinfection of drinking and wastewater include chlorination, ozonation, UV irradiation, and gamma irradiation [24, 27, 29].

Given the array of existing disinfection methods, tree gum kondagogu-capped ZnO NP were synthesized using the alkaline precipitation method at variable gum concentrations. The produced NP at optimal conditions were characterized using UV-visible absorption spectroscopy, dynamic light scattering, zeta potential, X-ray diffraction, Fourier transform infrared spectroscopy, and transmission electron microscopy techniques. Further, the in vitro antibacterial activity of the gum stabilized NP was studied towards the wastewaterborne bacteria, *Escherichia coli* and *Bacillus subtilis* with resazurin broth assay.

2 | Materials and Methods

2.1 | Materials

Gum kondagogu (KG), grade 1 (Girijan Co-operative Corporation Ltd., Hyderabad, India), glucose, zinc acetate dihydrate, sodium hydroxide (SD Fine, Mumbai, India), bovine serum albumin (BSA) (Sigma-Aldrich, Bengaluru, India), nutrient broth (NB), nutrient agar (NA), HiCrome coliform agar (CA), resazurin, and ciprofloxacin hydrochloride monohydrate (HiMedia, Mumbai, India) were utilized in the current study. All the aqueous solutions were made with ultrapure water collected from the Purelab Flex 3 water polishing system (Elga, High Wycombe, England). Pressure cooker (TTK Prestige, Bengaluru, India) sterilized glassware, plasticware, and bacterial culture media were used during the work [18].

2.2 | Synthesis of Gum-Capped Zinc Oxide Nanoparticles (ZnO NP)

The as-received grade 1 gum kondagogu was ground into a powder and sieved to a particle size of 38 μ m. A 0.5% gum solution in ultrapure water was prepared by overnight mixing of gum powder at ambient temperature. The total reducing sugars and total protein content in the gum solution were quantified by the phenol-sulfuric acid method with glucose standard and Bradford method with BSA standard, respectively, and the values are expressed as μ g/mL [19]. The ZnO NP were synthesized employing a facile, dropwise alkaline precipitation method with sodium hydroxide (20 mM) using zinc acetate (10 mM) as a metal precursor and gum kondagogu as a stabilizing agent at varying gum concentrations (0.1%–0.5%) under continuous stirring for 2 h, with minor modifications [1, 16]. The milky white hydrocolloids were removed by centrifugation and washed thoroughly with ultrapure water, and the produced NP were dried at 80°C for 3 h. The zinc concentration in the produced NP was quantified using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Horiba, Ultima Expert, Longjumeau, France) at 213.856 nm.

2.3 | Characterization of Gum Kondagogu Stabilized ZnO NP

The UV-visible absorption (UV-vis) spectra of gum kondagogu-capped ZnO NP at variable gum concentrations (0.1%–0.5%) were determined from 200 to 800 nm by dispersing and diluting the samples 8 times with ultrapure water against a water blank (Analytik Jena AG, Specord 200 Plus, Jena, Germany). The hydrodynamic radius ($\bar{z}$ average) and zeta potential of the diluted NP solutions were determined (Malvern, Zetasizer Nano ZS90, Malvern, UK). The X-ray diffraction (XRD) pattern of the synthesized ZnO NP powder was recorded at 40 kV and 30 mA utilizing monochromatic Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at a 2θ range of 3°–70° and a scan rate of 1°/min (Rigaku, Ultima IV diffractometer, Tokyo, Japan). The Fourier transform infrared (FTIR) spectra of the powdered gum and NP were obtained at a wave number of 1000–4000 cm^{-1} with 4 cm^{-1} resolution (Bomem, MB100, Quebec, Canada). The transmission electron microscope (TEM) pictures of the produced NP solution drop





Synthesis of BODIPY-Linked *N*-Heterocyclic Carbene Metal Complexes for Cancer Chemotheranostics and Catalysis Applications

Shraddha SP Yadav,^[a] Ananda Guha Majumdar,^[b, d] Manish Ramesh Shingole,^[c, d] Seemita Banerjee,^[c, d] Mahesh Subramanian,^[b, d] Rohit Singh Chauhan,^{*, [a]} and Soumyaditya Mula^{*, [b, d]}

Fluorescent *N*-heterocyclic carbene (NHC) metal complexes are useful for various chemical and biological applications. In this study, we developed a simple strategy to synthesize BODIPY-linked NHC metal complexes involving Ag, Cu, Ni, and Pd. The synthesis began with the preparation of BODIPY-imidazolium salt as a precursor ligand. This ligand was used to obtain BODIPY-imidazolium silver carbene complex, which subsequently facilitated the syntheses of BODIPY-linked NHC transition metal complexes (Cu, Ni, and Pd) via the transmetalation method. This approach offers a versatile pathway for the synthesis of various other fluorescent carbene metal complexes. The applications of these BODIPY-linked NHC metal complexes were also explored. Chemotherapeutic anti-cancer activity of BODIPY-imidazolium silver carbene complex showed high cancer cell killing efficacy as compared to its precursor ligand. This

outcome confirmed that the attachment of the silver atom is essential to enhance the cytotoxic activities. Additionally, the fluorescence property of the BODIPY moiety is highly useful for cellular imaging, which establishes the silver complex as a potential chemotheranostic agent for cancer management. Furthermore, BODIPY-imidazolium copper carbene complex was explored as a non-noble metal-based catalyst for ammonia borane (AB) hydrolysis to generate hydrogen. This catalytic system was further applied for chemoselective reduction of the aromatic formyl groups in the presence of other reducible functional groups. Overall, this investigation presents a simple and efficient design strategy for the synthesis of different BODIPY-linked metal carbene complexes with potential applications in catalysis, cellular imaging, and cancer therapy.

1. Introduction

N-Heterocyclic carbenes (NHC) are well-known electron-donating ligands that are capable of forming complexes with transition metals as well as main group elements, providing arrays of materials useful for various applications.^[1] NHC metal complexes are generally synthesized by using heterocyclic

scaffolds such as imidazole, thiazole, triazole, benzimidazole, acyclic diamine, etc.^[1] Besides their easy and inexpensive synthesis, NHCs offer ample opportunity to functionalize at the nitrogen atom or carbon backbone of corresponding NHC precursors, enabling to tune their electronic and steric properties.^[2] Leveraging these functionalization flexibilities, organic dyes were previously attached with NHC complexes for their applications in cellular bioimaging,^[3] cancer therapy,^[3] sensing,^[3] photocatalysis,^[3] etc.

In the past few decades, the boron-dipyrromethene (BODIPY) class of dyes has been explored for countless applications.^[4] Superior photophysical and electrochemical properties are the main attractive features of this class of dyes.^[5] BODIPY dyes were also linked with various ligands capable of complexation with transition metals and main group elements to develop a variety of organometallic compounds. These complexes are widely used for photocatalysis, energy harvesting, photodynamic therapy, cellular imaging, etc.^[6] Attachment of different ligands with the BODIPY moiety is sometimes challenging, and also different ligands are required for complexation with different metal ions, which makes the synthetic methodology tedious. In this respect, *N*-heterocyclic carbenes (NHC) act as a universal ligand for various transition metals as well as main group metals. But reports on BODIPY-linked NHC metal complexes are still limited. In the recent past, a few reports were published on syntheses of BODIPY-linked NHC metal complexes and

[a] S. S. Yadav, R. S. Chauhan

Department of Chemistry, K. J. Somaiya College of Science and Commerce, Vidyavihar, Mumbai 400 077, India
E-mail: rohit.chauhan@somaiya.edu

[b] A. Guha Majumdar, M. Subramanian, S. Mula

Bio-Organic Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
E-mail: smula@barc.gov.in

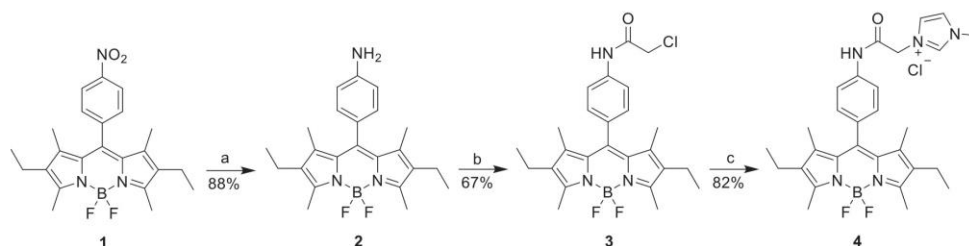
[c] M. R. Shingole, S. Banerjee

Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

[d] A. Guha Majumdar, M. R. Shingole, S. Banerjee, M. Subramanian, S. Mula
Homi Bhabha National Institute, Mumbai 400 094, India

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/asia.202500564>

© 2025 The Author(s). Chemistry - An Asian Journal published by Wiley-VCH GmbH. This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial-NoDerivs License](#), which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.



Scheme 1. Synthesis of BODIPY-imidazolium salt (4). Reaction conditions: a) 10% Pd/C, DCM/EtOH (1:1), 25 °C, 12 h; b) chloroacetyl chloride, DCM, 0–5 °C, 30 min; c) 1-methylimidazole, CH₃CN, reflux, 18 h.

their applications in catalysis, photodynamic and antimicrobial therapy, and chemodosimetry.^[7] In this work, our aim was to develop a new BODIPY-linked NHC ligand that will be useful for synthesizing different metal carbene complexes. This synthetic strategy was anticipated to provide an array of compounds with outstanding properties of both NHCs and BODIPY, useful for various applications. So we developed the synthetic protocol for the synthesis of BODIPY-imidazole-based NHC ligand and its corresponding NHC metal carbene complexes with silver, copper, nickel, and palladium.

The medicinal applications of silver-attached compounds are well documented in the literature.^[8] For instance, silver compounds have been used as antimicrobial agents for centuries.^[9] Also, silver complexes have demonstrated significant anticancer activities with improved pharmacological properties.^[10] But, pharmaceutical research on organometallic NHC-silver complexes is not well explored so far.

Recent studies have shown that NHC-silver complexes exhibit notable anti-cancer activity^[11] with higher efficacy, reduced side effects, and lower resistance development compared to established chemotherapeutic agents like cisplatin, carboplatin, and oxaliplatin.^[12] To the best of our knowledge, BODIPY-linked NHC-silver complexes have not yet been used as chemotherapeutic agents for killing cancers. Fluorescence properties of BODIPY dyes can also be used for cellular imaging, simultaneously to check the accumulation as well as localization of the complex in the tumour cells. Thus, we explored the cellular imaging as well as chemotherapeutic anticancer activities of the synthesized BODIPY-NHC silver complex. Also, anticipating the potential catalytic abilities of BODIPY-NHC transition metal complexes,^[12] their catalytic activities in ammonia borane (AB) hydrolysis to generate hydrogen were investigated towards chemoselective hydrogenation of organic functional groups. All these results are discussed below.

2. Result and Discussion

2.1. Synthesis and Photophysical Properties

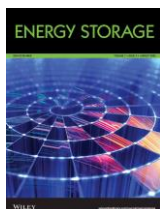
First, BODIPY-imidazolium salt (4) was designed as a versatile precursor for the synthesis of different NHC-metal complexes. The ligand 4 was synthesized in four steps starting from nitro-

BODIPY dye (1), which was synthesized as per the reported protocol (Scheme 1).^[13] Nitro-BODIPY dye (1) was reduced using a Pd-catalyzed hydrogenation reaction to furnish anilino-BODIPY dye (2).^[14] Reaction of chloroacetyl chloride with dye 2 gave chloroacetyl amido-BODIPY (3).^[15] Finally, BODIPY 3 was refluxed with 1-methylimidazole to furnish BODIPY-imidazolium salt (4) in good yield (Scheme 1).

All the compounds were characterized by ¹H and ¹³C NMR spectroscopy as well as by mass spectrometry. In the ¹H NMR spectrum of BODIPY 4, signals for both BODIPY as well as the imidazolium moiety were seen (Figures 1 and S9). For example, aryl protons of the BODIPY core resonated as doublets at 7.82 and 7.31 ppm with two proton integration each. Methyl proton signals were observed as singlets at 2.47 and 1.36 ppm for C3/C5 and C1/C7 protons, respectively. Methyl and methylene protons of the ethyl groups were resonated at 0.99 (triplet) and 2.35 ppm (quartet), respectively. All the aryl protons of the imidazolium moiety appeared as singlets at 9.01, 7.67 and 7.64 ppm which are attributed to the protons at the C2 (NCHN), C5, and C4 positions of the imidazole ring, respectively. The characteristic methyl and methylene protons attached to the imidazolium moiety were resonated as singlets at 3.99 and 5.25 ppm, respectively. The ¹³C NMR spectrum showed 6 aliphatic peaks and 12 aromatic signals with characteristic amide carbonyl resonance at 163.7 ppm and methylene signal at 50.9 ppm (Figure S10). Another signature peak for C2 (NCHN) of imidazolium ring was observed at 137.9 ppm, confirming the presence imidazole moiety in dye 4.^[16] The imidazolium salt is highly colored, strongly fluorescent and highly stable in both air and moisture, remaining stable in both the solid state and in solution.

The BODIPY-imidazolium salt (4) was utilized to synthesize the NHC-silver metal complex. One common approach for synthesizing NHC silver complexes involves the reaction of imidazolium salts with a silver source like Ag₂O, resulting in strong silver-carbon bonds.^[17] A similar approach was taken in our case, and the reaction of BODIPY-imidazolium salt (4) with Ag₂O in dichloromethane at room temperature furnished BODIPY-imidazolium silver complex (5) in a very good yield (70%) (Scheme 2). The conversion was confirmed by the NMR spectroscopy. The ¹H NMR spectrum of complex (5) showed an upfield shift in C-4 and C-5 proton signals of the imidazole rings (Figures 1 and S11). Additionally, the absence of a downfield NCHN signal in the ¹H NMR spectrum confirmed the successful





Energy Storage

11

WILEY

ENERGY STORAGE

SPECIAL ISSUE ARTICLE OPEN ACCESS

Unveiling Calcium-Decorated Psi-Graphene as a High-Capacity Hydrogen Storage Material: A First-Principles Investigation

Sruthi Thulaseedharan Jayasree¹ | Afsal S. Shajahan^{1,2} | Nandakumar Kalarikkal^{1,3} | Brahmananda Chakraborty^{2,4}

¹School of Pure & Applied Physics, Mahatma Gandhi University, Kottayam, India | ²High Pressure & Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Mumbai, India | ³International and Inter University Centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, Kottayam, India | ⁴Homi Bhabha National Institute, Mumbai, India

Correspondence: Brahmananda Chakraborty (brahma@barc.gov.in)

Received: 31 October 2024 | Revised: 14 June 2025 | Accepted: 2 July 2025

Funding: The authors received no specific funding for this work.

ABSTRACT

Our work investigates the potential of Ca-decorated Psi-Graphene for efficient hydrogen storage using first-principles electronic structure calculations and ab initio molecular dynamics simulations. The system exhibits an exceptional storage capacity of 13.44 wt% by adsorbing up to 82 H₂ molecules in a fully Ca loaded Psi-Graphene unit cell, significantly exceeding the Department of Energy (DOE) target. The last four hydrogen molecules of each single Ca atom have low binding energies under GGA approximation due to the only presence of Vander Waals interactions. The uniform binding energy of ~0.232 eV (under the GGA approximation) surpasses other Ca-decorated materials, attributed to H₂ polarization, hybridization of Ca 3d empty orbitals with H₂ σ orbitals, and the non-symmetric nature of Psi-Graphene. Additionally, strong Ca-substrate binding (~1.95 eV/atom) ensures system stability, as confirmed by density of states (DOS), projected density of states (PDOS), and Bader charge analysis. We have also performed Nudged Elastic Band (NEB) analysis to confirm that our system is not prone to metal clustering. The non-magnetic nature of isolated Ca and Psi-Graphene maintains a zero magnetic moment throughout the adsorption process. Ab initio molecular dynamics simulations further validate the thermal stability of the system up to 500 K. Using Van't Hoff equation, the desorption temperature falls within the range of 334.16–364.79 K between 5 and 12 bar pressure. These findings establish that Ca-decorated Psi-Graphene is a highly promising candidate for hydrogen storage applications.

1 | Introduction

Hydrogen as a clean and renewable fuel is increasingly studied for the potential replacement of depleting fossil fuels. Devastating environmental impacts like the greenhouse gas effect and climatic change are the outcomes of using fossil fuels. Hydrogen provides opportunities but is yet to emerge as a practical energy source. Most transportation runs in this economic era by gasoline. Vehicles working on electrical charge are now using as a temporary solution for meeting the deficiency and environmental impact of fossil fuels [1]. But they require some fossil fuel

for their electric charge production. Fuel cell vehicles (FCV) working by the intake of hydrogen does not require any use of fossil fuel; therefore, they would be a good alternative solution.

The benefits of a hydrogen economy include the release of water as a byproduct, the prevention of oil spills, the elimination of greenhouse emissions, the ability to address climate change, and lastly, a reduced reliance on foreign oil supplies from an economic standpoint [1–3]. Being the lightest, non-polluting, and most abundant element in nature, it enables energy security and have the highest energy density by weight of all common

This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial-NoDerivs](https://creativecommons.org/licenses/by-nc-nd/4.0/) License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

© 2025 The Author(s). *Energy Storage* published by John Wiley & Sons Ltd.

fuels. Hydrogen is a superior contender for fuel cell applications due to its wide flammability, low ignition energy, high air diffusivity, and significantly faster flame velocity than conventional gasoline [3, 4].

Hydrogen storage for mobile applications is the most difficult hurdle than that for stationary use. The major crisis includes low energy density by volume and high diffusivity in air, which makes it very fast to disperse off on any leakage [4]. High volumetric and gravimetric capacities are required for using as a fuel in mobile applications. By realizing the urge and research need for the transition to a hydrogen economy, in 2003, the US Department of Energy (DOE) released a target for hydrogen storage systems [5–8]. The DOE standards consider the volumetric and gravimetric capacities, refueling time, costs, cycle life, loss of usable hydrogen, safety, and efficiency. Even though tremendous research has been done on hydrogen storage, till now, we have a long way to go for “ideal” hydrogen storage material.

Conventional mechanical storage methods include compressed gas and cryogenic cooling. Now it has been improved to combined cryo-compression. Hydrogen should be kept for mobile applications in compact, lightweight systems that are strengthened to prevent explosion during collision. Since hydrogen has a volumetric capacity that is 3000 times smaller than that of gasoline due to its low energy density by volume [9–11]. Being the smallest molecule, hydrogen gas is highly diffuse and buoyant. Highly compressed hydrogen gas explodes violently when brought in contact with air [4]. The requirement of a high compression ratio questions the safety of storage and the integrity of the tank. High diffusivity and hydrogen embrittlement limit the weight of the tank to be high. This creates a crisis for the use of compressed gas storage. Energy density by volume could be doubled in liquid hydrogen storage as compared to compressed gas. The strong repulsive interaction between hydrogen brings its critical temperature to a low value of 33 K [12]. Because of the low critical temperature, liquid hydrogen can be stored in open systems. Generally, at room temperature, hydrogen warms up on expansion. Therefore, for cooling during expansion, the temperature should be below its inversion temperature of 202 K [12]. This limits its application as the liquefaction process is highly energy consuming and boil-off losses are very severe. Liquid hydrogen gains heat from the surrounding through a slow process and gets converted into gas. To avoid this, the pressure vessels should be insulated, which makes them heavier than compressed gas vessels. The volumetric ratio is less than that of gasoline and evaporates quickly on delivery and refueling time [1].

In solid state hydrogen storage methods, hydrogen combines with some materials, either chemically or physically, to give hydrides or to get molecular hydrogen adsorbed on the solid surface. Hydrogen can be obtained either through thermal simulation or by some other techniques. In a subject viewpoint, important parameters to consider in solid state hydrogen storage are that hydrogen contents in the solid should be high, pressure and temperature of hydrogenation and dehydration should be considered, hydrogen adsorption and dehydration properties should be studied, and kinetics of the reaction are also important [4]. The DOE criteria for hydrogen storage in solid state includes. (1) It should be able to hold at least 6.5% of its weight in hydrogen. (2) The hydrogen molecule should have a binding

energy in the range of 0.2–0.7 eV with the substrate [13–15]. Another crucial factor is the reversibility of uptake and release. Metal hydrides and complex hydrides are examples of materials for storing hydrogen that are chemically bonded. Even though both are safe methods, they have some disadvantages, such as metal hydrides forms metal oxide at the surface and acting as a barrier for hydrogen storage; the activation should be considered during the design of the tank system, as it is sensitive to air contamination [6]. Complex hydrides have a high hydrogen storing capacity. It is called “one-pass” hydrogen storage as hydrogen evolves upon contact with water. The main limitations of complex hydrides are that the desorption temperature is very high, the kinetic barrier for hydrogenation and dehydrogenation is high, and well knowledge about the atomic structure and thermodynamics of it is required [6]. Special equipment is needed for handling it due to its hygroscopic nature. The requirement of moisture-free inert atmosphere also counts as one disadvantage. Physisorption is a surface phenomenon. The major selection criteria for such materials are that they should have a high surface area, pore geometry, and pore volume are important criteria for their selection; the rate of hydrogen release must be high; they should have excellent cyclability; and also, materials should not change during adsorption and desorption. MOFs, zeolites, and carbon nanomaterials [16] are some used as physisorption material mediums for hydrogen storage. The main problem regarding MOFs is that the weight percentage is low at room temperature, with a need for cryogenic temperature and is highly sensitive to temperature and synthetic procedure [6]. The gravimetric capacity is low for zeolites. Also, the need for cryogenic temperature and the presence of cationic centers have a meager effect on hydrogen storage capacity [6].

The unique properties of some carbon allotropes make it an excellent area for research on hydrogen storage. Numerous distinctive allotropes of carbon, such as 0-D, C60, fullerene, 1-D CNT and nanoribbon, 2-D graphene, 3-D graphite, and so forth, can emerge from carbon forming sp, sp², and sp³ hybridization. A possible reversible hydrogen storage material is graphene-based structures. Its large specific area, fast kinetics, reversibility, chemical inertness, low weight, low price, and safety make it a good candidate. Graphene is the most stable carbon allotrope and is attracted due to its massless Dirac fermions and quantum Hall effect [17, 18]. The clear advantage of 2-D structures in hydrogen storage is the double side utilization. It could assist the hydrogen uptake by underling surface modifications. The binding energy between that of chemisorption and physisorption resulted in total reversibility at ambient conditions.

Psi-Graphene, a recent theoretically predicted 2-D allotrope of carbon, can be viewed as a disordered graphene layer with parallel aligned pentagonal and heptagonal rings of carbon atoms in a line which are separated by hexagons with one atom thickness [18]. It is made by polymerizing the carbon skeletons of s-indacene to produce rings with numbers 5, 6, and 7 [18, 19]. Psi-Graphene has been found to have lattice constants of $a = 6.70$ Å and $b = 4.84$ Å with 12 carbons per unit cell and P2mg planar symmetry [18]. Ψ -Graphene is metallic and is robust against external strain. It has the lowest energy and low diffusion energy barrier compared to 2-D carbon allotropes composed 5, 6, and 7 carbon rings [19]. It is reported that if the number of hexagonal rings is increased, then the thermal stability will enhance.





RESEARCH ARTICLE

ADVANCED
ENERGY & SUSTAINABILITY
RESEARCH

www.advenersystres.com

Tannic Acid Intercalated Tb Doped Graphene Oxide Layer: A Multifunctional Hybrid Photothermal Structure for Solar Energy Driven Water Purification, Power Generation, and Disinfection

Subhash Sarkar, Hirakendu Basu,* Amarnath Marimuthu, Sudeshna Saha, Rishu Bhati, Pallavi Chandwadkar, Celin Acharya, Sangita D. Kumar, and Chandra Nath Patra

The development of solar energy-driven multifunctional photothermal materials represents a key step toward bridging energy harvesting with environmental sustainability initiatives. Herein, a tactically designed tannic acid intercalated, terbium-doped graphene oxide (TA-Tb³⁺-GO) framework is presented. This framework demonstrates synergistic photothermal conversion and a permeable structure that facilitates proficient capillary action, permitting rapid water transmission and steam discharge. Surface temperature of the optimized TA-Tb³⁺-GO framework reaches over 60 °C within 5 min of exposure to 1 Sun, highlighting its potential as an effective a solar water purifier. It achieves an interfacial water evaporation rate of 1.4 kg m⁻² h⁻¹ under 1 Sun illumination, with of 98% conversion efficiency. Its cell viability tests reveal potential antimicrobial efficacy, successfully killing both Gram-positive and Gram-negative bacteria, suggesting its prospective for photothermal therapy. Moreover, when integrated with a commercial thermoelectric unit, the TA-Tb³⁺-GO framework exhibits exceptional photothermoelectric generation efficiency with an achieved power density of 5.8 Wm⁻², demonstrating its potential for electrical power generation. In summary, the framework's tremendous stability, lack of photoinduced leaching, ability to yield clean water out of seawater, antimicrobial features, and reutilization make TA-Tb³⁺-GO an archetype for sustainable freshwater and power production applications.

1. Introduction

Water and energy are crucial for sustaining life, fostering economic growth, and advancing society. The Earth's capacity to support civilization could face substantial challenges in the coming decades, particularly concerning the critical resources of clean water and electricity. Current technologies often struggle to provide sustainable, long-term solutions. Attempts to mitigate water scarcity can exacerbate energy challenges, and efforts to enhance water accessibility sometimes lead to environmental degradation.^[1] Consequently, significant initiatives have been directed toward developing green technologies to ensure clean water supplies. A promising approach to addressing water scarcity without harming the environment is solar-powered photothermal water evaporation by harnessing sunlight as a sustainable power source. However, traditional methods of heating water face limitations due to their low efficiency in converting solar energy, primarily

S. Sarkar
Radiation and Photochemistry Division
Bhabha Atomic Research Centre
Trombay, Mumbai 400085, India

H. Basu, S. Saha, S. D. Kumar, C. N. Patra
Analytical Chemistry Division
Bhabha Atomic Research Centre
Trombay, Mumbai 400085, India
E-mail: hirak@barc.gov.in

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/aesr.202500228>.

© 2025 The Author(s). Advanced Energy and Sustainability Research published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/aesr.202500228

H. Basu, R. Bhati, C. Acharya, S. D. Kumar, C. N. Patra
Homi Bhabha National Institute
Anushaktinagar, Mumbai 400094, India

A. Marimuthu
Plasma Research Laboratory
The Bombay Textile Research Association
Ghatkopar (W), Mumbai 400086, India

P. Chandwadkar, C. Acharya
Molecular Biology Division
Bhabha Atomic Research Centre
Trombay, Mumbai 400085, India

because of water's poor absorption of sunlight and significant heat loss in bulk systems.^[2] The development of nanostructured materials designed for enhanced solar absorption has reignited interest in solar-driven water evaporation technology. This renewed focus is fueled by growing concerns over environmental sustainability and the urgent need for energy conservation.^[3]

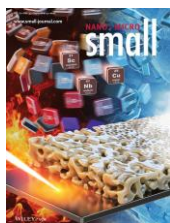
Developing photothermal materials requires precise engineering of their optical and thermal properties to achieve efficient light absorption, heat generation, and thermal stability. Recent advancements have focused on enhancing their effectiveness, durability, and versatility through innovative material designs, nanostructuring techniques, and functionalization strategies.^[4] The pursuit of superior photothermal capabilities has shifted toward nanoenabled materials, which exhibit unique thermal and optical properties. Solar electromagnetic radiation spans a wavelength range of 280–2500 nm, and different light-responsive thermal materials absorb specific wavelength regions based on their electronic energy levels or bandgap.^[5] This characteristic promotes optimal light energy conversion into heat energy. The principle of interfacial heating has significantly enhanced the efficiency of evaporation systems by using nanomaterials as efficient solar absorbers. By incorporating these solar absorber materials onto the water's surface, interfacial heating systems preserve thermal energy at the air-water junction, minimizing thermal dissipation to the bulk water.^[6] Furthermore, integrating waste heat conversion mechanisms into the design can generate electricity, highlighting the multifunctionality of well-designed nanoenabled photothermal materials in pathogen elimination and wastewater purification. Advances in layered materials and nanomaterials with semiconductor properties have expanded the active absorption range across the radiation spectrum, thereby improving photothermal evaporation efficiency. Metal oxide semiconductors and metal-doped 2D structures have been engineered to serve as photonabsorbing materials for solar distillation, leveraging electronic excitations within semiconductor band structures.^[7,8] This study focuses on synthesizing engineered nanomaterials, particularly transition metal or lanthanide-doped functionalized graphene oxide frameworks, to enhance photothermal effects. Within the group of carbon derivatives, graphene oxide (GO) and reduced graphene oxide (rGO) are especially significant. GO consists of a single layer of carbon atoms structured in a hexagonal pattern, featuring delocalized π electrons.^[9,10] The Hummer's method, which involves oxidizing graphite with a strong acidic solution under controlled conditions, is commonly used to produce GO.^[11] Mechanical treatment and water intercalation then modify the sheets, altering the original honeycomb structure and creating a network of hybridized carbon atoms with oxygen groups such as carboxy, epoxy, and hydroxy groups. Doping metal ions, particularly transition metals or lanthanides, onto the GO layers has proven effective in tuning the band structure to take in the full spectrum of sunlight, thereby enhancing the efficiency and effectiveness of the doped structure.^[12] However, finding a suitable dopant and determining its optimal composition remains a challenge. Doped GO can increase the density of mobile charge carriers throughout the photon absorption layer, which simultaneously activates thermal vibrations within the framework of the semiconductor lattice. This, in turn, enriches the activation between the π orbitals in GO, maximizing the heat conversion process. Moreover, the wavelength regions with low solar absorption can be further enhanced by incorporating an organic compound or

ligand.^[13] Tannic acid (TA), a naturally occurring light-sensitive compound, captures photons and releases energy into the nearby area. As a member of the polyphenol family, TA is low-cost, easy to manufacture, and nontoxic, making it a desirable material for environmentally friendly solutions.^[14] It may not be feasible to optimally use the wide electromagnetic spectrum for photothermal conversion using solely organic nanostructures. The multicomponent hybrid approach involving a GO 2D structure with an inorganic dopant and an organic molecule can therefore be very effective.^[15,16]

Breakthroughs in photoactive materials, thermal performance optimization at air-water interfaces, coupled with novel surface floating designs, can substantially elevate the complete competence of solar distillation for purification and sewage water management.^[17–19] In accordance with the arrangement of the material, it often exhibits exceptional antibacterial performance, rendering it a prime candidate for solar distillation processes. Nanomaterial-inspired light therapies have been demonstrated to be an extremely effective method for eliminating bacterial pathogens. When exposed to solar illumination, photothermal nanomaterials generate heat through the photothermal effect, which increases the degradation of microbial cell envelopes. This thermal effect results in the denaturation of proteins and the breakdown of bacterial cell structure.^[20] Low-dimensional structures with well-organized light-to-heat conversion properties offer advantages, such as minimal invasiveness, remote controllability, and high efficiency in killing bacteria. Specifically designed nanomaterials with photothermal capabilities can serve dual purposes: simultaneously purifying wastewater through evaporation and distillation while eliminating pathogens. Although few materials currently exhibit these dual functionalities, they represent promising innovations in the field of nanotechnology.^[21–25] A significant alternative application is leveraging the heat produced for electricity generation via the photothermoelectric (PTE) effect by integrating this material through a thermoelectric device. In contrast to technologies that produce electric energy using photovoltaics modules, solar thermoelectric generators (STEGs) offer the exclusive benefit of being solid state devices, making them suitable as portable power generators. Unlike photovoltaics, STEGs utilize the extensive solar spectrum (300–2500 nm). STEGs generate electrical energy based on the Seebeck effect, which is driven by the temperature difference (ΔT). To enhance performance, TEG modules focus on increasing ΔT via efficient photon-to-thermal conversion.^[26] An effective photothermal framework can alter the inherent temperature at the hot end of a TEG. A well-designed nanoenabled material offers multifunctionality, purifying wastewater, killing pathogens, and generating power through waste heat-to-electricity conversion.^[27] Versatile capabilities in a single material are crucial for developing efficient photothermal systems. For potable water production, a framework combining interfacial water evaporation and disinfection, along with solar energy conversion, can power nearby facilities, while 2D materials and nanosemiconductors enhance solar evaporation by absorbing a broad solar spectrum.^[28,29]

In our current work, we have developed a multifunctional photothermal network, Tb³⁺ doped GO intercalated with TA and for the investigation of its photothermal properties. TA, a naturally occurring polyphenol, was selected for its excellent chelating ability, photothermal responsiveness, and inherent antimicrobial





RESEARCH ARTICLE

NANO · MICRO
small
www.small-journal.com

Effect of Halide Variations on Cation Dynamics in MAPbX₃ (X = Cl, Br, and I)

Veerendra K. Sharma,* Ashutosh Mohanty, Victoria García Sakai, Madhusudan Tyagi, and D. D. Sarma

We investigate the temperature-dependent dynamics of methylammonium (MA) cations in MAPbCl₃ across all crystallographic phases. We identify two distinct motions: i) a threefold rotation around the C–N axis in the orthorhombic phase, with an activation energy of 16 meV, and ii) a fourfold rotation of the entire-molecule in the tetragonal/cubic phase, with an activation energy of 60 meV. To explore the halide effects, we compare MAPbCl₃ with MAPbBr₃ and MAPbI₃, revealing a strong correlation between rotational motion and halide composition. The onset of the threefold rotation in MAPbCl₃ spans a broader temperature range than in MAPbBr₃ and MAPbI₃ due to persistent octahedral distortions and Pb–Cl bond variations. Additionally, MAPbCl₃ exhibits a sharp transition in elastic intensity at the tetragonal-to-cubic phase transition, absent in MAPbBr₃ and MAPbI₃. A comparative analysis of activation energies and onset temperatures for the threefold rotation reveals a distinct trend: MAPbI₃ > MAPbBr₃ > MAPbCl₃. This aligns with the decreasing ionic radius from I[−] to Cl[−], reducing steric constraints and enhancing MA⁺ rotational freedom. The pronounced octahedral distortions in MAPbCl₃ create a more flexible framework, enabling facile cation reorientation and multiple rotational configurations even at lower temperatures, leading to a lower onset temperature and activation energy.

1. Introduction

The evolution of hybrid halide perovskite research, from early studies with limited fundamental understanding^[1] to recent advances^[2,3] which have enabled achieving attractive power conversion efficiencies, has invigorated this field of research. One of the most significant achievements in perovskite research is achieving the enhanced structural flexibility and improved stability of these materials, enabled by appropriate compositional tuning.^[4–6] The perovskite structure with chemical formula ABX₃ is shown in Figure 1, where the choice and combination^[6] of organic cations (A = MA⁺, FA⁺), inorganic cation (B = Pb²⁺, Sn²⁺), and halide anions (X = Cl[−], Br[−], and I[−]) can be used to improve stability and tailor optoelectronic properties. Structurally, all MAPbX₃ perovskites exhibit a high temperature cubic (*Pm-3m*) phase,^[7–9] an intermediate tetragonal phase (either *P4/mmm* or *I4/mcm*)^[7–9]

V. K. Sharma
Solid State Physics Division
Bhabha Atomic Research Centre
Mumbai 400085, India
E-mail: sharmavk@barc.gov.in

V. K. Sharma
Homi Bhabha National Institute
Anushaktinagar
Mumbai 400094, India

A. Mohanty, D. D. Sarma
Solid State and Structural Chemistry Unit
Indian Institute of Science
Bengaluru 560012, India

A. Mohanty
Department of Education
Indian Institute of Technology Kharagpur
Kharagpur 721302, India

V. G. Sakai
ISIS Pulsed Neutron and Muon Facility
Science and Technology Facilities Council
Rutherford Appleton Laboratory
Didcot OX11 0QX, UK

M. Tyagi
National Institute of Standards and Technology
Center for Neutron Research
Gaithersburg MD 20899, USA

M. Tyagi
Department of Materials Science and Engineering
University of Maryland
College Park, MD 20742, USA

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/smll.202504054>

© 2025 The Author(s). Small published by Wiley-VCH GmbH. This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial-NoDerivs](https://creativecommons.org/licenses/by-nc-nd/4.0/) License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

DOI: 10.1002/smll.202504054

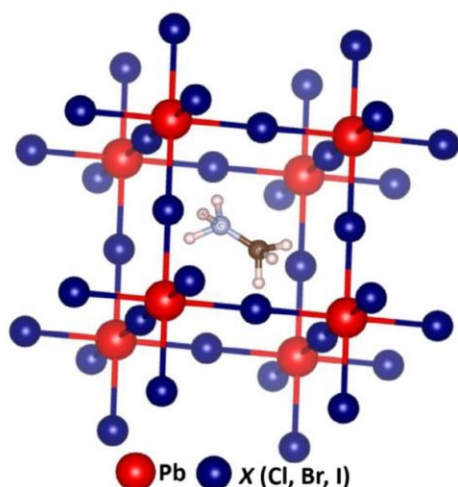


Figure 1. Representative structure of MAPbX₃ (X = Cl, Br, and I) in the cubic phase, where the methylammonium (MA) cation occupies the A-site, surrounded by corner-sharing PbX₆ octahedral units.

and a low temperature ordered orthorhombic phase (*Pnma*)^[10–12] However, MAPbBr₃ is an exception, exhibiting both intermediate tetragonal phases that is, *P4/mmm* and *I4/mcm*. Specifically, MAPbBr₃ undergoes a sequence of transitions: from orthorhombic (*Pnma*) to tetragonal-I (*P4/mmm*) at 147 K, followed by a transition to tetragonal-II (*I4/mcm*) at ≈155 K, before transforming into the cubic phase (*Pm-3m*) near 237 K.^[13] A comparison of phase transitions and their corresponding temperatures for different MAPbX₃ (X = Cl[−], Br[−], and I[−]) is summarized in Table 1. The optical band gap of these materials increases from 1.56 eV for iodides to 2.9 eV for chlorides.^[14–16] For this reason, Br- and Cl-based perovskite materials are in strong demand for light-emitting diodes, lasers and photodetectors.^[17–19] In addition to this, the incorporation of chloride into the lattice leads to higher structural stability of the perovskite scaffold^[20,21] and can aid in defect passivation,^[22] helping to mitigate the inherent deep trap states that can occur.^[23]

The interaction between the MA cation and the inorganic framework of PbX₆ octahedra plays a crucial role in dictating the electronic, thermal, and mechanical properties of these materials.^[24–26] In addition to this, the coupling between the reorientation dynamics of organic cations and the inorganic lattice significantly influences the electronic and transport properties.^[27–29] The MA cations interact with the inor-

ganic framework through H-bonding as well as via their large dipole moments.^[26] Several studies show that the successive temperature-dependent phase transitions in MAPbX₃ are associated with various structural changes linked to the orientation of the MA ion within the PbX₆ cage.^[30,31,24] Moreover, the orientational degrees of freedom of MA in MAPbX₃ are also reported to influence carrier diffusion lengths^[32–34] and hot carrier cooling timescales under photo-excitation.^[35] The molecular rotations of the A-site cations can induce distortions in the PbX₆ octahedral framework, leading to dynamic modifications in the band structure and significant phonon scattering. These phenomena play key roles in slowing carrier recombination, ultimately enhancing photovoltaic efficiency^[36] and drastically reducing thermal conductivity.^[26] Other investigations on similar aspects report that MA dipoles have rotational degrees of freedom at room temperature (RT), but reorientations freeze as they undergo a phase transition at low temperature.^[7,37–40] These findings emphasize the critical role of cation rotational motions in shaping the fundamental properties of hybrid organic–inorganic perovskites (HOIPs) materials and underscore the necessity of exploring this intriguing aspect of HOIPs to fully understand and optimize their performance.

Quasielastic neutron scattering (QENS) is a powerful technique for probing molecular dynamics in condensed matter systems at timescales from nanoseconds to picoseconds.^[41] QENS is particularly well-suited for studying cation dynamics in HOIPs as the hydrogen atoms within the organic cation are readily detectable due to their higher neutron scattering cross-section. This technique provides precise quantitative insights into characteristic correlation times and activation energies of dynamic processes but also sheds invaluable light on the geometrical mechanisms and spatial scales governing molecular motion. Extensive studies describing the dynamics of MA cations in MAPbI₃^[39,42–45] and MAPbBr₃^[46–48] have been reported but no general consensus has been reached on the exact mechanism that dictates molecular motion in these systems. For example, studies^[43,45] suggest that in the orthorhombic phase, the MA cation exclusively undergoes a threefold rotation around its C–N axis. At the orthorhombic-to-tetragonal phase transition, an additional fourfold reorientational motion of the entire MA molecule, mediated by the rotation of the C–N axis itself, is activated. Notably, the characteristic relaxation time associated with this threefold rotation exhibits a sharp decrease at the transition and becomes significantly faster.^[43,45] However, another study reported that even in the low-temperature orthorhombic phase, both three and fourfold rotations coexist, with no significant changes in cation dynamics across the orthorhombic-to-tetragonal phase transition.^[44] A different mechanism altogether was proposed by Li et al.,^[42] suggesting that in the orthorhombic phase, only the CH₃ group

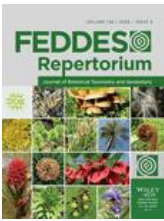
Table 1. Comparison of phase transition temperatures for the perovskite family MAPbX₃ (X = Cl, Br, and I).

Compound	Transition temperature [K]		
	Orthorhombic-tetragonal	Tetragonal-tetragonal	Tetragonal-cubic
MAPbCl ₃	173 K	NA	179 K
MAPbBr ₃	147 K	155 K	237 K
MAPbI ₃	162 K	NA	330 K



Scan the QR Code or Click for full text





RESEARCH ARTICLE OPEN ACCESS

Garcinia kusumae (Clusiaceae): A New Species From Assam, India

Jatindra Sarma¹ | Hussain A. Barbhuiya² 

¹State Expert Appraisal Committee, Assam, Ministry of Environment, Forest and Climate Change, Govt. of India, Guwahati, Assam, India | ²Landscape and Cosmetic Maintenance Section, Architectural and Structural Engineering Division, Bhabha Atomic Research Centre, Mumbai, Maharashtra, India

Correspondence: Hussain A. Barbhuiya (hahmed@barc.gov.in)

Received: 27 May 2025 | **Revised:** 25 June 2025 | **Accepted:** 27 June 2025

Funding: This work was conducted without any external funding support.

Keywords: Clusiaceae | *Garcinia* section *Brindonia* | new species | Northeast India

ABSTRACT

A new species, *Garcinia kusumae* (Clusiaceae), is described and illustrated from Assam, India. Detailed comparisons with morphologically similar species are provided to support its novelty. This discovery contributes to the underexplored diversity of *Garcinia* in Northeast India and highlights the importance of continued botanical exploration in the region.

1 | Introduction

Garcinia L. is the largest genus in the family Clusiaceae, comprising about 414 species of shrubs and trees (POWO 2025). It is pantropically distributed, with centers of diversity in Africa/Madagascar, Australasia, and Southeast Asia. The genus is notable for its remarkable floral diversity, frequent occurrence in lowland tropical rainforests worldwide, and significant pharmacological potential (Gaudeul et al. 2024). In India, the genus *Garcinia* is represented by 33 species and seven varieties (Mohan et al. 2023), while the state of Assam harbors 12 species and three varieties (Kanjilal et al. 1934; Sarma et al. 2016; Begum 2017; Shameer et al. 2021).

2 | Materials and Methods

While documenting species of the genus *Garcinia* in Assam, India, the first author encountered an undescribed taxon exhibiting distinct morphological characters not attributable to any known species. Specimens were collected following standard herbarium practices, including pressing, drying, and preservation (Jain and Rao 1977).

Morphological observations and measurements were conducted using a stereo zoom microscope and digital calipers. Comparative analysis was carried out with the aid of relevant literature, including regional floras, taxonomic revisions, and original species descriptions (Anderson 1874; Kurz 1877; Kanjilal et al. 1934; Maheshwari 1964; Long 1984; Singh 1993; Srivastava 1994; Mohan et al. 2023). Digital images of type material of closely related species were examined from major herbaria, accessed through online databases.

The new species described here is in accordance with the guidelines of the International Code of Nomenclature for algae, fungi, and plants (Turland et al. 2018). The holotype and paratype are deposited at HBARC (Thiers 2025) for future reference. Photographic documentation was undertaken both in situ and under controlled conditions to capture diagnostic features.

3 | Taxonomic Account

Garcinia kusumae J. Sarma & Barbhuiya sp. nov. (Figures 1 and 2).

This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial-NoDerivs](https://creativecommons.org/licenses/by-nc-nd/4.0/) License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

© 2025 The Author(s). *Feddes Repertorium* published by Wiley-VCH GmbH.

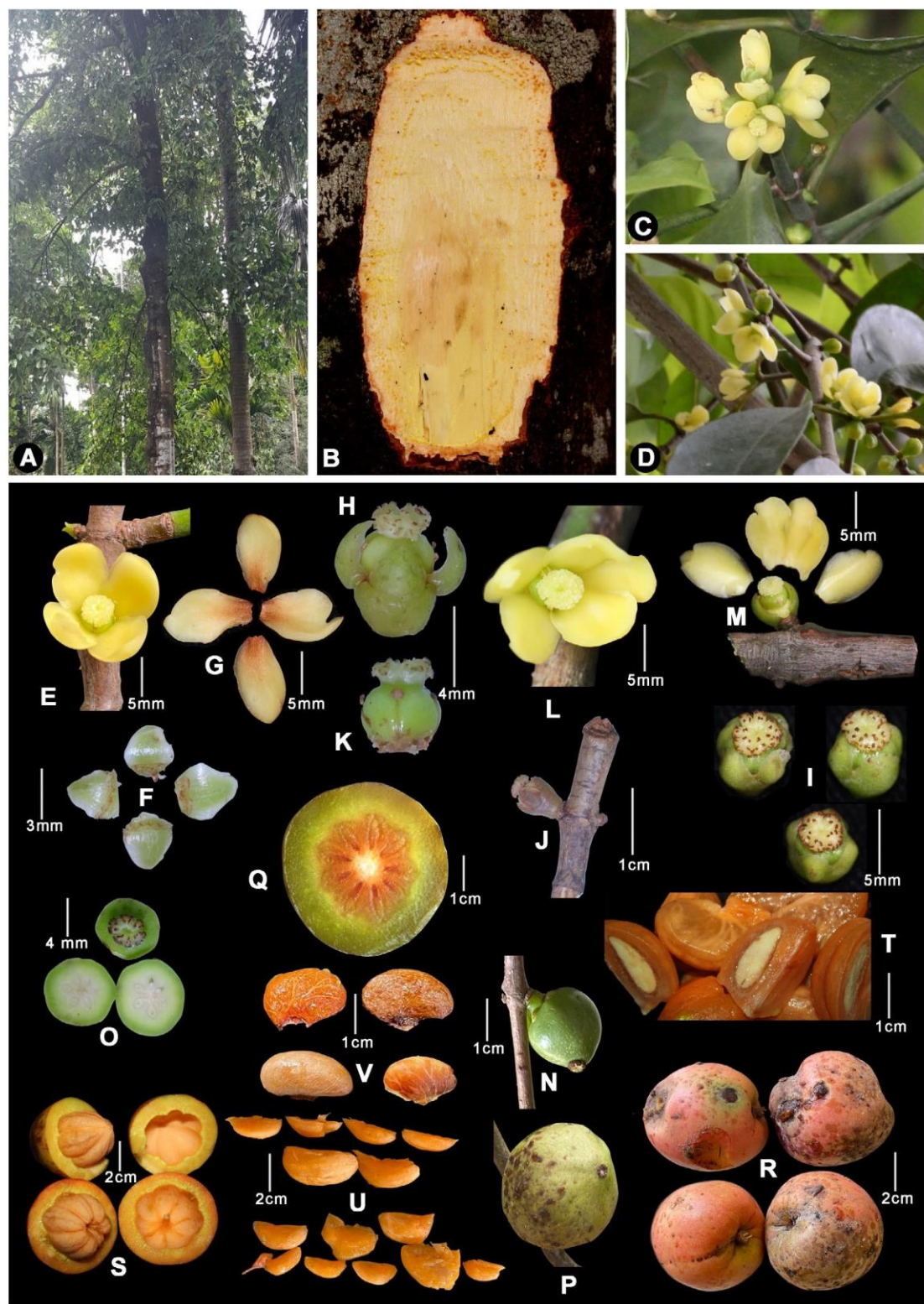
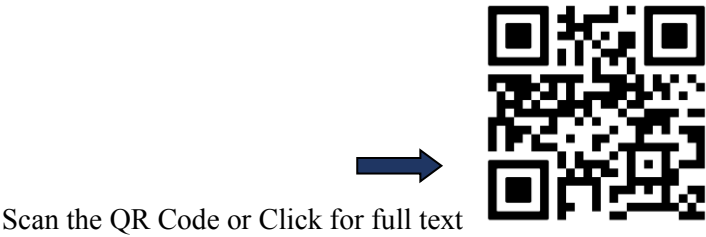
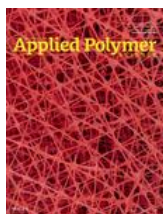


FIGURE 1 | Legend on next page.





RESEARCH ARTICLE OPEN ACCESS

Efficient and Fast Microplastic Separation From Aqueous Media by Electron Beam Assisted Developed Superhydrophobic Jute Fabric

Atanu Jha^{1,2} | Amol Thite³ | Subhendu Ray Chowdhury^{1,2}

¹Homi Bhabha National Institute, Mumbai, India | ²Radiation Technology Development Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India | ³The Bombay Textile Research Association, Mumbai, India

Correspondence: Subhendu Ray Chowdhury (rcsubhendu@gmail.com; rcsubhen@barc.gov.in)

Received: 22 March 2025 | **Revised:** 30 May 2025 | **Accepted:** 19 June 2025

Funding: This work was supported by the Bhabha Atomic Research Centre.

Keywords: applications | functionalization of polymers | grafting | irradiation | separation techniques

ABSTRACT

The accumulation of microplastics (MPs) in various aquatic environments is an alarming problem in the modern world. Hydrophobic surfaces are potential candidates to remove microplastics from water. This work reports the development of a superhydrophobic jute fabric by electron beam radiation-assisted chemical modification. The required extent of modification for the generation of superhydrophobicity is determined to be ~35 wt%, by varying surface wettability with the degree of modification. Study of tensile testing and surface morphology reveals no alteration of the basic structure and properties of the fabric after modification. The modified jute fabric is then employed for separating some common MPs from water and the successful removal of MPs has been demonstrated. The separation has been tried without solvents and with organic solvents. In the separation process, different organic solvents are found to facilitate the separation of MPs from water with a greater efficiency than the removal of MPs from the aqueous system without oil. In the presence of an oily solvent phase, instantaneous and highly efficient (> 95%) separation of MPs from water is demonstrated, as the MPs are accumulated in the organic phase. The modified jute fabric is found to be satisfactorily reusable for up to 30 using cycles. This simple, one-step, environment-friendly process of preparation of superhydrophobic jute and its successful application in separating MPs from water may be a sustainable solution for microplastic-related environmental issues.

1 | Introduction

Microplastics (MPs) are observed to be one of the most emerging pollutants of recent times. MPs are particulate objects with very small sizes (less than 1 mm), produced from partial degradation, weathering, recycling, processing, grinding, and sizing of plastics [1]. These pollutants are generated at various polymer processing industries, industrial effluent treatment plants, and dumping grounds. These MPs then diffuse to water bodies and persist for hundreds of years due to their non-biodegradable nature [2, 3]. MPs are found in freshwater,

lake water, rivers, seas, sewage drains, etc. Because of hydrophobicity and large surface area to volume ratio, the surface of MPs supports the adsorption of various pollutants namely toxic metals and hazardous organic chemicals [3, 4]. These MPs all over the world have created alarming situations due to their negative impact on the aquatic environment and human health. MPs have been spotted in the human body and unfortunately, on human blood as well in a recent finding. MPs can enter the human body through inhalation, ingestion, or through the open skin, causing cytotoxicity, disruption of the immune system, or even neurotoxicity, among other adverse

This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial License](#), which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

© 2025 The Author(s). *Journal of Applied Polymer Science* published by Wiley Periodicals LLC.

effects [5–7]. Accumulations of microplastics (MPs) in various water bodies and their adverse effects have recently gained significant attention. Scientific communities have developed various technologies to remove MPs from water. Widely used technologies for MPs separation are, membrane separation processes, electro-coagulation, photocatalysis, flocculation and air flotation-based separation [7–10]. However, these conventional techniques are not very efficient and require other additional techniques to achieve complete removal of MPs. Very fine MPs are not always been successfully removed by these methods [2, 11]. Sorption-based separation is found to be the easiest, efficient, cost-effective, and reliable option for separating MPs from aqueous media [2, 4, 12].

Because of easy availability, low cost, biodegradability, good mechanical properties, excellent design flexibility, and high volume-to-weight ratio jute fabric is one of the most promising natural sorbent materials [13–16]. It has been of significant interest to researchers and technologists due to increased environmental consciousness and exploration of newer applications using this material [17, 18]. There are some reports on removal of MPs by hydrophobic surfaces [3, 12, 19]. As surface of polyolefin is hydrophobic, i.e., of low surface energy; as it consists of long chain hydrocarbons which are of low surface energy [20]. Jute fabric has been superhydrophobically modified by various methods in the last few years. For example, superhydrophobicity is rendered to jute fabric by dip coating in tetraethyl-orthosilicate/hexadecyl trimethoxy silane (TEOS/HDTMS) [21]. Nawab et al., have hydrophobically modified jute fabric by dip-coating jute fibers with hydrocarbon and fluorocarbons [22]. Wang et al., have modified jute fabric by laccase-mediated grafting of octadecylamine (OA) [23]. In a recent work, hydrophobicity onto jute fabric is introduced by silica nano sol functional finishing using a pad-dry-cure method [24].

However, most of these reported methods of superhydrophobic jute fabric preparation are non-covalent coating-based modifications; therefore, coating falls apart in harsh environments. Moreover, these processes of modifications involve toxic chemicals, high temperature, multi-step reactions, etc. [17, 22, 24]. Therefore, a simple, economical, environment-friendly methodology for superhydrophobic jute fabric preparation without deteriorating its useful properties (especially porosity, thermal stability, and mechanical properties) is a challenge. In the recent past, our group has successfully tuned the surface wettability of polyolefins, flax fiber, polyurethane sponge, jute fiber, etc., by gamma radiation-induced modification [17, 20, 25]. Electron beam (EB) radiation has some specialities such as high dose rate, high throughput, easy scalability of products, and lesser safety maintenance compared to gamma radiation. Electron beam radiation has been found to be well-established and popular tool for modifying the surface properties of materials by radiation grafting, crosslinking, and curing-assisted changes [26–28]. These modifications lead to the introduction of properties such as bio-compatibility, different polarity, barrier property, enhanced dyeability, special wettability, and metal ion absorbing capacity, etc. [17, 20]. In this work, jute fabric is superhydrophobically modified by electron beam radiation. Unmodified and modified jute fabric is characterized by contact angle measurement, scanning electron microscopy (SEM), tensile testing, and thermogravimetric analysis (TGA). The degree of modification is optimized for the generation of

the desired extent of hydrophobicity. Different oily liquids and non-polar organic solvents are used to facilitate the separation of MPs. Then, the modified jute fabric is used to separate MPs from aqueous media; the utilization of superhydrophobic jute fabric for the separation of MPs has not been reported yet, to our knowledge. The efficiency of the modified jute fabric for MPs removal is investigated using low-density polyethylene (LDPE) and high-density polyethylene (HDPE) MPs, as polyethylene MPs are the most abundant and contribute more than 50% to the total amount of MPs worldwide [29]. The work is expected to provide an effective way for the removal of MPs from water.

2 | Materials and Methods

2.1 | Material Used

Dodecyl methacrylate (DMA, > 99% pure), Disperse blue 14 dye, ethanol, and ethyl acetate were purchased from Sigma Aldrich, India. All used chemicals were of analytical grade and were used as received without further purification. Woven jute fabric of 200 GSM was supplied by Bombay Textile Research Institute, India. Pristine jute fabric samples were washed thoroughly with ethanol before use. During the studies, double-distilled water was used for all the studies.

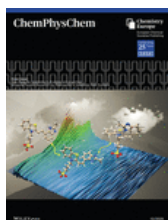
2.2 | Method of Modification

Electron beam (EB) radiation was used for the modification of jute fabric, considering the advantages of radiation technology over conventional techniques. Electron beam (EB) radiation from 5 MeV, 15 kW ILU type EB accelerator has been used for covalent integration of dodecyl methacrylate (DMA) onto jute. Direct/mutual irradiation method has been used for the modification. The total dose delivered was controlled by the beam current, voltage, speed of the conveyor on which the samples were placed, and the number of times the samples were passed under the beam. We followed the process as mentioned in our previous work to attain the desired degree of modification [30]. The controlled extent of modification was important to maintain the mechanical integrity and generation of hydrophobicity. At first, a known concentration of DMA was solubilized in ethanol-water solvent. Then the solution was stirred using a magnetic stirrer for 10–15 min, followed by ultrasonication for 15 min for better dispersion of DMA. Jute fabric pieces were immersed in the reaction mixture for 2–3 h. Jute fabric pieces soaked in the DMA-containing solution were put into plastic zip lock bags. Then the samples were irradiated. After radiation exposure, the samples were removed from the zip lock bags and washed with ethyl acetate solvent to remove unreacted DMA and formed homopolymers if there were any. Washed samples were then vacuum-dried at 70°C until a constant weight was attained.

Grafting yield (G%) was calculated gravimetrically using the equation.

$$\% \text{ grafting} = \frac{(W_f - W_i)}{(W_i)} \times 100 \quad (1)$$





100% for updates

ChemPhysChem

 Research Article
 doi.org/10.1002/cphc.202500016

 Chemistry
 Europe
 European Chemical
 Societies Publishing

www.chemphyschem.org

16

Development of Water-Dispersible CuS Nanoparticles for Chemo–Photothermal Therapy and Photoacoustic Application

Sonali Gupta, Bijaideep Dutta, Subhadip Paul, Ratan K. Saha, Kanhu C. Barick,*
and Puthusserickal A. Hassan*

Photothermal therapy (PTT) is a promising treatment option for cancer. However, biocompatibility, water dispersibility, and good photo-responsiveness are necessary for photothermal agents to be used in PTT. Herein, a soft chemical approach is reported for the design and development of phosphorylethanolamine-functionalized CuS nanoparticles (PEA-CuS NPs) using phosphorylethanolamine (PEA) as a surface passivation agent for combinatorial chemo–photothermal therapy. X-ray diffraction and transmission electron microscopy analyses proved the successful formation of the green covellite CuS phase with an average particle size of 13 nm, while Fourier transform infrared spectroscopy and light scattering measurements demonstrated their surface functionalization with the PEA ligand.

The PEA-CuS NPs have exhibited good photothermal heating efficacy upon irradiation of 980 nm laser light. Moreover, the in vitro studies have shown substantial cellular uptake of PEA-CuS NPs in MCF-7 cell lines and their dose-dependent cytotoxicity (83.3 and 65.4% cell-killing efficacy by 100 and 50 $\mu\text{g mL}^{-1}$ of PEA-CuS NPs, respectively) upon 980 nm laser irradiation (0.65 W power). The developed PEA-CuS NPs have also demonstrated very high acoustic signal under 690 and 530 nm laser light irradiation. Thus, these water-dispersible PEA-CuS NPs can be served as a promising candidate for image-guided combinatorial therapy involving chemotherapy and PTT.

1. Introduction

In terms of death rate, cancer is the second most frequent disease even though there are many therapeutic modalities accessible for its treatment.^[1,2] The main obstacles to obtain the best possible treatment results from the conventional chemotherapy and traditional medications include poor tumor-targeting ability, undesired side effects, and multidrug resistance.^[3–6] Because of its high tissue transparency, noninvasive manipulation, low normal cell toxicity, and reduced patient compliance, photoinduced therapy—photothermal therapy (PTT) and photodynamic therapy (PDT)—is becoming more and more popular.^[7–10] PTT employs photothermal agents (PTAs),

which generate heat and boost the temperature of the tumor micro-environment to 42–43 °C when exposed to near-infrared (NIR) light, thereby killing the cancer cells.^[11–17] On the other hand, in PDT, photosensitizers are used to generate reactive oxygen species (ROS) after being irradiated with a photon with a particular wavelength, and subsequently damage the cancer cells, acting as a therapeutic module.^[18–20] New concepts for cancer treatment have recently been made possible with the combination of chemotherapy and photothermal therapeutic modality. It has been shown that PTT combined with chemotherapy improves the therapeutic efficacy in comparison to their individual counterparts.^[21–24] To date, photothermal therapeutic systems have been created using a range of PTAs, including noble metal nanostructures, carbon-based materials, and semiconductor compounds. Among them, Au- and Pd-based nanostructures are expensive with poor photostability, and follow a complicated synthetic process, whereas carbon-based nanomaterials possess low photothermal conversion efficiency.^[25,26] The usage of semiconductor nanoparticles are also limited due to a certain degree of toxicity with the presence of toxic elements, like Cd, Hg, Pb, etc.^[27,28]

These issues have attracted the interest of researchers in developing copper chalcogenides (Cu_xS, Cu_xSe, and Cu_xTe, where $x = 1, 2$)-based PTAs, which exhibit plasmonic properties typically found in metal nanoparticles (such as Au and Ag), along with excitonic properties common to semiconductor nanoparticles.^[29–32] Unlike metals with free electrons, plasmonic behavior in copper chalcogenides arises from the collective oscillation of holes, a phenomenon triggered by oxidation that leads to the creation of Cu vacancies.^[33,34] In contrast to other metal-semiconductor heterostructures, this integration of electrical and photonic

S. Gupta, B. Dutta, K. C. Barick, P. A. Hassan
Chemistry Division
Bhabha Atomic Research Centre
Trombay, Mumbai 400085, India
E-mail: kcbarick@barc.gov.in
hassan@barc.gov.in

S. Gupta, B. Dutta, K. C. Barick, P. A. Hassan
Homi Bhabha National Institute
Anushaktinagar, Mumbai 400094, India
S. Paul, R. K. Saha
Department of Applied Sciences
Indian Institute of Information Technology Allahabad
Allahabad 211012, India

Supporting information for this article is available on the WWW under https://doi.org/10.1002/cphc.202500016

© 2025 The Authors. ChemPhysChem published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

properties in a single nanoscale entity opens up new possibilities for applications in quantum information processing, nonlinear optics, and light harvesting.^[35] Moreover, Cu_xS_y structures with different compositions have been extensively used for both in vitro and in vivo biomedical applications.^[36,37] This has resulted in the development of various preparation methodologies such as chemical precipitation, high temperature thermal decomposition, solvothermal synthesis, hot injection, and microwave-based processes for the preparation of Cu_xS_y NPs.^[30,38–41] Among these, the chemical precipitation-based soft chemical approach offers a simple and cost-effective route for synthesizing covellite CuS NPs. However, there are significant challenges that still lie in the preparation of water-dispersible CuS NPs of controlled shape and size with suitable surface functionality for chemo–photothermal therapy applications. Therefore, the development of surface-functionalized colloidal stable CuS NPs is worthwhile.

In this aspect, we report the development of water-dispersible phosphorylethanolamine-functionalized CuS NPs (PEA–CuS NPs), using a soft chemical approach that not only provides long-term colloidal stability of particles but also generates a particular site for binding of the anticancer drug, doxorubicin hydrochloride (DOX). The developed PEA–CuS NPs exhibited strong NIR absorption and good photothermal heating efficacy under the irradiation of NIR light (980 nm). These PEA–CuS NPs, in associating with DOX, showed enhanced toxicity toward breast cancer cells (MCF-7) under NIR light, indicating good chemo–photothermal efficacy. Moreover, these PEA–CuS NPs showed an admirable ability to generate an acoustic signal when exposed to laser light over a varied concentration range. Specifically, the excellent photostability, good photoacoustic (PA) signal-generating ability, and integrated chemo–photothermal efficacy make them potential agents for cancer therapy.

2. Experimental Section

2.1. Materials

Cu (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), sodium sulfide (Na_2S), sodium hydroxide (NaOH), and dimethyl sulfoxide (DMSO) were purchased from SDFCL, India. O-phosphorylethanolamine (PEA) was purchased from TIC Pvt. Ltd., India. Dulbecco's modified eagle medium (DMEM), fetal bovine serum (FBS), antibiotics, MTT reagent, DAPI dihydrochloride, and dialysis membrane-60 were procured from HiMedia Laboratories Pvt. Ltd., India. DOX and MCF-7 cells were received as kind gifts from the Advanced Centre for Treatment, Research and Education in Cancer (ACTREC), Navi Mumbai and Radiation Biology & Health Science Division (RB&HSD), BARC, Mumbai, respectively.

All the aqueous solutions were prepared using deionized water (DI) from a Millipore Milli Q system (resistivity $\approx 18 \text{ M}\Omega \text{ cm}$). The acetate buffer (AB, pH 5.0), phosphate buffer (PB, pH 6.5), and phosphate buffered saline (PBS, pH 7.4) were prepared using standard protocols. All the chemicals used were of AR grade unless otherwise specified, and used as such without further treatment.

2.2. Synthesis of PEA–CuS NPs

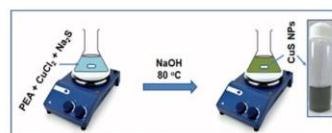
Highly water-dispersible, PEA–CuS NPs were synthesized using a soft chemical approach, with PEA serving as the surface passivating agent. Aqueous colloidal-stabilized CuS NPs were achieved at a molar ratio of $\text{Cu}^{+2}:\text{S}^{2-}:\text{PEA}$ of 1:3:3. In a typical synthesis, 0.169 g of PEA was dissolved in 100 mL of Milli Q water with stirring for 15 min at 80 °C. Subsequently, 2 mL of 0.2 M CuCl_2 (0.4 mmol) was added to the above solution. After 20 min, a 0.1 M NaOH solution was added dropwise to maintain a basic pH of 8–9, and the reaction was continued for another 10 min with stirring at the same temperature. Then, 6 mL of 0.2 M Na_2S (1.2 mmol) was introduced, and the reaction solution was stirred for an additional period of 60 min at 80 °C. The resulting dark-green PEA–CuS NPs solution was dialyzed against the Milli Q water for 24 h to remove unreacted chemicals and by-products. A portion of this solution was dried at 50 °C in an oven for further characterization. Solution-phase analyses were performed directly on the dialyzed PEA–CuS NPs suspension. The schematic representation of the synthesis of the PEA–CuS NPs is shown in Scheme 1.

2.3. Characterizations

The structural/microstructural studies and surface functionalization were performed by X-ray diffraction (XRD, Rigaku X-ray diffractometer), transmission electron microscopy (TEM, Themis 300 G3, Thermo Scientific) and Fourier transform infrared spectroscopy (FTIR, Bomen MB series). The average hydrodynamic diameter (H_D) and zeta potential (ZP) measurements were performed using Litesizer (Anton Paar). The absorption spectra were recorded using an UV–vis–NIR spectrophotometer (JASCO V-670 UV–vis–NIR spectrophotometer). The concentration of Cu in the aqueous suspension and powder form of the PEA–CuS NPs were measured using atomic absorption spectrometer (AAS, Analytik Jena).

2.4. Photothermal Heating Efficacy and Drug Loading/Release Studies

Photothermal heating studies were conducted by irradiating a 1 mL aqueous suspension of the synthesized PEA–CuS NPs with NIR light (980 nm). The concentrations of the PEA–CuS NPs, expressed as Cu, were 50, 100, and 150 $\mu\text{g mL}^{-1}$, and the suspensions were exposed to varying laser powers ranging from 0.45 to 0.85 W. The temperature change in the solution was recorded every 10 sec using an optical fiber-based temperature sensor, with an accuracy of ± 0.1 °C. To assess photostability, an aqueous suspension of the PEA–CuS NPs (50 $\mu\text{g mL}^{-1}$ Cu, 0.65 W) was



Scheme 1. Pictorial representation of the synthesis protocol of the PEA–CuS NPs.





Wiley
Case Reports in Pathology
Volume 2025, Article ID 1510607, 7 pages
<https://doi.org/10.1155/crip/1510607>

17

WILEY

Case Report

Multifocal Medullary and Papillary Thyroid Carcinoma Occurring as a Collision Tumor: A Case Report

Sayali Gadre,¹ Raji T. Naidu¹, Prachi R. Gaddam¹, Neha Mittal,² and Susan Cherian¹

¹Department of Pathology, Bhabha Atomic Research Centre Hospital, Mumbai, Maharashtra, India

²Department of Pathology, Tata Memorial Centre, Mumbai, Maharashtra, India

Correspondence should be addressed to Raji T. Naidu; drrajipillai@gmail.com

Received 14 December 2024; Revised 7 August 2025; Accepted 9 August 2025

Academic Editor: Suraiya Saleem

Copyright © 2025 Sayali Gadre et al. Case Reports in Pathology published by John Wiley & Sons Ltd. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Collision tumors are rare tumors comprising two morphologically distinct tumors within the same organ without histological admixture. Thyroid collision tumors are extremely rare. We present a case of a 64-year-old male patient with a radiologically suspicious, TI-RADS-TR4 lesion in the right lobe of the thyroid. Fine needle aspiration cytology (FNAC) from the lesion was diagnosed as medullary thyroid carcinoma. Total thyroidectomy with central and right lateral neck dissection was performed. On histopathological evaluation, a collision tumor was identified. Components of the collision tumor were multifocal medullary thyroid carcinoma (MTC) and multifocal infiltrative follicular variant of papillary thyroid carcinoma (PTC). Several hypotheses have been suggested regarding the pathogenesis of the collision tumor. Further management and prognosis of the tumor depend on the component with the higher stage and more aggressive behavior. The case report emphasizes the need for thorough sampling of uninvolved areas in the specimen for microscopic evaluation and staging of each component.

Keywords: collision tumor; medullary; papillary; thyroid carcinoma

1. Introduction

Collision tumor is a neoplastic lesion comprised of two or more distinct cell populations that maintain distinct borders. [1] Thyroid collision tumors (TCTs) consist of two histologically and morphologically distinct tumors occurring in the thyroid with no histological admixture. These tumors are very rare and constitute lower than 1% of all thyroid tumors [2]. Approximately 70 cases of TCTs have been reported in the literature to date. The most frequent association encountered in TCTs is the synchronous presence of MTC and PTC components [3]. The PTC component of TCT, in most reported cases, is papillary microcarcinoma (m-PTC). MTC and PTC are two distinct neoplasms of the thyroid which originate from follicular and parafollicular C cells, respectively. The cells of origin, histopathological features, and prognosis of these tumors are different [4]. We present a rare case of TCT comprising of multifocal medul-

lary thyroid carcinoma diagnosed on FNAC and multifocal infiltrative follicular variant of papillary thyroid carcinoma, which was incidentally detected after surgery.

2. Case Report

A 64-year-old male patient was detected to have a moderately suspicious (TI-RADS-TR4) lesion in the right lobe of the thyroid on ultrasonography (USG) during workup for left submandibular sialadenitis. A USG-guided FNAC was done from the same lesion and a cytological diagnosis of medullary thyroid carcinoma was given. Cytological findings revealed a dispersed population of plasmacytoid cells with moderate granular cytoplasm, eccentric hyperchromatic nuclei, and coarsely stippled chromatin (Figure 1).

A CT scan of the thyroid done subsequently showed an irregular, ill-defined, poorly delineated, hypoenhancing lesion in the right lobe and one hypoenhancing nodule in

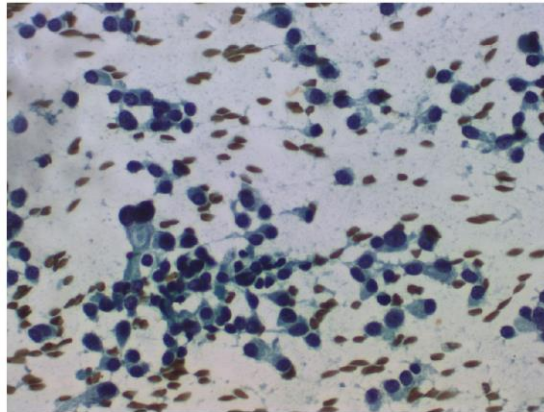


FIGURE 1: Fine needle aspiration cytology showing predominantly dissociated cells with hyperchromatic, eccentric nucleus, coarsely stippled chromatin, and moderate cytoplasm. Binucleate tumor cells are seen (Pap, $\times 400$).



FIGURE 2: Total thyroidectomy specimen. (a) A blackish firm area (black arrow) in the right lobe of the thyroid of $0.5 \times 0.5 \times 0.4$ cm dimension. (b) Two grey whitish firm nodules (black arrow) in the left lobe measuring $1.2 \times 1 \times 0.8$ cm and $0.7 \times 0.5 \times 0.5$ cm, respectively. The smaller nodule abuts the thyroid capsule.

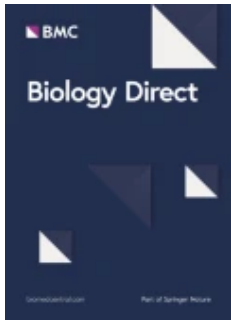
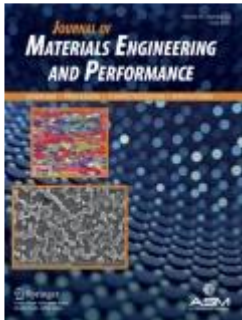
the left lobe of the thyroid. The serum calcitonin level performed at this time was 102 ng/L, normal range being ≤ 19 pg/mL or ≤ 19 ng/L (SI units) and ≤ 14 pg/mL or ≤ 14 ng/L (SI units). Thyroid function tests and serum parathyroid hormone level done were within normal limits. The patient underwent total thyroidectomy along with central and right lateral lymph node dissection as surgical management. On gross examination of the total thyroidectomy specimen received, a blackish firm area was seen in the right lobe measuring 0.5 cm maximum dimension (Figure 2a), and two nodules were seen in the left lobe measuring 1.2 and 0.7 cm (Figure 2b).

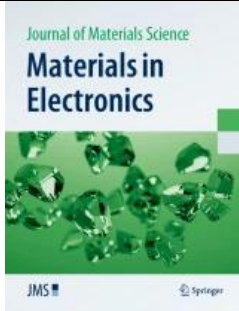
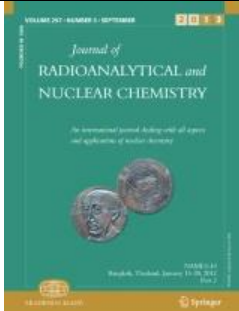
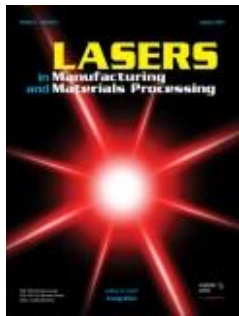
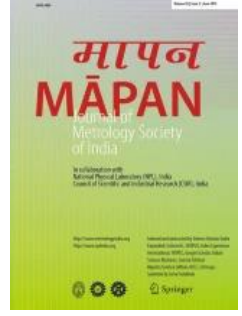
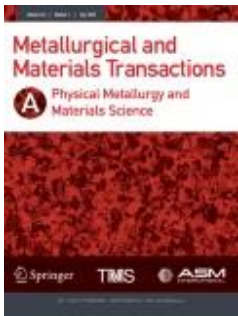
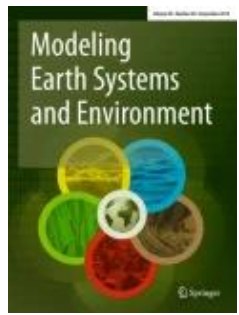
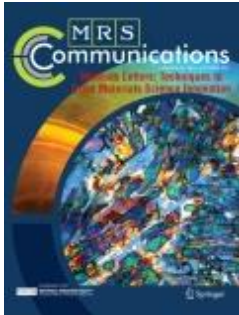
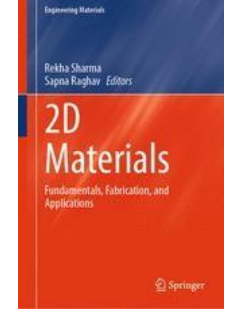
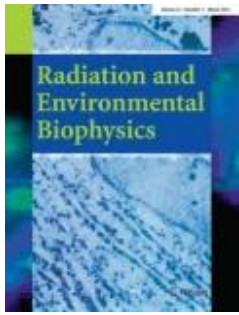
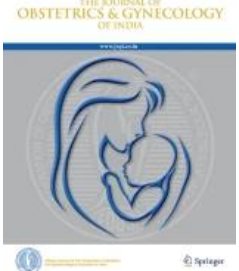
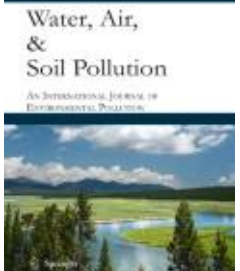
On microscopic examination, the right lobe nodule (0.5 cm) and the left lobe nodule (1.2 cm) showed features of medullary thyroid carcinoma (Figure 3a). The left lobe nodule measuring 0.7 cm in greatest dimension showed histological features of infiltrative follicular variant of papillary thyroid carcinoma (Figure 3b). Another 0.5 cm area in the isthmus also showed features of infiltrative follicular variant of papillary thyroid carcinoma. Both the tumor components were grossly and histologically separate (Figure 3c). Microscopic extrathyroidal extension was seen in both components. There were no lymphovascular emboli or perineural invasion. Three out of six lymph nodes from the right central

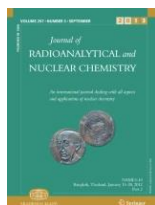


Scan the QR Code or Click for full text

SPRINGER NATURE

			
Applied Physics A	Applied Physics B	Biology Direct	BioNanoScience
			
BMC Plant Biology	Current Genetics	Current Microbiology	Emergent Materials
			
European Journal of Clinical Microbiology & Infectious Diseases	Interactions	International Journal of System Assurance Engineering & Management	JOM
			
Journal of Cluster Science	Journal of Materials Engineering and Performance	Journal of Materials Research	Journal of Materials Science

			
Journal of Materials Science: Materials in Electronics	Journal of Polymer Research	Journal of Radioanalytical and Nuclear Chemistry	Journal of Thermal Analysis and Calorimetry
			
Lasers in Manufacturing and Materials Processing	MAPAN	Medical Oncology	Metallurgical and Materials Transactions A
			
Modeling Earth Systems and Environment	Molecular Biology Reports	MRS Communications	NPJ 2D Materials and Applications
			
Radiation and Environmental Biophysics	Radiological Physics & Technology	Scientific Reports	The European Physical Journal A
			
The Journal of Obstetrics and Gynecology of India	Water, Air, & Soil Pollution		



A coincidence ion beam analysis methodology for high resolution depth profiling of nickel using a resonance in the $^{58}\text{Ni}(\text{p}, \gamma)^{59}\text{Cu}$ reaction

A. A. Sukumar¹ · D. V. Lakshmipathy¹ · Y. Sunitha¹ · Sk Jayabun¹ · J. V. Ramana¹ · G. L. N. Reddy^{1,2} 

Received: 19 April 2025 / Accepted: 23 July 2025 / Published online: 2 August 2025
 © The Author(s) 2025

Abstract

A coincidence mode Ion Beam Analysis (CIBA) methodology has been standardised for the depth profiling of nickel. The methodology is unique, as the 1424 keV resonance in the $^{58}\text{Ni}(\text{p}, \gamma)^{59}\text{Cu}$ reaction was utilised for interference free determination and depth profiling of nickel, using four channel high-speed digitizer, in coincidence spectroscopy mode (CI-NRRA). The aforementioned reaction, with a Q value of 3.42 MeV, emits characteristic γ -rays of 4817.7 keV, 4326.6 keV, and 491.1 keV energy. The 4326.6 keV, 491.1 keV γ -rays, emitted concomitantly, in the two-step cascade transition of the 4817.7 keV excited state, were detected in coincidence mode. Angular correlation studies were carried out to maximize coincidence events. Nickel depth profiling was carried out in Ni/Si, Cr/Ni/Si, Nb-W-Ta/Ni/Si films and Ni bulk targets. CI-NRRA facilitated the removal of interferences from chromium (Cr) and silicon (Si). The present study, which enables high resolution depth profile of Ni in various substrates, is the first of its kind to carry out Nuclear Resonance Reaction Analysis (NRRA) in coincidence mode for the depth profiling.

Keywords Coincidence ion beam analysis · Digitizer · Nuclear resonance reaction analysis (NRRA) · Coincidence · Depth profiling · Nickel

Introduction

Coincidence techniques are used in nuclear physics, in radioactivity metrology, and nuclear analytical measurements to enhance the precision and reliability of particle detection in experimental setups. These techniques are particularly valuable for reducing background noise and isolating specific nuclear events of interest. The coincidence technique involves detection of two or more related events that occur simultaneously or within a very short time window. By carrying out simultaneous detection in multiple detectors, the technique ensures that the recorded events are correlated, originating from a same/single nuclear decay or a reaction. This significantly reduces random background signals.

Coincidence circuits are typically employed to define the time window for event correlation. This method is especially useful for rejecting background radiation, as it ensures that only signals unique to the primary detector are recorded [1, 2].

Employing coincidence techniques makes it possible to achieve greater sensitivity, precision, and interference-free determination of elemental composition in nuclear analytical experiments. Ion Beam Analysis (IBA) is a powerful non-destructive nuclear analytical technique used for the determination of elemental composition and depth profiles. Common IBA methods include Rutherford Backscattering Spectrometry (RBS), Particle-Induced X-ray Emission (PIXE), and Nuclear Reaction Analysis (NRA). However, relatively limited literatures are available on the application of Coincidence Ion Beam Analysis (CIBA) for materials characterization. The Elastic Recoil Coincidence Spectroscopy (ERCS) technique has been applied for the highly sensitive determination and depth profiling of light elements ranging from hydrogen to oxygen in self-supporting thin metallic films and thin polymer-foils containing different heavier elements [3–6]. One of the earliest studies

✉ G. L. N. Reddy
glnreddy@barc.gov.in

¹ National Centre for Compositional Characterisation of Materials (NCCCM), BARC, Hyderabad 500062, India

² Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

reported the detection of hydrogen at concentrations as low as a few parts per million (ppm) in thin metallic films and foils [3]. However, to the best of our knowledge, no studies have been published to date on the application of Nuclear Resonance Reaction Analysis (NRRA) in coincidence mode. In this paper, we report a methodology on the application of a resonance in the $^{58}\text{Ni}(\text{p}, \gamma)^{59}\text{Cu}$ reaction in coincidence mode (Coincidence Ion Beam Analysis, CIBA) for the depth profiling of nickel. The present work is unique in two respects. Firstly, a resonance in a nuclear reaction has been investigated in coincidence mode for depth profiling. Secondly, a four-channel high-speed digitizer with simultaneous acquisition capabilities and a flash ADC has been utilized. This system allows data to be saved in list mode with time stamps, enabling both online and offline coincidence/anticoincidence measurements for carrying out CIBA.

Nuclear resonance reaction analysis is a prominent technique employed for depth profiling with superior depth resolution. While NRRA is extensively applied in analyzing low-Z elements, the technique's potential remains seldom utilized for elements with high or medium atomic numbers. Our laboratory in India has standardised methodologies for high-resolution depth profiling of several medium-Z elements [7–10]. We report a methodology for high-resolution depth profiling of nickel, based on resonances in the $^{58}\text{Ni}(\text{p}, \gamma)^{59}\text{Cu}$ reaction in samples containing nickel isotopes in their natural abundances (^{58}Ni : 68.1%, ^{60}Ni : 26.2%, ^{61}Ni : 1.1%, ^{62}Ni : 3.6%, ^{64}Ni : 1.0%). Nickel is an important alloying element in materials used for high-tech applications such as molten salt reactors (MSR) and nuclear micro-reactors (MR). Nickel, as an implanted ion, plays a crucial role in modifying the physical properties of structural materials [11]. Additionally, nickel and its oxide films have applications in sensors, semiconductors, and other technologies. In all these studies, the determination of composition, film thickness, and depth profiles of nickel holds significant importance in comprehending the underlying physical processes.

Among the various resonances in the $^{58}\text{Ni}(\text{p}, \gamma)^{59}\text{Cu}$ reaction, we have studied relatively intense resonance that occur at proton energy (E_p) of 1424 keV, with Q values of 3420 keV, with compound-nucleus excitation energy (E_x) of 4817.7 keV [12]. The 4817.8 keV excited state decays to a lower excited state of 491.1 keV as well as to the ground state with branching ratios of 50% and 35%, respectively [12, 13]. The cascade transition of 4817.7 keV excited state emits a 491.1 keV γ -ray in coincidence with a 4326.6 keV γ -ray. Whereas the transition to the ground state emits a 4817.7 keV γ -ray. The 491.1 keV and 4326.6 keV γ -rays were measured in coincidence mode using two detectors and the digitizer. Angular correlation studies were also performed to maximize the coincidence events. The excitation/

yield curves for the 1424 keV resonance were constructed in thin Ni film targets.

Experimental

To carry out the experiments, energetic proton beams were extracted from 3 MV Tandem accelerator (HVEE, Europa). The excitation curve for the $^{58}\text{Ni}(\text{p}, \gamma)^{59}\text{Cu}$ reaction was constructed using a proton beam with an energy range of 1400–1650 keV. The experiment involved bombardment of Ni containing targets (Ni isotopes in natural abundance) with a collimated proton beam (3.0 mm diameter) at normal and 45° incidence, with a current ranging from 500 to 800 nA. The proton beam energy was incrementally increased in 0.5 keV steps. The characteristic γ -rays of energy 491.1 keV, 4326.6 keV and 4817.7 keV were detected using 7.6 cm $\times$ 7.6 cm bismuth germanate (BGO) detector and high purity germanium (HPGe) detector, with a relative efficiency of 54% and energy resolution of 1.8 keV (at 1332 keV of ^{60}Co), positioned at different angles ranging from 0° to 135° relative to the incident proton beam. The distance between the target and the detector was maintained at 5.0 cm. For precise measurement of proton beam current, the targets were placed inside a Faraday cup arrangement [14]. The spectral data were collected for a charge of ≥ 100 μC at each proton beam energy. While, HPGe detector is being used, the area under the peak of the characteristic γ -rays (491.1 keV, 4326.6 keV and 4817.7 keV) constituted as the signal. Whereas, for the BGO detector, the total counts within the 3000 keV to 5000 keV energy region (Region of Interest: ROI), encompassing full energy peak, as well as both single and double escape peaks of 4326.6 keV and 4817.7 keV γ -rays, constituted as nickel signal.

The depth ' x ' at which the resonance occurs for a proton beam with energy E_p was calculated using Eq. (1):

$$x = \frac{E_p - E_R}{S(E_p)} \quad (1)$$

where $S(E_p)$ is the stopping power of the film/bulk target for proton beam with E_p .

The accelerator terminal voltage and the energy of the ions was calibrated using the resonances at 872 keV, 2010 keV and 3038 keV in the $^{19}\text{F}(\text{p}, \alpha)^{16}\text{O}$, $^{24}\text{Mg}(\text{p}, \text{p}'\gamma)^{24}\text{Mg}$ and $^{16}\text{O}(\alpha, \alpha)^{16}\text{O}$ reactions, respectively [15].

The γ -ray spectra from the detectors were obtained using CAEN DT5781 digitizer, which is a compact desktop system integrating 4 independent 16 k channel Digital MCAs for nuclear spectroscopy. The digitizer eliminates the use of the spectroscopy amplifiers. The pre-amplifier (Pre-Amp) signal from the detector is fed directly to the digitizer. The other features are: 4 detector inputs with the



OPEN A comprehensive study on the impact of He ion irradiation on the microstructure and mechanical properties of a Ni-Cr-Mo alloy

Sanjay Saini^{1,4}, Ranjini Menon^{2,4}, S. K. Sharma^{3,4}, P. Y. Nabhiraj^{2,4}, Suman Neogy^{1,4} & A. P. Srivastava^{1,4}✉

The impact of helium ion irradiation on the evolution of microstructure and mechanical properties of a Ni-45%Cr-1.4%Mo (wt%) alloy has been investigated. Analysis via transmission electron microscopy (TEM) of a pristine sample revealed an uneven distribution of alpha-Cr phase precipitates along with a few isolated planar arrangements of dislocations within the fcc γ -Ni matrix phase. A detailed study of irradiated samples established the presence of radiation-induced defect clusters, dislocation loops, network dislocations as perceptible irradiation effects. X-ray diffraction (XRD) and positron annihilation spectroscopy (PAS) studies also confirmed lattice swelling as an effect of irradiation in this alloy, likely caused by helium-stabilized vacancy cluster. A line profile analysis method which takes into account of planar defects, was employed on GIXRD (Grazing Incidence X-ray Diffraction) data to analyze changes in microstructural parameters such as domain size, microstrain, dislocation density and lattice parameter as a function of irradiation dose. All of these irradiation-damage manifestations led to the increase in the hardness of the alloy in nano-indentation experiment. Overall, the findings of this work provide significant insights into the radiation-induced microstructural changes and their effect on the hardening behavior of the studied Ni-Cr-Mo alloy.

Keywords Nuclear materials, Ion-implantation, Radiation effects, Microstructure

Ni-based alloys and their modifications have emerged as promising structural materials, possessing excellent creep properties at elevated temperatures and adequate swelling resistance^{1–5}. Their potential for use in nuclear reactors is undeniable; however, they are prone to substantial ductility loss under irradiation, which may severely limit their application. Despite this limitation, the invaluable characteristics of Ni-based alloys still position them as potential candidates for structural materials in heat exchangers or core components where the dose of irradiation is limited to a few dpa (displacement per atom) at most. The majority of published studies on Ni-based alloys concern Ni-Cr-Fe-Mo systems such as Inconel 625, Inconel 718, Hastelloy X, Nimonic PE16, etc. and Ni-Cr-Fe systems such as Alloy 600, Alloy 690, Inconel X-750, Alloy 903, Incolloy 800, Nimonic 80 A, etc.^{4,6,7}. Notably, a critical concern with Ni-based alloys in nuclear environments is the production of helium due to Ni (n, α) Fe transmutation reaction, which leads to He-embrittlement^{8–11}.

The recent advancements in the design of Ni-based alloys, particularly NiCrMo compositions, have shown improved swelling resistance and microstructural stability under high-dose irradiation conditions. Gurovich et al. have investigated the structural evolution of the 42XNM (Ni-Cr-Mo) alloy during neutron irradiation up to 12 dpa at ~ 300 °C and brought out the role of He bubble formation in microstructural changes due to irradiation¹¹. This alloy system is being used in nuclear reactors as a control rod shell and is being considered for fuel element shell in Gen IV reactors^{3,5}. We have already reported irradiation response of a modified alloy composition (Ni-42 wt% Cr) against proton irradiation to a very low dose of ~ 0.07 dpa¹².

The 42XNM (Ni-41.1%Cr-1.18%Mo) alloy is considered a promising structural material for Generation IV nuclear reactors due to its favorable properties under extreme conditions, where irradiation effects play a critical role. To ensure the safe functioning of reactors, it is crucial to have a comprehensive understanding of the impact of high dose ion irradiation in such materials. In this context, heavy ion irradiation is widely used to effectively

¹Materials Science Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India. ²Variable Energy Cyclotron Centre, Kolkata 700064, India. ³Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India. ⁴Homi Bhabha National Institute, Trombay, Mumbai 400094, India. ✉email: apsri@barc.gov.in

simulate the microstructural and mechanical changes induced by neutron irradiation^{13–20}. The damage due to heavy ion irradiation can be effectively evaluated using advance characterization techniques such as grazing incidence X-ray Diffraction (GIXRD), transmission electron microscopy (TEM), positron annihilation spectroscopy (PAS), and nanoindentation, as they can probe the thin irradiated layers and provide critical insights into the material's response to irradiation^{21–23}. The line profile analysis of XRD enables determination of changes in the key microstructural parameters such as domain size, dislocation density, and micro-strain through the broadening of diffraction peaks. On the other hand, PAS is a well-established technique for identifying vacancy-type defects due to the strong affinity of positrons for open-volume sites^{22,23}. These techniques offer critical insight into irradiation-induced microstructural changes through non-destructive analysis. Moreover, to directly observe and confirm the presence of such defects, TEM is often employed, providing high-resolution imaging and detailed compositional characterization. Further, nanoindentation has also proven to be one of the effective tools for evaluating the mechanical properties of irradiated materials with small sample volumes. In nano-indentation, the continuous stiffness measurement (CSM) mode gives the hardness of irradiated materials as a function of depth in the order of nm.

In the current study, we have selected a potential candidate with modified alloy composition Ni-45Cr-1.4Mo (wt%) for investigation. This alloy has been exposed to He ion irradiation at room temperature to achieve a range of irradiation doses up to 17.1 dpa of peak damage. This study aims to provide an in-depth understanding of the microstructural and mechanical responses of Ni-45Cr-1.4Mo alloy subjected to high-dose He ion irradiation by comprehensively elucidating the effects of irradiation-induced damage probed through a variety of advanced depth-resolved characterization techniques such as GIXRD, TEM, PAS, and nanoindentation.

Experimental

A sheet of Ni-45Cr-1.4Mo (wt%) alloy was vacuum-sealed in a quartz tube and subjected to heat treatment at 1150 °C for 10 min, followed by quenching in water. To prepare the samples for irradiation experiments, samples with dimensions of 10 × 10 × 1 mm were cut from the heat-treated sheet. The surfaces of these samples were prepared employing standard metallographic procedures followed by electropolishing with a solution of 10% perchloric acid and 90% methanol (v/v) at 20 V and –40 °C.

The samples were irradiated using He ion beam from a 6.45 GHz electron cyclotron resonance (ECR) ion source available at Variable Energy Cyclotron Centre, Kolkata. Three samples were exposed to He ion beam of energy 65 keV under 10^{–6} mbar vacuum to achieve total doses of 3 × 10¹⁶, 2 × 10¹⁷, and 7 × 10¹⁷ ions/cm², respectively, at an implantation rate of 3.5 × 10¹² ions/cm²-sec at room temperature.

Since the damage due to ion irradiation is limited to few hundreds of nanometers from the exposed surface of the sample, these were characterized by Grazing Incidence X-ray Diffraction (GIXRD) technique with a PANalytical system employing CuKα X-rays of 1.545 Å wavelength. The diffraction profiles of unirradiated and irradiated samples were obtained in the 2θ range of 40–95 with a 0.02 step size.

For further insight into microstructural changes, un-irradiated and irradiated samples was examined using a 300 kV JEOL 3010 TEM. TEM samples were prepared by mechanically grinding from the unirradiated side to get thin foil (80–100 μm) and subsequently 3 mm diameter discs were punched from these foils. The discs were then thinned to the point of perforation using the twin jet electropolishing process, in which Lacomit peelable varnish was applied to the irradiated side to prevent its polishing and ensure thinning only from the unirradiated side. This procedure ensured that the irradiated zone of the samples is transparent to electrons. Electropolishing was performed at 20 V and –45 °C using an electrolyte consisting of 10% perchloric acid in methanol. In addition to the imaging of microstructural features, EDS (energy dispersive spectroscopy) analysis of the composition of second-phase precipitates and that of the matrix phase was also performed.

The samples were also subjected to depth-dependent Doppler broadening measurements using a slow positron beam of variable energy. All the measurements were performed at room temperature using incident positron energies ranging from 0.2 to 17.2 keV with a high purity Ge detector having an energy resolution of 1.4 keV at 514 keV of ⁸⁵Sr. The Doppler broadening spectrum at different implantation energies or implantation depths (total counts ~ 5 × 10⁵) was characterized by two line-shape parameters, viz., S- and W-parameters. The S-parameter was evaluated by taking the ratio of counts in the low momentum region (511.000–0.684 keV) to the total counts under the annihilation peak, whereas the W-parameter was evaluated by taking the ratio of counts under a 4.564 keV window centered at (511.000–13.692 keV) in the high momentum region to the total area of the annihilation peak.

The hardness of unirradiated and irradiated samples was evaluated using the nanoindentation technique employing a Berkovich diamond indenter (UNHT, CSM, Switzerland). The continuous stiffness measurement method was used to measure the hardness of the irradiated samples as a function of depth. The indentation was carried out up to a depth of 450 nm from the irradiated surface. At least 10 indentations were performed at each depth and the average of these measurements was considered for interpretation. The spacing between two successive indents was kept at 50 μm to prevent interference with plastic zones formed by adjacent indents.

Results

The nominal composition of the Ni-Cr-Mo alloy obtained by chemical analysis is given in Table 1. A widely known Monte-Carlo simulation-based software SRIM-2008²⁴ has been used to estimate the depth profile of the distribution of implanted He ions and vacancies formed during irradiation and the same is shown in Fig. 1. The irradiation damage has been evaluated in terms of dpa (displacements per atom) using the following formula:

$$dpa = (\nu_{\text{NRT}} \times 10^8 \times \Phi) / N_o \quad (1)$$





OPEN

A persistent radon anomaly signal preceding the destructive 7.7 M_w earthquake in Myanmar on March 28, 2025

B. K. Sahoo^{1,3}, B. K. Sapra^{1,3}✉, Arshad Khan¹, M. P. Ratheesh¹, D. H. Kumbhar¹, J. J. Gaware¹, S. D. Kanse¹, Sumitra Phanjoubam⁴ & D. K. Aswal^{2,3}

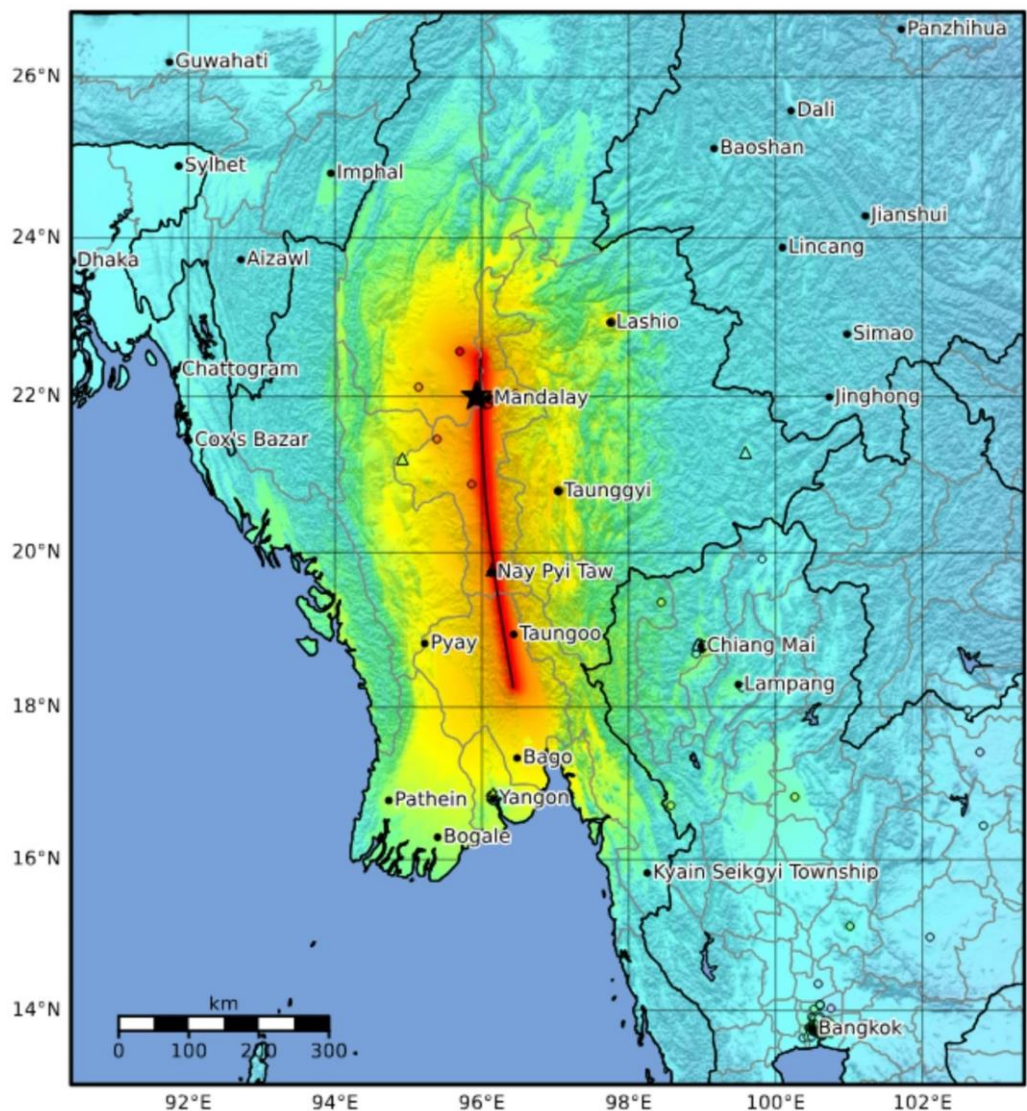
On March 28, 2025, a devastating earthquake doublet of moment magnitude 7.7 and 6.7 struck the Sagaing Region of Myanmar, causing extensive damage and significant casualties across Southeast Asia. In the months preceding this seismic event, a continuous radon monitoring system—BhaROSA—installed in Imphal, India, as a part of the Indian Network for Detecting Radon Anomaly signal (INDRA), recorded a pronounced and statistically significant novel radon anomaly signal. The anomaly signal commenced on December 5, 2024, with a gradual buildup, followed by a sharp rise on February 28, 2025. Multiple peak alerts were observed prior to the mainshock (7.7 M_w) on March 28, 2025, after which the signal declined rapidly, returning to baseline levels—suggesting a potential correlation with pre-seismic crustal stress accumulation and release. The anomaly signal exhibited a normalized squared deviation of 35.14 from the baseline value, far exceeding natural variability at the time of main shock. The radon signal, with a build-up period of approximately 109 days and a decay of ~96 h, closely matched the spatial and temporal characteristics of the dilatancy-diffusion model. A pooled analysis of radon anomalies from ten earthquake events, including this major event, across multiple Indian observatories of INDRA reveals a robust positive correlation ($r = 0.96$, $R^2 = 0.93$) between radon buildup duration and earthquake magnitude. These findings strongly suggest that radon emissions are sensitive indicators of impending seismic activity and radon build up period can be a good indicator of magnitude of earthquake. The study highlights the potential of continuous radon monitoring in tectonically active regions like Northeast India and Myanmar as a viable component of earthquake precursor research and early warning systems.

Keywords Radon anomaly, Earthquake precursor, BhaROSA, Sagaing fault, Myanmar earthquake 2025

On March 28, 2025, at 06:20:52 UTC, a powerful earthquake with a moment magnitude 7.7 struck the Sagaing Region of central Myanmar (<https://earthquake.usgs.gov/earthquakes/eventpage/us7000pn9s/executive>). The epicenter was located near Sagaing Township, approximately 14 km north-northwest of Sagaing city and just 16 km west of Mandalay, Myanmar's second-largest city. The earthquake occurred along the highly active Sagaing Fault, a major tectonic boundary between the Burma and Sunda plates, and was recorded at a shallow depth of approximately 10 km. Its shallow hypocenter and strike-slip faulting mechanism contributed to widespread, catastrophic damage across central Myanmar and extended to neighbouring countries, including Thailand, China, and Vietnam. The intensity shaking map of main event (7.7Mw) is shown in Fig. 1.

This earthquake marked the most significant seismic event in Myanmar since the 1912 Maymyo earthquake¹ and stands as the second deadliest in the country's modern history, surpassed only by the 1930 Bago earthquake². The mainshock reached a maximum Modified Mercalli Intensity (MMI) of X (Extreme), as recorded in areas near the rupture zone, including Mandalay and parts of the Sagaing Region. The ground shaking was strong enough to be felt across much of Southeast Asia, including as far as Bangkok, Thailand—over 1,000 km from the epicenter—where geological conditions amplified long-period seismic waves, resulting in notable structural

¹Radiological Physics and Advisory Division, Bhabha Atomic Research Centre, Mumbai 400094, India. ²Health, Safety and Environment Group, Bhabha Atomic Research Centre, Mumbai 400094, India. ³Homi Bhabha National Institute, Mumbai 400094, India. ⁴Department of Physics, Manipur University, Canchipur, Imphal, Manipur 795003, India. ✉email: bsapra@barc.gov.in

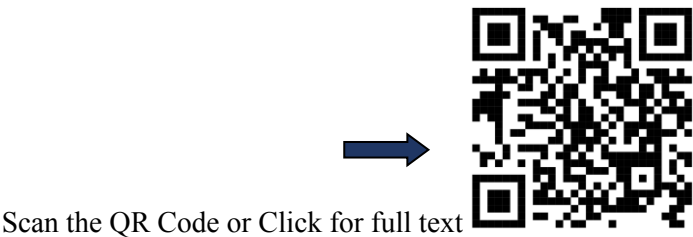


SHAKING	Not felt	Weak	Light	Moderate	Strong	Very strong	Severe	Violent	Extreme
DAMAGE	None	None	None	Very light	Light	Moderate	Moderate/heavy	Heavy	Very heavy
PGA(%g)	<0.0464	0.297	2.76	6.2	11.5	21.5	40.1	74.7	>139
PGV(cm/s)	<0.0215	0.135	1.41	4.65	9.64	20	41.4	85.8	>178
INTENSITY	I	II-III	IV	V	VI	VII	VIII	IX	X+

Fig. 1. Macro-seismic Intensity Map of Myanmar earthquake 7.7 M_w that occurred on March 28, 2025, at 06:20:52 UTC (Big Data Viz (Ver 0.1) Interface, Ellyptech, India, URL: www.ellyptech.com/init/products/bigdataviz).

damage and casualties. The earthquake claimed the lives of over 3000 people in Myanmar³. In addition, over 7,800 people were injured, and hundreds more were reported missing.

The rupture extended along an estimated 460–500 km section of the Sagaing Fault, which runs from the Andaman Sea through Myanmar to the Himalayan collision zone (<https://earthquake.usgs.gov/earthquakes/eventpage/us7000pn9s/executive>). Satellite data and seismic modeling indicate the event was a “supershear”





Journal of Cluster Science (2025) 36:215
<https://doi.org/10.1007/s10876-025-02943-7>

ORIGINAL PAPER



Adsorption Behaviour of Sarin on $\text{Zn}_{12}\text{O}_{12}$ and $\text{Cu}_{12}\text{O}_{12}$ Nanoclusters: A Theoretical Study Based on DFT Approach

Pramod Sharma^{1,3} · Chinagandham Rajesh² · Chiranjib Majumder^{1,3}

Received: 3 March 2025 / Accepted: 13 October 2025 / Published online: 28 October 2025
 © The Author(s) 2025

Abstract

Here we present adsorption and decomposition behaviour of sarin, a nerve gas molecule, on $\text{Zn}_{12}\text{O}_{12}$ and $\text{Cu}_{12}\text{O}_{12}$ cluster, as representative model for ZnO and CuO surface, using DFT formalism. LCAO-MO based approach has been adopted in the present study. For both the cluster systems investigated, sarin is found to interact with these clusters via dative bond involving lone-pair of phosphoryl oxygen as donor and Zn/Cu atom as acceptor. Sarin is found to undergo decomposition on these clusters via dissociation of O–isopropyl bond. The intrinsic reaction coordinate (IRC) analysis was performed for characterizing the transition states associated with decomposition of adsorbed sarin on $\text{Zn}_{12}\text{O}_{12}$ and $\text{Cu}_{12}\text{O}_{12}$ clusters. Gibbs free energy of activation ($\Delta G^\ddagger$) for decomposition of sarin is estimated to be 31.62 and 28.30 kcal/mol, for $\text{Zn}_{12}\text{O}_{12}$ and $\text{Cu}_{12}\text{O}_{12}$ clusters respectively. Our studies indicate that though decomposition of sarin on these substrates is thermodynamically favourable, the reaction rate of sarin decomposition is slow at room temperature. Thus implying requirement of higher temperature for the decomposition reaction, to be kinetically feasible.

Keywords DFT · Sarin · Decomposition · Organophosphorus Compounds · Clusters · $\text{Zn}_{12}\text{O}_{12}$ · $\text{Cu}_{12}\text{O}_{12}$

Introduction

Nerve gas agents (NA) are organophosphorus compounds - similar to pesticides, which interfere with the functioning of central nervous system and are classified as Chemical Warfare Agents (CWA). Conventionally CWA(s) are mitigated using gas masks, employing metal oxide impregnated activated carbon as filtration material [1]. However to develop efficient sorbents for mitigation of these NA(s) it is necessary to understand the surface chemistry and interactions of these molecules with various kinds of materials [2, 3].

Over the years catalytic oxidation of nerve gas agents using metals, clusters, surfaces of metal oxides, zeolites, MOFs [4–7] as substrates, has been extensively investigated. For these studies DMMP is commonly used as structural simulant for organophosphorus chemical warfare agents because of its comparatively much lower toxicity. Hence, several studies have been carried out on interaction of Dimethyl methylphosphonate (DMMP) with various substrates [8–11], though similar studies involving interaction of sarin with different substrates are comparatively sparse. In order to find a suitable material for decomposition of sarin, it is imperative to understand its interaction with different substrates. In this pursuit both experimental and computational efforts have been carried out by several groups on the adsorption and decomposition of nerve gas agents on a variety of surfaces, including metal oxides, clays and MOFs, to understand and design new filters and methods to mitigate these toxins. Nikmaram [12] carried out comparative study on dissociative adsorption of sarin on small Zn_nO_n and Cd_nO_n ($n=1,4$) clusters. Based on these studies higher interaction energies were reported for Zn_4O_4 and Cd_4O_4 clusters, with sarin molecule. Sarin predominantly interacts via oxygen of P=O group of sarin with ZnO clusters, while fluorine atoms of sarin interacts primarily with

✉ Pramod Sharma
 pramod@barc.gov.in

✉ Chiranjib Majumder
 chimaju@barc.gov.in

¹ Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

² RMC, Bhabha Atomic Research Centre, Mumbai 400094, India

³ Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

CdO clusters, causing its facile decomposition. Michalkova et al. [13] have investigated adsorption and decomposition of sarin on MgO surface, using representative cluster as model systems. Le et al. have carried out DFT calculations, investigating adsorption of sarin on three different surfaces of TiO₂ (anatase) and concluded that sarin chemisorbs on all three surfaces of TiO₂ by the formation of a dative bond between the phosphoryl oxygen and a five-coordinated titanium atom on the surface [14]. Roman et al. have carried out quantum chemical modelling for understanding decomposition of sarin on pristine MoO₃ [15] surface and have reported that DMMP and sarin molecules decompose via different decomposition mechanism. While for DMMP breaking of P-F bond is predominant, decomposition of sarin proceeds via elimination of propene molecule. Of late ZnO has become a material of interest following work of Holdren et al. [16] related to facile decomposition of DMMP on ZnO surface at room temperature, based on the experimental findings, which were also supported by DFT studies. ZnO nanoclusters of varying size have also been explored for applications in drug delivery and gas sensor development. These studies signify decrease in band-gap with increase in size of ZnO clusters, thus favouring interaction between the gaseous molecules and the cluster via charge-transfer process. Also larger size ZnO clusters ((ZnO)_n, *n* = 18, 60) have been projected as promising candidates for targeted drug delivery, due to strong interactions between the cluster and the drug molecules. [17–19]. Surface adsorption and decomposition of DMMP on CuO surface has also been extensively investigated, using in situ ambient pressure X-ray photoelectron and infrared spectroscopy techniques. Extensive room temperature decomposition of DMMP on CuO surface was observed and the mechanism of DMMP decomposition on CuO surface has been explained based on density functional calculations [20]. Moreover, ZnO and CuO are considered inexpensive, efficient, and durable catalyst for a variety of chemical reactions [21, 22].

In this work, computational investigations have been carried out to understand adsorption/decomposition of sarin on cluster of ZnO and CuO, utilizing Zn₁₂O₁₂ and Cu₁₂O₁₂ as model clusters. These clusters were preferred because of their higher stability and ability to form cluster assembled materials. [23]. Also these model cluster systems were chosen (as compared to clusters of larger size) due to their convenient optimum size, to save on computational cost. Though for larger size ZnO clusters, it is assumed that their ability to lose electrons decreases and their affinity for electrons generally increases [19]. Density functional theory (DFT) calculations were carried out using LCAO-MO approach, for understanding interaction of sarin with Zn₁₂O₁₂ cluster/Cu₁₂O₁₂ clusters, as well as to explore the mechanism and estimate the energy barriers for the dissociation of sarin on these cluster substrates.

Computational Methods

Computational studies were carried out at B3PW91 hybrid density functional level of theory (DFT), for studies related to interaction of sarin with Zn₁₂O₁₂/Cu₁₂O₁₂ clusters, as implemented in the program suite GAMESS [24]. Since for metal clusters, results obtained using B3PW91 functional were reported to be in-line, with more accurate coupled-cluster calculations [25]. Dunning type Aug-cc-pVDZ basis sets were placed on light atoms, while LANL2DZ basis set was used for Zn and Cu. LANL2DZ basis set is the most commonly preferred basis set in computational chemistry calculations involving heavy elements, as it effectively manages both relativistic effects and the core electrons of heavier elements. Geometric optimization of Zn₁₂O₁₂/Cu₁₂O₁₂ clusters, sarin molecule and several Zn₁₂O₁₂ (Cu₁₂O₁₂)-sarin adsorption complexes (both upon molecular and dissociative adsorption) were carried out. The adsorption energies (*E*_{ad}) of sarin upon interaction with Zn₁₂O₁₂ and Cu₁₂O₁₂ nanoclusters was calculated as follows –

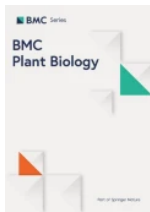
$$E_{ad} = E_{\text{sarin-cluster}} - (E_{\text{cluster}} + E_{\text{sarin}}) + E_{\text{BSSE}} \quad (1)$$

Where *E*_{sarin-cluster} is total energy of adsorbed sarin gas on cluster i.e. Zn₁₂O₁₂ or Cu₁₂O₁₂, while *E*_{cluster} and *E*_{sarin} are total energies of isolated cluster and sarin gas respectively. *E*_{BSSE} is the basis set superposition error (BSSE), calculated using the counter poise method [26]. All the transition states obtained displayed single imaginary frequency. The obtained transition states were further validated by carrying out intrinsic reaction coordinate (IRC) calculations, where the transition states transformed to the designated reactant and products. For characterizing the nature of bonding interactions AIM (Atoms-in-molecules) [27] and noncovalent interaction (NCI) analysis were performed using Multiwfn software [28].

Results and Discussion

The optimized geometries of Zn₁₂O₁₂ and Cu₁₂O₁₂ clusters, along with optimized geometry of sarin molecule are shown in Fig. 1. The optimized ground state geometry of Zn₁₂O₁₂ cluster is a cage like structure with T_h symmetry, comprising of six squares and eight hexagons. Structurally, two different types of Zn-O bonds were found within the cluster, one is shared by the two six-membered rings while the other is shared between the four and six membered ring. Their bond lengths were found to be 1.91 Å and 1.98 Å. The geometric parameters of the optimized structure are consistent with previous reports [29]. While the optimized geometry of Cu₁₂O₁₂ clusters represents an open ended





RESEARCH

Open Access



Agronomic improvement using gamma ray induced mutagenesis is associated with changes in phytochemical and phytohormonal profiles in functional rice variety 'Gathuwan'

Anjali Chauhan^{1,3}, Rahul Checker^{2,3*}, Parmeshwar K. Sahu^{4,5}, Raviraj Singh Patel⁴, Samrath Baghel⁴, Deepak Sharma^{2,3}, Deepak Sharma⁴ and Bikram K. Das^{1,3*}

Abstract

Background Gamma ray induced mutation breeding has emerged as an excellent method for expedited development of improved varieties of rice, a staple food for more than half the world's population. However, the assessment of radiation induced variations are primarily phenotypic in nature. In this direction, evaluation of the metabolic signature of bio-active ingredients, which confer beneficial properties to rice, could be employed as a tool to select varieties which not only retain the health benefits of the parent variety but also exhibit better agronomic traits. The present study was, therefore, aimed at evaluating the metabolomic changes in the mutants of Gathuwan, an indigenous Indian rice with immunomodulatory properties. The mutant varieties were developed through gamma irradiation, and liquid chromatography-tandem mass spectrometry (LC–MS/MS)-based metabolic profiling was performed.

Results A total of 274 differentially expressed compounds were identified among Gathuwan and four of its mutants (mutant 6, mutant 7, mutant 8 and mutant 12), indicating that gamma irradiation induced stable metabolic alterations. Significant differences were observed in the phytochemical composition of mutants relative to the parent, emphasizing the importance of metabolic screening in functional rice breeding. Cluster analysis and phytochemical profiling revealed that mutant 6 was metabolically closest to the parent variety. Additionally, distinct phytohormonal variations among the mutants were observed which may account for the phenotypic differences in growth and development.

Conclusions Our study demonstrates that radiation-induced improvement in agronomic traits are accompanied by distinct alterations in phytochemical and phytohormonal profiles in stable rice mutants. These metabolic changes

*Correspondence:

Rahul Checker
 rchecker@barc.gov.in
 Bikram K. Das
 bkdas@barc.gov.in

Full list of author information is available at the end of the article



© The Author(s) 2025. **Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

support the functional potential of the mutants and provide insights into the biological mechanisms underlying their traits. Among the mutants, mutant 6 emerges as a promising candidate due to its similarity to the parent in metabolite composition. Therefore, inclusion of metabolomic profiling as a selection criterion offers a powerful tool to identify robust and functionally superior rice varieties.

Keywords Rice, Gamma rays, Mutation breeding, Metabolomics, Phytochemicals, Phytohormones

Background

Rice is consumed by more than half of world's population for calories and basic nutrition. In 2022–23, worldwide consumption of rice was 520.4 million metric tons, of which a significantly large proportion was consumed by developing nations (<https://www.statista.com>). Large scale dependency on rice makes it a crucial contributor to the global food security and captivates more emphasis toward sustainable rice production. However, two important aspects which need to be considered for ensuring food security in future are that rice is a crop with vast diversity in agro-morphological traits along with nutritional and sensory qualities. The most widely consumed form of rice is polished rice, wherein the processing stripes off most of the nutritive elements. Numerous studies have shown unpolished rice to be healthier than the polished rice due to retention of bran and germ, the anatomical fractions of rice containing many nutrients and phytochemicals [1–3]. Emerging evidence indicates that among the plethora of existing rice cultivars, the traditional ones which have adapted and stood the test of time over thousands of years, produce biochemicals with beneficial effects on human health and disease conditions [4]. Many traditional rice varieties from countries like India, China, Thailand, Sri-Lanka etc. have been found to exhibit therapeutic effects as diverse as anti-oxidative, anti-allergic, anti-cancer, anti-diabetic, immune-stimulatory, cardioprotective, hepatoprotective etc., supporting activity based ethnic classifications of rice [5–9]. However, the lower yield of traditional varieties is a major drawback for their long-term commercial viability. Poor plant and panicle architecture along with long maturity duration are the factors responsible for the low yield. Hence there is a clear need to identify novel strategies that can be applied to overcome the undesirable traits associated with rice varieties having health promoting properties.

In this direction, inducing desired heritable changes in the phenotype of plants using physical mutagenic agents is an effective way to overcome the limitations of rice landraces within comparatively shorter span of time. Although radiation induced mutagenesis is a random process, it has the potential to generate wide combinations of traits providing opportunity to select and propagate the desirable one. Therefore, gamma ray induced mutagenesis has been extensively used for the improvement of yield, harvest time and efforts, nutrient use

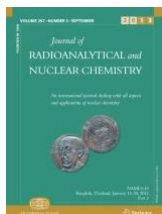
efficiency, stress tolerance and nutritional and organoleptic qualities in various crops [10–12], thus contributing significantly to food sustainability. Gamma rays induce broad spectrum mutations which manifests as diverse phenotypic, physiological and biochemical changes [13–15]. In crop improvement programs, major emphasis is laid on either phenotypic or physiological alterations. However, gamma rays have also been shown to alter contents of various biochemicals present in these varieties and also affect plant responses to various stresses [16–18]. These biochemical are often implicated in regulating the biological activities of different parts of plants and also known to be responsible for health promoting effects in humans [19–22]. In a study by Kim et al. (2004), metabolic changes led to balanced amino acid composition by enhancing the levels of limiting amino acids (lysine and tryptophan) in rice, along with increased protein content [23]. Kongdin et al. (2023) also showed the effect of gamma rays on phenolic compound accumulation in rice under stress conditions [24]. Taken together, these observations indicate that the mutant varieties may possibly acquire a different metabolic signature as compared to the parent variety due to altered biochemical pathways, particularly in case of plants of nutraceutical worth.

It is well accepted that the metabolome of a plant is an aggregation of all the metabolites (primary and secondary) and is responsible for shaping the morphology and functional properties of the plant. Therefore, in recent years, there has been an increased focus on deciphering the metabolic signature of plant products associated with their biological activity in different organisms. A large number of metabolic investigations are being conducted in rice for diverse purposes such as metabolic profiling, discriminating different rice cultivars, plant interaction with biotic and abiotic factors, stress response and integrated studies to understand functional gene-metabolite relationships [25–30]. Hence, utilizing a metabolomics guided approach can prove to be a valuable tool for the improvement of indigenous rice having medicinal properties.

In the present study, mutation breeding using gamma rays was employed to improve the agronomic traits of Gathuwan rice, a traditional rice variety originally collected from Abhanpur district of Chhattisgarh, India. It is being maintained as a part of India's largest rice germplasm collection at Indira Gandhi Krishi Vishwavidyalaya (IGKV), Raipur, Chhattisgarh. We have recently showed



Scan the QR Code or Click for full text



Journal of Radioanalytical and Nuclear Chemistry (2025) 334:5771–5783
<https://doi.org/10.1007/s10967-025-10313-w>



Assessment of TFWT and OBT in terrestrial plants at Tarapur, a tropical NPP Site in India, and a comparative analysis with model-computed concentrations

A. Baburajan¹ · R. H. Gaikwad¹ · V. K. Varakhedkar¹ · I. V. Saradhi² · A. Vinod Kumar²

Received: 21 May 2025 / Accepted: 27 July 2025 / Published online: 19 August 2025
 © The Author(s) 2025

Abstract

Tritium, a key radionuclide from pressurized heavy water reactors, disperses rapidly and is absorbed by organisms as Tissue-Free Water Tritium (TFWT) and Organically Bound Tritium (OBT). This study examines the measured TFWT and OBT concentrations in terrestrial plants around Nuclear Power Plant (NPP) site at Tarapur, India, from 2016 to 2018 and compared with the computed concentrations. A Gaussian Plume Model (GPM) was used to compute air tritium concentrations, incorporating meteorological data and site-specific model parameters. The key parameters include fractional water content (WCp), water equivalent factor (WEQp), and the OBT-to-TFWT ratio (Rp). Results show higher concentrations near the NPP, with measured values exceeding computed estimates may be due to GPM limitations and environmental variability. A statistical evaluations (mean fractional bias: −0.095) of computed to measured air tritium (2014 to 2018) confirmed systematic underestimation by computation, highlighting the need for field measurements and site-specific parameterization in tritium transport modelling.

Keywords TFWT · OBT · Site-specific data · Terrestrial plants · Tritium transport model

Introduction

In a Pressurized Heavy Water Reactor (PHWR), tritium is a key radionuclide that is released into the atmosphere. Tritium, a radioactive isotope of hydrogen, undergoes beta decay to form helium-3, emitting a beta particle with a maximum energy of 18.6 keV and an average energy of approximately 5.7 keV. It has a half-life of 12.312 years [1]. Tritium is of ecological significance due to its rapid dispersion in the environment and absorption by living organisms. Once released, it settles on the ground through processes such as diffusion and precipitation [2]. Tritium in the form of hydrogen gas (HT) is quickly converted into tritiated water (HTO) by microbial activity in the soil [3, 4]. Plants absorb

tritium through two main pathways: root uptake from soil and foliar absorption of atmospheric HTO [5, 6]. Once in the atmosphere as HTO or T₂O, tritium readily exchanges with the tissue-free water of organisms, leading to its transformation into Tissue-Free Water Tritium (TFWT) within minutes to hours [7]. Over time, tritium also integrates into organic plant matter during photosynthesis in a slow phase, forming Organically Bound Tritium (OBT) [8–10]. This form of tritium is chemically bound to carbon atoms in plant tissues and has a longer retention period compared to tritiated water. Among the different pathways of OBT formation, photosynthesis in green leaves plays a major role, using HTO as a precursor.

The movement of tritium through the environment and its assimilation by plants depend on various environmental and plant-specific factors. While several models attempt to describe tritium transport and distribution within plant systems, no universal model applies to all environmental conditions. The International Atomic Energy Agency (IAEA) TECDOC-1616 [11] proposes a generic specific activity model designed for specific conditions, assuming that tritium concentrations within different environmental compartments remain in equilibrium. This model is commonly used for

✉ A. Baburajan
 babu_aramana@yahoo.co.in

¹ Environmental Survey Laboratory, Environmental Monitoring and Assessment Division, Bhabha Atomic Research Centre, TAPS Colony, TAPP (P.O.), Tarapur, Palghar, Dt.) 401504, India

² Environmental Monitoring and Assessment Division, BARC, Trombay, Mumbai 400085, India

routine dose assessments of populations living near nuclear power plants (NPPs) due to tritium emissions. A schematic diagram of specific activity model for tritium transport for routine release is provided in Fig. 1 [12].

The atmospheric transport model consists of three main compartments: air, soil, and plants. Within plant systems, tritium exists in two primary forms: TFWT, which is exchangeable with water, and OBT, which remains bound within plant tissues. Several site-specific parameters influence tritium transfer, including the air-to-soil transfer ratio (CRs), fractional water content in plants (WCp), water equivalent factor (WEQp), and the OBT-to-TFWT ratio (Rp). These factors vary significantly based on environmental conditions, necessitating the determination of location-specific transfer ratios. The site-specific parameters derived in this study have been integrated into a tritium transport model, which is used to estimate TFWT and OBT concentrations in terrestrial plants. These computed values are then compared with actual field measurements to assess the model's accuracy.

Experimental

Site description

Tarapur, a major nuclear site located on the west coast of India (19°50'N, 72°39'E), situated approximately 100 km north of Mumbai. The site hosts multiple nuclear facilities, including two Boiling Water Reactor (BWR) units, each with a capacity of 160 MWe, collectively known as Tarapur Atomic Power Station Units 1 and 2 (TAPS 1&2). Additionally, it houses two Pressurized Heavy Water Reactor (PHWR) units, each generating 540 Mwe, referred to as Tarapur Atomic Power Station 3 and 4 (TAPS 3&4). Other key facilities at the site include the Power Reactor Fuel Reprocessing Plant (PREFRE), the Advanced Fuel Fabrication Facility (AFFF), and Waste Management Facilities. As

shown in Fig. 2, the sampling points are distributed within 5 km of the nuclear power plant.

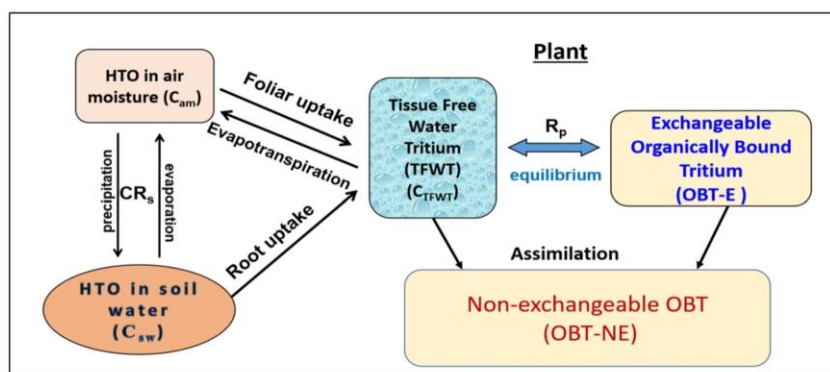
Calibration

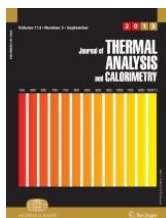
HTO samples were analyzed using a Quantulus Model Q-1220 liquid scintillation spectrometer (PerkinElmer, USA). The system had a background count rate of 0.8 CPM within the window region of 50–170, achieving an optimal Figure of Merit (FOM) value of 551. The FOM was calculated using the formula E^2/B , where E represents counting efficiency in percentage and B denotes the system background in counts per minute (CPM). The counting efficiency for HTO was approximately 21% when using a 10 mL sample combined with 10 mL of scintillator. The minimum detectable activity (MDA) at a 3 σ confidence level for a counting time of 100 min was determined to be 2 Bq·L⁻¹. Routine calibration of the liquid scintillation analyzer (LSA) is well explained in Baburajan et al. [13].

Quality assurance

In addition to routine calibration of the LSA, the laboratory actively participates in inter-laboratory proficiency tests conducted by the International Atomic Energy Agency (IAEA). These tests involve measuring tritium alongside other radionuclides, with the most recent program being IAEA-TERC-2024-01. In this assessment, the laboratory reported a tritium activity of 20.6 ± 3.03 Bq·kg⁻¹, closely aligning with the target value of 19.5 ± 1.0 Bq·kg⁻¹, and successfully met the test criteria with a relative bias of +5.64%. Also participated in OBT inter-comparison exercise organized by International Tritium Working Group for the determination of OBT in sediment sludge sample (GAU-Radio Analytical—International Working Group on OBT, 2014) in 2014. The result on OBT reported 167 ± 9 Bq·kg⁻¹ (dry) (Sample code # 20) was in agreement with the reference value of 168 ± 22 Bq·kg⁻¹ (dry) and passed all the test criteria [14].

Fig. 1 General Scheme of tritium transport and cycling in the vegetation [12]





Calorimetric investigation of ternary oxides in the CuO–V₂O₅ system

P. M. Aiswarya^{1,2} · S. Narang^{1,2} · Rimpi Dawar^{1,2} · P. D. Babu³ · R. Mishra^{1,2}

Received: 31 December 2024 / Accepted: 14 August 2025 / Published online: 14 October 2025
 © The Author(s) 2025

Abstract

In the present study, we present the experimental investigation on thermochemical stability of five compounds in Cu–V–O ternary system i.e., CuV₂O₆(s), Cu₂V₂O₇(s), Cu₃V₂O₈(s), Cu₅V₂O₁₀(s) and Cu₁₁V₆O₂₆(s). The molar heat capacity of these compounds was determined in the temperature range 2–770 K employing relaxation calorimetry in conjunction with differential scanning calorimetry. The standard molar entropies of formation of the compounds were determined by low temperature heat capacity measurements from 2 to 300 K using relaxation calorimetry. A high temperature oxide melt solution calorimeter was employed to determine the standard molar enthalpy of dissolution of these compounds in sodium molybdate solvent. Using the experimentally obtained thermochemical data, the standard molar enthalpy of formation of these compounds were derived.

Keywords CuO–V₂O₅ system · Molar heat capacity · Magnetic entropy · Oxide melt calorimetry · Enthalpy of formation

Introduction

The ternary oxides in the CuO–V₂O₅ system have been extensively investigated for various applications, such as ion exchange materials, antibacterial additives, and dye photolytic degradation materials [1–3]. Their small band-gap (~2 eV) and remarkable stability against photocorrosion have made them attractive photoanodes for solar fuel generation [4]. They exhibit higher photoelectrochemical stability compared to many other vanadates, and hence, are employed as anodes for photo-electrochemical water splitting applications [5–7] and hydrogen generation [6]. Due to their advantageous electrochemical properties, copper vanadates are also being investigated as cathode materials for high-energy lithium-ion batteries and electrochemical sensors [8–10]. Furthermore, they are reported to be useful in

magnetic memory and display devices [11] and as catalysts for the oxidation of the exhaust gases of internal combustion engines and thermal power plants [12].

While there has been a lot of research on the physical properties and crystal structures of compounds in the CuO–V₂O₅ system, it has been less investigated from a thermodynamic perspective. The phase diagrams reported so far on the CuO–V₂O₅ system contradict each other in terms of the existence and stability of ternary phases in the system. The recent phase equilibria [13–17] reported on this system show the presence of five ternary oxides, namely, CuV₂O₆(s), Cu₂V₂O₇(s), Cu₃V₂O₈(s), Cu₅V₂O₁₀(s) and Cu₁₁V₆O₂₆(s). Among these, both Cu₂V₂O₇(s) and Cu₃V₂O₈(s) are reported to exhibit polymorphism. But disagreements exist regarding the number of polymorphs and their respective transition temperatures as detailed in Table 1. Moreover, many of the thermochemical properties of these copper vanadates have remained poorly investigated. The only experimental thermochemical data available on these compounds are the heat capacities of CuV₂O₆(s) [14, 18, 19], Cu₂V₂O₇(s) [19–22], Cu₃V₂O₈(s) [23–25] and Cu₅V₂O₁₀(s) [26] compounds. A thorough experimental investigation of their thermochemical properties is essential to predict their stability and effectiveness in reactive environments, and it can also enable the calculations to optimize the thermodynamic relations in the system. In this context, a detailed calorimetric investigation leading to the determination of the standard molar enthalpy

P. M. Aiswarya and S. Narang contributed equally to this work.

✉ Rimpi Dawar
 rimpid@barc.gov.in

¹ Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

² Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

³ UGC-DAE Consortium for Scientific Research, Mumbai Centre, Trombay, Mumbai 400085, India

Table 1 Literature data on the polymorphic transitions displayed by Cu₂V₂O₇(s) and Cu₃V₂O₈(s) compounds

References	Information on the polymorphism of Cu ₂ V ₂ O ₇ (s)
Brisi and Molinari [13]	α-Cu ₂ V ₂ O ₇ to β-Cu ₂ V ₂ O ₇ transition at 933 K Could not isolate high-temperature Cu ₂ V ₂ O ₇ β-phase
Mercurio-Lavaud and Frit [17]	Isolated the α and β Cu ₂ V ₂ O ₇ (s) phases with transition temperature at 985 K
Clark [27]	Reported three polymorphs for Cu ₂ V ₂ O ₇ (s): low temperature orthorhombic α-Cu ₂ V ₂ O ₇ , intermediate monoclinic-I β-Cu ₂ V ₂ O ₇ and high temperature monoclinic-II γ-Cu ₂ V ₂ O ₇ Formation of β-Cu ₂ V ₂ O ₇ phase at temperatures less than 823 K Formation of α-Cu ₂ V ₂ O ₇ phase between 823 and 953 K Formation of γ-Cu ₂ V ₂ O ₇ at temperatures higher than 953 K Reversible α to γ transition at 978 K Relatively slow γ to α transition Reversible β to α transition at 878 K α to β transition is relatively slow
Petrova [28]	Observed three polymorphs for Cu ₂ V ₂ O ₇ : α, β and β' phases Both α and β phases stable at room temperature High temperature β' phase (monoclinic II) forms between 978 and 985 K and is stable up to the melting point (1053 K)
Slobodin [8]	Synthesized the β-Cu ₂ V ₂ O ₇ by solid-state reaction at 773 K β-Cu ₂ V ₂ O ₇ to α-Cu ₂ V ₂ O ₇ irreversible transition at 883 K α to γ-Cu ₂ V ₂ O ₇ transition between 971 and 980 K γ to α-Cu ₂ V ₂ O ₇ transition between 912 and 881 K, α-phase is a structurally distorted phase Distorted α-Cu ₂ V ₂ O ₇ to β-phase transition between 881 and 884 K
Denisova [19]	Observed polymorphic transitions in Cu ₂ V ₂ O ₇ (s) during heat capacity measurements, which showed two maxima at 899 and 986 K corresponding to α to β' and β' to β transitions
Rao and Palanna [29]	Reported existence of γ-orthorhombic Cu ₃ V ₂ O ₈ phase α-Cu ₃ V ₂ O ₈ is stable between 708 and 783 K β-Cu ₃ V ₂ O ₈ is stable between 808 and 818 K γ-Cu ₃ V ₂ O ₈ is stable at high temperatures above 818 K
Andrzej Jezierski [7]	Observed the triclinic (α) and monoclinic (β) phases of Cu ₃ V ₂ O ₈ (s) α to β phase transition at 733 K

of formation and molar heat capacity of all five ternary compounds in the CuO–V₂O₅ system is performed in the present work.

Experimental

Materials and synthesis

For the preparation of ternary compounds in the CuO–V₂O₅ system, powders of reagent-grade CuO(s) and V₂O₅(s) were used. These metal oxide powders were subjected to prior heating at 573 K for 6 h to remove any adsorbed moisture. To carry out high-temperature solution calorimetric experiments, a molten solvent of composition 3Na₂O·4MoO₃ was used. This molten solvent was prepared from an intimate mixture of Na₂CO₃(s) and MoO₃(s) in the respective molar ratio. A list of all the chemicals employed in this study, along with their source and purity, is provided in Table 2.

The five ternary compounds in the CuO–V₂O₅ pseudo binary system, namely, CuV₂O₆(s), Cu₂V₂O₇(s), Cu₃V₂O₈(s), Cu₅V₂O₁₀(s), and Cu₁₁V₆O₂₆(s), were synthesized by the solid-state reaction of CuO(s) and V₂O₅(s)

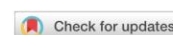
powders. The starting metal oxide powders were accurately weighed in their respective stoichiometric proportion and ground well to prepare a homogeneous mixture. The intimate mixture was then compacted into pellets and heated in platinum crucibles under atmospheric conditions. Different calcination temperatures and durations of heating were employed for the synthesis of different Cu–V–O compounds. Details of compositions and the reaction conditions employed are provided in Table 3.

In order to reduce the volatilization of V₂O₅(s) at high temperatures, heating was carried out in steps. The mixture was ground intermittently to ensure the completeness of the reaction. After the heating process, the samples were furnace-cooled to room temperature. The pellets were then crushed and ground into powders and were subjected to further experimental evaluation.

Sample characterization

The formation of the synthesized compounds was verified employing a Rigaku room temperature X-ray diffractometer with Cu Kα radiation. The diffraction patterns were recorded in the 2θ range 10 to 80° with a step size of 0.008°.





OPEN Cardio-renal protection and mechanisms of the antihypertensive activity of Alcalase-derived moth bean hydrolysate in DOCA-salt induced hypertensive Wistar rats

Nancy Goyal^{1,3}, Jitesh Singh Rathee², Sachin N. Hajare^{1,3}✉ & S. Gautam^{1,3}

Hypertension remains a major global health concern, often leading to severe cardiovascular and renal complications. In this study, we investigated the antihypertensive and cardiorenal protective effects of AF4, a bioactive Alcalase derived peptide fraction (<1 kDa) derived from moth bean protein hydrolysate, in a DOCA-salt hypertensive rat model. AF4 administration significantly reduced systolic blood pressure in a dose-dependent manner, with the minimum effective dose (75 mg/kg body weight/day) selected for further mechanistic evaluation. Treatment with AF4 improved various physiological parameters, including heart rate, cardio-myocytes conduction, electrocardiogram (ECG) abnormalities, and kidney function markers. Biochemical analyses revealed that AF4 act as ACE inhibitor, led to reduction of angiotensin II plasma levels, and subsequently endothelin-1, and vasopressin, while enhancing nitric oxide (NO) bioavailability. The antioxidant capacity of AF4, both direct and enzyme-mediated, reduced oxidative stress and inflammation by lowering ROS, TNF- α , and IL-6 levels, thereby preventing endothelial dysfunction and vascular damage. Histopathological analysis of cardiac and renal tissues demonstrated that AF4 mitigated fibrosis, myocardial infarction, and renal sclerosis, further confirming its protective effects. Overall, AF4 displayed significant antihypertensive potential through its multifaceted actions on RAAS modulation, oxidative stress reduction, and inflammation control, providing a promising candidate for the management of hypertension and associated organ damage.

Keywords Hypertension, DOCA-salt hypertensive rat, Systolic blood pressure, Electrocardiogram, Inflammation

Hypertension remains one of the leading risk factors for cardiovascular diseases (CVD), contributing to approximately 20% of global deaths, as reported by the Global Burden of Disease 2020. Despite the alarming statistics, hypertension often goes undiagnosed, untreated, or undertreated in nearly two-thirds of affected individuals, underscoring its critical role as a preventable cause of CVD¹. It is a multifaceted condition, involving complex interactions within the cardiovascular, renal, and vascular systems, along with disturbances in the antioxidant defence mechanisms. These pathological alterations not only increase blood pressure but also contribute to progressive organ damage, particularly in the kidneys and heart. Given the intricacies of hypertension and its global health burden, effective management strategies are urgently needed to prevent and mitigate its detrimental effects.

In recent years, the potential of natural compounds (bioactive peptides, phenolics, and other plant-derived substances) has garnered significant attention for their antihypertensive and cardioprotective properties.

¹Food Technology Division, Bhabha Atomic Research Centre, Mumbai 400085, India. ²Bio-Organic Division, Bhabha Atomic Research Centre, Mumbai 400085, India. ³Homi Bhabha National Institute, Anushakti Nagar, Mumbai 400094, India. ✉email: shajare@barc.gov.in

These compounds offer promising therapeutic alternatives with fewer side effects compared to conventional antihypertensive drugs. Among these, bioactive peptides derived from food proteins have demonstrated antihypertensive potential through multiple mechanisms, including antioxidant and angiotensin converting enzyme (ACE) inhibition.

Moth bean (*Vigna aconitifolia*), a draught tolerant minor legume that grows in arid regions, consists of high contents of bioactive compounds (phenols, peptides)^{2,3}. Previous studies, have highlighted the beneficial effects of moth bean phenolic extracts, particularly their anti-diabetic and antioxidant properties^{2,4}. Our earlier work also demonstrated the ACE-inhibitory and antioxidant effect of < 1 kDa peptide fraction of moth bean hydrolysate derived from Alcalase treatment, designated as AF4^{4,5}. In that work, moth bean protein concentrate was enzymatically hydrolyzed using different proteases. Among them, the hydrolysate generated with Alcalase-exhibited highest ACE-inhibitory activity along with considerable antioxidant capacity. To further enrich the bioactive peptides content, the hydrolysate was fractionated on the basis of molecular weight that led to generation of 4 fractions: AF 1 (protein hydrolysate); AF2 (< 10 kDa fraction); AF3 (< 3 kDa fraction); AF4 (< 1 kDa fraction). Among these four fractions, AF4 showed highest ACE inhibitory activity. To investigate the therapeutic potential of AF4 in vivo, DOCA (Deoxycorticosterone acetate)-salt hypertensive rat model was employed. DOCA-salt model is a well-established hypertensive model that involves DOCA administration, salt water intake and uni-nephrectomy. This model helps in induction of severe hypertension in rats in less time that impact blood volume, kidney dysfunction, oxidative stress, inflammatory conditions, as well as heart and vascular pathology⁶. Hemodynamic overload is a key determinant in functional and morphological changes in cardiac and kidney, causing high blood pressure⁷.

This study aimed to evaluate the antihypertensive effect of AF4 and elucidate the underlying mechanisms in a DOCA-salt hypertensive rat model. The research primarily focused on the modulation of the renin-angiotensin aldosterone system (RAAS), particularly angiotensin II, oxidative stress, and inflammatory responses⁸ along with its impact on endothelin-1 (ET-1), vasopressin, and nitric oxide (NO) levels. It also examined markers of cardiac and renal injury to understand AF4's therapeutic potential in hypertension. The findings highlight the role of AF4 in regulating blood pressure, reducing oxidative stress, and inflammation, supporting cardiovascular health as a natural intervention.

Materials and methods

Drugs, chemicals, reagents and assay kits

All the chemicals used in the study were of analytical grade. Ketamine and xylazine were procured from Themis Medicare Ltd., Mumbai, India and Indian Immunologicals Ltd, Telangana, India, respectively. Sodium thiopentone was obtained from Neon Laboratory Ltd., Mumbai, India while heparin and sodium chloride (AR grade) was procured from HiMedia Laboratories Pvt. Ltd., Mumbai, India. Deoxycorticosterone acetate (DOCA) was from Tokyo Chemical Industry, Shanghai, Japan and dimethyl sulfoxide (DMSO) was from Merck, Germany. Phenyl methyl sulfonyl fluoride (PMSF), dimethylformamide (DMF), formaldehyde solution (37%) and Bradford's reagent were procured from Sigma Aldrich (Sigma, St. Louis, MO, USA). Rat endothelin-1 (ET-1) and vasopressin assay kits were obtained from Krishgen Biosystems (Mumbai, India). Creatine Kinase (CK)-MB, and Creatine Kinase (CK)-NAC assay kits were sourced from Coral Clinical Systems (India), while angiotensin II, Interleukin -6 (IL-6), and Tumor necrosis factor (TNF)-alpha determination kits were purchased from Cloud-Clone Corp. (TX, USA). Kits for Super oxide dismutase (SOD), catalase, and total antioxidant capacity assays were obtained from Elabscience Biotechnology Inc. (TX, USA). Additionally, nitric oxide (NO) and nitric oxide synthase (NOS) level determination kits were acquired from Abcam Inc (MA, USA).

Moth bean hydrolysate Preparation

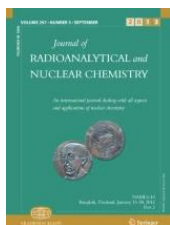
Moth bean protein hydrolysate was prepared by enzymatic hydrolysis of defatted moth bean seed powder using Alcalase, as previously described in our study⁴. Briefly, the seed powder was suspended in distilled water at a protein-to-enzyme ratio of 10:1 (w/w) and subjected to hydrolysis at pH 8.0 and 45 °C for 3 h. The enzyme activity was terminated by heating the solution at 95 °C for 15 min to denature the enzyme. The hydrolysate was then centrifuged to remove insoluble materials, and the resulting supernatant was collected. The supernatant was filtered by using 1 kDa molecular weight cut-off ultrafiltration membrane. The permeate was subsequently lyophilized and stored at - 20 °C until further use.

Experimental design and ARRIVE statement

Healthy male Wistar rats of 190–220 g weight were obtained from the animal facility at BARC, Mumbai, India following clearance from BARC Animal Ethics Committee (BAEC/33/21 dt. 01/12/2021). The animals were accommodated under standard conditions (22 ± 1 °C, 12-hour light/dark cycle, 75% humidity) with *ad libitum* access to food and water. Though the maximum humidity recorded was 75% which is slightly higher than the recommended, the overall health of the animals was normal and stringent husbandry practices were followed to keep them healthy. All experiments were conducted following the guidelines of the National Institutes of Health (NIH, 1996) for the care and use of laboratory animals and the authors strictly complied with the ARRIVE guidelines.

Before undergoing uni-nephrectomy, rats were screened for variations in systolic blood pressure, and only those exhibiting normal blood pressure were selected for this study. The DOCA-salt hypertensive rat model was developed as per the previous reports⁶, briefly rats were anesthetized with a mixture of ketamine (70 mg/kg body weight) and xylazine (7 mg/kg body weight) administered intraperitoneally. A small incision was made on the left dorsal side to remove the left kidney, and the ureter was ligated with thread. Left kidney was excised out and the incision site was then sutured in layers with sterile suture (Ethicon PROLENE No. 3 – 0), and the kidney was blotted dry and weighed. Starting the next day, the rats received subcutaneous injection of DOCA (30 mg/





Journal of Radioanalytical and Nuclear Chemistry (2025) 334:4751–4763
<https://doi.org/10.1007/s10967-025-10255-3>



Comparative study on sugars for high-dose measurements using diffuse reflectance spectrometry

S. H. Shinde¹ · Sandip Mondal¹ · Sneha Chandrasekhar¹ · Probal Chaudhury²

Received: 10 February 2025 / Accepted: 25 June 2025 / Published online: 15 July 2025
 © The Author(s) 2025

Abstract

This study optimizes grain size, irradiation conditions, and environmental factors for accurate diffuse reflectance spectrometry (DRS) dosimetry in fructose, glucose, and sucrose. A grain size of 250–500 µm showed minimal reflectance variation. Reflectance spectra confirmed stable dose–response relationships, with unirradiated sugars remaining stable for 350 days. Post-irradiation reflectance decreased by 15% within 65 h but remained consistent afterward. Temperature variations (–5 to 60 °C) had no significant impact. Dose fractionation and rate changes did not alter responses, confirming DRS reliability. This study supports DRS as a precise dosimetry tool with applications in food safety and radiation processing.

Keywords Fructose · Glucose · Sucrose · Diffuse reflectance · Radiation processing · High dose dosimetry · Spectrophotometric read-out

Introduction

In the past, sugar gained significant attention as a potential emergency dosimeter for the general population following large-scale radiological accidents, such as the Chernobyl disaster. Sugar was used to estimate radiation doses in Pripyat residents after the Chernobyl accident [1–3]. Similarly, in 1994, an accident occurred in Kiisa, Estonia, where a high-activity Cs-137 source was discovered in the kitchen of a private residence. Due to insufficient data, dose calculations were uncertain. The methods used for dose assessments during radiation sickness, including biological dosimetry, were not sufficiently accurate and were not applied to all affected individuals. As a result, sugar was utilized to measure the integrated dose in the kitchen [4].

When exposed to ionizing radiation, sugar molecules in solid or liquid states can undergo chemical transformations due to the high-energy radiation, leading to defects in crystal lattice, molecular breakdowns, formation of free radicals or other reactive species. These radiation-induced

changes may alter the molecular structure or crystal lattice of the sugar, which is reflected in a change in its colour [5–7]. These structural modifications can be quantified using various analytical techniques, including ESR, UV–Vis spectrophotometry, luminescence spectrometry, viscometry, refractometry, and chromatography [8–15]. Sugar dosimetry is cost-effective, requiring minimal specialized equipment. Compared to Electron Spin Resonance (ESR), sugar dosimetry using diffuse reflectance spectrometry (DRS) is significantly more cost-effective and accessible, as ESR requires highly specialized and expensive instrumentation along with expert operation and maintenance, whereas DRS relies on a relatively affordable UV–Vis spectrophotometer and uses readily available sugars as dosimetric materials. DRS offers rapid, reproducible measurements suitable for high-dose applications such as food irradiation and radiation processing, making it a practical alternative for routine or emergency dosimetry where ESR is impractical due to cost, complexity, and infrastructure demands. Sugar dosimeters are highly sensitive and can provide precise measurements for various types of radiation (e.g., X-rays, gamma rays, neutrons), depending on the specific formulation and conditions.

Among the mentioned methods, ESR is not cost-effective due to the need for an expensive ESR spectrometer. The cost of an ESR spectrometer stems from the combination of high-end microwave and magnetic components, precision engineering, and specialized operational requirements,

✉ S. H. Shinde
 shshinde456@gmail.com

¹ Radiation Safety Systems Division, Bhabha Atomic Research Centre, Mumbai 400085, India

² Health Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India

making it significantly more expensive than many other spectroscopic techniques. Other techniques, such as luminescence, viscosity, refractive index measurements, and chromatography, often exhibit greater measurement uncertainty, lower reproducibility, are time-consuming or are affected by environmental conditions, making them unsuitable for routine or industrial dosimetry where reliable and repeatable dose assessments are critical. Common table sugar (sucrose) consists of two main molecular components—glucose and fructose—and each of these sugars has demonstrated distinct dosimetry properties in electron paramagnetic resonance (EPR) studies [16]. Additionally, diffuse reflectance has been reported as an effective method for measuring dosimeters [17]. Therefore, a comparative dosimetry study was conducted on sugars viz: fructose, glucose, and sucrose; using diffuse reflectance as the read-out technique. This approach involves measuring the light scattered from the material's surface to quantify structural and chemical changes induced by radiation exposure [16–19]. However, there has been limited research on applying diffuse reflectance techniques to sugar-based dosimeters.

To address this gap, the present study aims to evaluate the feasibility and effectiveness of using fructose, glucose, and sucrose as economical, reliable dosimetric materials by employing diffuse reflectance spectrometry (DRS) of fructose, glucose, and sucrose; as a low-cost, accessible read-out method for high-dose radiation measurements. By evaluating the light scattered from the surface of irradiated sugar samples, this approach aims to quantify structural and chemical changes resulting from high-dose radiation exposure. The study explores the feasibility of using these sugars as reliable, economical dosimeters, thereby offering a practical alternative to conventional ESR-based methods.

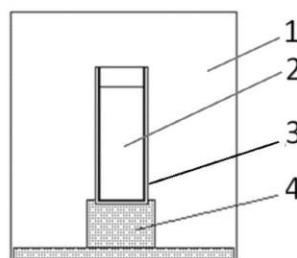
Experimental

Sugars (monosaccharides and disaccharides) viz: fructose, glucose, and sucrose of analytical grade were acquired from Merck, Germany, and used without further purification.

Irradiation was performed using a Gamma Chamber 1200 (GC1200), calibrated using the Fricke dosimeter [20], a widely recognized reference standard as per ISO/ASTM 51026 [20]. This setup ensures dose accuracy and reproducibility, consistent with previous works (e.g., [9, 10]), where Fricke dosimetry was also used for calibration in high-dose sugar dosimetry. Fricke dosimeter consisted of a Fricke solution sealed in airtight polypropylene containers, each with dimensions of 13 mm outer diameter, 1 mm wall thickness, and 54 mm height. Samples were placed in polypropylene containers and packed into a Perspex jig to ensure reproducible geometry and electronic equilibrium during irradiation (Fig. 1), a method similarly applied by Zagórski and Rafalski [18] for consistent sample alignment in DRS studies.

Reflectance spectra were measured using a Shimadzu UV-3600 Plus UV–Vis spectrophotometer equipped with an ISR-603 integrating sphere, following the method used by Piliero et al. [19] in DRS-based dosimetry for GAFchromic films. The reflectance was recorded in the 375–640 nm range using barium sulphate as a reference, but without mixing the sugars with BaSO₄—streamlining the procedure while maintaining spectral integrity as supported by Meeten and North [14] in refractance-based dosimetry. The samples were irradiated with gamma rays at doses ranging from 1 to 46 kGy, with multiple samples at each dose level to ensure accuracy and reproducibility. The dose range of 1–46 kGy was selected based on the individual dosimetric responses of the sugars under study—glucose, fructose, and sucrose—as well as the typical dose levels used in high-dose radiation processing. The lower limit of 1 kGy was chosen to evaluate the detection threshold and sensitivity of the sugars at the onset of radiation exposure, which is relevant for low-dose applications like food preservation. The upper limits were extended based on the maximum linear or usable response observed in each sugar type, ensuring that the full dynamic range of reflectance changes could be captured. Moreover, the range aligns with typical dose levels used in industrial applications such as food irradiation, sterilization of medical products, and polymer modification, where doses from 1 to 50 kGy are commonly employed.

Fig. 1 Irradiation setup



1. Irradiation volume of GC1200 2. Fricke dosimeter 3. Build-up 4. Perspex Jig





J Mater Sci: Mater Electron (2026) 37:116



Comparison of electrochemical properties of bismuth oxide/sulfide core@shell and heterostructure composites as anode material for lithium-ion batteries

Akhilesh C. Joshi^{1,3}, Dimple P. Dutta^{2,3,*}, and B. Vishwanadh⁴

¹ Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

² HRDD, Knowledge Management Group, Bhabha Atomic Research Centre, Mumbai 400085, India

³ Homi Bhabha National Institute, Mumbai 400094, India

⁴ Materials Science Division, Bhabha Atomic Research Centre, Mumbai 400085, India

Received: 22 October 2025

Accepted: 24 December 2025

Published online:

6 January 2026

© The Author(s), 2025

ABSTRACT

Core-shell ($\text{Bi}_2\text{O}_3/\text{Bi}_2\text{S}_3$) and heterostructure composites of bismuth oxide (Bi_2O_3) and bismuth sulfide (Bi_2S_3) have been produced using wet chemical method. The performance of both materials as anode material for lithium-ion battery (LIB) have been evaluated. The $\text{Bi}_2\text{S}_3/\text{Bi}_2\text{O}_3$ heterostructure composite exhibited superior electrochemical performance compared to $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{S}_3$ core-shell for LIB. It demonstrated high coulombic efficiency, high capacity, superior capacity retention, excellent rate capability, and long cycle stability. Higher capacity of $\sim 530 \text{ mAh g}^{-1}$ was obtained for $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{S}_3$ heterostructure composite compared to $\sim 335 \text{ mAh g}^{-1}$ for $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{S}_3$ core-shell anode after a run of 500 cycles. Polysulfide shuttling is more prevalent in the core-shell $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{S}_3$ in which the outer shell is predominantly Bi_2S_3 compared to $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{S}_3$ heterostructure composite. As sodium-ion battery anode, the $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{S}_3$ heterostructure composite delivers a reversible discharge capacity of 421 mAh g^{-1} at current rate of 100 mA g^{-1} after 200 cycles. Materials characterization and electrochemical analysis revealed that enhanced energy storage properties of $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{S}_3$ heterostructure composites are accredited to the synergistic effect of upgraded charge transfer in the heterostructures and reduced polysulfide leaching compared to the core-shell structures. The results showed that $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{S}_3$ heterostructure composites have high potential for application as advanced anodes for Li-ion and Na-ion storage.

Address correspondence to E-mail: dimpled@barc.gov.in

1 Introduction

At present, there is a growing utilization of portable electronic devices among the general population. This trend has resulted in an increased demand for the development of energy sources that are lightweight, portable, have a long lifespan, and exhibit high energy density. Lithium-ion batteries (LIBs) essentially fulfill most of these requirements and are widely employed in various portable devices, including mobile phones, laptops, smartwatches, and more [1]. Typically, in commercially available LIBs, the anode is made of graphite. Nevertheless, this material presents certain drawbacks, such as a limited theoretical specific capacity of 372 mAh g^{-1} and inadequate rapid charging capabilities [2]. Consequently, numerous research studies have been conducted to identify other materials of interest. The anode materials in LIBs fundamentally operate based on three mechanisms: intercalation, conversion, and alloying [3]. The mechanism of intercalation is prevalent in layered or framework materials characterized by open structures that contain a significant number of vacant spaces. The benefits of intercalation-type anodes include minimal volume changes and mechanical strain, which consequently enhance the cycle stability of the battery [4]. However, anode materials that utilize intercalation, such as graphite and hard carbon, exhibit relatively low capacity [5]. The mechanism of the conversion reaction is a process wherein electrochemical reaction take place between Li^+ ions and the electrode material, resulting in the creation of new compounds. Metal oxide electrode materials, particularly Transition Metal Oxides (TMOs), typically function according to this mechanism [6]. The mechanism encompasses a relatively high specific capacity, prolonged cycle life, substantial volume change, and low conductivity. In the alloying mechanism, the formation of alloys between the electrode material and Li^+ ions influence the characteristics of the electrochemical reaction [7]. The anode materials, which include Si, Sb, Bi, and Sn, are precisely materials that partake in alloying reactions with Li^+ ions. Though alloying-type anodes demonstrate a remarkably high specific capacity, the large volume change that occurs during lithiation/delithiation poses a significant disadvantage for these materials. It is to be noted that compounds of elements such as Si, Sn, Bi, Sb, and Zn exhibit both alloying and conversion mechanisms [8]. Due to the synergy of these two mechanisms, these active materials exhibit excellent

potential for use as electrodes in battery with high theoretical capacity, such as Sb_2O_3 (1103 mAh g^{-1}), ZnO (978 mAh g^{-1}), and SnO_2 ($\sim 782 \text{ mAh g}^{-1}$).

Bismuth occurs naturally in the earth's crust as bismuthinite in which bismuth sulfide (Bi_2S_3) is the prime constituent. Bi_2S_3 has gained attention as LIB anodes due its high theoretical capacity of 625 mAh g^{-1} . Similarly, bismuth oxide (Bi_2O_3) with its large theoretical capacity of 690 mAh g^{-1} could be a promising anode material for LIB [9, 10]. The prime reason that confines the application of Bi_2S_3 and Bi_2O_3 in LIB or sodium-ion battery (SIB) is its huge volume alteration during the charging/discharging processes and its meager conductivity. Both bismuth sulfide and bismuth oxide convert to bismuth with concomitant formation of $\text{Li}_2\text{S}/\text{Na}_2\text{S}$ or $\text{Li}_2\text{O}/\text{Na}_2\text{O}$ and then the bismuth forms Li_3Bi / Na_3Bi alloys. $\text{Li}_2\text{O}/\text{Na}_2\text{O}$ is largely electrochemically inert and acts as a rigid buffer which provides stabilization but also trap Li^+/Na^+ and results in lower initial coulombic efficiency (ICE). Comparatively, $\text{Li}_2\text{S}/\text{Na}_2\text{S}$ is more ionically conductive and the trapping of Li^+/Na^+ ions is (partially) reversible but it suffers from polysulfide leaching. Several researchers have reported the development of high-performance Bi_2S_3 and Bi_2O_3 by tuning their structure, surface, and composition [11, 12]. Heterostructures composed of sulfide and oxide has interesting applications in energy associated fields due to their improved performance and effortlessness of fabrication. Heterostructures have built-in heterointerface which creates internal electric fields that accelerates charge transfer and lowers overpotentials. However, reports on development of $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{S}_3$ heterostructure is relatively less [13, 14].

In the present work, $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{S}_3$ material pair was selected due to the highly complementary physicochemical properties of the two components and their proven synergistic behavior in electrochemical systems. Bi_2O_3 offers high theoretical capacity, multiple accessible redox states, and excellent structural stability, but its practical performance is often limited by low electrical conductivity. In contrast, Bi_2S_3 is a narrow-bandgap semiconductor with significantly higher electronic conductivity and favorable ion diffusion characteristics, yet it tends to suffer from volume expansion and polarization when used alone. Coupling Bi_2O_3 with Bi_2S_3 in a heterostructured configuration effectively integrates the strengths of both materials while mitigating their individual limitations. The formation of an internal built-in electric field at the oxide-sulfide interface





Interactions (2025) 246:88
<https://doi.org/10.1007/s10751-025-02303-x>

CONFERENCE PROCEEDING



Development of a high-performance chemiresistive H₂S sensor based on sandwich type SnO₂: CuO film realized using hybrid PVD approach

Damu V. Rupnar^{1,2} · Deepak Goyal¹ · Pradip Sarawade² · Niranjan S. Ramgir¹

Accepted: 21 July 2025 / Published online: 14 August 2025
 © The Author(s) 2025

Abstract

This study presents the development of a high-performance chemiresistive hydrogen sulphide (H₂S) gas sensor realized using a hybrid physical vapor deposition (PVD) technique. In particular, the sensor fabrication process integrates two complementary PVD methods; namely Direct Current (DC) sputtering for tin (Sn) deposition and thermal evaporation for copper (Cu) deposition, forming a heterostructured sensing layer that exhibited enhanced gas adsorption and charge transfer properties. The developed sensor exhibited a sensor response (SR) of 22,000 (R_a/R_g) towards 500 ppm of H₂S with a rapid response and recovery times of 1 and 6 min, respectively. The sensor performance was evaluated against the 4-S sensor selection or Ramgir criteria to check its feasibility for commercial deployment. Identical response kinetics observed over multiple cycles or repeated high-concentration H₂S exposure (500 ppm) further establishes the excellent repeatability and reproducibility thereby assuring reliability of the developed sensors. Further, the long-term operational stability measurements assessed over a period of six months indicated that the sensor consistently maintained a SR of 2200 towards 10 ppm H₂S with negligible degradation. Selectivity studies revealed that the sensor exhibited a significantly higher response toward H₂S compared to other interfering gases, including methane (CH₄), chlorine (Cl₂), ammonia (NH₃), and ethylene (C₂H₄). The synergistic combination of Sn and Cu, deposited via the dual PVD approach, significantly enhances the sensor's sensitivity, selectivity, and durability. The fulfilment of the 4-S sensor selection criteria makes the sensor a promising candidate for realizing a device suitable for industrial and environmental H₂S monitoring applications.

Keywords Chemiresistive gas sensor · Hydrogen sulphide (H₂S) · DC sputtering, thermal evaporation · SnO₂: CuO

✉ Niranjan S. Ramgir
 niranjanpr@yahoo.com

Damu V. Rupnar
 Damur412.dr@gmail.com

¹ Gas Sensing Devices Section, Technical Physics Division, Bhabha Atomic Research Center, Mumbai 400 085, India

² Department of Physics, University of Mumbai, 400 098 Kalina, Mumbai, India

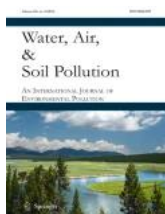
1 Introduction

Hydrogen sulphide (H₂S) is a highly toxic and corrosive gas that poses serious health and environmental risks, particularly in industries like oil and gas, sewage treatment, pulp and paper, and heavy water plants [1]. Exposure can cause respiratory issues, dizziness, nausea, and at high levels may result in unconsciousness or even death caused by disruption of oxygen utilization in cells. In confined spaces like manholes and pipelines, H₂S can quickly accumulate leading to severe health effects and structural damage. Due to its role in forming corrosive sulfuric acid, its monitoring and safe usage is very crucial. Despite its high toxicity, H₂S is crucial in various industrial applications. In industrial processes, such as the kraft pulping method or the Girdler-Sulfide (GS) process, it presents both health hazards and equipment degradation risks [2]. It aids heavy water production for nuclear reactors and is removed from crude oil in gas processing. In pulp production and sewage treatment it is monitored continuously to check or prevent hazards. Controlled use thus ensures industrial benefits while minimizing risks. Accordingly, demands development of reliable and deployable H₂S sensor [3].

The H₂S sensors generally developed are highly application specific and classified as high-range (50–500 ppm) or low-range (0–50 ppm) sensors. High-range gas sensors offer significant advantages over low-range sensors, particularly in industrial applications where high concentrations of H₂S are common. While low-range sensors are suitable for detecting trace amounts of H₂S in controlled environments particularly for health safety applications. They often suffer from saturation and reduced accuracy at elevated concentrations, making them unreliable for high-exposure scenarios. In contrast, high-range sensors provide a broader detection capability, ensuring accurate measurements even in extreme conditions, such as in oil refineries, sewage treatment plants, and chemical industries [4]. Additionally, high-range sensors typically have a longer lifespan, as they are designed to withstand repeated exposure to high H₂S levels without rapid degradation, whereas low-range sensors may require frequent recalibration or replacement due to sensor poisoning. By offering superior durability, stability, and precision in detecting dangerous H₂S levels, high-range sensors play a crucial role in industrial safety, infrastructure protection, and regulatory compliance, making them a more reliable choice for harsh operational environments. However, prior to commercial deployment the sensors are checked for their ability to fulfil the stringent 4-S sensor selection or Ramgir criterion [5]. For safety or health applications, the dangerous limits of H₂S are often defined as short term exposure (STEL) and long term exposure limits (LTEL) corresponding to 15 and 10 ppm of H₂S exposure for period of 10 min and 8 h, respectively [1, 2].

Accordingly, in the present work, we report the development of high range H₂S sensor (50–500 ppm) utilizing a novel approach of using the DC sputtering to deposit the host matrix of Sn and Cu sensitizer layer using thermal evaporation. Use of DC sputtering ensures controlled and uniform deposition of Sn. And use of Cu as a sensitizer results in the formation of well dispersed p-n heterojunctions which are responsible for the observed enhanced sensor response characteristics. The sandwich type sensor is further evaluated against 4-S sensor selection criterion for its possible commercial deployment.





Water Air Soil Pollut (2026) 237:360
<https://doi.org/10.1007/s11270-025-09021-8>



Distribution and Leaching Behavior of Trace Elements and Radionuclide in Waste Rocks of a Uranium Mine: Implications for Environmental Risk Assessment and Mitigation

Samim Molla · Aditi Chakrabarty Patra · Ranjit Kumar · V. S. Srivastava · S. K. Jha

Received: 11 November 2024 / Accepted: 15 December 2025 / Published online: 7 January 2026
 © The Author(s) 2026

Abstract The distribution pattern of trace elements in waste rocks of a uranium mine in the Singhm region, India, and their leaching behavior in the presence of natural and anthropogenic leaching agents were evaluated in the study. Tessier's Sequential extraction revealed that heavy elements that largely exist in residual and reducible phases are stable; those in exchangeable fractions pose a higher risk due to their mobility. More than half of the cobalt (54.0–79.9%), copper (70.7–91.9%), iron (85–94%), manganese (50–75%), and nickel (61.3–90.4%) were present in the residual phase. The mobility factor was found to decrease with increasing particle size for most elements, suggesting lower leaching potential for larger particles. The leaching potential studies with rainwater showed that ionic concentrations decreased with increasing liquid-to-solid ratios from 0.5 to 10, indicating a dilution effect. The gamma spectrometric analysis of waste rocks showed that ^{226}Ra with the highest (948–16,2145–30 Bqkg $^{-1}$)

and ^{232}Th with the lowest (72–132–9 Bqkg $^{-1}$) activity levels among the measured radionuclides. The study will help to assess the environmental risks and develop effective long-term mitigation strategies to prevent contamination of soil, water, and air. The findings also provide critical input for environmental risk assessment frameworks and guide mitigation approaches such as selective waste segregation and controlled reuse of mine waste rocks.

Keywords Uranium mine · Waste rock · Leaching · Trace elements · Radionuclides

1 Introduction

Banduhurang uranium mine is the country's first and only open-cast type uranium mine, which gives a unique opportunity to study the environmental effects of the mine wastes. In an open-cast mine, three types of waste, namely solid, liquid, and gaseous waste, are generated (Das et al., 2024). Waste rock is produced in open-pit mining during the removal of overburden and the production stage, where the uranium grade in rock is lower than the cut-off grade (0.02% U_3O_8). The waste rocks are transported to the surface and stored in a designated waste yard, which is exposed to all environmental conditions, including rainfall. The waste from the mine primarily consists of uranium series radionuclides and various common minerals, but typically exhibits greater porosity

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11270-025-09021-8>.

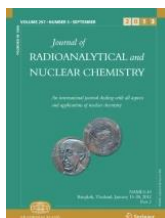
S. Molla (✉) · A. C. Patra · R. Kumar · V. S. Srivastava · S. K. Jha
 Health Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India
 e-mail: samimm@barc.gov.in

S. Molla · A. C. Patra
 Homi Bhabha National Institute, Mumbai 400094, India

and permeability compared to the original material, i.e., ore. Consequently, the chemical and radioactive components in waste rocks may be mobilized during prolonged redox and weathering activities (Lieu, 2004). The mobilization would be even more significant under acid conditions, as acidity is one of the most important factors influencing the release of toxic elements from solid wastes (Förstner, 1986). The acidic environment may also result from the oxidation of sulfidic minerals found in the waste rocks; the degree of acid production relies on the sulfide concentration in the waste rocks (Alpers et al., 1994; Jambor, 2003). The acidic pH level may accelerate the migration of radioactive and toxic elements from waste rocks (Krampah et al., 2019). Consequently, the radionuclides and other metals in the waste rocks can be released into the ambient environment, and thus waste rocks may become a substantial source of surface and groundwater contamination (Liu et al., 2015). Further, acid rain may influence the release of contaminants. The H^+ ion in acid rain affects the affinity between mineral surfaces and metal ions (Harter & Naidu, 2001). Furthermore, the H^+ ion affects the solubility and speciation of trace metals by the exchange of cations from binding sites, the formation of ion pairs, and the dissolution of metal carbonates (Appel & Ma, 2002). Previous studies have demonstrated the significant effect of acid rain on metals released from various matrices such as mill tailings (Kaniki & Tumba, 2019; Shaw et al., 2011). Trace elements and radionuclides discharged into the environment from mining and industrial activities pose significant ecological and human health risks due to their persistence, bioaccumulation, and potential for radiotoxicity. These contaminants can degrade soil and water quality, affecting biodiversity and increasing long-term exposure risks to nearby populations (Battle et al., 2016; Li et al., 2024). The use of total elemental concentration in waste rock as a criterion for assessing its environmental impact may lead to an erroneous conclusion. Sequential extraction is a method of speciation analysis that can provide insight into the binding and mobility of potentially toxic elements in the environment (Howe et al., 2002). Thus, Tessier's sequential extraction method was utilized in the current study to partition several trace elements into five fractions: exchangeable, carbonate-bound, Fe–Mn oxide-bound, organic matter-bound, and residual (Ali et al., 2024). Exchangeable

and carbonate-bound fraction represents the most labile portions, comprising loosely adsorbed ions and those co-precipitated with carbonates (Malov et al., 2021). Fe–Mn oxide-bound (reducible) fraction encompasses trace elements chemically adsorbed or co-precipitated onto iron and manganese oxyhydroxides. Under oxidizing surface conditions, Fe–Mn oxides scavenge trace metals (e.g., As, Pb, Zn, Cu) through adsorption or surface complexation and help in effective immobilization (Gómez & Ruiz, 2023). Fe–Mn oxides act as critical geochemical buffers for Ra mobility in uranium mine waste rock. These oxide phases act as both sinks and sources of radium depending on prevailing geochemical conditions, especially redox potential, pH, and the presence of complexing agents. Under oxidizing conditions, Fe(III) and Mn(IV) oxides are prevalent and exhibit a strong affinity for Ra^{2+} through surface complexation or co-precipitation. These oxides can effectively scavenge radium from porewater and incorporate it into the solid phase. However, under reducing conditions, commonly encountered in buried waste rock piles or saturated zones, Fe(III) and Mn(IV) oxides undergo microbial or abiotic reductive dissolution, leading to the release of previously adsorbed or co-precipitated Ra^{2+} (Chen & Kocar, 2018). The organic matter-bound (oxidizable) fraction comprises metals complexed with organic ligands. Their liberation requires oxidative breakdown of organic matter, making them sensitive to changes in redox conditions or microbial degradation (Awad et al., 2021; Okoro et al., 2012). Most trace elements in mine waste—particularly uranium, thorium, and refractory metals—tend to reside in this residual phase, rendering them essentially immobile under ambient conditions (Singh et al., 2025). The experiment was carried out in 4 different size fractions to evaluate the effect of particle size on the leaching characteristics of uranium. The leaching potential of waste rocks was also assessed by liquid–solid partitioning as a function of the liquid-to-solid ratio using a parallel batch procedure (U.S. Environmental Protection Agency, 2012) using rainwater as the leachant for 48 h at room temperature. This testing approach was designed to obtain an extract (i.e., eluate) from a solid substance to evaluate the solubility and release of uranium and other elements under controlled laboratory conditions. To mimic the general atmospheric exposure situation of waste rocks, rainwater was used as the





Dosimetry studies on amino acids using diffuse reflectance measurements for high doses

Sandip Mondal¹ · S. H. Shinde¹ · Sneha Chandrasekhar¹ · Probal Chaudhury¹

Received: 28 August 2025 / Accepted: 9 December 2025 / Published online: 2 January 2026
 © The Author(s) 2025

Abstract

This study investigates alanine, glycine, and glutamine as high-dose gamma radiation dosimeters using diffuse reflectance spectroscopy (DRS). DRS provides a non-invasive, cost-effective method for rapid dose estimation. Amino acid powders were irradiated from 0.1 to 100 kGy, and their reflectance spectra in the range of 300 to 510 nm, were analysed. Non-linear dose–response curves were observed, with alanine, glycine, and glutamine showing peak sensitivities at different dose ranges. Measurements were within 6.3% suggesting good reproducibility, stability over time and temperature, and unaffected by dose fractionation. These results highlight amino acids' potential for reliable, long-term radiation dosimetry in routine monitoring applications.

Keywords Amino acid dosimeter · Diffuse reflectance · Radiation Processing · High dose dosimetry · Spectrophotometric read-out

Introduction

High-dose radiation dosimetry plays a critical role in industrial irradiation, food sterilization, and radiation-processing applications. Organic materials such as amino acids form stable free radicals when exposed to ionizing radiation, making them suitable candidates for solid-state dosimetry. Among these, alanine has been widely used as a reference dosimeter, particularly with EPR/ESR read-out, due to its high stability and dose-linearity. Regulla and Deffner first demonstrated the robustness of alanine-ESR dosimetry, which later formed the basis for ISO/ASTM 51607 standards [1–3]. However, EPR systems are expensive and not widely accessible, creating a need for simpler and cost-effective read-out methods.

Several alternative methods have been explored. Lyoluminescence, although sensitive, suffers from fading and strong dependence on sample dissolution, oxygen content, and temperature, limiting its routine applicability [4, 5]. The ferrous–xylenol orange (FX) spectrophotometric method offers another indirect read-out, but it requires dissolution of the

sample, careful solution handling, and consumes material, making it unsuitable for rapid or high-throughput measurements [6, 7].

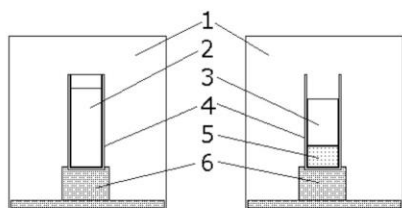
In contrast, diffuse reflectance spectroscopy (DRS) has emerged as a rapid, non-destructive, and cost-effective technique for probing radiation-induced changes in solids. DRS has been successfully used for polymer films and radiochromic materials, and earlier work by Zagórski and Rafalski demonstrated its suitability for quantifying irradiated labels. More recently, DRS systems have been adopted for dosimetry of materials such as Gafchromic films, reaffirming its potential for routine dose assessment. Amino acids—particularly alanine, glycine, and glutamine—show distinct UV–visible reflectance changes after irradiation, making them promising candidates for DRS-based high-dose dosimetry [8–10].

Despite these advances, limited studies have systematically compared the DRS response of alanine, glycine, and glutamine across a broad dose range or evaluated operational factors such as dose rate, dose fractionation, pre- and post-irradiation temperature, and long-term stability. These parameters are crucial for establishing a reliable dosimetry system suitable for routine industrial application.

The present work addresses this gap by investigating the diffuse reflectance response of alanine, glycine, and glutamine irradiated from 0.1 to 100 kGy using a high-dose

✉ S. H. Shinde
 shshinde456@gmail.com

¹ Radiation Safety Systems Division, Mumbai, India 400085



1. Irradiation volume of GC1200 2. Fricke dosimeter 3. Sample container
4. Build-up 5. Perspex spacer 6. Perspex Jig

Fig. 1 Irradiation setup. 1 Irradiation volume of GC1200, 2. Fricke dosimeter, 3 Sample container, 4 Build-up, 5 Perspex spacer, 6. Perspex Jig

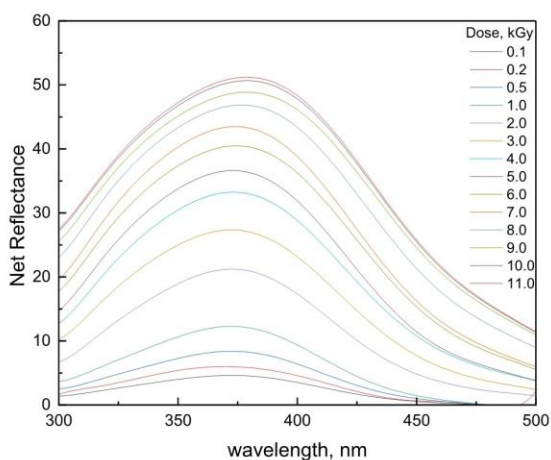


Fig. 2 Net reflectance spectra for Alanine

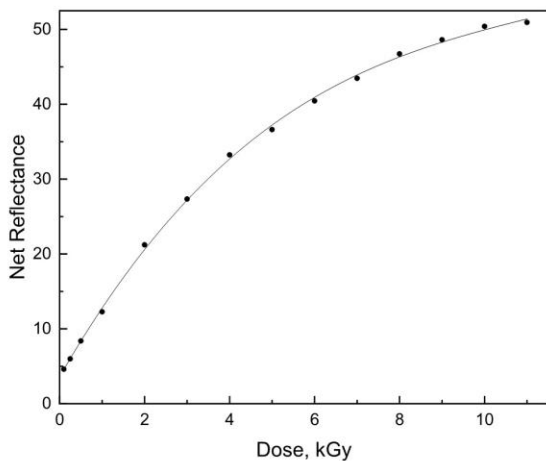


Fig. 3 Dose-response for Alanine

Co-60 gamma source. Net reflectance changes at their respective wavelengths of maximum sensitivity are analyzed, and the effects of dose rate, fractionation, and storage conditions are systematically evaluated. The study demonstrates the feasibility of using these amino acids as simple, stable, and rapid read-out high-dose dosimeters, offering an accessible alternative to more complex analytical techniques.

Experimental

Analytical-grade alanine, glutamine, and glycine were sourced from Merck, Germany, and used without further purification. Irradiations were performed using two different Co-60 Gamma Chamber-1200, which were calibrated

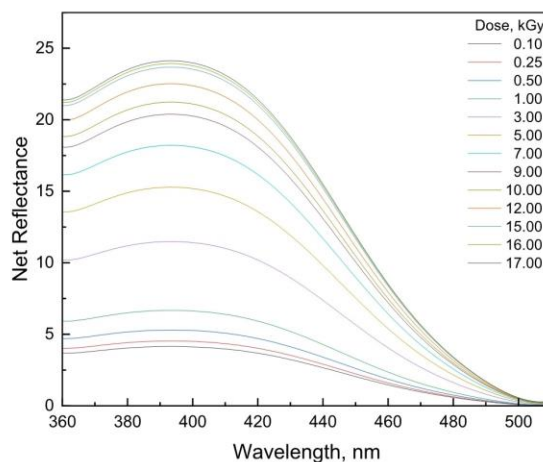


Fig. 4 Net reflectance spectra for Glycine

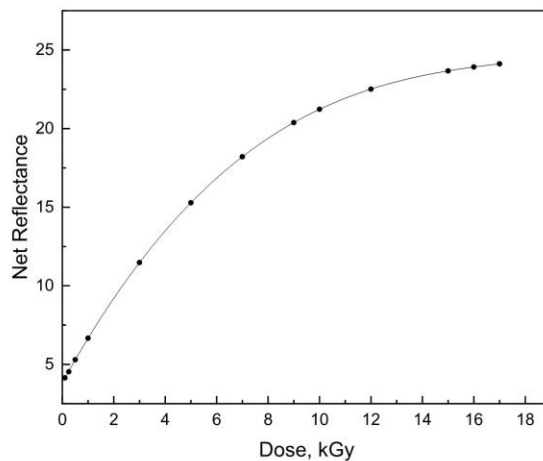


Fig. 5 Dose-response for Glycine





J Mater Sci (2025) 60:25114–25133

Ceramics



Effect of borosilicate glass environment on creep behaviour of alloy 690 at temperatures over 800–1000 °C

M. Karri^{1,2}, A. Verma^{1,2}, J. B. Singh^{1,3,*} , and C. V. Singh⁴

¹ Homi Bhabha National Institute, Anushakti Nagar, Mumbai 400094, India

² Mechanical Metallurgy Division, Bhabha Atomic Research Centre, Mumbai 400085, India

³ Glass & Advanced Materials Division, Bhabha Atomic Research Centre, Mumbai 400085, India

⁴ Materials Engineering Division, CSIR-National Metallurgical Laboratory, Jamshedpur 831007, India

Received: 29 July 2025

Accepted: 24 October 2025

Published online:

20 November 2025

© The Author(s), 2025

ABSTRACT

The creep behaviour of Alloy 690 has been studied in a borosilicate glass environment using hollow cylindrical samples, at temperatures ranging from 800 to 1000 °C under constant load conditions of applied stresses between 16 and 56 MPa. This study aims to elucidate the role of borosilicate glass on the creep deformation behaviour of Alloy 690. The highly corrosive nature of molten borosilicate glass was found to significantly reduce the creep life (t_f) of Alloy 690 by approximately one-third and to double the minimum creep rate ($\dot{\epsilon}_m$), compared to similar tests conducted in air. The degradation of creep properties observed in the molten borosilicate glass environment was attributed to stress-assisted grain boundary oxidation, which primarily accelerated the initiation and propagation of surface cracks. A relatively low activation energy (~ 223 kJ/mol) in the present study, suggested minimal role of Cr_{23}C_6 carbides precipitation on creep deformation. Alloy 690 exhibited power-law creep behaviour under the tested conditions, emphasizing the role of climb-assisted dislocation creep. Furthermore, the creep data in the molten glass environment was found to conform to both the Monkman–Grant and Larson–Miller relationships.

Introduction

A Ni–Cr–Fe based Alloy 690 derives its desired corrosion resistance and useful mechanical strength from alloying additions of high concentration of chromium in its austenite matrix. Alloy 690 usually forms blocky

particles of primary carbides and /or nitrides during solidification [1], which are not detrimental to the mechanical properties of the alloy. Alloy 690 was primarily developed as a potential alternate of Alloy 600 for steal generator tubes application in pressurised water reactors in nuclear power plants. This

Handling Editor: Andréa de Camargo.

Address correspondence to E-mail: jbsingh@barc.gov.in

development had happened to overcome the shortcoming of poor corrosion resistance of Alloy 600 to various forms of corrosion attacks like stress corrosion cracking, intergranular stress corrosion cracking, intergranular attack, pitting, etc. [2–8]. Such application also require good creep resistance under normal operating conditions as well as under accidental scenario. Alloy 690 experiences least creep deformation under normal operating conditions of steam generator tubes that operate under 9–15 MPa pressure at a temperature range of 250–300 °C. However, structural integrity of the alloy could be severely challenged in an accidental scenario due to creep deformation encountered during uncontrolled temperature increase as high as 800 °C [9].

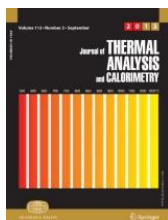
Alloy 690, owing to high chromium content, has also been recognized as promising material to fabricate mettler pots for the vitrification application to immobilize a high-level nuclear waste in a borosilicate glass matrix before its disposal. Vitrification process generally takes place in the temperature range of 800–1100 °C in which borosilicate glass is extremely corrosive. During the vitrification process, Alloy 690 experience various forms of damage caused by: (i) exposure of the alloy to corrosive borosilicate glass melt at high temperatures (800–1100 °C) and; (ii) creep damage at high temperatures (800–1100 °C) and low stresses during prolong process cycles. Most of the published work reports independent effect of molten glass and creep on various forms of damage to the Alloy 690 [10–14]. For instance, exposure of the Alloy 690 to corrosive borosilicate glass melt at high temperatures have been reported to bring distinct microstructural and chemical changes at different depth levels from the exposed surface [10–12, 14]. These changes include formation of NiCr_2O_4 spinels on the continuous and adherent Cr_2O_3 film that form on the alloy's exposed surface as well as chromium-depletion from the alloy's sub-surface regions [10–12, 14]. To a large extent, corrosion behavior of the Alloy 690 in a molten borosilicate glass is primarily governed by the growth and dissolution of the Cr_2O_3 surface film. At temperatures higher than 1000 °C, the Cr_2O_3 film transforms into non-protective and granular nature to severely degrade the corrosion resistance properties of the alloy [14].

Creep studies of Alloy 690 have been mostly carried out in air at temperatures from 650–1200 °C [13, 15–24]. Most of these studies were driven by development of Alloy 690 for steam generator tube

application. However, considering the potential application of Alloy 690 in vitrification equipment, it becomes essential to understand the creep behaviour of the Alloy 690 in a borosilicate glass environment for temperatures and stresses that are usually encountered in such applications. Sourabh and Singh [13] have studied creep behaviour of Alloy 690, covering temperatures and stresses that are important in the vitrification application. They have found that creep deformation of the alloy in the vicinity of vitrification temperatures was assisted by dislocation climb controlled mechanism [13]. The alloy has been found to undergo creep damage by necking at lower temperatures and lower stresses, while by a mixture of transgranular ductile failure (necking) and intergranular failure (cavitation) modes above 800 °C [13].

The present work aims to investigate the creep behaviour of Alloy 690 under a borosilicate glass environment over a range of temperatures from 800 to 1000 °C and stresses from 16 to 56 MPa. These stresses were selected in order to mimic the creep deformation behaviour of melter pots of Alloy 690 under service conditions. Usually, the melter pot of Alloy 690 under normal operating conditions experiences stress of ~ 2 MPa that mostly arises from sustained loads such as its self-weight, weight of the molten glass, etc. However, Thorve et al. [25] have estimated a maximum allowable stress of ~ 43 MPa for the operational life of the metallic melter pots. Thus, the stresses selected in the present study aims to develop a broader understanding of creep deformation behaviour of Alloy 690 in the simulated service conditions. This study, therefore, addresses the following objectives: (i) effect of corrosive glass environment on the creep parameters such as creep life, minimum creep rate, creep mechanism, fracture behaviour etc.; (ii) assess the compliance of the Monkman–Grant relationship [26] and the Larson–Miller parametric relationship [27] in molten glass environment of the alloy and establish their relationships for predicting the creep life in glass environment; (iii) bridge the gap between creep deformation behaviour of Alloy 690 in molten borosilicate glass with those carried out in air [13]. For this purpose, a specially designed hollow cylindrical specimens inspired from the work by Ren [28] have been used to ensure identical loading conditions of hollow specimens with that of solid specimens of a given material. According to this condition, the hollow and the solid specimens must possess nearly same A/V ratio, where A is the area of the gauge





Journal of Thermal Analysis and Calorimetry
<https://doi.org/10.1007/s10973-025-15128-1>

32



Effect of Ni addition on dehydrogenation behavior of MgH_2

Bhaskar Paul¹ · Pankaj Shrivastava¹ · Shubham Kumar¹ · Jugal Kishor¹ · Sanjay Kumar¹ · Sanjib Majumdar¹

Received: 29 June 2025 / Accepted: 21 November 2025
 © The Author(s) 2025

Abstract

Magnesium hydride (MgH_2) is an attractive and widely researched hydrogen storage material because of its high hydrogen capacity and lower cost of production coupled with the availability of Mg. However, higher desorption temperature and sluggish kinetics are the limitations of widespread use of MgH_2 as hydrogen storage material. The present study deals with the effect of the addition of Ni on the dehydrogenation behavior of as-synthesized MgH_2 from coarse commercial-grade magnesium powder (purity 99.8%). Optimization of the process parameters for the conversion of Mg powder to MgH_2 in bulk quantity and characterization of MgH_2 were carried out. Mg_2NiH_4 phase could be formed by ball milling in planetary ball mill of as-synthesized MgH_2 and Ni powder. Thermal analyses such as TG-DTA, DSC, and pressure–composition isotherms were used to understand the dehydrogenation behavior of MgH_2 and MgH_2 -Ni. The release of hydrogen was found to start from 220 °C for MgH_2 -Ni by the combined action of the addition of Ni in MgH_2 and particle size reduction because of ball milling.

Keywords Magnesium hydride · TGA · Hydrogenation–dehydrogenation · Thermal analysis · Hydrogen storage material

Introduction

A large number of materials have been investigated for solid-state hydrogen storage applications, including physical adsorbents, complex hydrides, alloy hydrides, and metal hydrides [1–3]. Among the metal hydrides, magnesium-based hydrogen storage materials have been widely studied for their higher storage capacity (≈ 7.6 mass% for pure MgH_2) on the material level, low cost, abundance, non-toxic nature, and good reversibility [4–6]. Although MgH_2 could attract the scientists and engineers worldwide, still it could not be commercialized as per its potential. The primary drawbacks are limited cost-effective and commercial-scale production facilities and higher dehydrogenation temperatures. The first drawback is related to direct hydrogenation of magnesium powder and production method of Mg powder. Hydrogenation of finer Mg powder is easier. Mg powder is produced using several methods, primarily mechanical crushing and atomization of molten metal [7]. The cheapest and most widely used commercial method for

bulk magnesium powder production is mechanical crushing (scratching, cutting–grinding, milling–grinding, etc.) especially for industrial applications, where particle morphology is less important. Atomization of magnesium which is able to produce very fine Mg powder is a technologically difficult process because of high reactivity of Mg. On the other hand, because of the lower capital investment, simpler process, and established technology, mechanical processing of magnesium ingots is more popular industrially. Mechanically processed magnesium powders are irregularly shaped with a wider range of sizes. The particle size of commercially available industrial grade mechanically processed magnesium powder ranges from 100–300 μm . For industrial level scaling up of magnesium-based hydrogen storage material development, the raw material should be chosen which is cheaper and easily available without the technological hindrances. Therefore, technology for the hydrogenation of commercially available Mg powder should be developed for the ultimate use of MgH_2 in large scale real hydrogen storage applications. The underlying issue of restricted commercial application is the high dehydrogenation temperature of as-synthesized MgH_2 . Because of the sluggish kinetics, magnesium hydride (MgH_2) releases hydrogen slowly and desorption takes place at high temperatures, around 703 K at 1 bar of pressure in as-synthesized condition. Therefore,

✉ Bhaskar Paul
 bpaul@barc.gov.in

¹ MP&CED, Bhabha Atomic Research Centre,
 Mumbai 400085, India

as-synthesized MgH_2 has to be treated to overcome the shortcomings related to higher desorption temperature [8–15].

In the current study, attempts were taken in this research to study the hydrogenation behavior of mechanically processed coarse powder followed by post hydriding treatment to reduce the dehydrogenation temperature. Nickel has gained much attention as an alloying addition because of its ability to form intermetallic hydrides, which enhances the modified the desorption route and decreases the activation energy [16–18]. In earlier experimental studies, nickel nanoparticles have been utilized successfully to improve the kinetics of the MgH_2 hydrogen absorption/desorption process [19–26]. However, in the most explored research, nano-nickel compounds were produced at a very small scale under tuned conditions which were used further for use as a catalyst for MgH_2 . However, it is essential to investigate the possibility of using commercial Ni to develop cost-effective MgH_2 -Ni dilute composite hydrogen storage materials. The present investigation deals with use of the commercial-grade Ni powder as catalysts for as-synthesized MgH_2 and characterization with respect to the morphological changes, phase, particle size, and dehydrogenation behavior.

Experimental

Preparation of magnesium hydride

Commercial-grade magnesium powder (purity > 99.8%, 200 mesh size) was used for hydrogenation in a specially designed rotary reactor at 623 K with a hydrogen pressure of 2.5 MPa after activation. The indigenously designed and developed hydriding setup consists of a rotating reaction chamber with PID controlled heater, mass-flow controller, pressure gauge, hydrogen leak detector, and hydrogen chamber as a hydrogen source with known volume. High-purity hydrogen gas (99.999%) was used for the hydrogenation experiment in 0.5 kg batch scale. Small quantity of samples was removed in between and characterized for the extent of hydrogenation.

Catalyzing as-synthesized MgH_2 and characterization of the MgH_2 -Ni

As synthesized MgH_2 powder was transferred to a planetary ball mill pot after the conversion of > 96% of Mg powder to MgH_2 was confirmed by the thermogravimetric analysis. MgH_2 powder was mechanically milled with Ni powder (stoichiometric quantity for formation of Mg_2Ni phase as 33 at.% of Ni) in a planetary ball mill under an argon atmosphere. The milling was carried out using hardened steel balls of 5 mm and 10 mm in diameter. The

ball-to-powder mass ratio was kept at about 40:1. The milled powders were characterized with respect to their size, phase, microstructure, and dehydrogenation temperature by different characterization tools; laser diffraction method, XRD (XRD, MPD), SEM (SEM, Camscan MV2300CT/100, UK), TG (TG, Setsys evolution 24, Setaram Instrumentation, France), and DSC (DSC, Q100 from TA Instruments), respectively. The TG-DTA and DSC analyses were performed from ambient to 723 K (heating rate of 10 K min^{-1}) under the argon flow of 25 mL min^{-1} . Before starting the heating process, the TG-DTA chamber was evacuated to 10–3 mbar and subsequently flushed with high-purity argon gas.

Dehydrogenation kinetics were studied in an indigenously developed Sievert-type apparatus. The hydrogen desorption tests were not carried out under a vacuum, which is conventionally done, but pressure was allowed to increase in the known volume after dehydrogenation. From the back calculation of increased pressure, the amount of the hydrogen content could be derived.

Result & discussion

Conversion of Mg powder to MgH_2 in bulk quantity

In the previous study, optimization of process parameters was carried out for the conversion of Mg powder to MgH_2 on a small scale (20 gm) [4]. Subsequently, the process of conversion of commercial magnesium to MgH_2 on bulk scale was developed by the use of indigenously designed rotary-type reactor in 0.5 kg scale. Rotation of the reaction chamber was found to be helpful for attaining temperature uniformity as well as pulverizing the powder facilitating faster hydrogenation by the creation of fresh surfaces. Temperature uniformity was found to be the key parameter for the complete conversion of Mg to MgH_2 . The formation of MgH_2 was confirmed through XRD and TGA analysis. Figure 1 shows the TG plot revealing the dehydrogenation behavior of as-synthesized MgH_2 . The dehydrogenation temperature of MgH_2 was found to be about 703 K in as-synthesized condition, and the dehydrogenation was endothermic in nature, as shown by the DTA plot (Fig. 1). Just after the completion of dehydrogenation, an increase in mass was observed in TGA plot. This gain can be correlated with the partial oxidation of the highly reactive, freshly formed nascent magnesium. The oxidation reaction likely occurred because of the presence of trace amounts of oxygen in the flowing argon gas. Conversion of about 95% could be achieved by following the hydrogenation at 623 K and under a hydrogen pressure of 25 bar.





ORIGINAL RESEARCH ARTICLE

Effect of Solutionization Temperature on the Interfacial Microstructure of a Hot Roll Bonded Alloy 690/Carbon Steel Clad Steel Plate



LAXYA GUPTA, NACHIKET KESKAR, and BIKAS C. MAJI

Fabrication of a Ni-based superalloy Alloy 690 cladded ASTM SA516 GR60 carbon steel (GR60) clad steel plate was carried out through vacuum hot roll bonding at 1323 K for the first time. The as-rolled clad plate showed excellent metallurgical bonding at the joining interface, however, a precipitation zone within the Alloy 690 layer containing Cr_{23}C_6 carbides was observed, which is detrimental to the intergranular corrosion resistance. A comprehensive approach integrating thermodynamic calculations and numerical simulations of long-range diffusion of alloying elements was employed to optimize the post rolling solutionization heat treatment temperature. Thermodynamic calculations predicted the possibility of reduction in Cr-carbide amount on solutionization in the temperature range of 1373 K to 1573 K. Guided by these calculations, as-rolled specimen was solutionized at 1373 K for 4 hours, however, the width of the Cr_{23}C_6 carbide precipitation zone was found to increase instead of decreasing due to enhanced Cr and C diffusion. On the other hand, solutionization at 1473 K for 4 hours resulted in a substantial reduction in Cr_{23}C_6 precipitates on Alloy 690 side. Formation of a thin stabilized γ -FCC (γ_s) was noticed on the GR60 side after solutionization at 1373 K due to net influx of Ni from Alloy 690 alloy, which separates the original joining interface from the bulk GR60. The width of this γ_s region further increased after 1473 K-4 hours solutionization due to enrichment of Ni within GR60 layer. Overall, a higher solutionization temperature (1473 K) was found to be more effective to reduce the Cr-carbide amount in Alloy 690 cladded GR60 plates than that usually employed 1373 K for monolithic Alloy 690 plate.

<https://doi.org/10.1007/s11661-025-07954-7>

© The Author(s) 2025

I. INTRODUCTION

ALLOY 690 [containing Ni-(28–30) wt pct Cr-(8–10) wt pct Fe] is a Ni-based superalloy that finds extensive applications in steam generator tubing and tube sheets,^[1] glass vitrification equipment,^[2] equipment for nitric acid production,^[3] etc. It has replaced the Alloy 600 as a preferred material of construction for steam generator tubing in nuclear power plants due to its higher resistance to stress corrosion cracking (SCC). The higher SCC resistance of Alloy 690 as compared to Alloy 600 has been attributed to its relatively higher Cr content.^[4] It also finds numerous applications in various components of nuclear reprocessing plants such as Joule melters for glass vitrification of high-level nuclear waste

(HLW) due to its higher corrosion resistance to molten glass at high temperatures.^[2] Higher corrosion resistance in acidic environments makes this a suitable material of construction for many equipment in aggressive acid production units.^[3] However, the presence of costly alloying elements such as Ni and Cr in high quantities makes Alloy 690 much costlier as compared to steels and limits its widespread use in various industrial applications as a structural material. Therefore, a partial replacement of Alloy 690 in combination with a cheaper grade of steels, such as carbon steels, can economize the use of this material while exploiting its useful properties. An excellent, industrially scalable, high throughput and cost-effective method to achieve this partial replacement is to clad Alloy 690 over carbon steel through hot roll bonding (HRB). HRB is usually carried out under a protective atmosphere such as Argon,^[5] Hydrogen,^[6] or vacuum^[7–9] to prevent oxide formation at the joining interface and achieve a sound metallurgical bonding. Among these, the vacuum hot roll bonding (VHRB) process developed at JFE corporation, Japan^[10] is the most prevalent industrial practice now a days, where a package assembly consisting of cladding and backing materials is hot rolled while maintaining a static vacuum

LAXYA GUPTA, NACHIKET KESKAR, and BIKAS C. MAJI are with the Mechanical Metallurgy Division, Bhabha Atomic Research Centre, Mumbai 400085, India. Contact e-mail: bikchan@barc.gov.in

Manuscript submitted February 17, 2025; accepted August 18, 2025.

Article published online September 2, 2025

at the contact surfaces. While reports on the cladding of Ni-based superalloys through electron-beam powder bed fusion,^[11] laser melting,^[12] hot pressing,^[13] and weld overlay^[14] are widely available in literature, report on VHRB of Ni-superalloys remains scarce^[8] and not at all available for Alloy 690. Moreover, cladding of Alloy 690 using techniques that involve melt deposition of Alloy 690 over a substrate results in coarse dendritic microstructure^[11,15] of the Alloy 690, which may lead to poor mechanical properties of the clad layer. A major concern while using these cladding techniques is the significant dilution of composition at the interface due to intermixing of substrate and Alloy 690 leading to hot cracking at the interface.^[14] Moreover, a wide heat-affected zone also forms on the substrate side,^[14] which significantly deteriorates the mechanical properties of the cladding as well as the backing layers. Therefore, these cladding techniques can only be used for providing the corrosion resistance but the deposited layer cannot be used as a load-bearing structural member. Recently, heterogeneous materials^[16] having a good combination of ductile and brittle material is being investigated to circumvent the inverse relation between strength and ductility. In this regard, VHRB being essentially a solid-state joining process having a narrower width interface can provide an excellent avenue to impart corrosion resistance to carbon steels through cladding Alloy 690 while improving the mechanical properties along with significant cost savings.

However, one potential challenge in VHRB of Alloy 690 and carbon steel can be the formation of a Cr-rich precipitation zone near the interface due to the diffusion of carbon from the carbon steel side toward the Alloy 690, which can deteriorate the corrosion as well as mechanical properties of the material specially at the interface. This phenomenon has been observed to occur in the Inconel 625 and Hastelloy by Lopez *et al.*^[13] and Tachibana *et al.*,^[17] which ultimately affect the corrosion resistance at the interface. Thus, post rolling solutionization treatment becomes absolute necessity to minimize the impact of these carbides. Industrially, bulk Alloy 690 is mill annealed at 1373 K (1100 °C) to dissolve these carbide precipitates, however, this temperature may not be sufficient enough to dissolve the Cr-rich carbides due to their increased stability with increasing carbon concentration. Therefore, identification of an optimized solutionization heat treatment either through experimentation or in combination with theoretical calculation is of absolute necessity to minimize the impact of carbide precipitation on the final product.

Therefore, in the present study an attempt has been made to fabricate a steel clad plate having Alloy 690 as a cladding layer and ASTM A516 GR60 (hereafter will be referred to as GR60) as a backing layer through VHRB technique. GR60 was chosen as the backing layer as it is widely used as materials of construction for manufacturing of pressure vessels in numerous industrial applications.^[18] Thermodynamic calculations were utilized to identify suitable temperature regime for post rolling solutionization treatment in order to minimize the width of the precipitation zone. Simulation of multicomponent

diffusion process during hot roll bonding and solutionization heat treatment was carried out to elucidate the microstructural evolution at the interface.

II. MATERIALS AND METHODS

A. Starting Materials

Alloy 690 and GR60 were utilized as the cladding and backing materials, respectively, for the fabrication of the clad plate. The nominal compositions (in wt pct) of both these starting materials are listed in Table I. Both these materials possess widely different microstructures, phase transformation characteristics, and mechanical and thermophysical properties. Alloy 690 shows a stable FCC-austenitic microstructure [Figure 1(a)] throughout the temperature range from RT to melting point along with minor carbide precipitates. On the other hand, GR60 shows a BCC-ferritic (α)-pearlitic microstructure at RT [Figure 1(b)], which transforms into the FCC-austenitic phase (γ) at a temperature above 1123 K (850 °C) (see electronic Supplementary Figure S1). As a result of their distinct composition and microstructure, both these materials have widely different mechanical and thermophysical properties, which have also been summarized in Table II. Alloy 690 generally possesses a higher ultimate tensile strength (UTS), yield strength (YS), and elongation as compared to GR60. It also shows a slightly higher thermal expansion coefficient and much lower thermal conductivity as compared to the GR60.

B. Fabrication of Clad Plate and Solutionization Treatments

A triple-layered Alloy 690/GR60 clad plate was fabricated through VHRB using a sandwiched assembly (60 × 60 × 32 mm) consisting of a GR60 plate (60 × 60 × 16 mm) placed between two Alloy 690 plates (60 × 60 × 8 mm). The contact surfaces of these plates were ground using SiC emery paper and ultrasonically cleaned using acetone to obtain oxide free surfaces. The sandwiched assembly was welded from all sides using tungsten inert gas (TIG) welding and a static vacuum of $\sim 10^{-2}$ torr was created using a rotary vacuum pump to minimize the chances of oxidation at contacting surfaces during VHRB. The evacuated assembly was hot roll bonded at a temperature of 1323 K (1050 °C) and strain rates of 1 to 5 s⁻¹. The hot rolling temperature and strain rate regime were chosen based on the dynamic recrystallization domain reported for Alloy 690.^[20] A two high laboratory rolling mill having 300 mm diameter rolls revolving at 45 revolution per minute was used for roll bonding. Roll bonding was carried out in multiple passes until the plate thickness was reduced to ~ 8 mm (~ 75 pct reduction). The per pass thickness reduction was varied in such a way so that the strain rate can be maintained within 1 to 5 s⁻¹. Strain rate calculations for this purpose were performed using standard formula for rolling under sticking friction condition.^[21] The sandwiched assembly was





TECHNICAL ARTICLE

Effect of Trigger Material on the Uranium Metal Produced by Deterministic Triggering of Magnesiothermic Reduction of UF₄

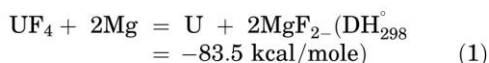
PASUPULETI KALPANA^{1,2,3} SONAL GUPTA,² U.R. THAKKAR,²
 S.K. SATPATI,¹ and RISHI VERMA¹

1.—Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India. 2.—Homi Bhabha National Institute (HBNI), Mumbai 400094, India. 3.—e-mail: pkalpana@barc.gov.in

There are several well-established methods for the purification and extraction of uranium metal. One is magnesiothermic reduction, which involves converting uranium tetrafluoride (UF₄) into uranium metal using magnesium as a reducing agent. This process is conducted in a sealed vessel with external heating, which is continued until the reaction is initiated. The literature shows that the reaction can be externally triggered beyond a specific average charge temperature after pre-heating to achieve the same level of purity and quality. In this study, we analyze the influence of trigger location and trigger material on the purity and consolidation of uranium metal. Specifically, we study the effects of different trigger materials, including graphite, nichrome, Kanthal, and silicon carbide, on ingot formation. The impact of firing location on the final ingot quality is also assessed. Results indicate that top-zone firing led to poor ingot consolidation, whereas initiating the reaction from the middle or bottom zones yielded better ingot quality with higher average weights (≥ 4.65 kg).

INTRODUCTION

Magnesiothermic reduction (MTR) is a commonly used method to produce uranium metal from uranium tetrafluoride, where magnesium reduces UF₄ according to the following equation:



The reaction is self-propagating and high temperature. Uranium is a heavy metal compared to MgF₂; hence, density-based separation can be achieved if both the products are in a molten state. Although the reaction is exothermic, to ensure the products are both in a molten state, the charged mixture must be pre-heated.^{1–6} The melting points of uranium and MgF₂ are 1133°C and 1264°C. Upon pre-heating up to 270°C, both uranium and

magnesium fluoride formed will be in a molten state, and for good slag metal separation, pre-heating up to 450°C is required.⁴ The TG-DTA study showed that the reaction is initiated at 650°C, i.e., the melting point of magnesium.⁷ Therefore, deterministic reaction triggering (DRT) helps in reducing the effect of undesirable reactions and eliminates the need to wait for an indefinite period, thus reducing energy loss. DRT causes localized heating at a desired pre-heating temperature by introducing a heating element, which operates on low voltage.⁴ The study of DRT explores the reduction of uranium tetrafluoride (UF₄) to uranium metal using a deterministic and controlled firing approach. The work emphasizes process optimization, reaction parameters, and yield consistency, providing insights into reducing impurities and maximizing metallic uranium recovery. A systematic approach to temperature control, reducing agent selection, and reaction kinetics is presented.

In this paper, the influence of the trigger material, e.g., nichrome, Kanthal, silicon carbide, and graphite, on the uranium metal quality has been

studied for a 5-kg batch size. Also, selection and sizing of suitable trigger material for a specific batch size and for desired product quality have been discussed. DRT also opens an avenue to establish the optimum location of the reaction trigger to ensure good slag metal separation, i.e., the influence of location of trigger on the consolidation. In this paper, an experimental study of the effect of trigger location on the ingot quality for a 5-kg batch size has also been done.

MATERIALS AND METHODS

Selection criteria for trigger materials.

The following criteria were used to select a suitable trigger material.

1. The material should have all the properties of an effective heating element.^{8–10}
2. The minimum quantity should suffice for triggering the reaction. This will reduce the impurity intrusion in the product.
3. Since the trigger is a sacrificial component, the material should be low-cost and abundantly available.

Based on the above criteria, a few materials have been identified and evaluated:

1. **Graphite** Graphite is a commonly used heating element. In conventional magnesiothermic reduction of UF_4 setup, a graphite crucible is used to collect the molten metal (uranium). Hence, graphite element used as a trigger will not significantly add any additional new impurity to the product. Apart from this advantage, graphite also has a very high melting point of 3000°C . Here, a 15-g graphite coil was used. The coil sizing is discussed in the design section, and the design criteria were selected to ensure the temperature of the charge (reactant mixture of $\text{UF}_4 + \text{Mg}$) around the trigger element was increased to the desired value before any degeneration of the trigger element started. A COMSOL simulation tool¹¹ was used to ensure the above-mentioned essential condition was met.

2. **Silicon carbide** Silicon carbide, with a high melting point of approximately 2730°C , is thermally stable and chemically inert with respect to uranium, even at elevated temperatures. These properties make it a promising candidate for use as a trigger material. However, due to its brittle nature, excessive reduction in weight compromises its mechanical strength. Therefore, a compromise weight of 15 g was selected for experimental trials.

SiC exhibits negligible solubility in uranium and does not chemically interact with it, minimizing the risk of contamination.¹² The thermodynamic response of the SiC coil during initiation was studied to evaluate the time required for triggering the reaction.

3. **Nichrome** Nichrome has a reasonably high melting point of 1400°C . Limits for nickel and chromium are both 100 ppm as per ASTM 753.

Nichrome's malleability allows easy fabrication into precise coil geometries using minimal material, thus reducing potential impurity intrusion. The impurity intrusion using a nichrome wire of different gauges, 0.3 mm and 0.8 mm, respectively, was reported in Ref. 4. The results of this study were also used as a reference. A simulation study was done to estimate the optimum size of the element suitable for triggering the reaction. The plots of charge temperature around the coil for different gauges were generated to understand the influence of the wire thickness on the time for triggering the reaction without melting the wire itself. The temperature profiles of the charge and the coil element were simulated using OCTAVIA.

4. **Kanthal** This material has a reasonably high melting point. Limits for iron, aluminum, and chromium are 250 ppm, 150 ppm, and 100 ppm, respectively. The density of Kanthal is less than that of nichrome; at the same time, the resistivity of Kanthal is higher than that of nichrome. Kanthal wire needs less weight to achieve the same resistance (and in turn produce the same heat) as nichrome. Furthermore, the alloy is made up of three different materials, reducing the impurity burden on a particular element. Hence, a 24SWG (Standard Wire Gauge) Kanthal wire was used as a trigger element. Apart from the trigger element, other materials were used for the experiments. Uranium tetrafluoride (UF_4) used for the study was formed by hydrofluorination of UO_2 using anhydrous hydrogen fluoride. The material was then passed through an expulsion furnace at 250°C to remove residual moisture and HF. The quality parameters of the UF_4 used for the experiments are as described in Ref. 4.

Magnesium (Mg) in the form of chips was used as the reducing agent. Very fine magnesium powder is difficult to handle and highly reactive, whereas blocks or large chips offer a reduced reaction surface area. The particle size distribution of Mg is chosen on the basis given by Harrington et al. (p 253).¹³

Magnesium fluoride (MgF_2) was used as the lining material for the reaction vessel. The material acts as an electro-thermal insulator for the reaction vessel. The lining for the reactor is made using a mold and a vibrator. To obtain a lining with the desired strength, the particle size distribution of the MgF_2 was optimized. The distribution used for this experiment is given by Harrington et al.¹³

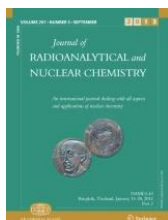
The particle size distributions of MgF_2 (used for reactor vessel lining) and Mg (chips) were measured using ASTM sieve analysis, and we ensured that they were similar to the material chosen in Ref. 4.

EXPERIMENTAL SETUP

The reaction vessel, made of steel SA516 with an MgF_2 lining for insulation, housed the UF_4 and reducing agent mixture with a 4-inch MgF_2 capping. The vessel was sealed, insulated, and placed in a



Scan the QR Code or Click for full text



Journal of Radioanalytical and Nuclear Chemistry (2025) 334:5545–5553
<https://doi.org/10.1007/s10967-025-10297-7>



Evaluation of gross α and gross β activities in air particulate matter at Trombay, Mumbai

V. B. Yadav¹ · V. M. Joshi¹ · Vandana A. Pulhani^{1,2} · A. Vinod Kumar^{1,2}

Received: 7 April 2025 / Accepted: 18 July 2025 / Published online: 31 July 2025
 © The Author(s) 2025

Abstract

This study presents a comprehensive assessment of atmospheric particulate radioactivity in Trombay, Mumbai, conducted from 2016 to 2022. Particulate samples were collected using high volume samplers and analysed for gross α and β activities. Average activities were 0.19 $\pm$ 0.11 and 1.77 $\pm$ 0.86 mBq m⁻³, respectively. A positive correlation ($r^2=0.37$; Spearman coefficient=0.66) indicated common or related sources. The mean α/β ratio was 0.11 $\pm$ 0.05. Seasonal trends showed elevated activity in winter. However, no statistically significant change in average activity was observed over time. The findings suggest stable natural sources dominate atmospheric radioactivity, with variations influenced by seasonal and meteorological conditions.

Keywords Particulate matter · Gross α · Gross β · Atmospheric radioactivity

Introduction

Particulate matter (PM) is a complex mixture of solids and liquids suspended in the atmosphere and is increasingly becoming a serious concern because of its harmful effects on human well-being, especially in urban areas where PM concentrations often reach high levels [1–5]. Particles of different dimensions, with particular concern for PM_{2.5} (atmospheric particles with aerodynamic diameter 2.5 μ m or smaller) and PM₁₀ (atmospheric particles with aerodynamic diameter 10 μ m or smaller) because they can infiltrate the respiratory system after inhalation [6, 7]. Presence of Radioactive Material (RM) in the particulate introduces additional health considerations [8].

Atmospheric radioactivity comes from sources such as natural radionuclides (⁴⁰K and the actinium, uranium, and thorium series radionuclides and their decay products) which were released or re-suspended from the Earth's crust into the atmosphere, cosmic radionuclides (¹⁴C, ⁷Be, ³H etc.),

cosmic radiation and volcanic eruptions [9–11]. Anthropogenic radionuclides may also enter the atmosphere in the event of nuclear accidents, radiological diffusion devices or “dirty bombs” [12]. Among other anthropogenic radionuclides, ¹³⁷Cs has a particular importance due to its long half-life, biological uptake and widespread diffusion after nuclear accidents and nuclear tests [13, 14]. After release in atmosphere, these radionuclides get attached to atmospheric particles, becoming part of particulate matter.

The sources and levels of natural radioactive particles in the air exhibit geographical variation. In urban settings, a diverse range of activities such as vehicular traffic, industrial operations, and commercial endeavors contribute to air pollution. In rural areas, the use of wood, crop residues, and dung as domestic fuel, along with dust from unpaved roads, constitutes the primary sources of air pollution [15]. These emitted pollutants often carry trace amounts of naturally occurring radioactive materials (NORM), thereby contributing to atmospheric radioactivity. NORM primarily consist of radionuclides from three natural decay series (²³⁸U, ²³⁵U, ²³²Th and their daughter products) and some other naturally occurring radioactive isotopes (⁴⁰K, ⁸⁷Rb, ¹⁴C, ³H, etc.). The measured levels of atmospheric particle radioactivity are dependent upon numerous factors, including indoor and outdoor conditions [16], seasonal fluctuations [17, 18], particle size fractions, and geographic locations [19]. Radon (²²²Rn) and thoron (²²⁰Rn)

✉ V. B. Yadav
 vbyadav@barc.gov.in

¹ Environmental Monitoring and Assessment Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

² Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

are gaseous decay products of the radium isotopes ^{226}Ra (a daughter product of the ^{238}U decay series) and ^{224}Ra (a daughter product of the ^{232}Th decay series), respectively. These radionuclides diffuse through the soil, enter the atmosphere, and eventually decay into solid progeny. These progenies can attach to existing aerosol particles, forming radioactive aerosols.

The radioactivity of airborne particles is often quantified in terms of radiological indexes such as gross α and gross β activities which provides a quick means to assess the aggregate composition of the alpha and beta emitting radioactive substances [20]. These indicators also serve as common screening techniques for monitoring atmospheric particulate radioactivity due to their low cost, simplicity, and rapid response [21–23]. Gross α and gross β activity measurement, though does not exactly pinpoint specific radionuclide source or isotope, offers a simple means of tracking radioactivity trends over time [20]. While short-term assessments of air quality furnish valuable information of pollution levels, prolonged observations are requisite for capturing seasonal fluctuations, trends, and potential alterations in pollution sources over time [18]. Long-term studies, spanning several years furnish pivotal insights into the efficacy of environmental policies, the impact of technological advancements, and the dynamic behavior of pollutants and radionuclides in the atmosphere [18].

The city of Mumbai, India's financial hub, exemplifies the rapid pace of urban expansion and industrial advancement. In this context, our study delves into a long-term monitoring of atmospheric radioactivity at Trombay, Mumbai, India, spanning from 2016 to 2022. The coexistence of nuclear establishment with industrial operations and urban development in this region underscores the significance of monitoring atmospheric radioactivity and particulate matter to assess environmental safety and public health. Prior investigations into particulate matter and air pollution in Mumbai have been conducted by various researchers dealing with air pollution and its impact on health [24], variation in $\text{PM}_{2.5}$ level [25], theoretical prediction of pollution [26], Chemical characterization and source identification [27], emission inventory of particulate matter and gaseous pollutants [28], source apportionment [29–31], organic aerosols and atmospheric processing [32]. Nevertheless, to our best knowledge scarce literature exists on the measurement of radioactivity in the particulate matter and their long-term trends in Mumbai.

Our research endeavors to bridge this knowledge gap by presenting an in-depth analysis of a 7 years dataset, offering valuable insights into temporal patterns of gross α and gross β , activity concentrations in Trombay, a coastal site of Mumbai. The study also includes the measurement of the activity concentration of ^{137}Cs in the particulate matter. The study involves collection and analysis of particulate matter

(PM) utilizing high-volume samplers and measurements of radioactivity in particulate matter.

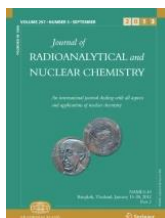
Study area and sampling

The study area, Trombay, along the eastern suburbs of Mumbai, remains well-known for its surrounding industrial activities. It is surrounded by water bodies, with Mumbai Harbour Bay to the east (approximately 1 km distant) and the Arabian Sea to the west (around 12.5 km away). Sampling was carried out the terrace (approximately 20 m above ground level) of a building at Trombay, Mumbai, India. During the period 2016 to 2021 samples were collected on a monthly basis except in monsoon season (June to September) due to sampling constraints. However, during year, 2022, weekly sampling was carried out throughout the year, with the sampler protected under a sheltered enclosure during rainy season. The collection of particulate matter with a diameter of less than or equal to $10\text{ }\mu\text{m}$ (PM_{10}) was accomplished on pre-combusted (heated to $400\text{ }^{\circ}\text{C}$ for a continuous 6-h duration in a Muffle Furnace) $8'' \times 10''$ glass fiber filter (GF/F) using high-volume respirable sampler, at a flow rate of $1.0\text{ m}^3\text{ min}^{-1}$.

Measurement

A waiting period of five days was observed to allow for the decay of short-lived radioisotopes before measurement. A small segment of the filter paper (2.8 cm diameter circular piece), was counted in a low-background gross α and gross β radiometer (UMF-2000). This radiometer enabled the simultaneous measurement of alpha and beta activity using a silicon ion-implanted detector with an area of 1000 mm^2 . The radiometer incorporates active shielding (along with passive shielding) against background radiation with the use of gas discharge detector (GM counters) and anti-coincidence circuit. Routine background assessments of the detector were conducted using clean filters and background correction was applied to both gross α and gross β measured activities. Calibration of the radiometer for gross α and gross β measurements was carried out using a standard radioactive source of α - β activity (ONCH 238, No. 1737, supplied with the instrument). The source contains ^{238}U (along with its decay products ^{234}Th and ^{234}Pa), ^{234}U and ^{235}U radionuclides, with alpha and beta activities of 28 Bq and 27 Bq, respectively. The ^{137}Cs activity in monthly collected filter papers were measured using $4'' \times 4''$ thick well type thallium-activated sodium iodide scintillator detector. The resolution of the detector was better than 8% at 662 keV for ^{137}Cs gamma photon. The average efficiency was calculated as 28.5% for 0.662 MeV gamma energy using the certified





Journal of Radioanalytical and Nuclear Chemistry (2026) 335:1283–1295
<https://doi.org/10.1007/s10967-025-10666-2>



Evaluation of vacuum distillation column performance using radiotracers

Sunil Goswami^{1,2} · U. K. Sahoo³ · V. K. Sharma¹ · Rajesh Kumar^{2,4}

Received: 20 May 2025 / Accepted: 25 November 2025 / Published online: 23 December 2025
 © The Author(s) 2025

Abstract

A radiotracer investigation was carried out to investigate flow dynamics of water in a vacuum distillation column (VDC) meant for production of heavy water. Residence time distribution (RTD) of heavy water was measured using bromine-82 as a radiotracer. The measured RTDs were used to determine the MRTs and examine the radial distribution of water within the beds inside the VDC. Axial dispersion model was used to simulate the measured RTD curves and flow patterns within the different section of the column. Results of RTD analysis showed significant maldistribution in liquid phase flow in the distillation column.

Keywords Heavy water · Vacuum distillation column · Residence time distribution · Mean residence time · Radiotracer · Bromine-82 · Radial distribution · Axial dispersion

Introduction:

Heavy water (D_2O) plays a critical role in nuclear reactor technology, particularly in Pressurised Heavy Water Reactors (PHWRs), where it serves both as a moderator and a primary heat transfer medium (coolant) [1, 2]. Its low neutron absorption cross-section and excellent moderating properties enable the use of natural uranium as fuel, making PHWRs an efficient and cost-effective option for nuclear power generation [3, 4]. Typically, PHWRs require about 750–850 kg of D_2O per electrical megawatt (MWe) of installed capacity [5]. Since D_2O is not consumed during reactor operation, the primary driver for its demand is the construction of new PHWRs, annual losses due to leakage and operational inefficiencies account for less than 1% of the total inventory [6]. Beyond nuclear applications, D_2O is extensively used

in scientific research and industrial applications. It is used for synthesizing a wide range deuterated drugs, which have higher stability and improved therapeutic performance. It also serves as a stable isotope tracer in biological and environmental studies and is essential in NMR spectroscopy through deuterated solvents for accurate chemical analysis [7].

Heavy water is produced through various isotopic separation processes, the most commercially viable methods being the water–hydrogen sulphide (H_2S) exchange and the ammonia–hydrogen exchange processes. The H_2S -based method [8, 9], also known as the Girdler sulphide process, relies on isotopic exchange between deuterium in hydrogen sulphide gas and ordinary water. This process occurs in counter-current towers under moderate temperatures (30–130 °C) and high pressures (around 30 Atm.), where deuterium preferentially concentrates in the liquid phase, enabling enrichment through multiple stages. The second most popular method is the ammonia–hydrogen exchange process [8, 10]. This process is carried out at very low temperature (~ - 25 Deg. C) and high pressure (~285 kg/cm² or atm) in presence of catalyst- potassium Amide solution (~ 25 gm KNH_2 per kg of Liquid Ammonia). The deuterium-enriched ammonia is subsequently cracked into H_2 , D_2 & H_2 in ammonia-cracker in presence of Fe-catalyst at high temperature (~710 Deg C.) & high pressure (~160 atm.) making this method especially

✉ Sunil Goswami
 gsunil@barc.gov.in

¹ Isotope and Radiation Application Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

² Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

³ Heavy Water Board, Anushaktinagar, Mumbai 400094, India

⁴ Heavy Water Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

suitable for integration with hydrogen production in fertilizer plants.

The heavy water produced from these methods is typically enriched up to 10–30%, necessitating further purification to reach reactor-grade concentration (99.85%) [8, 11]. For this final enrichment, vacuum distillation is widely employed due to its operational simplicity, mild conditions, and low risk of product loss. Although vacuum distillation is unsuitable for primary enrichment due to its low separation factor and high energy demand, advancements in structured packing materials—particularly corrugated designs and improved surface wettability—have significantly enhanced efficiency of the process [12]. These improvements allow for lower height equivalent to a theoretical plate (HETP), reduced pressure drop, and better liquid–vapour contact, making it feasible to upgrade D₂O in a single-column setup instead of using a cascade of sieve tray columns. In this study, in a heavy water production plant, a vacuum distillation column consisting of 14 stages of structured packing was found to be operating below its design efficiency. The effectiveness of vapour–liquid contact in such columns heavily depends on the uniform distribution of liquid over the packing. Maldistribution issues like bypassing or channelling can severely compromise column performance. To identify the root causes of inefficiency and to understand the liquid-phase flow behaviour within the column, it was decided to investigate, the liquid phase flow pattern and measure the residence time distribution (RTD) using a radiotracer technique [13–20].

Experimental

Vacuum distillation column

The final enrichment of heavy water is carried out by performing continuous distillation under sub-atmospheric condition. The schematic diagram of the plant is shown in Fig. 1. The distillation plant consists of feed evaporator, vacuum distillation columns, reboiler, reflux condenser and product condenser along with vacuum pumping system for sub atmospheric pressure operation. Distillation column is of 1050 mm diameter having 14 sections of 3 m height each. Each section is packed with phosphor bronze wire mesh structured packing of 2.5 m height and equipped with a liquid collector and distributor on the top to collect liquid coming from the next upper section and redistribute it uniformly over the entire cross section to have a uniform liquid distribution over the packing. The phosphor bronze structured packing used in the column provides a very high specific surface area for vapour–liquid mass transfer, resulting in improved contact between the phases and enhanced isotopic exchange efficiency. Its excellent mechanical strength,

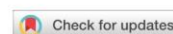
corrosion resistance, and wetting characteristics further contribute to stable column performance and lower pressure drop during operation. However, contact efficiency of the structured packing is mainly dependent on uniform distribution of liquid over the packing and any maldistribution of liquid over the packing such as bypassing, channelling etc. can deteriorate the column performance significantly. The column is operated at negative pressure (vacuum) that is maintained by a vacuum pump and the column top pressure is maintained at 110–120 mm of Hg.

Initially low isotope purity (IP) heavy water is boiled in the reboiler at the bottom of the column and allowed to ascend through the distillation column. After reaching at the top of the column, it is condensed in a reflux condenser and the condensed reflux liquid is fed back into the column through the distributor mounted at the top of the section L-14. The reflux liquid descends through the 14 sections within the column and is fed to the boiler after reaching at the bottom of the column. This process is run continuously. The counter-currently flowing vapour and liquid phases come in intimate contact with each other within the column resulting in vapour–liquid mass transfer. The lighter isotope of hydrogen component (H) from liquid phase is transferred to the vapour phase and the heavier isotope deuterium (D) from vapour phase is transferred to the liquid phase. This mass transfer sets up a concentration gradient along the column producing enriched heavy water (D₂O) of nuclear grade (99.85%) at the bottom of the column and light water at the top of the column. Once the steady state concentration profile is established within the column, feed is introduced into the column. The feed which is heavy water (30% enriched) produced in the primary chemical exchange method, is vaporised at a pre-determined rate and fed into the column between any of the two sections of the column where the feed concentration matches with the column concentration profile. Necessary feeding provisions are made to introduce the feed between any of the two sections. Based on the overall material balance, a part of the reboiled vapour is collected as product (D₂O) of nuclear grade at the bottom of the column and a part of the condensed liquid from reflux condenser is collected as reject at the top of the column.

Radiotracer experiments

A series of four radiotracer experiments was carried out to investigate flow dynamics of heavy water through the 13 different packed bed sections of the column. Bromine-82 [*t*_{1/2}: 36 h, γ : 554 keV (70%); 619 keV (40%); 776(85%)] as ammonium bromide dissolved in aqueous solution was selected to be used as radiotracer and about 200 MBq (~5 mCi) was used in each experiment. In run 1, the radiotracer was injected into the distributor mounted above





OPEN Experimental and theoretical insight into the complexation of tetra secondary butyl diglycolamide (TSBDGA) with trivalent f cations into ionic liquid

Adityamani Nagar¹, Anuj Shukla², A. Srivastava^{3,4}, Arijit Sengupta^{3,4}✉, Dipita Karmakar^{3,4}, Sk. Musharaf Ali^{4,5}, Willem Verboom⁶ & Prasanta K. Mohapatra^{3,4}

Ionic liquids have been emerged of as potential 'green' alternatives to the volatile organic compounds used in liquid-liquid biphasic extraction of metal ions. Their unique properties bring interesting chemistry during extraction of metal ions with respect to tuning the extraction mechanism, speciation, kinetics and energetics associated to it. Diglycolamide based ligands exhibited high selectivity towards the trivalent f cations due to their aggregation behaviour in the diluents. In view of this, it is imperative to understand the complexation of trivalent f cations into ionic liquid with tetra secondary butyl diglycolamide (TsBDGA). TsBDGA was found to form 1:1, 1:2 and 1:3 species predominantly with trivalent f cations. However, the complexation constant values for Nd³⁺ were found to be lower than those of the Eu³⁺ ion, as ascribed to lanthanide contraction. The complexation was found to be spontaneous in nature. On complexation, the local asymmetry around Eu³⁺ was found to increase and the diffusion coefficient values were reduced. The complexation was also indicated by shifts in the carbonyl stretching frequency in the FTIR spectra. Computation analyses were performed to optimize the energy, bond length and 3D structures of the Nd³⁺ as well as Eu³⁺ complexes in gas phase and solution phase alongwith the calculation of the Mulliken Partial atomic charge.

Keywords TSBDGA, UV-vis spectroscopy, Photoluminescence, DFT, Cyclic voltammetry

Partitioning of actinides is one of the proposed strategies for reduction in long term surveillance of highly radiotoxic waste generated from the back end of the nuclear fuel cycle¹⁻³. The first step of the Plutonium Uranium Reduction EXtraction (PUREX) process is the co-extraction of hexavalent uranium and tetravalent plutonium by 30% tri-*n*-butyl phosphate (TBP) in *n*-dodecane. The organic phase containing U and Pu are subjected to change in oxidation state of plutonium from + 4 to + 3 to achieve the mutual separation from hexavalent uranium. The initial raffinate contained all the minor actinides, lanthanides, activation and fission products. In order to avoid long term surveillance, the partitioning and transmutation strategy has been followed. In actinide partitioning, the trivalent lanthanides and actinides were co-extracted into the organic phase resulting their separation from the rest of the other metal ions. In the text this was referred as the first step for actinide partitioning. In the subsequent step, the trivalent actinide and lanthanides which were separated from rest of the other metal ions were subjected for their mutual separation i.e. separation between trivalent lanthanides and actinides. Due to the complex nature of the matrices, presence of different metal ions and associated high radio-toxicity, efficient and selective separation plays key role in order to have desired performance of the nuclear fuel cycle. The first step of the partitioning pertains to the co-extraction of the trivalent lanthanides and actinides from aqueous acidic streams due to their similar chemical behaviour⁴⁻⁶; while the second step pertains to the mutual separation of them⁷⁻⁹. Different partitioning agents have been under consideration for the co-extraction

¹UM-DAE Centre for Excellence in Basic Sciences, Mumbai 400098, India. ²Health Physics Division, Bhabha Atomic Research Centre, Mumbai 400094, India. ³Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India. ⁴Homi Bhabha National Institute, Mumbai 400094, India. ⁵Chemical Engineering Division, Bhabha Atomic Research Centre, Mumbai 400085, India. ⁶Molecular Nanofabrication group, Department of Molecules & Materials, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, Enschede 7500 AE, The Netherlands. ✉email: arijita@barc.gov.in

of trivalent lanthanides and actinides. Carbamoyl methyl phosphine oxide (CMPO) based materials exhibited potential in this regards compared to the only phosphine oxide type of ligands, which are effective mostly in lower acidic region, not in accordance with most of the spent fuel feed acidity (3–4 M HNO_3)^{10–12}. Though CMPO was effective in higher feed acidity, however, the acid insensitive extraction of trivalent f cations due to intermolecular buffering led to the back extraction highly challenging. Moreover, the presence of P in the ligand makes the CMPO not incinerable completely. In order to fulfill the criteria of C, H, O, N principle, the P = O functionality was replaced by another amide moieties resulting malonamide (MA) type of ligands^{13–15}. These MAs exhibited poorer extraction efficiency of trivalent f cations compared to the CMPO, however, the back extraction issue was resolved.

In order to improve the extraction efficiency of the MAs type of ligands; it was proposed to enhance the denticity of the ligand by introducing one etheric O atom between two amide moieties resulting in diglycolamide type of ligands (DGA)^{16–18}. This group of ligands not only improved the extraction efficiency of trivalent f cations; but also exhibited some unique properties of better extraction efficiency of trivalent f cations compared to the tetravalent, which is unconventional in nature. The formation of micellar aggregation in the organic diluents resulted in the unconventional trend¹⁹. Several attempts were made to understand the phenomena and optimize the extraction scheme. The anchoring of multiple DGA functionalities onto molecular or atomic facets have been employed^{20–23}. The structural modification in the tetra-alkyl groups of DGA functionalities also exhibited different extraction efficiency mainly guided either by the electronic factor associated to inductive effect or the steric factor near the functional groups responsible for coordination^{24,25}. Hence, in the present case one of such DGA ligands with secondary butyl as substituted alkyl groups (TsBDGA) was chosen for investigation on the complexation, speciation, etc. with trivalent lanthanides in order to understand the separation scheme in a better way.

In order to resolve the issue of ongoing environmental concern for using volatile organic compounds (VOCs), solvents, etc in the commercial scale, several research were conducted to modify the industrial schemes in 'greener' way. Ionic liquid based research has been evolved as the potential 'green' alternatives to these VOCs; as it generates lesser atmospheric micro-pollutants due to low vapor pressure compared to the VOCs^{26–28}. Apart from the advantageous properties, the high degree of radiation, chemical and thermal stability along with high degree of solubilizing nature reducing the propensity of 3rd phase formation during solvent extraction, ionic liquid based research gained importance in nuclear establishments^{29–32}. A large potential window provides opportunity for direct deposition of f cations from ionic liquid phase selectively³³. The tuning of properties by small structural modification was found to modify the nature of extracted species, efficiency of extraction and even the mechanism of the extraction^{34–37}. Hence, the kinetics and thermodynamic aspects can also be modified depending upon the nature of the structural modifications. However, the functionalized ionic liquids and ionic liquid based membranes also exhibited unique separations in different domains of separation science and technology^{38–40}.

The most exploited ionic liquids in f cation research pertains to alkyl methylimidazolium based ionic liquids, where, 1 and 3 positions of the imidazolium ring was attached to the methyl and other alkyl group, respectively. The nature of the alkyl group can induce the different mechanism for the biphasic mass transfer and hence, is of interest to study. The constituent anion chosen in the present case was NTf_2^- instead of PF_6^- . The PF_6^- based ionic liquid exhibited instability in presence of excess water⁴¹ or acid and the highly viscous nature compared to the NTf_2 analogues make the mass transfer sluggish⁴². In view of this, the complexation of trivalent f cations were investigated using TsBDGA into $\text{C}_6\text{mimNTf}_2$ through different spectroscopic (UV-vis, photo-luminescence, FTIR etc.) as well as electrochemical ways. In order to support the experimental findings computational approach was also followed through density functional theory (DFT).

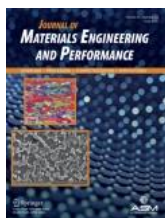
Results and discussions

The complexation of TsBDGA with trivalent f cations into $\text{C}_6\text{mimNTf}_2$ has been investigated through UV-vis titration using Nd^{3+} as a probe, photo luminescence titration using Eu^{3+} as probe, FTIR spectral analyses of Nd^{3+} as well as Eu^{3+} complexes and electrochemical investigation of Eu^{3+} complex employing cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The complexation was compared with other tetra-alkyl DGA based ligands where alkyl groups are isopropyl (TIPDGA), isobutyl (TIBDGA) and iso amyl (TIADGA). The computational calculations were performed for Nd^{3+} and Eu^{3+} complexes of TsBDGA into $\text{C}_6\text{mimNTf}_2$ having ML_1 , ML_2 and ML_3 speciation. The chemical structures for different DGA ligands and the ionic liquids are shown in Fig. 1.

UV-Vis spectroscopic investigations

Figure 2a illustrates the UV-Vis spectroscopic data collected during complexation studies of TsBDGA ligand with Nd^{3+} ions in $\text{C}_6\text{mimNTf}_2$ solvent at 27 °C (300 K). The concentration of $\text{Nd}(\text{NTf}_2)_3$ was 2.7 mM and that of TsBDGA into $\text{C}_6\text{mimNTf}_2$ was 100 mM. The baseline Nd^{3+} absorption displays a characteristic peak at 575 nm, corresponding to f-f electronic transitions ($^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$, $^2\text{G}_{7/2}$)⁴³. The environmental sensitivity of these transitions makes this wavelength region ideal for tracking coordination events throughout the titration process. Figure 2a reveals peak position shifts in all experimental systems. Spectral evolution demonstrates three key features: initially, displacement of the primary peak (accompanied by intensity reduction), subsequently, appearance of a new absorption band at ~580 nm with enhanced intensity, and finally, development of two additional peaks at 575 and 587 nm. Beyond these changes, no further spectral evolution was noted except for a general decrease in overall intensity. The spectral data were quantitatively analyzed using the HypSpec 2008 software, and the fitting results confirm the formation of multiple coordination species, specifically 1:1 (ML_1), 1:2 (ML_2), and 1:3 (ML_3) metal-to-ligand complexes. The deconvoluted spectra for each species of the TsBDGA complexes of Nd^{3+} is given in Fig. 2b. The speciation curves of different stoichiometric complexes are given by





JMEPEG (2025) 34:21741–21754
<https://doi.org/10.1007/s11665-025-11744-y>

©The Author(s)
 1059-9495/\$19.00



ORIGINAL RESEARCH ARTICLE

Exploring Anisotropy in Zr-2.5%Nb Pressure Tube Material through Hardness Measurements: Role of Microstructure and Hydrogen Concentration

Arnomitra Chatterjee and R.N. Singh

Submitted: 8 April 2025 / Revised: 23 June 2025 / Accepted: 1 July 2025 / Published online: 30 July 2025

Zr-2.5Nb pressure tube material exhibits strong anisotropy in mechanical properties owing to its microstructure and texture. In this work, an effort has been made to delineate the contributions from both these factors in the overall anisotropy of the material by imparting suitable heat treatments. The hardness and Young's modulus of as-received and heat-treated material were estimated along three orthogonal directions through nano-indentation and have been correlated with the materials microstructure and texture. Micro-hardness measurements have been carried out on pressure tube samples charged with different hydrogen concentrations to explore if the presence of hydrogen has any influence on the anisotropy of the material. The combined effect of hydrogen and heat treatment on anisotropy has also been investigated.

Keywords anisotropy, hydride, micro-hardness, nano-hardness, texture, Zr-2.5%Nb alloy

1. Introduction

The low neutron absorption cross section, adequate strength and good corrosion resistance at reactor operating condition (Ref 1-3) have made Zr-2.5%Nb alloy the structural material for pressure tube (PT) in Pressurized Heavy Water Reactor (PHWR). The metallurgical parameters of the material in terms of size and shape of grains, texture, etc., are tailored by adapting proper fabrication route to achieve the dimensional stability of the component in service condition. The fabrication process designed for Indian PHWR pressure tubes includes a series of thermo-mechanical treatments that regulates final microstructure and texture of the tubes. The fabrication route for the pressure tube has also evolved over time (Ref 4). Figure 1 shows the flowchart of fabrication process followed for the particular pressure tube considered in this work. This route is very much similar to the modified route II of CANDU reactor pressure tubes (Ref 5). The final microstructure of the component thus fabricated contains heavily elongated and textured α phase surrounded by a thin network of β phase along the grain boundaries (Ref 5, 6). The microstructure and texture resulted from the fabrication process impose strong anisotropy in mechanical properties of the material along with the inherent hcp crystal structure of α zirconium. The formulation of constitutive equations in predicting in-reactor deformation of the component under multi-axial load demands an extensive

knowledge of the anisotropy. Hence, the study of anisotropy of the PT has been an active field of research (Ref 6-9). Li and Holt (Ref 7) investigated the anisotropy of thermal creep in this material and established profound texture dependence in creep anisotropy. Holt et al. (Ref 8) explored the anisotropy of in-reactor deformation of Zr-2.5%Nb pressure tubes. Shewfelt (Ref 9) investigated the anisotropy in Zr-2.5%Nb PTs used in CANDU reactors by tensile and creep tests. Through his results, he established the difference in deformation mechanism along longitudinal and transverse direction in terms of prismatic slip and twin, respectively, up to 500 °C, resulting in anisotropy in tensile properties. The creep properties exhibited anisotropy as higher creep rate along longitudinal direction up to 550 °C. However, owing to the change of creep mechanism to grain boundary sliding at still higher temperature in case of transverse samples corresponding creep rate surpassed that of longitudinal samples. Causey et al. (Ref 10) investigated anisotropy in in-reactor creep behavior in the PT material in detail. Patel et al. (Ref 11) also explored the anisotropy in the creep properties of Zr-2.5%Nb PT from IPHWR, and they could conclude that creep resistance was more in transverse direction compared to the longitudinal one. Singh et al. (Ref 12) worked extensively on anisotropy in flow behavior of PT used in Indian PHWR540 reactor through tensile tests on samples fabricated along axial and transverse direction. The transverse direction of the tube was found to show higher strength and lower ductility than that along longitudinal direction up to 623 K above which strength was almost comparable in both the directions. Anisotropy in tensile and fracture toughness properties of Zr-2.5%Nb pressure tube has been studied by Bind and Singh (Ref 13) which showed transverse direction exhibited higher strength and lower fracture toughness compared to the longitudinal direction. Dutta and Robi (Ref 14) also performed tensile tests on Zr-2.5%Nb alloy over a wide range of temperature to investigate the anisotropy in strength and work hardening of the material. Several other works have been carried out to understand the anisotropy in mechanical properties of the PT material (Ref 15-

Arnomitra Chatterjee and **R.N. Singh**, Mechanical Metallurgy Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India. Contact e-mail: amitrac@barc.gov.in.

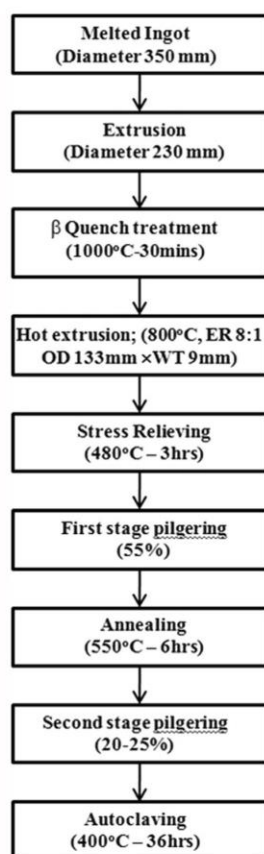


Fig. 1 Fabrication route for the Zr-2.5%Nb alloy pressure tube considered in this work

17). However, it must be noted that the use of standard sized samples for the pressure tube geometry allowed the mechanical property to be evaluated in longitudinal and transverse direction only. There are some works where miniature samples have been used to study the anisotropy of the material. Automated ball indentation and small punch test technique were used by Kulkarni et al. (Ref 18) to compute the correlation coefficient of ABI with tensile test along different loading directions. Through their work, they could establish that both SPT and ABI techniques could capture the anisotropy of the material. Murty et al. (Ref 19) studied the anisotropy in mechanical properties of Zircaloy-2 by constant stress impression test along axial, radial and hoop direction and identified the hoop direction to have highest yield stress. The study of anisotropy in strain hardening behavior revealed the radial direction to have highest strain hardening exponent and strength coefficient. Oviasuyi and Klassen (Ref 20) made use of spherical indentation technique to study the stress-strain response of anisotropic Zr-2.5%Nb alloy. However, there have not been many works reported where hardness-based techniques have been utilized to study the anisotropy in the Zr-2.5%Nb alloy. Bose and Klassen (Ref 21) used micro-indentation to explore the effect of texture on the anisotropy in mechanical anisotropy

of the Zr-2.5%Nb pressure tube material along three orthogonal directions. They generated data set on variation of yield strength and creep rate with temperature, especially along radial direction. It has been noted that the anisotropy of the PT material has not been probed with nano-indentation even though it has been a very useful method to extract mechanical properties from a very small volume of material. However, this technique has been adapted to study several other aspects of the Zr-2.5%Nb alloys. Wang et al. (Ref 22) investigated orientation dependent evolution of plasticity in case of irradiated Zr-2.5%Nb alloy by nano-indentation. Sahoo et al. (Ref 23) made use of nano-indentation in evaluating properties of individual phases α and β .

As the anisotropy aspect of Zr-2.5%Nb alloy PT material holds an important role in predicting the component behavior in service condition, there has been another very important factor in assessing the lifetime of PT: hydride embrittlement. During reactor operation, hydrogen is released and that is picked up by the PT material over the time of operation (Ref 24). The solubility of hydrogen is almost negligible in Zr (Ref 25, 26), and it is precipitated as hydride in the material. Thus, it would be very interesting to investigate if there is any mutual dependence of these two aspects of PT material; whether the anisotropy of the material would evolve with the change in hydrogen concentration or hydride formation in the material.

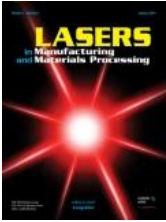
In this work, for the first time an attempt has been made to study the anisotropy in the mechanical properties of the Zr-2.5%Nb alloy PT material by nano-indentation to quantify the contribution of microstructure and texture in the anisotropy of the material by imparting different heat treatments. The material is charged with different concentrations of hydrogen, and the anisotropy in terms of micro-hardness measurement has been carried out to investigate if the presence of hydride has any influence on the anisotropy of the material.

2. Experiments

The material used in the present study is Zr-2.5%Nb pressure tube (PT) material for IPHWR220 in as-received (AR) condition manufactured by Nuclear Fuel Complex, Hyderabad. Small pieces of rectangular samples of 10 mm long (longitudinal-L), 8 mm width (transverse-T) and a thickness of around 3.5 mm (radial-R) were cut from the AR PT. The AR samples were heat treated at 550, 700 and 800 °C for 6, 2 and 0.5 h, respectively, and finally allowed to furnace cool in an effort to delineate the contribution of microstructure and texture in anisotropy of the material. The microstructure and hardness studies were carried out on three orthogonal planes along longitudinal normal (LN), transverse normal (TN) and radial normal (RN) as schematically shown in Fig. 2.

The coupons of AR Zr-2.5%Nb PT material have been charged with hydrogen for six different target concentrations of 25, 50, 70, 100, 150 and 200 wppm, respectively. The coupons were polished up to 1200 grit SiC paper to achieve the optimum surface roughness for hydrogen charging. Hydrogen was charged in a modified Sievert's apparatus (Ref 27, 28) at 363 °C. The difference between initial and final partial pressure of hydrogen gives the estimate of hydrogen picked up by the material during the charging process. Small pieces of average mass of ~ 180-200 mg were cut from these charged coupons





Lasers in Manufacturing and Materials Processing (2025) 12:1037–1060
<https://doi.org/10.1007/s40516-025-00319-3>

RESEARCH



Exploring Manual Laser Oscillation Welding of Stainless Steel in Different Joint Configurations

Aniruddha Kumar¹

Received: 23 May 2025 / Revised: 16 September 2025 / Accepted: 24 September 2025 /
 Published online: 16 October 2025
 © The Author(s) 2025

Abstract

In this work, we report on handheld laser welding of AISI 304 L stainless steel sheets and pipes using various joint configurations. Sheet welds were performed using butt, corner, “T”, lap, and edge joints with a 2 kW continuous-wave handheld laser welding system. AISI 304 filler wire with a diameter of 1 mm was employed during welding. The process was carried out manually by manoeuvring the welding torch along the joint, utilizing an oscillating beam at a constant speed. The effects of oscillation amplitude, oscillation frequency, and laser power on weld pool shape and penetration were investigated. Weld quality was evaluated through X-ray radiography, optical microscopy, tensile pull testing, and micro-hardness measurements. Porosity was observed in welds produced under argon shielding gas. In contrast, using high-purity nitrogen gas resulted in porosity-free welds. Tensile tests showed that welds made with nitrogen shielding sustained a peak load of 23 kN, 26 kN and 12 kN for butt, “T” and lap joint welds respectively before fracture, significantly outperforming those welded under argon. Microstructural analysis revealed a duplex structure, with ferrite as the minor phase distributed in various morphologies within the austenitic matrix. All standard joint configurations were successfully welded using the handheld laser welding system.

Keywords Hand Held Laser · Fiber Laser · Oscillation Welding · Stainless Steel · Nitrogen

✉ Aniruddha Kumar
aniruddhak@barc.gov.in; nontee65@yahoo.com

¹ Fuel Fabrication, Bhabha Atomic Research Centre Tarapur, Maharashtra 401 502, India

Introduction

With significant advancements in laser technology over the past few decades, laser welding has emerged as a widely adopted technique in industries where high weld strength and consistent weld quality are critical. The development of fiber laser technology—with its excellent beam quality and high brilliance—has further enhanced process capabilities. Remote laser welding using oscillating beams enables the joining of components with poor fit-up, stabilizes the melt pool, and reduces defects such as porosity and spatter [1–3]. Compared to conventional arc welding methods, laser welding offers higher speeds, lower thermal distortion, and superior aesthetic weld quality, often minimizing the need for post-processing [4].

Despite its advantages, the adoption of laser welding has been limited due to high equipment costs, complex beam delivery systems, and the requirement for skilled operators. Consequently, traditional arc welding methods such as Gas Tungsten Arc Welding (GTAW), Gas Metal Arc Welding (GMAW), and Shielded Metal Arc Welding (SMAW) continue to be widely used. Among these, GTAW remains a preferred choice for welding thin stainless-steel sheets due to its simplicity and high weld quality. However, it is constrained by slow welding speeds, high heat input, and a susceptibility to weld defects such as incomplete fusion, cracks, and distortion [5, 6]. Techniques like Activated Flux TIG (A-TIG) [7, 8] and Plasma Arc Welding (PAW) [9] have been introduced to address some of these limitations, and hybrid processes combining low-power lasers with plasma arcs have shown improved efficiency in welding thin stainless steel sheets [10].

The recent introduction of hand-held fiber laser welding (HLW) systems present a promising alternative to both conventional arc welding and costly robotic laser systems [11]. HLW combines the precision of laser welding with the flexibility of manual operation, allowing high-speed welding of components up to a few millimetres thick. These systems offer enhanced manoeuvrability, making them suitable for in-situ repairs, complex geometries, and low-volume production. Equipped with features such as beam oscillation, automatic wire feeding, and integrated safety systems, HLW devices ensure consistent weld quality while reducing operator fatigue and skill dependency.

Handheld laser welding (HLW) has emerged as a promising alternative to conventional welding techniques due to its flexibility, precision, and ease of operation, especially in small-scale and custom fabrication environments. Early developments in HLW, dating back to the 1970s, have gained renewed attention following advancements in compact fiber laser sources, ergonomic torch designs, and smart control systems. Xin et al. [12] developed a PLC-based handheld laser welding system with capabilities for both spot and continuous welding, demonstrating enhanced control and reduced operator workload. Puester et al. described safety requirements for hand held laser processing devices in their work [13]. A more specialized application was presented by Reis et al. [14], where a smart handheld laser device was used for ultra-thin foil welding, emphasizing precise thermal management and minimal distortion, making it suitable for microelectronics and biomedical components. Feasibility studies on materials such as aluminum alloys was done by Berrizbeitia et al. [15]. The authors confirmed HLW's potential for joining thin sections of highly conductive





OPEN

First evidence of coexistence of Pseudo Pelger Huët anomaly and balanced translocation in a two decades retrospectively exposed human subject

Rajesh Kumar Chaurasia^{1,4}, Ranjana S. Pathak^{2,4}, Anjana Goel², Kapil B. Shirsath¹, Nagesh N. Bhat^{1,3}, Arshad Khan¹ & Balvinder K. Sapra^{1,3}✉

This study investigated the long-term stability of cytogenetic and morphological markers, including dicentric chromosomes (DC), unbalanced translocation (UT), balanced translocation (BT), and Pseudo Pelger-Huët Anomaly (PPHA), in a radiation worker exposed to an acute dose of ^{60}Co - γ radiation. Initial dose assessment, one week after exposure via Thermoluminescent dosimeters (TLDs) and DC, yielded a physical dose of 438.8 mGy and a biological dose of 398 mGy respectively. A follow-up biodosimetry evaluation, conducted 24 years postexposure, yielded a dose estimate of 449 mGy on the basis of BT, closely matching the initial TLD measurement (+ 2.3% relative error). In contrast, the DC, UT, and micronuclei (MN) frequencies fell within the background range, confirming their instability over time. We also assessed the presence of PPHA in blood smears from the same volunteer. PPHA, a morphological marker of neutrophils originating exclusively in vivo from bone marrow progenitor cells, demonstrated a more than twofold increase in frequency compared to background levels, suggesting an association with radiation exposure. This is the first report of concurrent BT and PPHA persistence in the same individual, demonstrating the suitability of these biomarkers for retrospective detection of past radiation exposure. BT offered reliable dose reconstruction decades after exposure. We could not translate the PPHA yield into an absorbed dose, as no in-house dose-response curve was established.

Keywords Radiation exposure, Retrospective biodosimetry, Balanced translocations, Pseudo Pelger-Huët anomaly, Long-term dose estimation

Accurate dose estimation following radiation exposure is essential for health monitoring, regulatory compliance, and medical intervention, particularly in cases of accidental, occupational, or environmental exposure¹. Cumulative radiation doses pose long-term health risks, making precise dose reconstruction critical for radiation workers, radiotherapy patients, and other exposed populations². Cytogenetic techniques such as the dicentric chromosome assay (DCA), cytokinesis blocked micronuclei (CBMN) assay, and fluorescence in situ hybridization (FISH) have been developed to address this need¹. DCA, the gold standard for short-term biodosimetry, detects dicentric chromosomes (DCs) formed by ionizing radiation-induced DNA double-strand breaks. However, DCs gradually decline as damaged cells are cleared or complete their life cycle, limiting their long-term utility^{1,3}. Similarly, MNs, extranuclear bodies formed from chromosomal fragments (or whole chromosomes), also decrease in frequency over time, further restricting their application in long-term retrospective biodosimetry^{1,4}. More stable chromosomal markers, such as translocations, offer a solution for long-term dose estimation. Balanced translocations (BTs), in particular, are stably maintained through successive cell divisions, making them reliable markers for cumulative radiation exposure from years to decades (up to lifetime)⁵. Peripheral blood lymphocytes are eventually eliminated after completing their lifespan, which result in the loss of BT signals from peripheral blood. However, new lymphocytes produced from precursor bone marrow cells possess these stable

¹Radiological Physics and Advisory Division, Bhabha Atomic Research Centre (BARC), Mumbai, India. ²Department of Biotechnology, GLA University, Mathura, India. ³Homi Bhabha National Institute (HBNI), Mumbai, India. ⁴Rajesh Kumar Chaurasia and Ranjana S. Pathak: These authors contributed equally to this work. ✉email: bsapra@barc.gov.in

aberrations (BTs are stable aberrations, involve no genetic loss, only gene rearrangements)⁶. These precursor cells continue to produce functional blood lymphocytes with stable aberrations and hence the frequency of peripheral blood lymphocytes with such stable aberrations remains maintained over longer periods^{7,8}. FISH is crucial for detecting BTs, making it indispensable for long-term biodosimetry, especially in radiation workers with potential long-term exposure, and in other cumulative exposure cases, and large-scale epidemiological studies^{5,7}.

The decay kinetics of DCs, MNs, and unbalanced translocations (UTs) have been extensively studied, with significant variability reported in their temporal dynamics⁹. While DCs, MNs and UTs are useful for short-term dose assessment, they exhibit rapid decay due to cell turnover (typically lasting 2–3 years), complicating long-term dose reconstruction¹⁰. Conversely, BTs demonstrate notable stability, persisting in peripheral lymphocytes for years to decades postexposure¹¹. Although partial-body exposure and other factors can influence BT stability, their robustness makes them critical for retrospective dose estimation in long-term studies¹².

In addition to established cytogenetic markers, recent studies have identified radiation-induced morphological markers. Notably, Goans et al. (2015) reported that pseudo-Pelger-Huët anomaly (PPHA) is a radiation-induced morphological biomarker¹³. Their analysis of archival peripheral blood smears from the 1958, Y-12 criticality accident revealed that PPHA morphology in neutrophils emerged within 12 h postexposure, highlighting its potential as a marker of acute radiation exposure¹⁴. Further evidence from the Y-12 incident indicated that PPHA could persist as a long-term biomarker, with one patient exhibiting the PPHA marker for up to 16 years postexposure, suggesting a stable radiation-induced alteration^{14,15}. The Pelger-Huët anomaly was first described by Karl Pelger (1928) and G.J. Huët (1931) as an autosomal dominant mutation^{16,17}. PPHA is characterized by round, oval, or bilobed nuclei joined by a thin chromatin bridge. While PPHA affects all granulocytes, it is most pronounced in neutrophils. This is generally attributed to decreased expression of the lamin B receptor (LBR), a component of the nuclear lamina whose expression increases during normal granulocyte maturation. PPHA originates in the bone marrow and is caused by a dominant mutation in the lamin B receptor (LBR) gene, which is located on chromosome 1q42.12¹⁸.

This article presents a case study of a radiation worker exposed to acute ⁶⁰Co-γ radiation, with initial dose assessment using DCA and a TLD. It evaluates the long-term stability of cytogenetic (DC, UT, and BT) and morphological (PPHA) markers, 24 years postexposure. Notably, this study provides the first evidence of simultaneous BT in lymphocytes and PPHA in neutrophils, demonstrating their persistence over time. These findings emphasize the potential of BT and PPHA as long-existing biomarkers for retrospective radiation dose estimation.

Materials and methods

Study design

Approximately 2 decades ago, a middle-aged industrial radiation worker was acutely exposed to ⁶⁰Co-γ radiation. Initial dose estimation used physical (TLD) and biological (DCA) dosimetry (Table 1; Fig. 4-supplementary material). Recently, 24 years post-exposure, biodosimetry assessed the long-term stability of radiation-induced markers, including chromosomal aberrations (BT, UT, DC, MN) in lymphocytes and PPHA in neutrophils (Figs. 1 and 2).

This study investigated chromosomal markers, including DC, UT, BT and MN, in lymphocytes and the morphological marker PPHA in neutrophils from a willingly participating radiation worker (age-27 years, gender-male) exposed inadvertently to an acute dose of ⁶⁰Co-γ radiation 24 years ago. It aimed to assess the long-term in vivo stability of these markers for accurate dose estimation. The initial dose was estimated one week after exposure, with a reassessment conducted 24 years later using blood sample from the same volunteer. The initial dose estimation was performed using DC analysis with Giemsa staining, while the follow-up assessment utilized both FISH- and Giemsa-based methods. FISH analysis measured BT, UT, and DC, whereas Giemsa staining evaluated DC and MN. Age- and sex-matched controls (positive and negative) were included in both the initial and follow-up dose estimations. The term “control” refers to blood samples obtained from unexposed healthy volunteers. The initial control blood sample was collected from one volunteer at the time of the first exposure. After 24 years, a subsequent control blood sample was collected from a different healthy, unexposed volunteer matched for age and gender. The control volunteers were not the same for the initial and later blood collections. The inclusion of age- and sex-matched positive and negative controls aimed to ensure the reliability and consistency of cytogenetic dose estimation in cases of defined radiation exposure levels. These controls served as a reference for comparison with data obtained in the exposed individual. Additionally, their inclusion helped evaluate intra-laboratory reproducibility and validate the robustness of the biodosimetry techniques used in both the initial and follow-up assessments. The negative control was not exposed, while the positive control received in vitro 0.5 Gy of ⁶⁰Co-γ radiation at a dose rate of 0.4 Gy/min via a Blood Irradiator-2000 manufactured by the Board of Radiation & Isotope Technology (BRIT), DAE, India.

Irradiation was carried out following recommended guidelines^{1,3}. A water-equivalent phantom with 3 mm buildup (polymethyl methacrylate (PMMA) plate placed on top of the phantom) was used to ensure electronic equilibrium for the samples. Both the phantom and samples were pre-warmed and maintained at 37 °C throughout the procedure. Dose and dose rate were measured using a Fricke dosimeter in the same irradiation geometry, with calibration traceable to national standards and aligned with international primary standards. All irradiations were performed on the same day.

The subject is absolutely fine and in good health conditions, with no symptoms of any oncological conditions after 24 years of exposure. A recent differential blood count was conducted and found to be within the normal range, further supporting the absence of any hematological abnormalities.





Fission product mass distribution studies in $^{35}\text{Cl} + ^{176}\text{Yb}$ and $^{35}\text{Cl} + ^{165}\text{Ho}$ reactions

S. Kumar^{1,a}, R. Tripathi^{1,3}, S. Patra^{1,3}, A. Mhatre¹, A. Kumar¹, K. Ramachandran², T. N. Nag¹, S. Santra^{2,3}

¹ Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

² Nuclear Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India

³ Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

Received: 13 March 2025 / Accepted: 30 July 2025

© The Author(s) 2025

Communicated by Silvia Leoni.

Abstract Many studies on the fission fragment mass distribution in the sub-lead and pre-actinide region have proposed the presence of asymmetric components in this mass region, primarily due to proton shells corresponding to $Z \approx 36, 38$. Present studies have been carried out to investigate the mass distributions in the $^{35}\text{Cl} + ^{176}\text{Yb} \rightarrow ^{211}\text{Fr}$ and $^{35}\text{Cl} + ^{165}\text{Ho} \rightarrow ^{200}\text{Po}$ reactions in the mass region around ~ 200 , a transition between the sub-lead and actinide region. Mass distribution studies have been carried out near the entrance channel Coulomb barrier using the recoil catcher technique, followed by off-line γ -ray spectrometry of the fission products. The broad Gaussian nature of the mass distribution in the $^{35}\text{Cl} + ^{176}\text{Yb}$ reaction indicates a dominant symmetric fission contribution. The mass distributions for the $^{35}\text{Cl} + ^{176}\text{Yb}$ and $^{35}\text{Cl} + ^{165}\text{Ho}$ reactions were found to be in gross agreement with GEF (Schmidt et al. in Nucl Data Sheets 131:107, 2016; Schmidt and Jurado in Rep Prog Phys 81:106301, 2018). The GEF model predicts a dominant symmetric fission contribution along with the contribution from the asymmetric fission mode corresponding to $Z \approx 38$. The most probable charge, Z_p was varied within a range of ~ 1.5 units with respect to that obtained using the unchanged charge density hypothesis to obtain the best agreement with GEF. However, a few experimental mass yields in the mass regions corresponding to $Z \approx 50\text{--}52$ and $Z \approx 54\text{--}56$ were observed to be still higher (more than $\sim 50\%$) compared to the GEF predictions. A similar enhancement observed in the corresponding fission product yields indicates possible contributions from the conventional asymmetric fission modes, in addition to the shell corresponding to $Z \approx 38$.

1 Introduction

The fission product mass distribution is intimately connected to the potential energy landscape of the fissioning nucleus. Subsequent to the observation of asymmetric mass distribution in the beta delayed fission of ^{180}Tl [3], a large number of studies have been carried out theoretically and experimentally in the pre-actinide as well as sub-lead mass regions [4–30]. The experimentally observed asymmetric mass distributions in the pre-actinide region have been explained based on the states of the fissioning nucleus in the vicinity of the saddle point [4–6] as well as of pre-formed fragments near the scission point [7–12]. In the first approach, shell gaps arising due to the interaction of $[30\Lambda\Omega]$ and $[41\Lambda\Omega]$ levels of the fissioning nucleus have been proposed to be the driving force for the contribution from asymmetric fission [4]. On the other hand, Wilkins et al. proposed fragment shell effects near the scission point to be the dominant factor responsible for the asymmetric fission in very early studies [7]. Recently, different neutron and proton shells have been proposed in the octupole deformed fragments near scission [11, 12]. Studies in the mass region around $A \approx 200$ are crucial for observing the transition from asymmetric fission in the sub-lead region to that in the actinide region, via the intermediate pre-actinide mass range. It might be possible to observe the role of the neutron/proton shells operating in the sub-lead as well as in the actinide region in the mass distribution of the fissioning nuclei around $A \approx 200$. The low-energy fission studies carried out by Schmidt et al. [13] over a wide range of nuclei from ^{205}At to ^{234}U showed dominant symmetric charge distributions for lower mass fissioning systems around the lead region. In contrast, significant contribution from asymmetric fission was observed in the higher mass region, showing a transition around ^{227}Th . There have been a large number of

^a e-mail: ksatyam@barc.gov.in (corresponding author)

studies in the recent past as well as some early studies spanning over a wide mass range around $A \approx 176\text{--}210$ [15–30]. Recently, detailed fission fragment mass distribution studies have been carried out by Bogachev et al. [27] and Kozulin et al. [28] covering fissioning systems ^{178}Pt , $^{180,182,182,190}\text{Hg}$ and $^{184,192,202}\text{Pb}$. Based on these studies, it has been proposed that the asymmetric components in the multi-modal fission in this mass region mainly arises due to the proton shells corresponding to $Z \approx 36$ and 38 (referred to as A1 mode), 45 and 46 (referred to as A2 mode) and 28/50 (referred to as A3 mode) [27, 28]. The proton shell corresponding to $Z \approx 50$, as observed in these studies, can also be related to the conventional SI asymmetric mode [31]. In the study of fission fragment mass distributions carried out by Itkis et al. [15], contributions from conventional SI and SII modes were observed in the fission fragment mass distributions in the light fissioning systems $^{205,207,209}\text{Bi}$, $^{208,210,212}\text{Po}$ and ^{213}At . In all these systems, mass distributions were observed to have a flat-top nature near symmetry, which is now attributed to the proton shell closure ($Z \approx 36\text{--}38$) [15, 30].¹Morfeuace et al. [32] studied the charge distributions of fission fragments for 100 exotic fissioning systems ranging from the sub-lead to the actinide region. The study demonstrated a transition to more asymmetric fission as we move towards neutron-deficient systems. The study highlighted the dominant role of deformed proton shell at $Z = 36$ of the light fragment in the fission of sub-lead nuclei [32]. The fission fragment mass distributions studies for $^{176,186}\text{Pt}$ at varying excitation energies by ²Duan et al. [33] inferred the role of the proton shells corresponding to $Z \approx 35$ for the light fragments and $Z \approx 43$ for the heavy fragments. In this study, the presence of asymmetric fission mode was observed at high excitation energies which was attributed to the contribution from higher chance fission with low excitation energies. Similarly, heavy-ion induced fission mass distributions for the even- Z fissioning nuclei ranging from ^{144}Gd to ^{212}Th studied by ³Buete et al. [34] attributed the proton shell gaps at $Z = 34$, 36 and $Z = 44$, 46 to be major guide for the fission mass distributions in the sub-lead region. However, the study didn't rule out the contribution from the proton shells associated with asymmetric modes SI and SII fission [34]. The proton number of fragments can be estimated using the unchanged charge density (UCD) hypothesis, which assumes the same N/Z ratio for fragments and the fissioning nucleus [35]. In a recent study on the fission of ^{178}Hg , it was pointed out that $\langle N \rangle / Z$ values may significantly deviate from calculations based on the UCD hypothesis due to charge polarization effects. However, the observed deviation for such a light mass fissioning nucleus was in the opposite direction compared to that observed in the actinide region [26]. Change

in the direction of the deviation reflects the shift of the Z_p values towards the neutron-deficient region in the light mass fissioning system. Based on these studies, strong roles of $Z = 28$ and $Z = 50$ shells were also observed in governing the mass distribution. The study was carried out using inverse kinematics at VAMOS++ where, mass and charge identification of one of the fragments were obtained from time-of-flight (TOF) measurement, while the fission partner was detected by the second detection (SED) arm consisting of a position-sensitive MWPC (PS-MWPC) backed with a Si detector [26]. The information about Z of the fission products (mostly for products with even N and even Z) can also be obtained using $\gamma\text{--}\gamma$ coincidence measurement of the prompt γ -rays emitted near the end of the yrast decay cascade [36, 37]. Also, the information about the proton number of the fission products can be obtained using radiochemical methods, which involves irradiation followed by off-line γ -ray spectrometry of the radioactive fission products. Off-line γ -ray spectrometry is an alternative or complementary approach to the on-line measurements and has been extensively used in the recent past [38–44]. In this method, the fission product of a given mass and proton number can be uniquely identified by identifying its characteristic decay γ -rays as well as following its half-life.

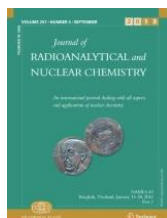
In the present study, the fission product mass distribution of the $^{35}\text{Cl} + ^{176}\text{Yb} \rightarrow ^{211}\text{Fr}$ reaction has been measured using off-line γ -ray spectrometry at $E_{\text{lab}} = 167.1$ MeV. Experimentally measured fission product cross-sections were modified to obtain the corresponding mass yields using the respective charge distribution parameters. Results from the $^{35}\text{Cl} + ^{176}\text{Yb} \rightarrow ^{211}\text{Fr}$ reaction have been compared with the results obtained for the $^{35}\text{Cl} + ^{165}\text{Ho} \rightarrow ^{200}\text{Po}$ reaction at 161.7 MeV beam energy from a separate experiment, to obtain a comprehensive understanding of the role of different shells in the pre-actinide region. A detailed comparison of the experimental mass yields with those calculated using the GEF code [1, 2] has been carried out for both the fissioning systems.

2 Experimental details

The experiments were carried out at the BARC-TIFR Pelletron-LINAC facility at Tata Institute of Fundamental Research, Mumbai, India. For the $^{35}\text{Cl} + ^{176}\text{Yb}$ reaction, a self-supporting ^{176}Yb target (Yb target 96.6% enriched in ^{176}Yb isotope) of thickness ~ 2.2 mg/cm² was mounted on a target stand. A Pb foil of thickness ~ 17.5 mg/cm² was used as a forward catcher foil to capture the fission products in the forward direction. The energy of the ^{35}Cl beam emerging from the target was much below the fusion barrier for lead, thereby avoiding any possibility of fission products from $^{35}\text{Cl} + ^{\text{nat}}\text{Pb}$ reaction. For the collection of fission products recoiling out

^{1,2,3} The references have been included during the revision of the manuscript.





Journal of Radioanalytical and Nuclear Chemistry (2025) 334:5861–5868
<https://doi.org/10.1007/s10967-025-10289-7>



From minerals to the electrodes of lithium-ion battery: facile and precise determination of lithium by ${}^7\text{Li}(\text{p},\alpha){}^4\text{He}$ nuclear reaction

Yerroju Sunitha¹ · D. V. Lakshmipathy¹ · Sk Jayabun¹ · G. L. N. Reddy¹

Received: 26 May 2025 / Accepted: 17 July 2025 / Published online: 2 August 2025
 © The Author(s) 2025

Abstract

The determination of lithium in spodumene, a mineral of lithium, and a number of materials used in lithium-ion battery by ${}^7\text{Li}(\text{p},\alpha){}^4\text{He}$ nuclear reaction is described. The reaction is induced by 600 keV protons while the α -ejectiles are detected at 150° emission angle by a surface barrier detector. A mylar foil of ~ 10 micron thickness is used as a stopper foil to prevent the detection of backscattered protons and the α -ejectiles from $X(\text{p},\alpha)$ reactions ($X = \text{B}, \text{N}, \text{O}$ or F) occurring simultaneously with the ${}^7\text{Li}(\text{p},\alpha){}^4\text{He}$ nuclear reaction. Specimen-silver powder mixtures serve as the targets. The comparator approach is used for quantitation. It employs a linear calibration plot constructed over 1–9.5 wt.% ${}^7\text{Li}$ using lithium carbonate powder standards. The precision of the determinations is 1–3% while the combined uncertainty is $< 8\%$. Homogeneity of targets and the choice of stopping cross sections of the materials are crucial for determinations with good analytical attributes. Non-destructive nature, rapidity, amenability to both bulk solid matrices and coatings and superior analytical merits make this method suitable for the routine determination of Li in materials.

Keywords Lithium · Nuclear reaction · Spodumene · Lithium ion battery · Lithium titanate

Introduction

The advent of lithium-ion battery (LIB) as an efficient system has renewed the interest in the determination of lithium in materials [1]. A LIB is an electrochemical device that employs a lithium based chemical compound, such as LiCoO_2 , LiNiO_2 or LiFePO_4 , as the cathode [2–4]. These materials function as the source of lithium ions for charge transport. So far as the anode materials of LIBs are concerned, graphite is the most preferred choice. However, recent cell configurations, designed specifically for heavy electric vehicles have adopted a yet another lithium compound lithium titanate (LTO), as the anode material [3]. It is instructive to mention that lithium hydroxide (LiOH) and lithium carbonate (Li_2CO_3) serve as the precursors for nearly all lithium compounds while these themselves derived from minerals [5]. Spodumene ($\text{LiAlSi}_2\text{O}_6$), eucryptite (LiAlSiO_4) and the recently discovered jaderite ($\text{LiNaSiB}_3\text{O}_7(\text{OH})$) containing 3.73, 5.51 and 3.16 wt.% Li respectively are the

commercially important minerals of the element [6]. Notably, lithium has a low natural abundance (20–40 ppm) in the earth's crust and, therefore, falls under the category of scarce elements.

The determination of lithium in various materials—from the ores and the minerals to lithium hydroxide, lithium carbonate, and the electrode materials—is crucial for an optimum resource utilization, the fabrication of high-quality products and failure analysis. Importantly, the determination of lithium is required not only in the cathode materials but also in the anodes, graphite or LTO, that reversibly host Li-ions during cell operation. Analytical measurements are also crucial in formulating strategies for the recovery of Li from spent cathodes. The recovery and recycling of Li is an active area of research due to the limited availability of the element and the environmental concerns arising from the LIB waste [7].

A number of analytical techniques and methodologies for the determination of Li in different types of matrices are reported in literature [8]. A succinct yet comprehensive account of these techniques and methods is presented in a recent review article [1]. Unfortunately, it does not include (probably due to space constraints) ion beam analysis (IBA) whose credentials for the determination of Li have long been

✉ Yerroju Sunitha
sunitha@barc.gov.in

¹ National Centre for Compositional Characterization of Materials, BARC, ECIL Post, Hyderabad 500062, India

established. A review article published on this topic about three decades back that remains relevant even today, is a vivid testimony of its capabilities [9]. Amongst several merits, the solid-state analysis capability of the method needs specific mention because the dissolution of ores, minerals or refractory materials (e.g. LTO) for their analysis by the wet-chemical methods is often tedious and time-consuming.

Among the IBA methods, particle induced γ -ray emission (PIGE) involving $^7\text{Li}(\text{p},\text{p}'\gamma)^7\text{Li}$ ($E_\gamma=478$ keV) scattering and nuclear reaction analysis (NRA) involving $^7\text{Li}(\text{p},\alpha)^4\text{He}$ reaction ($Q=17.3$ MeV) are eminently suitable for the determination of lithium from percentage down to trace levels [10–12]. However, its determination by PIGE in the minerals of Li and other materials composed of light elements such as B, F, Na, Al and Si, suffers from certain practical limitations. These may arise from two different accounts. Firstly, similar to Li, these elements are prolific prompt γ -ray emitters and, therefore, can cause elevated background around 478 keV γ -ray energy region. Also, the high-count rate can increase the dead time and cause pulse pile up during counting. To maintain these undesirable events within acceptable limits, the energy and current of the proton beam must be appropriately adjusted. Secondly, spectral interference can be a source of erroneous results. For example, the prevalence of B raises the possibility of the overestimation of Li because of the spectral interference due to the simultaneous occurrence of $^{10}\text{B}(\text{p},\alpha\gamma)^7\text{Be}$ (EC) ^7Li ($E_\gamma=478$ keV) reaction.

In the present study $^7\text{Li}(\text{p},\alpha)^4\text{He}$ reaction ($E_p=0.6$ MeV) was used for the determination of lithium at percentage levels in materials that are important from the point of view of lithium prospecting (e.g., spodumene) and LIB (e.g. lithium carbonate, lithium titanate and lithium cobalt oxide) technology. The reaction was selected for lithium determination in view of the following reasons: (a) high Q value of the reaction that enables interference free and, also, background free detection of the α -ejectiles and (b) favorable cross-section even at a low proton energy (e.g., 0.5 mb/sr at $E_p=0.6$ MeV) at 150° emission angle. Also, the method does not suffer from any pulse pile up problem and samples can be bombarded with fairly large beam currents for rapid analysis. We

have shown that the reaction produces a calibration curve of good linearity and provides facile Li determination, irrespective of the nature of the matrix, with robust statistical attributes. Additionally, the paper examines the influence of the stopping cross-section of the samples, a factor often overlooked, on the accuracy of lithium determination.

Methodological considerations

A Li bearing chemical compound or mineral of interest in the present study contains, in addition to Li, several other elements such as C, B, O, F, Al and or Si as major/ minor constituents. The isotopes of these elements undergo (p, α) reaction simultaneously with $^7\text{Li}(\text{p},\alpha)^4\text{He}$ reaction and can interfere in its determination due to kinematic reasons. Table 1 shows these reactions along with their respective Q values, cross-sections and the energies of α -ejectiles at 150° emission angle [13].

Some important observations drawn from the Table 1 on the features of the reactions and their influence on the determination of lithium can be summarized as follows. Firstly, the reactions involving the both isotopes of lithium i.e. ^6Li and ^7Li and, ^{11}B follow inverse kinematics. Secondly, the determination of lithium through ^6Li which has 7.5% natural isotopic abundance is difficult in spite of the larger cross section of the $^6\text{Li}(\text{p},^3\text{He})^4\text{He}$ reaction. The limitation arises due to the extensive spectral interference by the reactions listed in Table 1. On the other hand, the $^7\text{Li}(\text{p},\alpha)^4\text{He}$ reaction has a large Q value. As a result, the α -ejectiles are entitled with high energy and do not suffer from any interference. Thus, $^7\text{Li}(\text{p},\alpha)^4\text{He}$ reaction can be used for the reliable estimation of lithium in materials.

So far as the choice of proton incident energy is concerned, it depends primarily on (a) the cross-section of the reaction, (b) analyte (Li) concentration and (c) interferences from other (p, α) reactions. Since the objective is to determine Li at percentage or sub-percentage levels any energy in 0.5–0.8 MeV range is suitable for the measurements. Also, to ensure better energy separation between the α -ejectiles

Table 1 List of some of (p, α) nuclear reactions along with their Q values and cross-sections at $E_p=0.6$ MeV at 150° scattering angle. In addition, the energies of α -ejectile emitted at 150° angle at $E_p=0.01$ and 0.6 MeV are also listed

Nuclear reaction	Q -value (MeV)	α -ejectile energy (MeV)		Energy (keV) lost by α -ejectiles in 10 μm mylar ($E_p=0.6$ MeV)	Cross-section (mb/sr) ($E_p=0.6$ MeV)
		$E_p=0.01$ MeV	$E_p=0.6$ MeV		
$^6\text{Li}(\text{p},^3\text{He})^4\text{He}$	4.02	2.23	2.07	205	2.89
$^7\text{Li}(\text{p},\alpha)^4\text{He}$	17.34	8.55	7.95	72	0.5
$^{11}\text{B}(\text{p},\alpha)^8\text{Be}$	8.58	5.66	5.55	96	52
$^{15}\text{N}(\text{p},\alpha)^{12}\text{C}$	4.97	3.69	3.81	129	11.4
$^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$	3.98	3.12	3.32	143	10
$^{19}\text{F}(\text{p},\alpha)^{16}\text{O}$	8.11	6.45	6.59	84	0.6





Medical Oncology (2025) 42:501
<https://doi.org/10.1007/s12032-025-03058-9>

ORIGINAL PAPER



Hypoxia-drives reversible cell cycle arrest in lung cancer cells via modulation of cellular redox and gene expression

Dharmendra Kumar Maurya^{1,2} · Varshita Mehta^{1,3} · Babita Singh¹

Received: 8 June 2025 / Accepted: 17 September 2025 / Published online: 29 September 2025
 © The Author(s) 2025

Abstract

Hypoxia is a well-recognized clinical feature of solid tumors, including lung cancer, and is associated with poor prognosis due to its role in promoting resistance to chemotherapy and radiotherapy. To investigate the cellular consequences of hypoxia, we cultured A549 lung adenocarcinoma cells under 1% O₂ and examined their growth, cell cycle distribution, and redox status. Hypoxia significantly reduces cell proliferation and induced G1 phase cell cycle arrest, suggesting a cytostatic effect. Biochemical analysis showed a 2.64- and 2.04-fold increase in total and mitochondrial reactive oxygen species (ROS) levels, respectively, along with an elevated total thiol levels under hypoxic conditions compared to normoxia. To assess the reversibility of the hypoxic response, we performed a reciprocal oxygen exposure experiment where cells initially grown under hypoxia were re-exposed to normoxia, and vice versa. To explore the underlying molecular mechanism, we analyzed transcriptomic datasets (GEO accession: GSE48134 and GSE42416) which revealed that hypoxia downregulated key genes involved in energy metabolism (e.g., PDK4, G6PD), cell cycle progression (e.g., CCND1, CDK2), and redox regulation (e.g., GCLM, TXNRD1, NQO1, GCLC). Further, few of redox-related genes were validated by RT-PCR in A549 cells cultured under hypoxia and normoxia for 24 h. Importantly, cyclic hypoxia (intermittent hypoxia-reoxygenation) conditions showed partial restoration of some of these transcripts, supporting the transient nature of hypoxic stress, consistent with our in vitro observations. Furthermore, transcriptome profiles from adenocarcinoma patients (GEO accession: GSE30979) also match our cell line observations. Thus, our results clearly show that hypoxia causes a temporary cell cycle arrest in lung cancer cells, which is reversible when oxygen is restored.

Keywords Adenocarcinoma · Hypoxia · Cycling hypoxia · Cellular redox · Transcriptome profile

Introduction

Oxygen is an indispensable molecule for aerobic life to drive cellular bioenergetics and homeostasis [17]. A pathological condition in which the body or a part of the body is underprivileged for enough supply of oxygen is defined as hypoxia [10]. It is a state of oxygen deprivation that is commonly encountered by cancer cells during the development and progression of tumors [10]. Hypoxia can have

numerous consequences in organisms, one such happening is the relapse of cancer due to resistance against chemotherapy and radiotherapy [4]. Tumors often outgrow their blood supply, leading to decreased oxygen levels and the development of hypoxic regions within the tumor. Pathological hypoxia disrupts the normal homeostasis and is mostly observed in tumors, at the site of inflammation, and also in ischaemic diseases [2, 3]. This hypoxic microenvironment plays a critical role in the survival, growth, and progression of cancer cells [15]. Studies have shown that cancer cells in hypoxic regions are more resistant to chemotherapy and radiation therapy, making it important to understand the response of cancer cells to hypoxia [4]. Hypoxia can trigger a range of cellular responses, including increased angiogenesis, increased cell survival, and changes in cell metabolism and gene expression. These changes are mediated by hypoxia-inducible factor (HIF), a transcription factor that is activated in response to hypoxia [12, 18]. HIF regulates a

✉ Dharmendra Kumar Maurya
 dkmaurya@barc.gov.in; dkmauryabarc@gmail.com

¹ Radiation Biology & Health Sciences Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

² Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

³ KJ Somaiya College of Science & Commerce, Vidyavihar, Mumbai 400081, India

number of genes that are involved in cell survival, angiogenesis, and metabolism, leading to changes in the behavior of cancer cells in hypoxic regions [6]. In lung cancers i.e., with respect to both SCLC and NSCLC, a high level of HIF-1 α and HIF-2 α is observed, both of which are linked with poor prognosis [11].

The purpose of this study is to investigate the response of A549 lung cancer cells to hypoxia and to understand the cellular and molecular mechanisms that drive these responses. We evaluated the effects of hypoxia on the growth, cell cycle, redox status, and antioxidant enzyme activity of the A549 cells. Since oxygen consumption, energy demand, and redox status are closely related, we also analyzed identify the differentially expressed genes related to hypoxia response. We conducted transcriptomic analysis on A549 cells grown under normoxia-hypoxia cycles and on samples from hypoxic lung adenocarcinoma patients. Transient hypoxia response refers to the cellular response of cells to a temporary decrease in the availability of oxygen. Under conditions of hypoxia, cells undergo a series of physiological changes that allow them to adapt and survive. This response is controlled by a complex network of signaling pathways and transcription factors, including the hypoxia-inducible factor (HIF) pathway, which plays a central role in mediating the cellular response to hypoxia. Understanding the mechanisms underlying the transient hypoxia response in A549 cells can provide insights into the biology of lung cancer and may help to develop new strategies for the treatment of this disease.

The study of the response of A549 lung cancer cells to hypoxia is crucial for improving our understanding of the complex interactions between cancer cells and the microenvironment and for developing more effective strategies for the treatment of lung cancer. The results of this study will contribute to our understanding of the cellular and molecular mechanisms underlying the response of cancer cells to hypoxia and may provide insights into the development of more effective therapies for the treatment of lung cancer. Our results showed that alterations in hypoxia-induced redox parameters and cell cycle patterns are temporary and can be restored by returning to normoxic conditions. Additionally, the findings of this study may provide clue for the development of new strategies for reducing the resistance of cancer cells to chemotherapy and radiation therapy, as well as for enhancing the efficacy of these treatments.

Materials and methods

Chemicals

Consumable for cell culture such as Dulbecco's modified Eagle's medium (DMEM), trypsin, antibiotics, and

fetal bovine serum (FBS) were obtained from Hi-Media (Hi-Media Pvt., Mumbai, India). Hoechst 33342, and carboxyfluorescein diacetate succinimidyl ester (CFSE) was procured from Molecular Probes (NY, USA). Carboxy-dichlorofluorescein diacetate (DCF-DA) and propidium iodide (PI) were purchased from Sigma Chemical Co. (MO, USA). All other chemicals used were of analytical grade and procured from local reputed manufacturers.

Cell culture and treatment with hypoxia

The A549 lung cancer cell line was maintained in DMEM supplemented with 10% FBS and 1% penicillin–streptomycin at 37 °C in a humidified incubator with 5% CO₂. The cells were seeded into 6-well plates at a density of 2.5×10^5 cells per well and were allowed to adhere overnight. The cells were then subjected to hypoxia by incubating them in a hypoxic chamber at 1% O₂ for 24 to 72 h. The control cells were incubated under normoxic conditions (21% O₂) in a standard incubator.

Measurement of cell viability and proliferation

To determine the effect of hypoxia on cell viability, the cells were subjected to a cell viability assay using the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay. This assay measures the activity of mitochondrial dehydrogenases, which are an indicator of cellular viability. For MTT assay, 5×10^3 A549 cells were cultured in a 96-well plate and incubated either under normoxia or hypoxia for 72 h. Four hours before completion of incubation, 10 μ l of MTT (10 mg/ml) was added in each well to monitor cell proliferation by measuring the absorbance [9]. The absorbance of the formazan product produced by the MTT assay was measured at 570 nm using a microplate reader. For counting the nuclei, 2.5×10^3 A549 cells were cultured in a 96-well plate and incubated either under normoxia or hypoxia for 72 h. After completion of the incubation period, cell nuclei were stained with Hoechst 33342 dye, and nuclei were analyzed using a high throughput cell analyzer (TTP Labtech Ltd). Cell proliferation was determined using CFSE dye dilution assay, which measures the decrease in the CFSE fluorescence of proliferating cells. For studying the cell proliferation, cells were stained with CFSE dye and cultured under normoxia and hypoxia for 72 h. After completion of the incubation period, cells were harvested and analyzed using a flow cytometer and the data were analyzed using FlowJo software. Cells that underwent more division will have lower mean fluorescence intensity compared to less divided cells.





Molecular Biology Reports (2025) 52:883
<https://doi.org/10.1007/s11033-025-10996-0>

ORIGINAL ARTICLE



Identification of known and novel genetic variants in sensorineural hearing loss: insights from whole exome sequencing in Indian families

Kurva Jagannath^{1,4} · Nalini Bhat² · Anu Ghosh^{3,4} · Harshada Tawade² · Susan Cherian¹ · Suresh Shettigar¹

Received: 19 June 2025 / Accepted: 28 August 2025 / Published online: 10 September 2025
 © The Author(s) 2025

Abstract

Background Hearing loss (HL) is one of the most common congenital anomalies and is a complex etiologically diverse condition. Molecular genetic characterization of HL remains challenging owing to the high genetic heterogeneity. This study aimed to screen for potential disease-causing genetic variations in a cohort of Indian patients with congenital bilateral severe-to-profound sensorineural HL.

Methods and results The study cohort consisted of 105 individuals, including 31 patients from 25 families with congenital HL classified as severe to profound bilateral. The patients were identified based on clinical evaluation and family history. Whole exome sequencing (WES) was performed to detect the genetic variations within these families. Variant co-segregation was examined using Sanger sequencing, and amino acid conservation was assessed using Clustal Omega. The 3D protein structure prediction was performed for the novel missense variants. WES and subsequent data analysis identified five novel variants and five previously reported pathogenic variants. The novel variants included a homozygous 23 bp frameshift deletion (*CDH23* c.6571_6593del), compound heterozygous stop-gain variant (*SLC26A4* c.1416G>A), and three homozygous missense variants (*CDH23* c.811 A>T, *COL4A6* c.227G>A, and *CLIC5* c.401 A>G). Co-segregation was confirmed within families. Frameshift deletion and stop-gain variants were classified as pathogenic, while missense variants were categorized as variant of uncertain significance. Pathogenicity prediction tools and amino acid conservation analyses further supported the pathogenic potential of the novel variants.

Conclusions The identification of novel and previously reported variants in familial cases underscores the importance of WES in genetic analysis of HL. These findings enhance our understanding of the genetic landscape of HL and could have implications for the diagnosis and genetic counselling of affected families.

Keywords Sensorineural hearing loss · Whole exome sequencing · Indian families · Novel variants · *CDH23* · *SLC26A4* · *COL4A6* · *CLIC5*

✉ Anu Ghosh
 anugh@barc.gov.in

Suresh Shettigar
 sureshs@barc.gov.in

¹ Cytogenetics and Molecular Genetics Lab, Pathology Unit, Medical Division (BARC Hospital), Bhabha Atomic Research Centre, Anushakti Nagar, Mumbai, India

² ENT Unit, Medical Division (BARC Hospital), Bhabha Atomic Research Centre, Anushakti Nagar, Mumbai 400094, India

³ Animal House Facility & Radiation Signaling Section, Radiation Biology & Health Sciences Division, Bio-Science Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

⁴ Homi Bhabha National Institute (HBNI), Anushakti Nagar, Mumbai 400094, India

Introduction

Hearing loss (HL) is a partial or total loss of the ability to hear sounds either bilaterally or unilaterally. Globally, HL is one of the most common congenital anomalies among newborns, with a prevalence of 2.21 per 1000, range 1–6 [1]. In India, the prevalence of HL in infants ranges from 1.6 to 8.8 per 1000 births [2]. HL in infants results in serious disabilities of speech development, thus impairing their quality of life. Early diagnosis and intervention can improve the well-being of children and allow for genetic counseling and future family planning.

HL is genetically heterogeneous. Genetic causes account for up to 80% of all congenital HL cases in developed nations [3]. Non-syndromic hearing loss (NSHL) accounts

for almost 70% of all genetic HL cases, 80% of which are inherited in an autosomal recessive manner [4]. To date, more than 180 genes have been reported in various HL databases (<https://deafnessvariationdatabase.org> and <http://hereditaryhearingloss.org/>) [5]. Most (~125) of these genes have been implicated in NSHL, whereas only a few (~36) have been linked to syndromic hearing loss (SHL). Additionally, nine genes were found to be associated with both NSHL and SHL.

Traditionally, linkage analysis, combined with Sanger sequencing, has been used for genetic identification. Sanger sequencing remains the gold standard for diagnosing single-gene disorders and is commonly used to confirm variants identified using next-generation sequencing (NGS) technologies. Recently, large gene panels (100–225 genes) and targeted NGS, which allow simultaneous identification of multiple gene variations, have been increasingly used for improved and effective detection and early clinical intervention in patients with HL. These methods allow for a high diagnostic yield and can thus, help in establishing customized population-specific screening kits for disorders with genetic heterogeneity, such as HL. Although targeted HL gene panel studies show promise, there is a possibility that we may overlook novel variations and their associated genes, which are not included in the panel. In this context, whole exome sequencing (WES) and whole genome sequencing (WGS) based analyses have proven valuable for identifying novel genes and variants, as well as for providing an in-depth understanding of the molecular etiology of HL [6]. Currently, WES is used to identify both known common and novel genes along with their variants that are associated with HL [7].

The present study aimed to identify potential disease-causing genetic variants associated with congenital bilateral severe-to-profound sensorineural hearing loss (CSNHL) in an Indian cohort through a comprehensive analysis of genetic variations. WES was performed on 105 individuals from 25 families, including 31 patients with CSNHL. Seventeen of these patients were pediatric (aged ≤18 years). Nine of the 25 families were consanguineous. Pedigrees were obtained from the families studied. Co-segregation of variants in the families was confirmed by Sanger sequencing. The results of this study not only substantiate our understanding of the molecular etiology of HL within the studied families but also offer efficient counseling for affected members.

Materials and methods

Patients and clinical evaluation

All HL patients were identified at the departmental hospital. Audiometric assessment, clinical evaluation, and patient history confirmed that the patients in this study were diagnosed with CSNHL (Supplementary Table 1). A total of 105 individuals from 25 families were enrolled, including 31 patients with CSNHL. Of the 31 patients (aged 1–49 years), 17 were children (aged ≤18 years) and 14 were adults, among whom were 6 parents. Pedigrees were drawn from 25 families using CeGaT Pedigree Chart Designer software (<https://cegat.com/>). This study was approved by the Institutional Ethics Committee (Project No: BHMEC/NP/10/2018). Written informed consent was obtained from all study participants, their parents, or legal guardians at the time of enrollment.

Whole exome sequencing and data analysis

Genomic DNA was extracted from 2 ml of blood using the QIAamp DNA Blood Midi Kit (Qiagen, Hilden, Germany). DNA quality was assessed using agarose gel electrophoresis, a Nanodrop 1000 spectrophotometer and QIAxpert and, quantified using a Qubit DNA BR Assay (Invitrogen). A whole exome library was prepared using the SureSelect XT Reagent Kit (Agilent, Cat# G9641B). A SureSelect XT Human All Exon V5+UTRs Kit (Agilent, Cat# 5190–6215) was used to capture all exon clusters, which were amplified on an Illumina flow cell and run on a HiSeq X platform (Illumina) to generate 2 × 150 paired-end reads with an average of 100X coverage. WES data analysis pipelines for calling short variants were implemented using the GRCh38 human reference genome according to GATK Best Practices. FastQC, Fastp, BWA-MEM, GATK, Picard, VEP, Microsoft Excel, Geneyx, and InterVar were used to analyze the WES data [8–14]. A detailed description of the data analysis methodology is provided in the WES data analysis process section in the Supplementary Information. Finally, high-confidence variants were classified as pathogenic, likely pathogenic, variants of uncertain significance (VUS), likely benign, or benign using InterVar based on the ACMG and AMP 2015 guidelines [15]. The variants analyzed using an in-house data analysis pipeline were confirmed using Geneyx software.

Co-segregation analysis of novel and previously identified pathogenic variants

Co-segregation of the variants identified in this study was confirmed in the families using Sanger sequencing. Sanger





Emergent Materials (2025) 8:7627–7635
<https://doi.org/10.1007/s42247-025-01189-3>

ORIGINAL ARTICLE



Improving power factor of multiwalled carbon nanotube films through dual doping and sequential energy filtering of charge carriers

Suman K. Mishra^{1,2} · Meetu Bharti³ · Bhanu Partap Singh⁴ · S. Bhattacharya^{2,5} · S. Samanta⁵ · P. Jha^{2,5} · V. S. Rawat^{2,3} · Ajay Singh^{2,5}

Received: 16 April 2025 / Accepted: 7 July 2025 / Published online: 22 August 2025
 © The Author(s) 2025

Abstract

Free-standing multiwalled carbon nanotubes (MWCNTs) sheet exhibits low thermoelectric power factor due to poor inter-junctions' connectivity. The present work demonstrates a simultaneous improvement of two anti-correlated thermoelectric parameters-Seebeck coefficient and electrical conductivity of free-standing MWCNTs sheet through dual doping with PEDOT: PSS and SnTe. The sequential energy dependent scattering of charge carriers at MWCNT/PEDOT-SnTe interfaces leads to a significant improvement of Seebeck coefficient. The enhanced carrier concentration along with the facile transport of the high energy charge carriers through PEDOT-SnTe composites due to improved connectivity between MWCNTs renders improvement of electrical conductivity. Such a synergetic combination of improved Seebeck coefficient and electrical conductivity resulted in a 7-fold enhancement in power factor of MWCNT/PEDOT: PSS-SnTe composite films.

Highlights

- Simultaneous improvement of Seebeck coefficient and electrical conductivity is observed in ternary composite MWCNT sheet.
- Sequential energy filtering of charge carriers at MWCNT/PEDOT-SnTe interfaces is responsible for improvement of Seebeck coefficient.
- SnTe crystallites in the PEDOT matrix acts like charge reservoirs that help in improving the MWCNTs inter-junction connectivity.

1 Introduction

Flexible energy harvesting materials are highly desirable to design smart wearable and miniature electronic devices in the modern era of urbanization and industrialization [1]. Thermoelectric materials that convert ambient heat into useful power can be promising energy harvesting materials in remote as well as inaccessible/indoor locations [2]. World-wide research, therefore, has been focused to the fabrication of new generation 'Wearable/flexible thermoelectric devices', which would not only be low cost, room temperature operable but also be able to harness heat of curved hot surfaces [3–7]. For meeting the requirement of such wearable applications, emerging flexible thermoelectric materials like carbon-based materials (single-walled/multi-walled carbon nanotubes sheets, graphene, conducting polymers) and screen-printed paste-type inorganic materials are considered as a better choice [8, 9]. Such carbon nanotube-based materials offer

✉ Meetu Bharti
meetubharti@yahoo.com

✉ Ajay Singh
ajay@barc.gov.in

¹ Advanced Tunable Laser Applications Division, Trombay, Mumbai 400085, India

² Homi Bhabha National Institute, Anushaktinagar, Mumbai, India

³ All India Jat Heroes' Memorial College, Rohtak 124001, Haryana, India

⁴ National Physical Laboratory, New Delhi 110012, India

⁵ Technical Physics Division, Bhabha Atomic Research Centre, 400085 Trombay, Mumbai, India



many advantages such as environment-friendliness, low thermal conductivity, and flexibility over their inorganic counterparts [10, 11]. However, the Seebeck coefficient as well as electrical conductivity of carbon nanotube-based materials is remarkably lower than that of inorganic counterparts [9]. Therefore, there is strong need to improve their Seebeck coefficient as well as electrical conductivity to improve their overall thermoelectric power generation efficiency. Due to trade-off relationship between Seebeck coefficient and electrical conductivity, improving these two parameters simultaneously becomes very challenging [12]. One of the possible solutions is the doping of the desired material to enhance the carrier concentration and to create energy filtering interfaces that can remarkably increase the Seebeck coefficient while maintaining the high electrical conductivity [13]. However, to have a simultaneous balance of high Seebeck coefficient and high electrical conductivity the following points needs to be considered for designing an energy filtering interface: (1) intimate contacts between matrix and secondary phase to establish a defect free interface that maintains high charge carrier mobility; (2) the interfacial barrier height at the interface should be of low to selectively scatter low-energy charge carriers; (3) high surface area of secondary phase so that an elongated potential barrier can be formed compared to at a low concentration of secondary phase. Based upon these criteria, many organic–inorganic nanocomposites have been demonstrated with higher power factors [14, 15]. For example, in Bi_2Te_3 –P3HT composite three times enhancement of power factor was achieved than pure P3HT [16]. Similar three times enhancement of power factor was obtained for Te-SWCNT composites [17, 18].

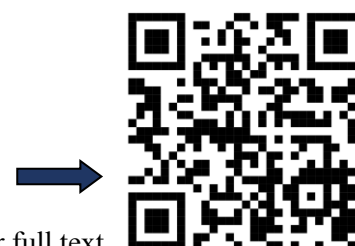
Such an energy-filtering based improvement of thermoelectric properties reported in various composite systems [11, 19–24] inspired us to reinforce the energy-filtering effect (constructing the interfaces containing the hierarchical potential barriers) in multiwall carbon nanotubes (MWCNTs) matrix. Very efficient results in power factor enhancements were also achieved for PEDOT: PSS and SWCNT composites by the researchers [22, 25]. In the present work PEDOT: PSS pre-mixed with DMSO along with SnTe powder synthesized in the lab was used to treat MWCNTs paper matrix. DMSO mixed PEDOT: PSS was considered due to better improved thermoelectric properties of the polymer as already reported [26–28]. DMSO being polar solvent not only removed the insulating hydrophilic PSS but also resulted in structural ordering of PEDOT and PSS chains, thus, allowing facile motion of charge carriers which enhances mobility of carrier. Co-treatment of MWCNTs paper with blended solution of inorganic SnTe and organic PEDOT: PSS-DMSO resulted in hybrid-composites of MWCNTs. The power factors values of ~ 0.2 , ~ 0.4 and $\sim 1.4 \mu\text{W}/\text{m}/\text{K}^2$ were observed respectively for

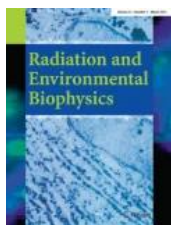
pure MWCNTs, MWCNT/PEDOT: PSS and MWCNT/PEDOT-PSS/SnTe nanocomposite sheet. The novelty of present work is the 7 times enhancement in the power factor of MWCNT films after its modification by PEDOT: PSS-SnTe composites. Detailed characterization revealed the improvement in the connectivity of MWCNT junctions along with the energy dependent scattering of charge carriers at MWCNT/PEDOT-SnTe interfaces is responsible for the improved power factor in MWCNT/PEDOT: PSS-SnTe composite films. In short, facile methodology of creating organic-inorganic interface to tune thermoelectric properties along with scalability of MWCNTs can certainly be useful for fabrication of new generation smart and wearable inexpensive thermoelectric power generators.

1.1 Experimental details

Chemical vapour deposition (CVD) technique was used to synthesize multiwalled carbon nanotubes (MWCNTs). Thermal decomposition of toluene in presence of iron catalyst that was obtained by the decomposition of organo-metallic ferrocene in a two-zone electric furnace inside the quartz reactor resulted in MWCNTs. To reduce the van der Waal forces among the MWCNTs, bundles of MWCNTs were dispersed in the aqueous solution of alkali-soluble emulsifier (ASE 60, from Premier pigments and chemicals). The dispersion was homogenized at 40,000 rpm for 15 min by laboratory homogenizer and thereafter, homogenized dispersion of MWCNTs was subjected to ultra-sonication for 2 h to separate the MWCNTs bundles. The separated and dispersed MWCNTs were filtered on a nylon mesh in a vacuum filtration unit and a fine network of MWCNTs was obtained in the form of paper of size $35 \text{ cm} \times 35 \text{ cm}$ and thickness $\sim 0.15 \text{ mm}$. The paper was allowed to dry overnight at room temperature and finally, peeled off from the nylon mesh after drying. The strips of desired dimensions were cut from the as-grown MWCNT paper for estimation of thermoelectric properties.

The p-type SnTe was prepared using vacuum melting at 900°C with base pressure of $\sim 10^6 \text{ mbar}$ and was used to prepare composite films of carbon i.e. MWCNTs paper. For this, carbon nanotube paper was cut in specific sizes ($\sim 30 \text{ mm} \times 30 \text{ mm}$) and pasted on clean glass slides to provide a flat surface to achieve the uniform thickness of hybrid films. Polymer poly(3,4-ethylenedioxythiophene): poly(styrenesulphonate) purchased from Ossila (M122 PH1000) and stored in the refrigerator was used as received for treatment of MWCNTs paper. All the samples have been prepared by varying concentration of SnTe in 5% DMSO-mixed PEDOT: PSS solution. SnTe (of different weight%) was added in DMSO mixed PEDOT: PSS and each solution was ultra sonicated for ten minutes before pouring on





Radiation and Environmental Biophysics (2025) 64:711–718
<https://doi.org/10.1007/s00411-025-01154-y>

RESEARCH



Influence of phantom material on the depth-dose profile and radiation quality factor of 126 MeV antiprotons – a FLUKA Monte Carlo study

Arghya Chattaraj¹ · T. Palani Selvam^{1,2}

Received: 23 May 2025 / Accepted: 27 September 2025 / Published online: 10 October 2025
 © The Author(s) 2025

Abstract

Antiprotons hold significant potential for radiotherapy due to their unique annihilation mechanism, which could offer dosimetric advantages. The objective of the present study was to assess how different phantom compositions affect the position of the Bragg peak and the biological effectiveness of antiproton beams in terms of the quality factor. This study investigated on-axis depth-dose profiles and the LET-based quality factor (Q_{LET}) for a 126 MeV antiproton beam in various phantom materials such as Water, Polystyrene, PMMA, RW1, WE210, Solid Water, and A150 using the FLUKA Monte Carlo code. The study also investigated the influence of elemental compositions of phantom materials on the relative contribution of antiprotons and secondary radiations to the total on-axis depth-dose profile. Additionally, the study discusses the variation in the in-flight annihilation cross-section across different phantom materials. The results show that depending on the phantom material, the position of the Bragg peak ranges from 11.49 to 11.82 g/cm². Furthermore, depending on the phantom material, Q_{LET} ranged from about 1.78 to 1.91 in the entrance region, from about 2.0 to 2.8 in the dose fall-off region, and from about 6.28 to 7.0 near the Bragg peak position. It is concluded that the study provides the theoretical basis of the understanding of depth dose profiles of antiprotons in various solid phantoms.

Keywords Antiprotons · Monte Carlo · Annihilation · Solid phantoms · Depth-dose profile · Quality factor

Introduction

Antiprotons are of considerable interest for radiotherapy due to their unique annihilation mechanism. The potential of antiprotons for radiotherapy was first proposed by Gray and Kalogeropoulos in 1984 (Gray and Kalogeropoulos 1984). Later, several studies were carried out to investigate the therapeutic advantages of antiproton beams for radiotherapy (Bassler et al., 2008a; Bassler et al. 2008b, c, 2010; Bassler and Holzscheiter 2009; Fahimian et al. 2009; Holzscheiter et al., 2004; Holzscheiter et al. 2016; Holzscheiter et al. 2006; Knudsen et al., 2008; Chattaraj and Selvam 2022). Most of these studies involved water phantoms.

However, the use of solid phantoms will be advantageous for routine dosimetry. The interaction cross-section of antiproton-nucleon annihilation producing a mixed-radiation field depends on the elemental composition of the phantom material (Gray and Kalogeropoulos 1984). Thus, the depth-dose profile of antiprotons in different phantom materials may be different. Note that no study has been conducted so far to investigate how the elemental composition of various phantom materials affects antiproton annihilation and, consequently, the resulting dose deposition pattern. In radiation dosimetry, precise placement of the dosimeter is essential to minimize the positional uncertainty. Given the rapid dose fall-off on either side of the antiproton Bragg-peak, accurately determining its position in the phantom material is crucial for precise dosimetry. Therefore, understanding the depth-dose profile of antiproton beams in different phantom is important.

The present study was aimed at investigating the influence of different phantom materials on the on-axis depth-dose profile of antiproton beams. Toward this goal, the depth-dose profile of 126 MeV antiproton beams in phantoms such as Water, ICRU-4 element, Polystyrene, PMMA,

✉ Arghya Chattaraj
 arghyac@barc.gov.in

¹ Radiological Physics and Advisory Division, Health, Safety and Environment Group, Bhabha Atomic Research Centre, Mumbai 400 085, India

² Homi Bhabha National Institute, Anushaktinagar, Mumbai 400 094, India

RW1, WE210, Solid water and A150 was calculated using the Monte Carlo-based FLUKA code. The study also investigated the influence of elemental compositions of phantom materials on the relative contribution of antiprotons and secondary radiations to the total on-axis depth-dose profile. Furthermore, the study included the calculation of the LET-based radiation quality factor (Q_{LET}) using the ICRP 60 formalism (ICRP, 1991) for investigating the influence of phantom materials on the biological effectiveness of the antiproton beams. Finally, in the study the variation in the in-flight annihilation cross-section across different phantom materials was investigated, providing insights into the antiproton dose deposition pattern.

Materials and methods

Simulation setup

The present study used the FLUKA code (version 2011–3.0) (Böhlen et al., 2014; Battistoni et al., 2015) for calculating depth-dose profiles and Q_{LET} values as a function of on-axis depth in different phantom materials. In the FLUKA simulations, a 126 MeV monoenergetic (momentum: 502 MeV/c) antiproton beam was incident on a $30 \times 30 \times 30 \text{ cm}^3$ phantom. The momentum spread ($\Delta p/p$) and divergence of the beam were 5×10^{-4} and 5 mrad, respectively. The chosen beam parameters such as momentum spread and beam divergence used in the present study were motivated by the antiproton beam at CERN (Bassler et al. 2008c). The field size of the beam on the surface of the phantom was $5 \times 5 \text{ cm}^2$. The elemental composition, mass fraction, physical density and effective Z/A of the phantom materials used in the present study are presented in Table 1.

Calculation of depth dose profile and quality factor

Depth along the central axis was divided into cylindrical voxels of dimensions 0.5 cm radius and 1 mm thickness. Absorbed dose (D) and Q_{LET} -weighted absorbed dose ($D \times Q_{LET}$) were scored in each voxel using the USRBIN Dose and DoseQLET scorers, respectively. The DoseQLET scorer considers an unrestricted LET (Linear Energy Transfer)-based Q value calculated based on the ICRP60 formalism (ICRP, 1991). The ratio of $D \times Q_{LET}$ to D gave Q_{LET} . The unrestricted LET includes all the primary and secondary particles as well as delta electrons produced through the interaction of antiprotons with matter. LET is an important dosimetric parameter for determining both the clinical RBE (Relative Biological Effectiveness) and Q (Wedenberg et al., 2013; Carabe et al., 2012; Chattaraj and Selvam 2024; ICRP, 2007; Arghya Chattaraj, 2025). LET depends on the target material as well as on the kinetic energy of the projectile charged particle. As the on-axis depth in a phantom increases, the kinetic energy of the charged particle decreases and hence LET increases. ICRP Publication 60 describes Q as a function of LET as shown below:

$$Q = 1 \quad \text{for } LET < 10 \text{ keV}/\mu\text{m}$$

$$Q = 0.3 \times LET - 2.2 \quad \text{for } LET = 10 - 100 \text{ keV}/\mu\text{m} \quad (1)$$

$$Q = 300/\sqrt{LET} \quad \text{for } LET > 100 \text{ keV}/\mu\text{m}$$

Any study of the biological effectiveness of a therapeutic beam relies on the RBE of deterministic effects (e.g. cell death) at high doses and dose rates. However, in the present study the ICRP 60-based Q_{LET} was calculated, which is generally associated with the low-dose RBE of stochastic effects such as carcinogenesis. Thus, the calculation of Q_{LET}

Table 1 Elemental compositions and their mass fraction, electron density ($\langle Z/A \rangle$) and mass density (ρ) of the investigated phantoms (Mishra and Selvam 2020; Schoenfeld et al., 2017; Dietze et al., 2013; Berger 1993). PMMA - Polymethylmethacrylate; Z – atomic number; A – mass number; ICRU – International commission on radiation units and measurements

Element	Z	A	Water ^a	Polystyrene ^a	PMMA ^a	WE210 ^a	Solid water ^a	A150 ^b	ICRU-4-elements ^b
H	1	1.008	0.112	0.07742	0.08054	0.0821	0.081	0.1013	0.101
C	6	12.01		0.92258	0.59985	0.6633	0.672	0.7755	0.111
N	7	14.01				0.0221	0.024	0.0351	0.026
O	8	15.99	0.888		0.31961	0.2065	0.199	0.0523	0.762
F	9	18.99						0.0140	
Mg	12	24.31					0.001		
Cl	17	35.46				0.004			
Ca	20	40.08				0.022	0.023	0.1840	
$\rho \text{ (g/cm}^3\text{)}$			1	1.06	1.19	1.006	1.036	1.127	1
$\langle Z/A \rangle$			0.555	0.538	0.539	0.540	0.540	0.547	0.551

^aMishra and Selvam 2020; Schoenfeld et al., 2017; Dietze et al., 2013

^bBerger 1993





MRS Communications (2025) 15:1445–1452
 © The Author(s), 2025
<https://doi.org/10.1557/s43579-025-00814-w>



Research Letter



Influence of ultrasonic vibration at different tensile deformation stages on the ductile fracture morphology of aluminum alloy

Arpan Das[✉], Scientific Information Resource Division (Knowledge Management Group), Bhabha Atomic Research Centre (Department of Atomic Energy), Mumbai 400 085, India; Homi Bhabha National Institute, Anushakti Nagar, Mumbai 400 094, India

Address all correspondence to Arpan Das at dasarpan1@yahoo.co.in; arpand@barc.gov.in

(Received 8 June 2025; accepted 22 August 2025; published online: 15 September 2025)

Abstract

Ultrasonic vibration (*UV*) in ductile materials during its deformation, generates/activates defects which influences void 'nucleation-growth' processes and eventually control the dimple geometry on fracture surfaces. Experimental measurements of dimple geometry in 2D on the published fractographs of a series of AA6061-T6 specimens with differently superimposed *UV*s (with different amplitudes and times) during different tensile deformation stages (i.e., elastic, yield, plastic and necking) have been performed and correlated with the corresponding mechanical properties. This research investigates the relationship between fracture features and the material's deformation response at different stages to elucidate the strong linkage between deformation and fracture. This study contributes to deeper insights into the ductile fracture micro-mechanisms of materials under the influence of *UV*s.

Introduction

Ultrasonic vibration (*UV*), well-known for its short-lived cycles, high-speed, high-frequency, controllable and user/environmental friendliness has come up as a highly powerful technique for stress-relief and surface-strengthening in several metal-forming operations for aluminum and copper alloys.^[1,2] *UV* can cause softening and hardening while deformation and 'this concept' is extensively exploited elsewhere.^[2] It has been investigated that the degree of acoustic-softening is closely related to amplitude,^[3] frequency,^[4] specimen size,^[4,5] temperature,^[6] material characteristics^[7,8] and grain morphology.^[9] Normally, *UV* induces volume-effects^[10] and surface-effects^[11] in plastic deformation. Volume-effect predominantly explains the effect of *UV* on materials' formability and the forming resistance, while surface-effect describes the lowering of friction between materials and tool which leads to the improvement of quality.^[12] Currently, significant volume of research-works largely focus on the ultrasonic-motion characteristics and surface-effect is corroborated by many experiments, but volume-effect is still not understood in open literatures. Normally AA6061-T6 alloy is used for aerospace, automotive, marine, electronic devices, reactor's core structures, fuel cladding, *etc.* Hence, it is important to understand the deformation behavior and eventual fracture characteristics of ductile materials under systematic imposition of *UV*s (with different degrees) at various deformation stages.

Recently, Wu et al.^[1] performed *UV*-tensile tests to explore the effect of *UV*-factors on tensile responses of AA6061-T6 alloy. Comparing the tensile responses and corresponding fracture morphologies, Wu et al.^[1] already concluded that *UV* has no solid effect (huge) on tensile properties of AA6061-T6. In current investigation, how the introduction of *UV*s (with

different amplitudes and duration) during different tensile deformation stages (i.e., elastic, yield, plastic and necking) influences the ductile failure micro-mechanisms/characteristics of AA6061-T6 has been quantitatively assessed/compared thoroughly. This brings out the novelty of current research.

Failure is the ultimate *continuum* of materials. Ductile fracture happens along the void 'nucleation-growth-coalescence' steps eventuating hierarchical micro/nano-layered dimples on the broken surfaces. These voids initiate and successively grow at inclusions, constituent particles, dislocation pile-up and other defects (stress-raisers in microstructure) under favorable influence of plastic strain and tensile hydrostatic-stress.^[13,14] The type, extent, geometry, strength and distribution of such stress-raisers, hence, play an important role in regulating not only the void initiation but the entire failure process also.^[13,14] Ductile failure is actively controlled by voids' spacing, triaxiality, geometry and the hardening characteristics (strain) of the material.^[13,14] Fracture characteristics of materials in particular depend on such staged progression of continuous damage accumulation during past deformation. Furthermore, the fracture geometry of broken free surfaces must be perceived as a product of microstructural defects and their interaction with local *stress-state*. Hence, it is corroborated that the fracture surface records the past incidents which occurs in the previous deformation events by keeping the *imprint* of 'characteristic-markings'.^[15] For example, recently, Macek et al.^[16] correlated the strain-loading sequence on the fatigue life of AA7075-T651 with its fracture pattern/topography. The geometric attributes present on the fracture surfaces clearly describe the crack growth history and the hindrances encountered during failure process. The complex and irregular morphologies of fracture surfaces can reasonably manifest the *state-of-energy* absorbed

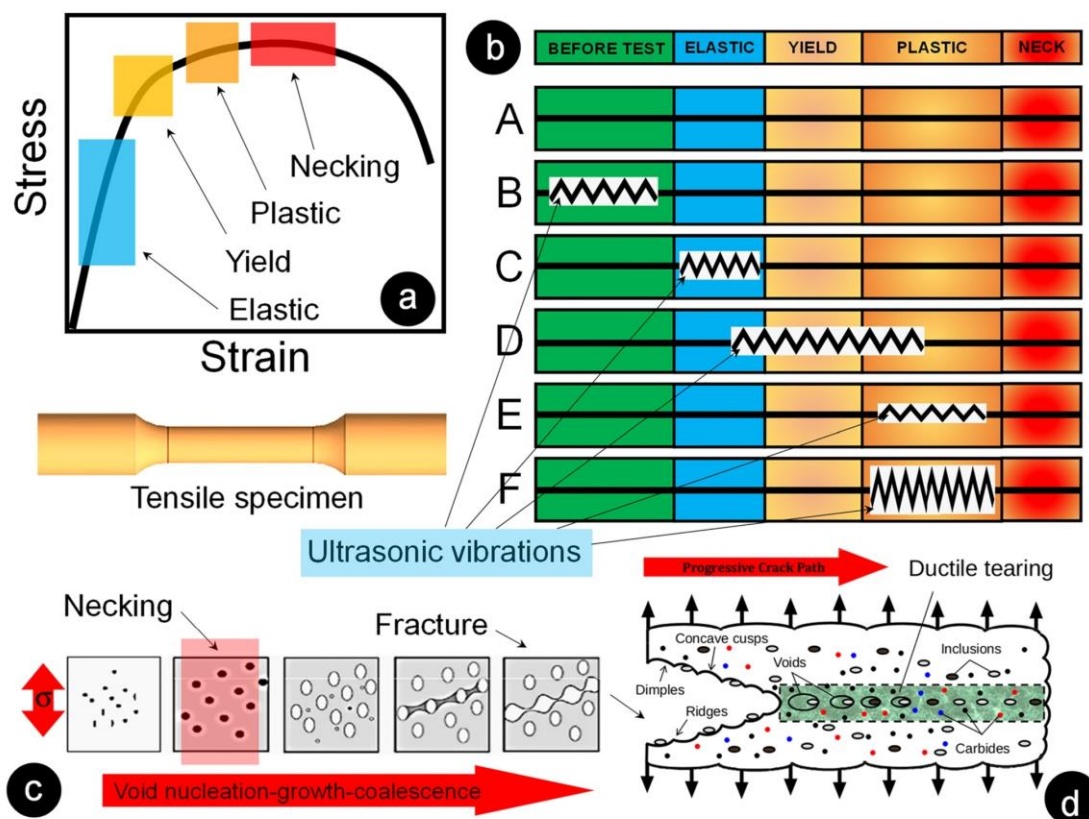


Figure 1. Schematic illustration of complete ductile fracture micro-mechanisms under imposition of UV. (a, b) UV applied at different stages of tensile deformation (i.e., elastic, yield, plastic and necking) on different tests by varying UA and Vt by Wu et al.^[1] and (c, d) void nucleation-growth and coalescence stages.^[19,20]

by the total failure event due to broken surfaces creation.^[17] Understanding such fracture patterns/characteristics of materials is very essential for predicting failure under stress, which directly influences design decisions and material selection. Quantitative fracture surface feature analysis generally reveals the root causes of failure, logically evaluates its integrity, and guides design improvements to enhance durability.

Material, method and analysis

For understanding the above theorem that ductile fracture characteristics can be correlated to respective mechanical responses of material, it is essential to change the type, geometry, morphology and density of void nucleating defects generated (or contained already) during plastic deformation in the microstructure. Such a strategy has been applied in AA6061-T6 (0.59Si-0.11Mn-0.24Cr-0.12Fe-0.24Cu-1.02Mg-0.07Zn-0.03Ti-bal. Al) (wt.%) by Wu et al.^[1] in their elegant article. Generally, this alloy has excellent mechanical

properties such as good corrosion resistance, high strength/weight ratio, excellent deformability and weldability.^[18] To thoroughly understand the influence of UV on the tensile responses of AA6061-T6, UV-tensile tests (of cylindrical solid specimens of gauge length 30 mm as per GB/T 228–2002 standard, applied displacement rate: 1 mm/min) were carried out by Wu et al.^[1] at different deformation stages (see Fig. 1), by systematically altering the vibration time (Vt) and ultrasonic amplitudes (UA). Detail experimental parameters are listed in Table 1 and thoroughly reported in Ref. 1. The UV axial tensile system, comprising electromechanical universal testing machine (UTM) and a UV-tensile device, is presented by Wu et al.^[1] in their Fig. 1. This setup ensures that the longitudinal acoustic wave propagates along tensile-stress direction. Details of the experiments are listed in Table 3 (reported in Ref. 1) and the excitation frequency of ultrasonic generator was kept 19,000 Hz during the entire test.^[1] All these experiments were performed by Wu et al.^[1] It has been logically presumed that the initial inclusion content





J Mater Sci (2025) 60:16480–16496

Metals & corrosion



Investigation of microstructural and magnetic property evolution in mechanically milled Co–Zr metallic ribbon

Sanjay Saini^{1,2}, A. P. Srivastava^{1,2,*}, P. S. Ghosh^{1,3}, Archana Sagdeo⁴, A. Ghosh³, D. Arvindha Babu⁵, S. V. Madge⁶, and S. Neogy^{1,2}

¹ Homi Bhabha National Institute, Anushakti Nagar, Mumbai 400094, India

² Materials Science Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

³ Glass and Advanced Materials Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

⁴ Raja Ramanna Centre for Advanced Technology, Indore 452013, India

⁵ Defence Metallurgical Research Laboratory (DMRL), Kanchanbagh, Hyderabad 500058, India

⁶ Indian Institute of Technology, Nagrota 181 221, Jammu, India

Received: 27 May 2025

Accepted: 14 August 2025

Published online:

5 September 2025

© The Author(s), 2025

ABSTRACT

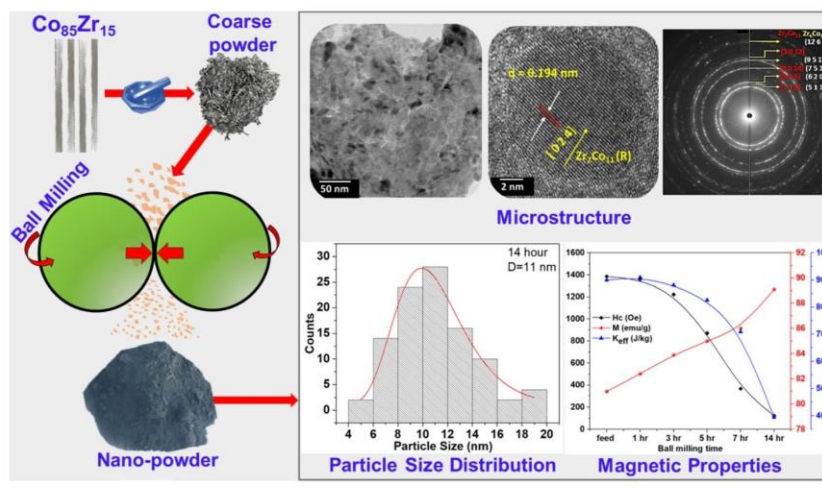
Zr₂Co₁₁ has emerged as a promising candidate for rare-earth-free magnetic materials with the exceptional energy products in thin-film nanocomposites. Despite this, its potential in bulk magnet form remains largely unexplored. Powder metallurgy offers a promising route to fabricate these alloys in bulk magnet form with controlled microstructure and soft and hard magnetic phase distribution essential for optimizing magnetic properties. This study investigates the effects of mechanical milling on the microstructure, and magnetic properties of a metallic ribbon having composition of Co₈₅Zr₁₅, aiming toward development of novel permanent magnet material. The microstructure and phase composition of both the as-cast ribbon and the milled powder samples were characterized using transmission electron microscopy (TEM) and synchrotron X-ray diffraction (XRD). The as-cast ribbon predominantly consists of the hard magnetic Zr₂Co₁₁ phase along with a soft magnetic Zr₆Co₂₃ phase. TEM analysis confirmed that mechanical milling reduced the ribbon to fine particles with an average size of 11 nm after 14 h of milling. With the increase in milling duration, the saturation magnetization was found to increase whereas the coercivity was found to decrease. This study shows that milling has a significant impact on the exchange coupling between soft and hard magnetic phases at nanoscale. To rationalize the experimental observations, first-principles calculations were performed considering rhombohedral structure of Zr₂Co₁₁ to estimate the change in the total magnetic moments in the unit cell as a function of isotropic compression/expansion, as well as to examine the effect of off-stoichiometry and defect formation. The ball milling process

Handling Editor: Nima Haghdadi.

Address correspondence to E-mail: apsri@barc.gov.in

parameters were optimized to achieve particle sizes close to the critical size of the soft and hard magnetic phases (~ 11 nm) required for effective magnetic coupling between the two so as to manifest the exchange spring behavior in nanocomposite magnets.

GRAPHICAL ABSTRACT



Introduction

Permanent magnets (PMs) are essential for a range of advanced technologies, particularly in the fields of renewable energy, automotive engineering and electronics. Their role in converting mechanical energy to electrical energy and vice versa makes them critical for electric motors, generators, and various other devices [1]. Historically, PMs such as AlNiCo, ferrites, etc., possessing energy product less than 10 MGOe have been most widely used because of low price and ease of availability. However, rare-earth (RE)-based permanent magnets, specifically NdFeB and SmCo magnets, dominate the market because of their energy product $(BH)_{\text{max}}$ of more than 20 MGOe [2, 3]. Recently, the supply risk of RE elements due to market volatility and high cost has driven research efforts toward rare-earth-free (RE-free) permanent magnets as viable alternatives [3–6]. Therefore, there is a need for the development of PMs having energy product more than 10 MGOe without containing rare-earth elements.

In this context, several RE-free hard magnetic phases, including FePt, FeNi, MnBi, MnAl, $\text{Zr}_2\text{Co}_{11}$, HfCo_7 , etc., have been proposed, and they are under

active research [7–11]. For example, Mn-based alloys such as MnBi and MnAl offer favorable properties such as high magnetocrystalline anisotropy, albeit researchers are facing limitations in achieving optimal coercivity and magnetic phase purity [3]. Iron nitride (Fe_{16}N_2) and carbide-based magnets are also considered potential candidates. They show high saturation magnetization but suffer from challenges in stable phase formation and maintaining high coercivity [3, 12].

The Co-based phases, particularly $\text{Zr}_2\text{Co}_{11}$ and HfCo_7 , have also emerged as promising candidates. These phases exhibit high magnetic anisotropy and high Curie temperature [13]. The earlier studies on the CoZr system have primarily focused on aspects such as the influence of various elemental substitutions, structural characterization, and their effects on magnetic properties [14–20]. In the CoZr system (with 10–25 at. % Zr), a eutectic phase transformation takes place at 1254 °C, and two peritectic transformations occur at 1331 and 1272 °C, respectively [21]. These phase transformations lead to the formation of $\text{Zr}_2\text{Co}_{11}$ and $\text{Zr}_6\text{Co}_{23}$ phases. Therefore, preparing a material containing only a single hard magnetic phase of $\text{Zr}_2\text{Co}_{11}$ poses challenges.





Current Genetics (2025) 71:29
<https://doi.org/10.1007/s00294-025-01334-9>

ORIGINAL ARTICLE



Is heptelidic (koningic) acid a microbial hormone that regulates secondary metabolism in the biocontrol fungus *Trichoderma virens*?

Ravindra Bansal^{1,2} · Sunil Kumar Sethy^{2,3} · Vitthal T. Barvkar⁴ · Prasun Kumar Mukherjee⁵ · Suvendu Mondal^{2,3}

Received: 7 May 2025 / Revised: 10 September 2025 / Accepted: 31 October 2025 / Published online: 19 November 2025
 © The Author(s) 2025

Abstract

Trichoderma virens, a plant-beneficial fungus, has the ability to produce volatile and non-volatile secondary metabolites that possess antimicrobial properties and contribute to promoting plant growth and development. Gliovirin, viridin, viridiol, and heptelidic acid are among its major non-volatile metabolites. In our previous study, we observed that the deletion of heptelidic acid synthase (*has1*), a terpene cyclase, abolished the biosynthesis of major non-volatile metabolites, in addition to heptelidic acid. Conversely, deletion of the *Tex7* gene, a non-ribosomal peptide synthetase, led to an increase in heptelidic acid production, along with other major secondary metabolites. Additionally, disruption of a GAPDH gene located within a secondary metabolite gene cluster abolished heptelidic acid biosynthesis and, consequently, all major secondary metabolites. These findings suggest that heptelidic acid might act as a microbial hormone that regulates secondary metabolism. To investigate this further, we conducted transcriptomic and metabolomic comparisons between the wild-type strain and a Δ has1 mutant lacking heptelidic acid biosynthesis. Transcriptome analysis revealed a major proportion of transcripts were down regulated. Of them, nine transcripts belonged to gliovirin biosynthesis cluster, 14 for viridin cluster and five for volatile sesquiterpene and heptelidic acid biosynthesis cluster; metabolite analysis couldn't detect any heptelidic acid along with viridin, viridiol and gliovirin in the Δ has1 mutant. Additionally, several other secondary metabolites were significantly down regulated. Our results are indicative of a possibility that heptelidic acid might function as a microbial hormone regulating secondary metabolism in this biotechnologically important fungus.

Keywords Gliovirin · Heptelidic acid synthase · Mutant · *Trichoderma virens* · Viridiol · Viridin

Introduction

Heptelidic acid, also known as koningic acid, is a sesquiterpene lactone originally isolated from the culture broth of *Trichoderma virens* (*Gliocladium virens*) (Itoh et al. 1980). The purified compound ($C_{15}H_{20}O_5$) was identified as an antibacterial metabolite exhibiting high toxicity against the anaerobic bacterium *Bacteroides fragilis*. Its structure was elucidated by spectrometry and X-ray crystallography (Stipanovic and Howell 1983). From a biocontrol perspective, Howell et al. (1993) examined a large number of *T. virens* isolates and classified them into two groups, i.e., the P and Q strains. The P-type strains were found to synthesize gliovirin and heptelidic acid, whereas the Q-type strains produced gliotoxin and dimethylgliotoxin. Both strain types produced viridin and viridiol. Heptelidic acid was also found to be an anti-oomycete, thereby broadening the antimicrobial spectrum of this fungal metabolite (Howell et al. 1993).

Ravindra Bansal and Sunil Kumar Sethy contributed equally. Joint first authors were arranged in alphabetic order.

✉ Prasun Kumar Mukherjee
 prasunmukherjee1@gmail.com

✉ Suvendu Mondal
 suvenduhere@yahoo.co.in

¹ Technology Transfer and Collaboration Division, Bhabha Atomic Research Centre, Mumbai 400085, India

² Homi Bhabha National Institute, Training School Complex, Anushaktinagar, Mumbai 400094, India

³ Nuclear Agriculture and Biotechnology Division, Bhabha Atomic Research Centre, Mumbai 400085, India

⁴ Department of Botany, Savitribai Phule Pune University, Pune 411007, India

⁵ Seacom Skills University, Kendradangal, Santiniketan, West Bengal 731236, India

In an interesting turn of event, heptelidic acid (HA) was found to be a specific inhibitor of glyceraldehyde 3-phosphate dehydrogenase (GAPDH), an enzyme that catalyzes the conversion of glyceraldehyde 3-phosphate to 3-phosphoglycerate in the energy-yielding glycolytic pathway (Endo et al. 1985; Sakai et al. 1988). HA irreversibly binds to the two sulfhydryl (cysteine) residues at the active site of GAPDH, thereby inactivating the enzyme (Sakai et al. 1988). As a mechanism of self-resistance, the genomes of the producing organisms harbor an additional GAPDH gene, which encodes an isoform relatively insensitive to HA (Sakai et al. 1990; Watanabe et al. 1993). Later, using theoretical modelling and experimental validation, the molecular basis for differential sensitivity between the two GAPDH isoforms was elucidated (Liberti et al. 2017; Ganapathy-Kanniappan 2018; Yan et al. 2020; Pachauri et al. 2020). The strong inhibitory effect of HA on GAPDH and its selective cytotoxicity against highly glycolytic cells through glucose-dependent ATP depletion (Kumagai et al. 2008) led to its exploration as a potential anti-cancer agent. Currently, HA is considered a promising drug candidate for tumor treatment by targeting the Warburg effect (Rahier et al. 2015; Liberti et al. 2017, 2020; Abdel-Wahab et al. 2019; Jing et al. 2022; Isozaki et al. 2022; Lin et al. 2023). This metabolite also exhibits apoptotic activity, antimalarial properties, and inhibitory effects on certain DNA polymerases (Nomura 1998; Tanaka et al. 1998; Nakazawa et al. 1997; Yamaguchi et al. 2010), underlying the importance of this compound as a drug candidate.

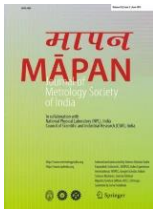
Using suppression subtractive hybridization and a *T. virens* mutant downregulated in secondary metabolism, we previously identified a gene cluster (designated as the vir cluster), with a GAPDH gene located adjacent to the terpene cyclase *vir4* (Mukherjee et al. 2006). Subsequently, following the publication of the *T. virens* genome, the full cluster was characterized, and it confirmed the presence of two GAPDH-encoding genes in the genome: one house-keeping and the other associated with the vir cluster (Crutcher et al. 2013). When *vir4* gene, which encodes a terpene cyclase, was deleted, production of several volatile sesquiterpenes was eliminated, although the biosynthesis of viridin, viridiol, and gliotoxin remained unaffected. This cluster was later shown to be involved in heptelidic acid biosynthesis in *Aspergillus oryzae*, another HA-producing organism (Shinohara et al. 2019). Subsequently, Yan et al. (2020) reported the vir cluster as the HA biosynthetic cluster in *T. virens*.

Based on gene knockout experiments, Bansal et al. (2021) proposed that another terpene cyclase Has1, is responsible for the first committed step, i.e., cyclization of farnesyl

pyrophosphate, in HA biosynthesis, while enzymes from the *vir4* cluster perform downstream modifications. In *T. virens*, deletion of the vir-cluster associated GAPDH (designated vGPD) abolished the biosynthesis of major non-volatile metabolites (viridin, viridiol, and HA) as well as volatile sesquiterpenes (Bansal et al. 2021). In addition, the deletion of *has1* abrogated non-volatile metabolite production, and downregulated volatile sesquiterpene biosynthesis. Interestingly, deletion of a non-ribosomal peptide synthetase *Tex7* in a Q strain of *T. virens*, previously thought to be an HA non-producer, resulted in abundant HA production (Taylor et al. 2020). The *tex7* mutants not only produced HA as the major metabolite but also exhibited elevated levels of other non-volatile metabolites such as gliotoxin, viridin, and viridiol. These findings suggest that the vir-cluster associated GAPDH (HA insensitive) acts as a positive regulator of HA biosynthesis, whereas *Tex7* functions as a negative regulator, and the secondary metabolism machinery in *T. virens* appears to be dependent on HA production itself.

In *Streptomyces griseus*, the secondary metabolite A-factor, a γ -butyrolactone, regulates secondary metabolism (Horinouchi and Beppu 1993, 1994; Horinouchi 2002). Several A-factor-like metabolites, all γ -butyrolactones, function as microbial hormones regulating secondary metabolism in various *Streptomyces* spp. (Horinouchi and Beppu 2007). The regulation mechanism involving these microbial hormones is well established. For example, the A-factor specifically binds to the receptor protein ArpA. ArpA acts as a transcriptional repressor for *AdpA* by binding to a specific DNA sequence in the promoter of *AdpA*. Binding of the A-factor to ArpA dissociates the protein, leading to the activation of the *AdpA* regulon, which results in secondary metabolism and morphological differentiation (Ohnishi et al. 1999, 2005; Horinouchi et al. 2000; Horinouchi and Beppu 2007). There has been at least one report on regulation of secondary metabolism by a natural product in fungi. The metabolite aureonitol acts as a transcription-regulator in biosynthesis of secondary metabolites in *Chaetomium globosum* (Nakazawa et al. 2013). However, such modulation of secondary metabolism has not been reported in most fungi, including the biotechnologically relevant fungi *Trichoderma* spp. To test the hypothesis that HA might regulate secondary metabolism in *T. virens*, we conducted transcriptomic and metabolomic analyses of a *T. virens* mutant deficient in HA biosynthesis (Δ has1). Our data indicate that the loss of HA biosynthesis correlates with the downregulation of multiple genes involved in volatile and non-volatile secondary metabolite biosynthesis, as well as abrogation of the corresponding metabolites in *T. virens*.





ORIGINAL PAPER

Leveraging the Aswal Model to Understand and Amplify the Impact of India's National Education Policy

D. K. Aswal and A. Chandra* 

Health Safety and Environment Group, Bhabha Atomic Research Centre, Mumbai 400085, India

Received: 18 April 2025 / Accepted: 28 June 2025 / Published online: 26 July 2025

© The Author(s) 2025

Abstract: India's ambitious initiative, “Viksit Bharat” (Developed India) by 2047, aims to transform the nation into a technologically advanced, economically robust, and socially inclusive society. Education stands as a central pillar of this vision. To ensure that quality education is accessible, equitable, and affordable for all, the National Education Policy (NEP) was introduced by the government in 2020, serving as a critical policy framework within the broader “Viksit Bharat” vision. While the NEP provides a comprehensive roadmap for India's educational transformation, a unified approach to ensure systemic quality and stakeholder integration is lacking. To fill this gap, this paper introduces the Aswal Model—a quality infrastructure-based framework originally developed for science and innovation—as a conceptual tool to analyse and amplify the NEP's impact. Rooted in the Quadruple Helix model of academia, industry, government, and civil society, the Aswal Model emphasizes the foundational role of metrology and quality infrastructure systems (QIS) in mediating stakeholder interactions. Using thematic analysis and policy documents, the study demonstrates how QI elements such as standardization, accreditation, and conformity assessment align with NEP's elements, including core focus areas—Early Childhood Care and Education, Higher Education, and Vocational Education. By embedding QI principles into India's education policy, the paper offers a novel interdisciplinary pathway for strengthening educational governance and knowledge generation. The findings contribute to both policy and metrology discourse by extending the application of quality infrastructure frameworks to education, providing actionable insights for regulators, technocrats, and institutional leaders.

Keywords: Education; Knowledge society; Quality infrastructure; National education policy; India

1. Introduction

India aims to attain developed nation status by 2047, its 100th year of independence [23]. Among the key drivers of this goal are the need for a resilient, inclusive, and innovation-driven economy [34] and quality education systems. A first step in this direction would be to enhance the Human Development Index (HDI) of India. HDI is a composite measure of development based on life expectancy, education, and per capita income to ensure a higher standard of living for all citizens. With India's current HDI at approximately 0.64, raising it above 0.8 would signal a developed nation status [41]. This would mean coming up with a comprehensive strategy that reinforces the educational system, advances scientific and technological

innovation, and generates inclusive economic opportunities across diverse regions. All of this amidst India's large population, democratic structure, and complex socio-economic environment.

One such holistic and comprehensive strategy is the Indian government's ‘Viksit Bharat’ [23]. The term ‘Viksit Bharat’ means ‘Developed India’. It represents the government's vision to transform India into a developed nation by 2047 [28]. The Viksit Bharat vision is built on 5 core principles—(i) Empowered Indians, (ii) Thriving and Sustainable Economy, (iii) Innovation, Science and Technology, (iv) Good Governance and Security and (v) Good International Relationships and Leadership.

In operational terms, the Viksit Bharat envisions [28]: (1) achieving a \$30 trillion economy with per-capita income of \$18,000–\$20,000, backed by sound public finances and a strong financial sector; (2) establishing world-class infrastructure in both rural and urban areas; (3) reducing government intervention in daily life, while

*Corresponding author, E-mail: anirudhc@barc.gov.in

promoting digital governance and economy; (4) nurturing global industry leaders and supporting indigenous innovation; (5) achieving self-reliance in defence and space, elevating India's global presence; (6) prioritizing green growth by expanding green energy and reducing carbon emissions; (7) equipping youth with skills and education to boost employment; and (8) partnering with global research and development to establish premier laboratories and rank at least ten Indian institutions in the global top 100.

This paper focuses on objective 7—education, a cornerstone of Viksit Bharat and an essential dimension of HDI.

In response to this imperative, the National Education Policy (NEP) 2020 was introduced by the Indian government to transform the educational landscape [26]. Although India's education system rests on a long-standing foundation, the NEP is designed to modernize it in line with sustainable development priorities and global competitiveness. While the policy is comprehensive in scope—addressing issues of access, equity, quality, and innovation—it lacks a clearly articulated, systemic quality assurance framework. Such a framework is essential for linking intent with measurable outcomes and for aligning various actors and institutions operating across different levels of the educational ecosystem.

To address this gap, the present paper explores a conceptual application of the Aswal Model—a quality infrastructure (QI)-based systems framework for knowledge production and innovation [2]. Originally developed in the context of science and technology policy, the Aswal Model emphasizes the enabling role of metrology, standardization, accreditation, and conformity assessment in building a trust-based, high-performance system. The model adapts the Quadruple Helix framework by explicitly integrating QI as a mediating force among academia, industry, government, and civil society.

By applying the Aswal Model to India's education system and NEP goals, we aim to illustrate how embedding QI elements can strengthen systemic coherence, promote stakeholder alignment, and amplify the policy's long-term impact. This conceptual approach may help policymakers, institutional leaders, and technocrats translate the NEP's vision into structured, measurable, and sustainable outcomes.

The article is organized as follows: Sect. 2 outlines the national context including NEP's key features and the idea of a knowledge economy and society. Section 3 discusses the methodology, which includes description of the Aswal Model and how it was applied to the Indian education system. Sects. 4 and 5. present the results and discussions of this application; and Sect. 6 concludes.

2. National Context

This section presents the NEP as the focal point for our model application, emphasizing its role in shaping India into a knowledge society—a core objective of the Viksit Bharat vision. Framing the NEP within this developmental context allows us to explore its alignment with the Aswal Model and place our analysis within broader theoretical frameworks for knowledge production and innovation.

2.1. National Education Policy for a Viksit Bharat

An important part of the Viksit Bharat vision is empowering youth with skills and education [28]. In support of this vision, the NEP was implemented in 2020 [26]. This is an upgradation of the erstwhile National Policy on Education of 1986. The NEP envisions an education system rooted in Indian ethos that contributes directly to transforming India sustainably into an equitable and vibrant knowledge society [20, 26].

Quality education is essential for equipping students with the skills and knowledge needed to succeed in a globalized world [15]. With this intent, the NEP outlines a transformative vision for education in India, focusing on quality, accessibility, and relevance. It focuses on a multidisciplinary approach, enhanced institutional autonomy, emphasis on research and innovation, and a commitment to inclusivity [26]. These goals are intended to position India as a leader in education, particularly higher education, and ready its youth for future opportunities and challenges. The salient features of the NEP can be grouped into several themes (see Fig. 1)

A. Access and inclusion

- Ensuring universal access at all levels of schooling from pre-primary to Grade 12.
- Equitable and inclusive education with special emphasis on Socially and Economically Disadvantaged Groups (SEDGs).
- A separate gender inclusion fund and special education zones for disadvantaged regions and groups.
- Achieving 100% youth and adult literacy.
- Expansion of open and distance learning to increase Gross Enrolment Ratio (GER).

B. Curriculum and pedagogy

- New curricular and pedagogical Structure (5 + 3 + 3 + 4).





International Journal of System Assurance Engineering and Management (2026) 17:166–191
<https://doi.org/10.1007/s13198-025-02960-9>

ORIGINAL ARTICLE



Machine learning based predictive model to enhance human reliability analysis for risk assessment of nuclear reactors

Vipul Garg^{1,2} · Gopika Vinod^{1,2} · Vivek Kant³

Received: 4 December 2024 / Accepted: 22 August 2025 / Published online: 7 October 2025
 © The Author(s) 2025

Abstract

The aim of Human Reliability Analysis (HRA) is to evaluate the likelihood of the human operator performing erroneous actions in terms of Human Error Probability (HEP). Human operators are vital in safely operating complex systems, such as nuclear power plants (NPPs). In order to account for the role of the human, HRA experts have developed a variety of methods primarily targeting the quantitative dimension of human behaviour, with limited focus on the qualitative. The most recent shift has been towards Machine Learning (ML)-based methods for predicting HEPs. Prominent among these new methods are Logistic Regression (LR) and Bayesian Networks (BN). Amongst ML methods, Artificial Neural Networks (ANN) are also a good candidate model but have not been adequately explored in HEP evaluation. This article presents a comparative analysis of the above three approaches. The results indicate that ANN based models can replicate the qualitative HRA in their HEP predictions. Therefore, if qualitatively appropriate HRA data is available, then ANN-based models, utilizing operator performance data maybe a good alternative for HEP evaluation. The comparative scheme developed in this article can serve as the basis for future comparison amongst methods that employ an amalgamation of qualitative and quantitative methods in HRA.

Keywords Human reliability analysis · Human error probability · Cognitive failure probability · Machine

learning · Qualitative analysis · Probabilistic safety assessment

1 Introduction

Probabilistic Safety Assessment (PSA) is an analytical approach to evaluate the risk emanating from complex systems. Human Reliability Analysis (HRA) is an indispensable part of Probabilistic Safety Assessment (PSA) which evaluates the likelihood of the human operator performing erroneous actions, in terms of Human Error Probability (HEP) that could perturb the facility or plant and drift it to an undesirable state. Human operators play a vital role in safe operation of complex systems such as nuclear power plants (NPPs) as well as other complex sectors (Zoltán & Rýdzi 2017; Robin Hamer 2021; Dekker 2019, 2011; Hollnagel 2014). However, sometimes, due to complex interplay with the technology and organizational practises, human operators may fail to meet the expected performance which could drift the system towards failure (Zoltán & Rýdzi 2017; D. Woods et al. 2010; Dekker 2014; Dekker 2004). In order to account for the role of the human, HRA experts have developed a variety of methods (Case Study on the Use of Psa Methods: Human Reliability Analysis, 1991; Swain 1987; Gertman et al. 2005; Hollnagel 1998).

While the artificial intelligence revolution unfolds widely in the technological sphere, there is also a growing need for developing these for safety and reliability. These new directions include the use for machine learning techniques to enable identification of the underlying factors related to incidents, accidents and system failures. The major challenge that we face currently is that most machine learning techniques are developed with a focus on data with one method being applicable to a lot of real world scenarios once the data is made amenable for processing. In contrast, in the safety and human reliability sector, there is a need for starting from the qualitative approach as it fits in with the

✉ Vipul Garg
vipulgarg@barc.gov.in

¹ Reactor Safety Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

² Homi Bhabha National Institute, Anushaktinagar, Mumbai 400 094, India

³ Department of Design, Indian Institute of Technology Kanpur, Kanpur, India

real-world experience of the workers in safety-critical sectors. The challenge in this case is that the qualitative based insights have to be coupled with quantitative based information about human activities to develop a predictive view of human reliability. In this case, predictive approaches will have to be developed starting from the human behavioural insights – both qualitative and quantitative. Most of the widely practised Human Reliability Analysis (HRA) methods generally predict Human Error Probability (HEP) based on expert-based calculations and judgements. These include introduction of multiplier weights and values to susceptible performance shaping factors to enhance the base or the nominal HEP. While these methods have a proven track record for HEP estimation, with the growth of Machine Learning (ML) methods, new avenues of HEP calculation can be sought. For example, if appropriately classified HRA data is present, then ML methods can be used to identify the patterns in data to derive HEP in given contexts. This presents a powerful way of addressing HEPs beyond that of traditional methods based on expert elicitation. Literature also suggests that safety experts globally are already anticipating the implementation of sophisticated ML techniques in future research (Riccardo Patriarca, Massaiu, Costantino, Gravio, & Boring, 2020).

Currently, some of the most common ML-based approaches prominently used in HRA literature include Logistic Regression (LR) (Wondea et al. 2020; James et al. 2022; Kim et al. 2022; Kim 2020) and Bayesian Networks (BN) (Groth & Swiler 2013; Abrishami et al. 2020a, b; Jo & Lee 2022; Podofilini et al. 2023). In addition, Artificial Neural Networks (ANN) is also a good candidate approach but has not been adequately explored. This paper contributes to the literature on HRA by comparing these three approaches for their suitability in predicting conditional cognitive function failure HEPs using a novel comparative scheme. The comparative scheme uses qualitative assessment, a crucial pre-requisite, as the starting point for HEP analysis and couples the ML-based approaches to investigate coherence and ensure suitability in providing the HEP results.

The results indicate that ANN based models are capable of replicating the qualitative HRA and provide consistent HEP predictions. In this endeavour, the research contribution of this article is as follows:

- 1) Presenting a novel comparative scheme for evaluating the ML-based approaches for predictive HRA.
- 2) Coupling qualitative analysis, as a crucial pre-requisite, with quantitative analysis to investigate coherence and ensure suitability between them.
- 3) Advancing ANN based approaches as a candidate approach for predictive HRA.

The rest of this article is divided into eight sections. Section 2 discusses the comparative assessment approach and the scheme adopted for the same. Section 3 briefly explains the template adopted to assist in qualitative analysis. Section 4 focuses on contemplation of the scenarios for simulation in an advanced reactor's control room, conduction of simulator experiments and elicitation of qualitative information pertaining to operator performance. Section 5 discusses different techniques contemplated and challenges encountered in predictive analysis. The final step is comparative quantitative analysis and its results are highlighted in Sect. 6. Section 7 summarizes the work and underscores the limitations and scope for future work. Section 8 concludes the work.

2 Background and related works

In accounting for the human in complex systems, HRA and PSA experts often confront the following challenges:

1. Currently, there exists no analytical model or equation that can accurately predict HEP. As a result, HRA methods generally make HEP predictions based on expert elicited equations, e.g. simple Performance Shaping Factors (PSFs) multiplication based equations in ASEP (Swain 1987), SPAR-H (Gertman, Blackman, Marble, Byers, & Smith, 2005), etc. Revising the PSFs or Base/Nominal Human Error Probability (BHEP/NHEP) of such equations with empirical data to improve the accuracy of HEP evaluation has its limitations. This is because relationship among the PSFs is complicated (Park J., 2024) and the accuracy is further restricted by the assumptions made while adopting such expert opinion based equations.
- 2.4 HRA in its current application in PSA is strongly oriented towards evaluation of HEP i.e. the predictive analysis. Liao et al. have highlighted the lack of focus of the majority of the widely practised HRA methods on qualitative assessment of the human operator performance (Liao et al. 2019a, 2019b, 2019c). Similarly, HRA experts often emphasize on conducting qualitative assessment before proceeding towards the predictive or the quantitative analysis to enhance the quality of HRA and to ensure coherence between them (Liao et al. 2019a, 2019b, 2019c).
3. A persistent challenge in HRA is inadequacy of human operator performance data. This is due to the fact that most of the initiating events modelled in PSA are infrequent events and some might not transpire during the entire lifecycle of the plant, owing to which the corresponding data is sparse (Hallbert & Kolaczowski





Microscopic structure of lead-silicate glass and its correlation with thermal, mechanical, and radiation shielding properties

Pooja Sahu^{1,2} · Musharaf Ali Sheikh^{1,2}

Received: 5 August 2025 / Accepted: 19 September 2025 / Published online: 30 October 2025
 © The Author(s) 2025

Abstract

Lead-silicate glasses are widely used in radiation shielding windows (RSW) as they offer high density and ability to attenuate γ -rays and X-rays while maintaining optical transparency. A detailed atomistic understanding is of importance for its wide technological applications. Therefore, classical molecular dynamics (MD) simulations in conjunction with ab initio MD (AIMD) simulation are carried out for binary lead silicate glasses with 30, 50, and 64 mol% PbO to elucidate the structure–property relationships. The calculated results show a 48.42% density increase and a significant rise in non-bridging oxygens (NBOs) confirming the network-modifying role of Pb^{2+} ions. The network modifying role of Pb^{2+} ions is also supported by Q^4/Q^3 to Q^0/Q^1 conversion and by the presence of multiple PbO_n ($n=1-7$) geometries with average ~ 4 -fold coordination. The emergence of a structure factor peak at $2.96 \text{ \AA}^{-1}$ and cluster size analysis indicate Pb clustering and a tendency to form a percolating network at a higher PbO concentrations. The formation of 2–8 membered Pb–O–Pb–O rings and the increasing intensity in total VDOS at 150 cm^{-1} suggest the partial covalent Pb–O network formation at higher PbO levels. Altogether, the results suggest that Pb^{2+} ions though primarily act as network modifiers, nevertheless, some Pb^{2+} ions may potentially integrate into the glass network structure at higher concentrations. These microscopic features explain the observed 16.68% decrease in T_g ; 62.5% increase in the thermal expansion coefficient (TEC) and 19.49% rise in Young's modulus (Y) while increasing PbO from 30 to 64 mol%. Thermodynamic analysis via two-phase thermodynamic (2PT) model reveals a 53.29% increase in vibrational entropy and a 106.52% increase in configurational entropy, supporting Pb-induced network depolymerization. The optical analysis demonstrates a 15.34% increase in refractive index, and 32.15% increase in dielectric constant with increasing PbO from 30 to 64%, while the reflection loss is increased from 7.62% to 11.53% due to higher density and more NBOs creation. The radiation shielding evaluations confirm that glasses with higher PbO content exhibit superior photon attenuation efficiency, particularly against low-energy photons dominated by photoelectric interactions.

Keywords Lead Silicate glass · MD simulations · AIMD simulations · Coordination and bond angle distribution · Glass transition temperature · Configurational entropy

1 Introduction

Lead-silicate glasses are widely employed in radiation shielding windows because the addition of PbO imparts high density and excellent attenuation of γ -rays and X-rays,

while retaining the optical transparency required for safe operation in nuclear power plants, medical radiology facilities, and research laboratories [1–3]. The application of radiation has expanded significantly in recent years, encompassing fields such as geological surveying [4], plant mutation studies [5], archaeology [6], energy production, medical diagnostics and treatment [7, 8], as well as food preservation [9]. This widespread usage has driven an increasing demand for efficient shielding materials capable of both protecting against harmful radiation and allowing continuous process monitoring. Historically, materials such as concrete were used for radiation shielding [10, 11]. However, the development of glass-based shielding

✉ Musharaf Ali Sheikh
 musharaf@barc.gov.in

¹ Chemical Engineering Division, Bhabha Atomic Research Centre, Mumbai, Maharashtra, India 400085

² Homi Bhabha National Institute, Mumbai, Maharashtra, India 400094

solutions introduced a paradigm shift, enabling transparency in addition to shielding functionality [12–15]. Lead-based compounds are widely adopted in conventional shielding glasses due to their high atomic number, providing excellent photon attenuation particularly in the low-energy regime, where the interactions are dominated by photoelectric interactions [2, 14]. Additionally, the low melting point of PbO facilitates easier glass fabrication. The minimal crystallization tendency of lead-silicate glasses while thermal treatment contributes to their extended operational lifespan [2]. Beyond RSW applications, high refractive index lead-silicate glasses are also extensively employed for imitating precious stones and creating valuable, durable objects, and advanced optical devices such as the Kepler telescope [16–18]. Nevertheless, these glasses exhibit some drawbacks, such as reduced fracture toughness, lower tensile strength, and degradation of optical transparency with increasing PbO content [17, 19, 20]. High PbO content also elevates glass density and viscosity, which complicates the melting and forming process by potentially inducing structural non-uniformity or defects. Current experimental studies largely focus on bulk property measurements and lack in-depth atomic-scale understanding of structure–property relationships in lead-silicate glasses [19, 21, 22]. Retaining both shielding efficiency and optical clarity, while overcoming inherent mechanical limitations, depends on careful composition design and understanding of structure–property correlations. Recently, a series of data driven machine learning (ML) studies have been conducted by Zhang and co-workers [23–28] to predict the composition-property relation of various polymer and glasses. The studies signify that the structure–property relationship is fundamental for advancing the development of next-generation Radiation Shielding Window (RSW) glasses. Additionally, understanding the structure–property relationships of RSW glasses is crucial, as radiation-induced structural changes can degrade glass quality over time.

The novelty of current research lies in applying the techniques of both classical and ab initio molecular dynamics simulations in conjunction with advanced thermodynamic modeling to reveal how PbO concentration affects network structure, thermodynamic properties, mechanical, optical and radiation shielding performance. This approach will enable the design of novel glass compositions with improved mechanical strength and radiation resistance while maintaining the high transparency. In the past, lead-silicate glasses with varying compositions of PbO and SiO₂ have been synthesized both experimentally [3, 29–32] and via MD simulation [31–33]. However, the exact role of lead elements in lead-silicate glasses is still debated. The studies of Furukawa et al. [34] suggest though Pb exist as PbO₄ structure in the glass matrix, but not necessarily

participates in the network formation in the glass structure. Existence of multiple Pb–O coordination geometry has been reported by many a studies [35, 36], however, whether Pb ions participate as network former or network modifier is still not conclusive. Few of earlier studies have postulated that the role of Pb²⁺ ions may depend on PbO concentration in the glass matrix [29, 34, 37–39]. The Pb²⁺ ions induced depolymerization and non-bridging oxygen (NBO) creation may strongly affect the attenuation properties and optical transparency the considered RSW glasses [40, 41], therefore it is important to explore the roles of Pb²⁺ ions in these glasses. Also, the impact of PbO concentration on the intermediate range order of glass structure is still not completely understood. Only a handful articles are available on the structural characterization of lead silicate glasses at intermediate range order [29, 42–44].

Considering all this, in present article, MD simulations have been used for prediction of long-term structural stability and property changes of lead silicate glass with varied PbO compositions: 30, 50 and 64 mol%. The studies focus on the evaluation of glass structure in terms of experimentally available short and intermediate ranged order parameters. Understanding how the atomic and molecular structure of glass influences its macroscopic properties—such as radiation attenuation, mechanical strength, optical transparency, and thermal stability—is the prime focus of present study which is essential for intelligent design of RSW glass compositions. The structural transition has been supported by evaluation of thermodynamic entropy components: configurational (S_{conf}) and vibrational (S_{vib}) entropy components using robust and very efficient two-phase thermodynamic (2PT) model [45, 46]. The results capture the short-to-medium range order of simulated glass using radial distribution function, structure factor, bond angle, Q^n and rings analysis. It is anticipated that the present results would be very beneficial in understanding the structural-property interrelationship of RSW glasses and its probable application in various fields of science and engineering.

2 Simulation methodology

2.1 Molecular dynamics (MD) simulation method

In the present study, lead-silicate glasses—70SiO₂.30PbO, 50SiO₂.50PbO and 36SiO₂.64PbO, corresponding to PbO concentration of 30 mol %, 50 mol % and 64 mol % were simulated to consider high to low silica content. Few of earlier studies have postulated that the role of Pb²⁺ ions may depend on PbO concentration in the glass matrix [29, 34, 37–39]. To confirm that three compositions with PbO content lower, equal and higher than SiO₂ network formers were





The Journal of Obstetrics and Gynecology of India
<https://doi.org/10.1007/s13224-025-02260-z>



CASE REPORT



Minimally Invasive Management of a Cesarean Scar Pregnancy: A Case Report and Review

Shruti Rane¹ · Anurag Bhate² · Fariza Shaikh³

Received: 8 August 2025 / Accepted: 28 September 2025
 © The Author(s) 2025

Abstract

Cesarean scar pregnancy (CSP) is a rare and potentially life-threatening form of ectopic pregnancy in which the gestational sac implants within the fibrous tissue of a previous cesarean section scar. It accounts for less than 1% of all ectopic pregnancies but poses significant risks including uterine rupture and massive haemorrhage if not diagnosed and managed promptly. With increasing cesarean rates worldwide, the incidence of CSP is on the rise, making early recognition crucial. While medical and surgical options exist, laparoscopic management offers a minimally invasive yet effective approach, particularly in hemodynamically stable patients. We present a rare case of cesarean scar ectopic pregnancy successfully managed via laparoscopy, highlighting the diagnostic challenges and surgical nuances involved.

Keywords Ectopic pregnancy · Caesarean scar pregnancy · Laparoscopy · Minimal access surgery · CSP · Obstetrics emergencies

Introduction

Cesarean scar pregnancy (CSP) is a rare and potentially life-threatening form of ectopic pregnancy in which the gestational sac implants within the fibrous tissue of a previous cesarean section scar. It accounts for less than 1% of all ectopic pregnancies but poses significant risks including uterine rupture and massive hemorrhage if not diagnosed and managed promptly. With increasing cesarean rates worldwide, the incidence of CSP is on the rise, making early recognition crucial. While medical and surgical options exist, laparoscopic management offers a minimally invasive yet effective approach, particularly in hemodynamically stable patients. We present a rare case of cesarean scar ectopic pregnancy successfully managed via laparoscopy,

highlighting the diagnostic challenges and surgical nuances involved.

Case Report

A 37-year-old multiparous female with previous 2 LSCS came to outpatient department with complaints of amenorrhea since 3 months, lower abdominal pain and per vaginal spotting since 24 h. On examination mild pallor was present, tachycardia up to 100 beats/min was present, blood pressure was 100/60 mm of Hg. On per abdominal examination tenderness present at hypogastric region. On pervaginal examination uterine size was around 8–10 weeks, bilateral fornices were free and non-tender also minimal spotting was present. Urine pregnancy test was done with was faintly positive. Urgent ultrasonography of pelvis was ordered and routine investigations were sent.

USG was suggestive of live scar ectopic pregnancy of 10 weeks with thick chorionic rim bulging at the serosal surface with considerable amount of blood flow in the trophoblastic rim extending in to serosal surface as shown in Fig. 1. Uterine cavity was empty bilateral adnexa was normal.

Hemoglobin was 7.2. Two packed red cells were transfused and 4 more were reserved. Patient and relatives were explained high risk consent and laparoscopic management

Dr. Shruti Rane is a MS, Obstetric & Gynaecology, Senior Resident, BARC-H; Dr. Anurag Bhate is a MS, DNB Obstetric & Gynaecology; Dr. Fariza Shaikh is a MS, Obstetric & Gynaecology.

✉ Shruti Rane
shrutisrane13@gmail.com

¹ Senior Resident, BARC, Mumbai, India

² Consultant ObGyn & Advanced Laproscopic Surgeon, Bhate's Shubhudeep Nursing Home, Mumbai, India

³ Consultant ObGyn, Jogeshwari Hospital, Mumbai, India

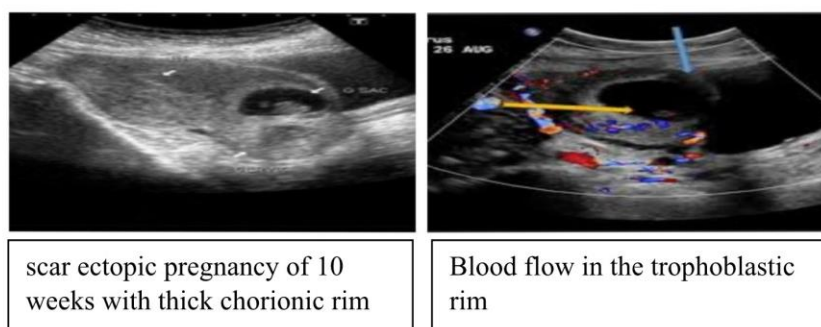
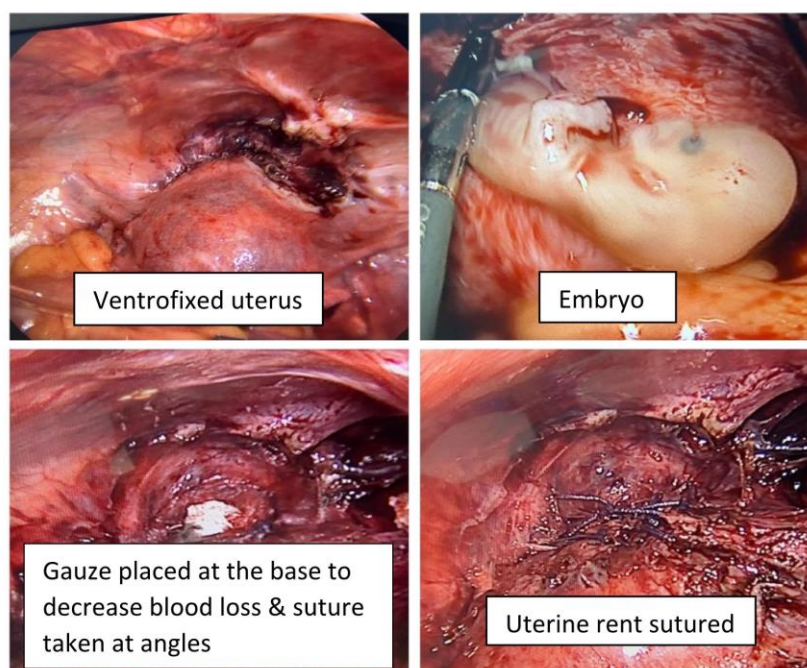


Fig. 1 Ultrasonography images

Fig. 2 Intra-operative pictures



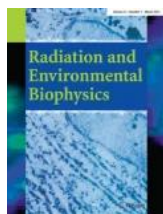
was decided. One central port 10 mm was placed and 3 accessories ports 5 mm were placed.

Intraoperatively uterus was ventro-fixed. Separation of uterus from anterior abdominal wall was done by using lateral window approach. Gestational sac was visible after releasing adhesions. Vasopressin was instilled into uterus and edges of sac to reduce bleeding. On opening the bulging scar inadvertently sac got ruptured and embryo along with other poc were expelled into abdominal cavity. Hemostasis

at scar site was achieved by taking hemostatic sutures at the lateral margin of the scar. Uterine scar was excised and edges were sutured with polyglactin 1-0. Hemostasis was achieved. All the products were removed via lateral port. Figure 2 shows intra-operative pictures. One whole blood was transfused intra-operatively. Estimated blood loss was 700–800 ml.

Postoperatively patient was immediately extubated. Rest of the post-op course was uneventful.





Radiation and Environmental Biophysics (2025) 64:379–389
<https://doi.org/10.1007/s00411-025-01138-y>

RESEARCH



Monte Carlo calculation of correction factors for determining the operational quantity $H_p(10)$ in solid phantoms for ISO narrow series photon sources

Vandana Shrivastava¹ · T. Palani Selvam^{1,2} · S. M. Pradhan^{1,2}

Received: 6 February 2025 / Accepted: 9 July 2025 / Published online: 30 July 2025
 © The Author(s) 2025

Abstract

Although previous studies already reported on backscatter and depth dose correction factors for a Polymethyl-methacrylate (PMMA) phantom to determine the operational quantity $H_p(10)$, more comprehensive evaluations for a wider range of tissue-equivalent phantoms are limited. Besides addressing this gap, the present study also provides phantom scatter correction factors for various phantoms. Correction factors were calculated to determine the $H_p(10)$ in solid phantoms (PMMA, Polystyrene, Solid Water, Plastic Water, Virtual Water, RW3, WE210, and A150) and the International Organisation for Standardisation (ISO)-recommended PMMA-walled water phantom involving detector materials such as air, LiF and $\text{Li}_2\text{B}_4\text{O}_7$ for ISO reference photon beams (N40, N80, N100, N150, N200, N250 x-rays and 662 keV gamma photon). The calculations were performed using the EGSnrc-based Monte Carlo code system. These correction factors include backscatter factor, depth dose factor and phantom scatter, for photon beams with normal incidence on the phantom. The calculated values of the backscatter and depth dose factors are in good agreement with published values for a PMMA phantom. The values of backscatter factor calculated in solid phantoms such as A150, Solid Water, Plastic Water, Virtual Water and WE210 were similar to those calculated in tissue phantom. The phantoms PMMA, Polystyrene and RW3 showed higher backscatter factor values in the energy range N40 - N100 as compared to the tissue phantom. The depth dose factors were comparable in all phantoms except in Polystyrene in which they were higher for N40 photons. The study shows that application of phantom scatter correction is important for phantoms such as PMMA (N40–N250), Polystyrene (N40–N150), RW3 (N40 & N80), Solid Water (N40 & N80), Virtual Water (N40 & N80) and WE210 (N40 & N80). A150, Plastic Water and PMMA-walled water phantoms behave like tissue-equivalent phantoms at all photon energies as the phantom scatter correction was in the range of 0.97–1.02, depending upon energy. This study demonstrates the importance of applying phantom scatter correction factors into the calculation of $H_p(10)$, particularly for low-energy photon beams.

Keywords Operational quantity · Phantom scatter · Monte Carlo · Radiological protection · Occupational monitoring

Introduction

For individual dose monitoring, the International Commission on Radiation Units and Measurements (ICRU) introduced the operational quantities, namely, individual dose equivalents $H_p(d = 10 \text{ mm})$, $H_p(d = 3 \text{ mm})$ and $H_p(d = 0.07 \text{ mm})$, for estimating the dose to the whole body, lens of the eye, and skin, respectively (ICRU 1985; ICRU 1988; ICRU 1992; ICRU 1993). $H_p(d)$ can be measured using a calibrated detector, worn on the body surface and covered with an appropriate thickness of tissue-equivalent material (ICRU 1993). $H_p(d)$ is defined in the ICRU

✉ Vandana Shrivastava
 vanash@barc.gov.in

¹ Radiological Physics & Advisory Division, Health, Safety & Environment Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

² Homi Bhabha National Institute, Anushaktinagar, Mumbai 400 094, India

sphere of 30 cm diameter, made up of ICRU-4-element (Hydrogen, Carbon, Nitrogen, and Oxygen) of unit density (1 g.cm^{-3}) that provides similar attenuation and scattering properties as that of body tissue (ICRU 1980; ICRU 1985). However, due to problems such as phantom fabrication, exact tissue substitutes, and placement of dosimeter, several other phantoms of different dimensions and materials are in use for calibration of dosimeters (ICRU 1992).

Several studies were devoted to calculate or measure backscatter factors which are needed for the determination of $H_p(d)$ (Bartlett et al. 1989, 1990; Grosswendt 1990; Traub et al. 1997).

Bartlett et al. (1989, 1990) calculated backscatter factors for ICRU, PMMA and MS20 phantoms of different shapes (sphere, slab and cube) using the Monte Carlo-based DEIPHOS computer program for mono-energetic photons (15 keV–662 keV) and photons of the ISO Narrow Series (N-series) by scoring kerma (kinetic energy released in matter) in air, tissue, LiF and $\text{Li}_2\text{B}_4\text{O}_7$ materials. Their study showed that for any personnel dosimeter, calibration on a 30 cm diameter spherical MS20 phantom closely mimicked calibration on the ICRU sphere (Bartlett et al. 1989). Traub et al. (1997) calculated backscatter factors for various phantoms such as ICRU, ISO, PMMA, tissue equivalent Plastic RS-1, RS-1/PMMA and PMMA/PTFE (Teflon) for various photon energies and x-ray beams (filtered and fluorescence). These authors showed that the RS-1/PMMA composite phantom is an almost exact match to ICRU tissue.

Will (1989, 1991) and Bartlett et al. (1989) carried out measurements of backscatter and depth dose factors in a PMMA slab phantom having a front face area of 30 cm x 30 cm and a thickness of 15 cm using an ionisation chamber and TLD dosimeters, to determine operational dose quantities. This study involved measurements of air-kerma free-in-air and dose equivalents (at $d=0.007$ and 1 g.cm^{-2}) for differently filtered x-rays and gamma radiation. Additionally, Monte Carlo (MC)-based calculations of $H_p(d)/K_a$ were performed in the above phantom by Grosswendt (1990) for an energy range from 2 keV to 1 MeV.

Regarding the use of appropriate phantoms for the measurement of $H_p(d)$, ICRU Report 47 (ICRU 1992) suggested the use of a $30 \times 30 \times 15 \text{ cm}^3$ PMMA rectangular phantom assuming that the backscatter contribution from PMMA material will be similar to that of tissue. However, studies using this PMMA slab phantom showed that the backscatter contribution is about 9% higher at 50 keV photons as compared to that for ICRU tissue (Kramer et al. 1994). The higher backscattered contribution from the PMMA slab phantom led to the development of the ISO water slab phantom with outer dimensions of $30 \times 30 \times 15 \text{ cm}^3$ with PMMA walls (front wall 2.5 mm thick, other walls 10 mm thick) (Alberts et al. 1994), which was also adapted

by ISO-4037-3 (1999). The second edition of ISO-4037-3 (2019) stated that the calibrations of personal dosimeters and response measurements as a function of radiation energy and direction of radiation incidence should be carried out in the above phantom. As the water slab phantom poses some problems such as bulging of the 2.5 mm PMMA front wall due to water pressure and leakage of water, the use of solid phantoms is advantageous (Traub et al. 1997). Note that the PMMA slab phantom with dimensions of $30 \times 30 \times 15 \text{ cm}^3$ is recommended for reference radiations with a mean energy equal to or above that of ^{137}Cs (662 keV) (ISO 1999, 2019).

Published studies on correction factors for measuring $H_p(10)$ are mostly limited to PMMA phantoms (Kramer et al. 1994; Ginjaume et al. 1996; Traub et al. 1997; Bartlett et al. 1989, 1990; Will 1989, 1991; Grosswendt 1990; Böhm et al. 1999). Note that when a solid phantom is different from the ICRU-4-element tissue, then a phantom scatter correction factor will also be applicable to account for differences in attenuation and scattering of photons between solid and ICRU phantoms. However, this correction is not addressed in the published studies mentioned above.

Consequently, the present study aimed to compute backscatter, depth dose, and phantom scatter correction factors for a range of solid phantoms (e.g., PMMA, Polystyrene, Solid Water, Plastic Water, Virtual Water, A150, RW3 and WE210) and the ISO PMMA-walled water phantom, using EGSnrc Monte Carlo simulations for ISO N40–N250 narrow-series photon beams (Ankerhold 2000; Peaple et al. 1989) and ^{137}Cs gamma radiation. The goal was to improve dosimeter calibration accuracy across different materials. The correction factors calculated are based on kerma scored in detector materials such as air, LiF and $\text{Li}_2\text{B}_4\text{O}_7$. The EGSnrc-based (Kawrakow et al. 2010) MC user-code DOSRZnrc (Rogers et al. 2010) is used in the present work.

Materials and methods

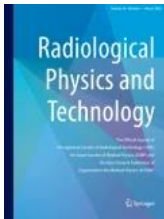
Determination of $H_p(10)$

The methodology described below (Eqs. 1–3) to determine the operational quantity $H_p(d)$ experimentally using a solid phantom is based on work published by Will (1991):

$$\frac{H_p(d)}{K_a} = B_a T_a(d) \left[\frac{\mu_{en}}{\rho} \right]_a^t \quad (1)$$

where B_a is the backscatter factor defined as the ratio of on-axis air-kerma on the surface of the tissue phantom $K_a(0;Q)$ and air-kerma free-in-air $K_a(Q)$, i.e. without phantom, 'a' indicates air and 't' indicates tissue and Q is the beam quality.





Radiological Physics and Technology (2026) 19:125–135
<https://doi.org/10.1007/s12194-025-00986-z>

RESEARCH ARTICLE



Monte Carlo-based dosimetric comparison of indigenous and commercial $^{106}\text{Ru}/^{106}\text{Rh}$ eye plaques using a mathematical eye phantom

Vandana Shrivastava¹ · Arghya Chattaraj¹ · T. Palani Selvam^{1,2} · M. S. Pathan^{1,2} · Rajesh Kumar^{1,2} · B. K. Sapra^{1,2}

Received: 26 August 2025 / Revised: 14 October 2025 / Accepted: 4 November 2025 / Published online: 18 November 2025
 © The Author(s) 2025

Abstract

This study evaluates and compares the dosimetric performance of the Bhabha Atomic Research Centre (BARC) $^{106}\text{Ru}/^{106}\text{Rh}$ eye plaques and a commercially available similar BEBIG CCA eye plaque using Monte Carlo simulations via the FLUKA code. Simulations were performed in both spherical water and mathematical eye phantoms to determine dosimetric parameters such as reference absorbed dose rates, percentage depth doses, off-axis dose profiles, and 2D dose mappings. The on-axis reference absorbed dose rates at 1 mm depth in the mathematical eye phantom was calculated as 10.712 ± 0.003 mGy/min-MBq for the BEBIG CCA plaque and 10.194 ± 0.003 mGy/min-MBq for the BARC plaque, showing close agreement between the two applicators. Off-axis and depth dose distributions confirmed that the BARC plaque delivers comparable dose profiles to the BEBIG plaque, with all critical eye structure doses, including the lens, retina, and cornea, well within established tolerance limits. The similarity in dose distributions between water and mathematical phantoms suggests that water can serve as a practical approximation for dosimetry evaluations. This study demonstrates that the BARC plaque provides dosimetric characteristics comparable to the BEBIG plaque, support its potential use in clinical ophthalmic brachytherapy.

Keywords $^{106}\text{Ru}/^{106}\text{Rh}$ eye plaque · Beta particle · Monte carlo · Eye dosimetry

1 Introduction

In the past, the intraocular cancers, particularly conditions such as malignant melanoma and uvea tumours used to be effectively managed by enucleation (complete removal of eye ball). However, utilization of brachytherapy for the treatment of intraocular cancer has emerged as a favoured approach over the more invasive enucleation procedure [1–3]. Choroidal melanoma predominantly afflicts adults, whereas retinoblastoma is predominantly observed in children. Collaborative Ocular Melanoma Study (COMS)

proved that plaque brachytherapy provides additional advantages of eye and vision preservation along with clinical outcome offered by enucleation [4–7].

The classifications of eye tumours are primarily based on the tumour's thickness and the maximum diameter of its base, following the guidelines outlined in ICRU 72 [3]. Small tumours (T1) are defined by a thickness ranging from 1 to 3 mm and a maximum tumour dimension of the tumour basis up to 10 mm. Medium-sized tumours (T2) exhibit a thickness between 3 and 5 mm, with the greatest tumour dimension of the tumour basis falling within the range of 10–15 mm. In contrast, large-sized tumours (T3) are characterized by a thickness exceeding 5 mm and a maximum tumour dimension of the tumour basis greater than 15 mm [3].

Choice of treatment for these tumours hinges on tumour size, height of the tumour apex, and its precise location [3]. These parameters subsequently guides the selection of an appropriate plaque size and radio-nuclide for brachytherapy treatment [1, 2]. ^{103}Pd and ^{125}I applicators are considered as

✉ Vandana Shrivastava
 vanash@barc.gov.in

¹ Radiological Physics & Advisory Division, Medical Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

² Homi Bhabha National Institute, Anushaktinagar, Mumbai 400 094, India

the most suitable choices for large-sized tumours [2,4–10]. Whereas $^{106}\text{Ru}/^{106}\text{Rh}$ beta applicators are commonly preferred [3, 11, 12] for treatment of melanomas of medium sized tumours due to their physical properties of beta radiation, which exhibits a short range, resulting in a substantial dose drop-off over distance and lower radiation exposure to surrounding healthy tissues.

The dosimetry parameters required for ophthalmic treatment are: (a) absolute dose rate to tissue or water at the surface of the applicator and at a certain reference depth along the central axis of the source perpendicular to the surface; (b) on-axis relative depth dose distribution in tissue or water close to the source; and (c) relative dose distribution as a function of off-axis position from the central axis [13]. According to ICRU report 72[3], the recommended method for specifying the radiation intensity of all therapeutic beta-particle sources is the reference absorbed-dose rate, which refers to the absorbed-dose rate to water at a specified reference point. In the case of beta planar and concave sources, the reference point is located at a distance of 1 mm from the centre of the source surface along the central axis.

A variety of commercial beta applicators—CCA, CCB, CCC, CCD, CCX/Y/Z, CXS, CGD, CIA, and CIB/CIB2 are available for ocular therapy [14]. Determination of dose distributions is challenging because of steep gradients over distance and the dimension of the detector [14]. Dosimetry using physical detector is time-intensive, prone to positioning errors and requires accurate calibration. Two approaches are commonly used for dosimetric calculations[14]: (a) Monte Carlo simulations, which model radiation transport with high accuracy; and (b) analytical point-kernel methods, which provides an estimation of the dose distributions but are less precise.

Several Monte Carlo-based studies on dosimetry of $^{106}\text{Ru}/^{106}\text{Rh}$ plaques are available in the literatures [4, 12, 14–17]. Hermida-López and Brualla[15] used PENELOPE to study the impact of the ^{106}Rh gamma spectrum using different plaque models such as CCA, CCC, CCX, CIA and showed its negligible contribution to eye dose. Barbosa et al. [12] employed MCNPX to calculate doses for CCA and CCB plaques in both AAPM and ABS TG-129 recommended mathematical eye phantom and a water phantom, comparing heterogeneous and homogeneous models. Mostafa et al.[16] used GATE to evaluate dose distributions from planar and concave plaques, highlighting the power of the Monte Carlo technique for precise dose calculations with different shapes of eye applicators. Mowlavi and Yazdani [17] applied MCNP4C to obtain isodose curves and dosimetric data for CCA and CCB plaques in a mathematical eye model.

Recently, Rajesh Kumar et al.[4]carried out dosimetry for indigenously developed round type BARC $^{106}\text{Ru}/^{106}\text{Rh}$

eye plaque.Using radiochromic film and diode detector in a custom phantom, they measured absorbed dose rate to water at various on-axis depths and non-uniformity of the activity distribution.Monte Carlo calculations with egs_brachy (part of EGSnrc Monte Carlo code system) confirmed measured depth-dose data.The measured depth-dose were also compared against manufacturer certificate values for CCA plaques. However, for treatment planning additional data such as off-axis dose distribution as a function of depth and 2D dose mapping at a plane are also required.

The present study addresses this gap area. The objective of this study is to conduct a comprehensive dosimetry in a mathematical eye phantom for BARC $^{106}\text{Ru}/^{106}\text{Rh}$ eye plaque and CCA eye plaque using FLUKA Monte Carlo code [18, 19]. The study includes calculations of absorbed dose rate at depths of 1 and 2 mm, percentage depth dose, off-axis dose profiles and 2D dose mapping. Furthermore, the study also presents doses to critical eye structures, namely, the eye lens, retina, choroid, and cornea. These dose data calculated for BARC eye plaque are compared with the corresponding data of CCA eye plaque.

2 Materials and methods

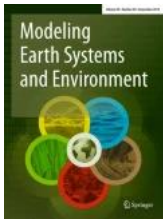
2.1 $^{106}\text{Ru}/^{106}\text{Rh}$ radionuclide

The ruthenium ophthalmic applicator contains radionuclide ^{106}Ru which is a pure β emitter with maximum energy of 39.4 keV and mean energy of 10 keV. Its half-life is 368.2 days and it disintegrates to ^{106}Pd via ^{106}Rh . The daughter ^{106}Rh is also a beta source having maximum and mean energies as 3.54 MeV and 1.412 MeV, respectively, providing the effective therapeutic irradiation [20, 21]. It is also emitting 0.34 photons per beta disintegration. The mean energy of gamma radiation is 0.600 MeV, where the greatest yield belongs to 0.512, 0.622, and 1.05 MeV transitions [20, 21]. The half-life of ^{106}Rh is 29.9 s. The combined beta spectrum of ^{106}Ru and ^{106}Rh is utilised in the simulations [21].

2.2 Description of $^{106}\text{Ru}/^{106}\text{Rh}$ ophthalmic applicators

This study incorporates two $^{106}\text{Ru}/^{106}\text{Rh}$ ophthalmic applicators, namely: CCA concave, manufactured by Eckert & Ziegler BEBIG GmbH and BARC eye plaque. CCA BEBIG model is a truncated spherical shell structure with 12.0 mm inner radius of the shell, along the symmetry axis. The outer and active diameters are 15.3 mm and 13 mm, respectively [4, 12, 22]. It is made of 3 layers with total thickness of 1.0 mm. These layers are made of silver having thicknesses of 0.1, 0.2 and 0.7 mm for front, middle and back layers,





Modeling Earth Systems and Environment (2025) 11:383
<https://doi.org/10.1007/s40808-025-02566-x>

ORIGINAL ARTICLE



Numerical hydrodynamic modeling of free surface flow by solving shallow water equations

Manish Chopra¹ · R. B. Oza¹

Received: 10 February 2025 / Accepted: 16 July 2025 / Published online: 13 August 2025
 © The Author(s) 2025

Abstract

A numerical model for solving the conservative form of the two-dimensional shallow water equations (SWEs) has been developed to simulate the hydrodynamics of surface water bodies and the flooding of adjacent land during extreme hydrological events. The solution is obtained using an Arakawa C-grid structure and an explicit finite difference technique with up-winding for advective terms. The model is verified by comparing its results with reported analytical and numerical solutions for standard one-dimensional and two-dimensional flow problems. It is demonstrated that the developed model accurately simulates surface water hydrodynamics for various scenarios involving hydrodynamic changes with varying shock strengths. The developed algorithm is shown to be superior to the Lax-Friedrichs and Lax-Wendroff schemes in terms of accuracy and stability. Moreover, the conservative form of the SWE is found to be better than the non-conservative form in handling discontinuities and sudden hydrodynamic changes.

Keywords SWEs · Hydrodynamics · Conservative and non-conservative forms · Numerical model · Finite difference · Explicit scheme

Introduction

Water bodies are regarded as shallow when their horizontal extent is much greater than their vertical extent, examples being estuaries, coastal seas, and inland flows. The Navier–Stokes equations are often utilized to fully describe flow dynamics. The Saint–Venant equations, commonly referred to as the SWEs, are one of the approximations of the Navier–Stokes equations for addressing large-scale overland flow problems and shallow water hydrodynamics (Safarzadeh Maleki 2014; Saint–Venant 1871). Considering that the horizontal length scale is much greater than the vertical length scale, the SWEs are derived by depth-integrating the Navier–Stokes equations. SWEs provide the spatial and temporal variation of horizontal velocities and surface water elevation. Two-dimensional (2D) SWEs have numerous applications in ocean and hydraulic engineering.

The most common applications include analyzing dam failures, storm water intrusion into open water channels, surface runoff, storm surges due to cyclones, tsunami propagation, overland flow, and estimating flow fields for impact assessment applications related to pollutant and thermal discharges (Alcrudo and Gil 1999; Zoppou and Roberts 1999; Synolakis et al. 2005). Storm surge, overland flood, and tsunami modeling studies are particularly important during the siting stage for any industry, especially for nuclear facilities located near surface water bodies.

Routine or accidental industrial discharges into surface water bodies may degrade water quality through contamination or by altering physical conditions such as temperature. Normally, contamination levels are too low to be measurable by standard instruments (Reichelt-Brushett 2023). To ensure and demonstrate that the environmental impact remains within regulatory guidelines, numerical modeling is a useful tool (Okpala and Yorkor 2013). Moreover, before a facility is constructed, its impact assessment can only be conducted by simulating different scenarios using numerical modeling. Knowledge of the flow field is a prerequisite for simulating the fate of pollutants or temperature distributions in the concerned water body. SWEs can be used to model the flow field for surface water bodies, which can then be

✉ Manish Chopra
 mchopra@barc.gov.in

R. B. Oza
 rboza@barc.gov.in

¹ Radiation Safety Systems Division, Bhabha Atomic Research Centre, Mumbai 400094, India

incorporated into transport models to assess the impact of such discharges.

The multi-dimensional importance of SWEs has fascinated the scientific and engineering community, leading to the development and utilization of various techniques to solve these equations. Numerous computational methods have been developed for SWEs, such as finite difference methods, finite volume methods, finite element methods, Godunov-type methods, and the lattice Boltzmann method (Versteeg and Malalasekera 1995). For instance, Xing and Shu (2005) developed an algorithm based on high-order finite difference WENO schemes that could preserve the steady-state solutions of SWEs with high accuracy. Gavete et al. (2007) developed a pseudo-spectral/finite difference adaptive method to solve spherical SWEs with high-order accuracy. Bates et al. (2010) proposed a simple inertial formulation that was shown to be computationally efficient for solving SWEs in flood inundation modeling applications. Lu and Qiu (2011) employed the Lax-Wendroff time discretization scheme within finite difference weighted non-oscillatory schemes to model 1D and 2D SWEs, including source terms. They reported that this scheme was non-oscillatory and computationally more efficient than the Runge–Kutta scheme. Crowhurst and Li (2013) demonstrated that finite difference methods can be used to solve SWEs, and that further improvements in results can be achieved through mesh refinement or optimization driven by a target error value. Namio et al. (2015) simulated the maximum water depths and discharge at specific locations under particular meteorological conditions. They employed the Lax-Wendroff scheme for solving nonlinear partial differential equations, i.e., SWEs, and carried out stability analysis, concluding that the results had positive implications. Li and Fan (2017) used a meshless scheme to solve SWEs. Their approach combined the split-coefficient matrix method, the second-order Runge–Kutta method, and the generalized finite difference method, achieving excellent results with reduced computational effort due to the absence of mesh generation. Huda and Pierre (2018) developed a new technique based on explicit centered finite difference and Leap-Frog schemes with a Robert-Asselin filter for solving 2D SWEs. They demonstrated the effectiveness of their technique by comparing the results of tsunami simulations with corresponding analytical solutions. Erwina et al. (2020) developed a staggered conservative scheme for solving 2D SWEs and demonstrated its appropriateness for varying shallow water flow scenarios through several test problems. Lundgren and Mattsson (2020) proposed a high-order explicit finite difference scheme for solving SWEs, achieving smooth yet robust solutions using their developed algorithm. Li et al. (2021) proposed a generalized finite difference method coupled with a flux limiter technique, which efficiently eliminated numerical oscillations. Riestiana et al. (2021) employed a finite difference method based on the Lax-Friedrichs scheme for simulating tsunami wave heights using 1D SWEs. Rajput et al. (2023) developed a solution for

2D SWEs with constant external body forces by employing the Crank-Nicolson method, enabling accurate prediction of the temporal and spatial profiles of water elevation and velocity. Rahou and Korichi (2023) provided a detailed comparative analysis of meshless Smoothed Particle Hydrodynamics (SPH) and mesh-based Finite Volume Methods (FVM) for 2D unsteady free surface flows. A good correlation with measurements and analytical estimates was observed in both cases; however, FVM was concluded to be superior in terms of accuracy and computational efficiency. The same group further evaluated the performance of the SPH method by conducting a parametric analysis of dam-break problems (Taibi et al. 2024).

Different numerical schemes have been evaluated with respect to their accuracy, precision, stability, and computational efficiency to identify the most suitable one for a particular problem. For instance, Saiduzzaman and Ray (2013) compared the capabilities of three numerical schemes—namely, the Lax-Friedrichs scheme, the Leap-Frog scheme, and the Lax-Wendroff scheme—for solving 1D SWEs. They concluded that the Lax-Wendroff scheme is more efficient than the Lax-Friedrichs and Leap-Frog schemes. Lu and Qiu (2017) compared the results of simulating 1D and 2D SWEs with source terms using high-resolution finite difference WENO schemes and two different time discretization methods, i.e., Lax-Wendroff (LW) and Runge–Kutta (RK). Their numerical findings demonstrated that the WENO5-LW methods are computationally more efficient for the same accuracy than those using WENO5-RK, and that LW could correctly model current flow and capture stronger discontinuities in water waves. Rahaman and Andallah (2018) used both Lax-Wendroff and Lax-Friedrichs schemes for solving SWEs. They observed that water height drops in the upstream direction and rises in the downstream direction for both the Lax-Friedrichs and Lax-Wendroff methods compared to the exact solution. Moreover, water velocity increases across both boundaries for both schemes. Very recently, Rajput et al. (2024) compared a forward time-centered scheme and the Lax-Wendroff method for solving extended 2D SWEs, including porosity and frictional resistance parameters. They concluded that the Lax-Wendroff method performs better in terms of accuracy and stability between the two.

Although a significant amount of literature is available on the numerical solution of SWEs, there is always scope for proposing or testing alternative numerical approaches to achieve better outcomes. Hence, the major objectives of the present work are: (1) to develop a numerical model that can solve the conservative form of the two-dimensional shallow water equations governing free surface fluid flow; (2) to compare the applicability of the conservative and non-conservative forms of SWEs for simulating flows with shocks; and (3) to compare the developed algorithm with other numerical algorithms reported in the literature for solving SWEs to assess the capability of the developed model. To achieve these objectives,




<https://doi.org/10.1038/s41699-025-00618-5>

Oxidative transformation of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene on gamma radiation exposure in aqueous media



Pragati Patil^{1,2}, Arijit Ghoshal^{1,2}, Nitin Gumber^{1,3}, Raj Kumar Mondal^{1,2}, Kedarnath Gotluru^{1,4}, Kumar Abhinav Dubey^{1,2} ✉ & Y. K. Bhardwaj^{1,2}

MXenes are promising for applications from energy storage to environmental remediation, yet their stability under ionizing radiation is largely unexplored. This study elucidates the fundamental mechanisms governing the radiation-induced transformation of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene through comprehensive spectroscopic, structural, and functional analysis. We demonstrate that radiation initiates a systematic oxidative transformation of the metallic MXene into semiconducting TiO_2 nanostructures. This process, driven by surface oxidation and Ti-C bond cleavage, is confirmed by the disappearance of MXene's characteristic plasmonic absorbance at 790 nm and the emergence of TiO_2 features. The degradation kinetics exhibit remarkable atmospheric dependency, accelerating significantly in oxygen-rich environment due to radiation-generated reactive oxygen species. This transformation severely deteriorate MXene's functional properties, causing a loss of electrical conductivity and a dramatic drop in methylene blue adsorption capacity from 87 to 31% at a 250 kGy dose. These findings establish a mechanistic framework for predicting MXene stability in radiation-intensive environments, providing essential guidelines for their implementation in radiation-intensive applications spanning environmental remediation, energy conversion, and space technologies.

Two-dimensional (2D) materials have emerged as a transformative class of nanomaterials characterized by their atomic or molecular thickness and lateral dimensions extending into the micron scale^{1,2}. Following the remarkable success of graphene, the 2D materials landscape has expanded significantly to encompass transition metal dichalcogenides (TMDs), hexagonal boron nitride, layered double hydroxides, and most recently, MXenes. This structural dimensionality confers exceptional surface-to-volume ratios and quantum confinement effects that manifest as unique electronic, optical, mechanical, and chemical properties distinct from their bulk counterparts.

MXenes represent an extensive family of 2D transition metal carbides, nitrides, and carbonitrides with the general formula $\text{M}_{n+1}\text{X}_n\text{T}_x$, where M denotes early transition metals (Ti, V, Nb, etc.), X represents carbon or nitrogen, and T_x signifies surface terminal groups ($-\text{OH}$, $-\text{O}$, and $-\text{F}$)^{3,4}. These materials are typically synthesized through selective etching of the A-layer (usually Al or Ga) from the corresponding MAX phases, generating 2D layers terminated with a mixture of functional groups. Among several MXenes synthesized to date, $\text{Ti}_3\text{C}_2\text{T}_x$ remains the most extensively studied

due to its excellent electrical conductivity, mechanical robustness, hydrophilicity, and versatile surface chemistry^{5,6}.

The exceptional properties of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene have catalyzed its integration into diverse technological domains including energy storage, electromagnetic interference (EMI) shielding, catalysis, sensing, and environmental remediation^{7–9}. Particularly in the context of water purification and environmental applications, MXenes demonstrate remarkable adsorption capacities toward various contaminants including heavy metal ions and organic dyes, attributed to their high specific surface area, abundant active sites, and tunable surface chemistry^{10–13}. The strong interactions between the delocalized π electrons in MXene sheets and the aromatic structures of organic dyes enable efficient adsorption through π - π stacking and electrostatic interactions¹⁴.

Despite these promising attributes, the practical implementation of MXene-based technologies is contingent upon understanding their long-term stability under diverse operational conditions^{15,16}. A critical yet underexplored aspect concerns the stability of MXenes when exposed to ionizing radiation, which represents a significant consideration for

¹Homi Bhabha National Institute, Mumbai, India. ²Radiation Technology Development Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India. ³Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India. ⁴Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India. ✉ e-mail: abhinav@barc.gov.in

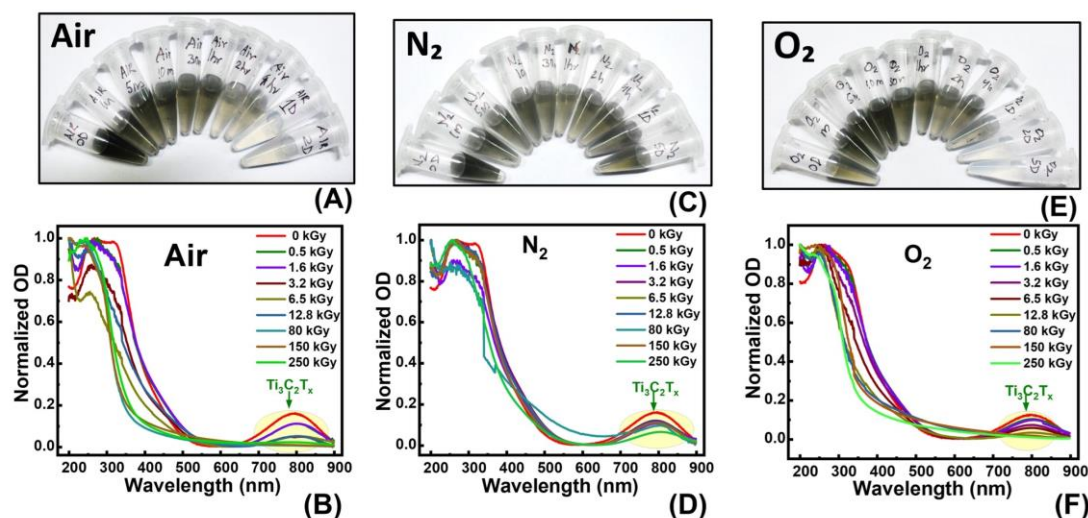


Fig. 1 | Atmosphere-dependent transformation of $\text{Ti}_3\text{C}_2\text{Tx}$ MXene on gamma irradiation. A, C, E Photograph series showing progressive color changes in air, N_2 , and O_2 atmospheres, respectively. B, D, F Corresponding UV-Vis absorption

spectra revealing differential conversion of MXene (absorption ~ 790 nm) to TiO_2 (absorption ~ 250 nm), with transformation rates following the order $\text{O}_2 > \text{air} > \text{N}_2$.

applications in nuclear environments, space technology, radiation therapy, and sterilization processes. Previous investigations have documented the susceptibility of various 2D materials to radiation-induced structural modifications; graphene exhibits defect formation and functionalization under gamma irradiation, while TMDs demonstrate phase transformations and chemical state alterations upon exposure to high-energy particles.

The behavior of MXenes under radiation remains relatively unexplored territory, with limited studies suggesting potential structural transformations¹⁷. These initial investigations indicate that radiation exposure may induce radiolytic processes that convert MXenes into their respective derivatives—a transformation pathway with profound implications for their functional properties. However, systematic investigations correlating radiation parameters (dose, ambiance) with structural evolution and consequent functional property modifications remain conspicuously absent from the scientific literature. The ambiance dependence of radiation-induced changes presents an intriguing dimension, as reactive oxygen species (ROS) generated during water radiolysis may accelerate oxidative degradation pathways. This environmental sensitivity introduces both challenges and opportunities: while potentially limiting MXene application in oxygen-rich irradiated environments, it simultaneously suggests avenues for controlled transformation into MXene/metal oxide composites with tailored properties through radiation processing¹⁸.

In this study, radiation-induced changes in $\text{Ti}_3\text{C}_2\text{Tx}$ MXene under gamma irradiation across a wide dose range (0.1–250 kGy) under different ambiance is reported. We elucidate the underlying mechanisms of structural reorganization through complementary spectroscopic, diffraction, and microscopic techniques, establishing direct correlations between radiation parameters and progressive phase transformation. Furthermore, the impact of these structural modifications on electrical conductivity and methylene blue adsorption capacity—functional properties central to MXene application in environmental pollution remediation—systematically evaluated. Additionally, findings reveal potential for radiation-induced engineering of MXene-derived composites with programmable functionality, expanding the technological landscape for these versatile 2D materials in radiation-intensive environments.

Results

Radiation-induced optical property changes in $\text{Ti}_3\text{C}_2\text{Tx}$ MXene

The spectroscopic signatures of $\text{Ti}_3\text{C}_2\text{Tx}$ MXene on gamma irradiation revealed distinct changes that are critically influenced by the ambiance during irradiation (Fig. 1). Pristine $\text{Ti}_3\text{C}_2\text{Tx}$ aqueous dispersions exhibit characteristic absorbance maxima at 320 nm and 790 nm, corresponding to the plasmonic response of delocalized electrons within the 2D titanium carbide structure¹⁹. These distinctive optical features stem from the material's intrinsic metallic conductivity and the presence of surface functional groups that modulate electron distribution across the 2D lattice²⁰.

Upon progressive gamma irradiation in air (Fig. 1A, B), systematic spectral evolution characterized by rapid attenuation of the 790 nm plasmonic signature following exponential decay kinetics was observed. This diminution coincides with the emergence of a pronounced absorbance feature at ~ 250 nm, characteristic of titanium dioxide nanostructure formation. Quantitative analysis reveals a critical radiation threshold of 3.5 kGy that marks a significant transition point in the material's electronic structure, beyond which the 790 nm plasmonic feature undergoes substantial degradation.

The transformation pathways exhibit remarkable ambiance dependence, as evidenced by comparative irradiation experiments under controlled nitrogen and oxygen environments (Fig. 1A–F). Under nitrogen atmosphere (Fig. 1C, D), spectral evolution proceeds with substantially reduced kinetics, preserving the characteristic MXene plasmonic features at higher cumulative doses. In stark contrast, oxygen-rich conditions (Fig. 1E, F) significantly accelerate the conversion process, with complete plasmonic signature loss occurring at significantly lower doses. This pronounced environmental sensitivity indicates that radiation-induced ROS serve as primary mediators in the oxidative transformation of $\text{Ti}_3\text{C}_2\text{Tx}$ basal planes and terminal functional groups. These findings demonstrate that the radiation-induced transformation of $\text{Ti}_3\text{C}_2\text{Tx}$ MXene follows distinct, ambiance-dependent pathways that can be selectively accessed through precise control of irradiation conditions. In aqueous, oxygen-rich environments, radiolytically-generated oxidative species drive progressive conversion to titanium dioxide nanostructures, while reducing conditions promote the formation of TiC/MXene nanocomposites with enhanced functional properties. The pronounced environmental sensitivity of MXene transformation pathways underscores the importance of atmospheric





Current Microbiology (2025) 82:557
<https://doi.org/10.1007/s00284-025-04541-2>



Phenotypic Characterization of Null Mutants of $\Delta cbpA$ and $\Delta cbpB$ in *S. enterica* Serovar Typhimurium

Indu Pant¹ · Shashidhar Ravindranath^{1,2}

Received: 21 March 2025 / Accepted: 27 September 2025 / Published online: 14 October 2025
 © The Author(s) 2025

Abstract

The phenotypic characteristics of the $\Delta cbpA$ and $\Delta cbpB$ mutants of *Salmonella enterica* serovar Typhimurium were comprehensively analyzed to elucidate the roles of these nucleoid-associated proteins in metabolism and stress responses. Both $\Delta cbpA$ and $\Delta cbpB$ mutants exhibited enhanced growth on carbon sources such as ribose, mannose, fructose, glycerol, galactose and sucrose compared to the wild-type strain. Conversely, the wild-type strain demonstrated superior growth on xylose. Notably, the $\Delta cbpB$ mutant experienced a prolonged lag phase of ~20 h when cultured in M9 medium supplemented with maltose. In M9 medium where alanine or arginine served as the sole nitrogen source, both mutants outperformed the wild-type strain in growth, indicating potential alterations in nitrogen metabolism pathways. The $\Delta cbpA$ and $\Delta cbpB$ mutants were non-motile and exhibited reduced cell sizes compared to the wild-type. Specifically, the $\Delta cbpA$ mutant was approximately 0.8 times smaller than the size of the wild-type, while the $\Delta cbpB$ mutant was about 1.3 times smaller. The D_{10} value, representing the radiation dose required to reduce the bacterial population by 90%, was 113 Gy for the wild-type, 140 Gy for $\Delta cbpA$ and 104 Gy for $\Delta cbpB$, suggesting differential radiation sensitivities among the strains. Upon heat exposure, the $\Delta cbpA$ mutant exhibited a fivefold reduction in viable cell number compared to the wild-type and $\Delta cbpB$, indicating increased heat sensitivity. No significant differences were observed among the strains in response to oxidative stress induced by hydrogen peroxide. After 72 h in 15% salt conditions, the wild-type strain showed a fivefold reduction in cell numbers, whereas both mutants exhibited only a fourfold reduction, suggesting enhanced salt tolerance. These findings underscore the pivotal roles of CbpA and CbpB proteins in regulating metabolic pathways and mediating stress responses in *S. Typhimurium*.

Introduction

Nucleoid-associated proteins (NAPs) are DNA-binding proteins that were initially overlooked in terms of their role in maintaining bacterial physiology. Traditionally, they were recognized primarily for their function in the structural organization of genetic material, while their involvement in modulating bacterial physiology and metabolism remained underappreciated [1]. The inability to initially understand the role of NAPs in bacterial physiology stemmed from their non-specific interactions with DNA. However, it is now evident that NAPs significantly influence cellular physiology by mediating genome compaction and relaxation [2, 3].

NAPs regulate critical cellular processes such as transcription, translation and replication which are vital for bacterial survival during periods of nutrient fluctuation commonly encountered in natural environments [4].

The CbpA protein was first discovered in *E. coli* [5]. This protein was associated with AT rich region; which introduces curves in the DNA [5]. CbpA exhibits DNA-binding affinity comparable to other nucleoid-associated proteins such as H-NS and HU. Its abundance has been observed to increase in nutrient-starved cells [6]. It reaches around 15,000 molecules per cells after two days of starvation [7]. But no function has been assigned to this protein in starved cells. The activity of CbpA protein is repressed by Fis protein in the rapidly growing culture. The CbpA protein is analogue of DnaJ protein. CbpM is another protein which helps CbpA protein in its DNA-binding and co-chaperone activities [8].

Similarly, right origin binding protein (Rob) or Curve DNA-binding protein B (CbpB) is another nucleoid-associated protein, which was identified after a random screening

✉ Shashidhar Ravindranath
 shashi@barc.gov.in

¹ Food Technology Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India

² Life Sciences, Homi Bhabha National Institute (DAE-Deemed University), Trombay, Mumbai 400094, India

of curved DNA-binding proteins from *E. coli* [9]. The expression of Rob protein enhances at the onset of stationary phase in Luria broth and phosphate starvation medium [9]. This protein shares 50% similarity in amino acid sequences to *soxs* and *mar* genes which have a role in oxidative and multiple antibiotic resistance operon. But apart from this, no other function has been assigned to this protein.

Among the DNA-binding proteins in *E. coli*, CbpA and Rob remain among the least studied, and their roles in stress responses and metabolic regulation are not well understood. Therefore, this study focuses on investigating the functions of CbpA and Rob in regulating cellular physiology in *S. Typhimurium*.

Materials and Methods

Bacterial Strains, Reagents and Growth Conditions

The Knockout strain of DNA-binding proteins (CbpA and CbpB) was constructed in wild-type strain of *Salmonella enterica* subsp. *enterica* serovar Typhimurium strain LT2 (MTCC 98). Luria broth and M9 medium (HiMedia, India) were used for all the growth-related experiments. The growth curves were performed at 37 °C at 150 rpm. LB agar plates supplemented with kanamycin (50 µg/mL) or carbenicillin (100 µg/mL) (HiMedia, India) were used as per requirement. All the reagents were autoclaved or filter sterilized before use.

Generation of Gene Knockout and Complemented Strains for the $\Delta cbpA$ and $\Delta cbpB$ mutants

The construction of $\Delta cbpA$ and $\Delta cbpB$ gene knockouts in *Salmonella enterica* serovar Typhimurium was accomplished using the Quick & Easy *E. coli* Gene Deletion Kit by Red®/ET® Recombination (Gene Bridges, Heidelberg, Germany) as described previously [10, 11]. The homology arms, each 50 base pairs long and matching the sequences adjacent to the chromosomal insertion site, are added to the functional cassette via PCR. The sequence for the functional cassette are provided in the kit [Red®/ET® Recombination, Gene Bridges (Heidelberg, Germany)] and primer sequence used are detailed in the Supplementary table (Table 1S). Then simultaneously, the *Salmonella enterica* serovar Typhimurium strain selected for null mutants creation is transformed with the pRedET expression plasmid and selected on ampicillin (100 µg/mL) containing plates and incubated at 30 °C. The *S. Typhimurium* transformed with pRedET was then used for further experiments. It was allowed to grow at 30 °C in Luria broth (LB) till it reaches an OD of 0.4. To induce expression of the Red/ET recombination genes, L-arabinose was added to a final concentration of 0.3%, and the culture

was incubated at 37 °C for 45 min to 1 h. Post-induction, cells were washed three times with ice-cold water to prepare electrocompetent cells. The purified PCR product containing the homology arms was electroporated into these cells using a voltage of 2500 V for 6 ms. To enhance transformation efficiency, the electroporation pulse was administered twice, as suggested by the kit protocol. Following electroporation, cells were immediately supplemented with fresh LB broth and incubated at 37 °C for 3 h to facilitate recombination. Subsequently, cells were centrifuged and plated on LB agar containing kanamycin (50 µg/mL). Only those colonies in which the target gene had been successfully replaced by the FRT-PGK-*gb2*-neo-FRT cassette grew on the kanamycin-containing plates.

To ensure that the kanamycin cassette is not causing any change in the phenotype of the cell, the *pcp20* vector was used for the removal of kanamycin cassette from the genome of knockouts following the method described previously [12]. The knockouts were confirmed using PCR-based methods and sequencing.

The *cbpA* and *cbpB* genes in *Salmonella enterica* serovar Typhimurium were complemented using pBAD TOPO and Pet-28a plasmid (Invitrogen, Massachusetts, USA) respectively. A 300 bp (gene coordinate; 4,842,684–4,843,870) upstream region of the *cbpB* gene, encompassing its native promoter, was amplified and cloned alongside the *cbpB* coding sequence and cloned into the pBAD TOPO vector in our laboratory. This recombinant plasmid was then transformed into the $\Delta cbpB$ mutant strain.

Similarly, a 500 bp (gene coordinate; 1,198,987–1,200,499); upstream region of the *cbpA* gene, containing its native promoter, was cloned upstream of the *cbpA* coding sequence. The resulting construct was introduced into the $\Delta cbpA$ mutant strain. Transformants were selected on LB agar plates supplemented with ampicillin (100 µg/mL). The complemented strains are referred to as *cbpA** and *cbpB** in the subsequent sections. Utilizing native promoters facilitated constitutive expression of the respective genes in the complemented strains. The complemented strain were confirmed by real-time PCR and restoration of phenotypes in both $\Delta cbpA$ and $\Delta cbpB$ mutants.

Phenotypic Characterization Using SEM

Fresh cultures of wild-type *S. Typhimurium*, $\Delta cbpA$ and $\Delta cbpB$ mutants were streaked onto LB agar plates. A single colony from each strain was then mounted onto an aluminum stub using double-sided carbon tape and examined under a scanning electron microscope (SEM) at various magnifications. Imaging was performed in variable pressure mode at 65 Pa and 20 kV. The SEM analysis was conducted using a Quanta 200 SEM (FEI Company, Hillsboro, OR, USA) at the facilities of Icon Analytical Equipment Pvt. Ltd., Mumbai,





BioNanoScience (2025) 15:469

<https://doi.org/10.1007/s12668-025-02090-3>

RESEARCH



Plant Gum Synthesized Phytogetic Silver and Palladium Nanoparticles Towards Decolourization of Rhodamine B and Methylene Blue Dyes

Aruna Jyothi Kora^{1,2}

Accepted: 10 July 2025 / Published online: 26 July 2025

© The Author(s) 2025

Abstract

Nanoparticles have gathered significant attention in current years for their versatile applications, including their use as catalysts for dye decolourization. Rhodamine B (RB) and methylene blue (MB) are common dyes employed in pulp, paper, textile, paint, pharma and other industries and their decolourization is essential to prevent environmental pollution. In this context, silver nanoparticles (Ag NP) of 5 nm and palladium nanoparticles (Pd NP) of 7 nm size were produced utilizing plant gum kondagogu as a reducing and stabilizing agent by pressure cooker autoclaving at optimal conditions. The synthesized NP were utilized as catalysts for the decolourization of RB and MB with sodium borohydride. The effect of varying concentration levels of Ag NP (0.5–5 µg/mL), Pd NP (0.025–0.3 µg/mL) and RB (2.5–7.5 µg/mL) and MB (5–15 µg/mL); and reaction time (1–8/0.25–2 min) was investigated at ambient conditions. Ag NP and Pd NP showed corresponding rate constant (*k*) values of 0.189 min⁻¹ and 0.367 min⁻¹; and 0.111 min⁻¹ and 0.304 min⁻¹ towards RB and MB, receptively. Efficient catalytic action is attributed to smaller particle size and exceptional stability of NP. Thus, the decolourization capability of NP can have wide functions in the ecofriendly ecological remediation of diverse wastewaters contaminated with noxious, mutagenic, carcinogenic, dangerous dyes and pigments.

Keywords Dye decolourization · Nanoparticles · Palladium · Plant gum · Silver · Catalyst

1 Introduction

Various manufacturing industries such as pulp, paper, paint, printing, rubber, textile, plastic, leather, concrete, cosmetic, food, pharma, aqua culture, medical etc. employ vast quantities of synthetic dyes for multiple applications because of their availability, low price, ease of bulk commercial production, wide colour choices, higher efficiency etc. [1, 2]. These industries mandate large volumes of water use at different steps and generate enormous quantities of effluents contaminated with dyes [3, 4]. For instance, Rhodamine B (RB) is a cationic, basic, water soluble, fluorescent dye from the xanthenes class. It is extensively employed as a fluorochrome,

biomarker, fluorescent tracer, histological stain, florescent probe, mitochondrial inhibitor, metal analytical aid, industrial colourant etc. [4, 6, 7]. The ecotoxicity studies indicated its toxicity towards various aquatic species [8]. Exposure to this xenobiotic, carcinogenic dye causes cell and tissue oxidative stress; eye and skin irritation; hypersensitive dermatitis, liver dysfunction, kidney failure, respiratory diseases, ovarian toxicity etc. in humans [7, 9]. The utilization of rhodamine B as a food adulterant for colour enhancement raises concern in India [10, 11]. It is not listed in the permitted food colourants and its use is prohibited by the Food Safety and Standards Authority of India (FSSAI) [12].

Methylene blue (MB) is a heterocyclic, aromatic, cationic, basic, water soluble thiazine dye classified under polymethine group [3, 4, 13]. It is finding its uses in vast areas such as anti methaemoglobinaemia agent, antimalarial agent, photodynamic and photosensitizing agent, biological, histological and live dead bacterial microscopic stain; visual diagnostic staining agent and tracer, industrial colouring agent, peroxide generator, analytical quantification aid, redox colouring indicator, antiseptic and disinfectant in aquaculture, data storage, holographic media in

✉ Aruna Jyothi Kora
koramaganti@gmail.com; koraaj@barc.gov.in;
ajkora@hbni.ac.in

¹ National Centre for Compositional Characterisation of Materials (NCCCM), Bhabha Atomic Research Centre (BARC), ECIL PO, Hyderabad 500 062, India

² Homi Bhabha National Institute (HBNI), Anushakti Nagar, Mumbai 400 094, India

electronics etc. [1, 2, 13, 14]. However, MB is mutagenic, teratogenic, carcinogenic, toxic and non biodegradable [2–4] and toxic to various aquatic species [2]. Elevated doses of MB cause hypertension, skin and eye irritation; blindness, respiratory distress, nausea, diarrhoea, vomiting, gastritis, jaundice, anemia, reduced cardiac output, renal blood flow etc. in humans [1, 3].

The presence of dyes in waters increases biological and chemical oxygen demand; drastically reduces sunlight penetration and decreases the photosynthesis of aquatic flora leads to reduced dissolved oxygen, reduced biodiversity and ecological imbalance in the native aquatic ecosystems [1–3]. As the dyes are persistent, it may lead to bioaccumulation and biomagnification [2]. Being a peril to aquatic organisms, the aesthetics of the water bodies are also affected making them unsuitable for human usage [3]. Many countries imposed a ban on the use of the dyes such as rhodamine B, malachite green, methylene blue [2, 3] in food, cosmetics and other consumer products. The regulatory bodies such as pollution control boards and the Food and Drug Administration (FDA), USA established guidelines for detection and prescribed maximum residue limits for the discharge of dye containing effluents into the water bodies [2].

This in turn demands the development of protocols for decolourization and removal of synthetic, toxic, persistent dyes from industrial effluents and their safer discharge into aquatic bodies [4]. Traditionally different methods such as evaporation, adsorption, biosorption, sedimentation, flocculation, sonication, precipitation, membrane filtration, ion exchange, ozonation, Fenton's oxidation, photocatalysis, irradiation, bioremediation etc. are used for wastewater effluent decolourization. However, they are not efficient due to complex molecular structure, thermal, light, microbial degradation resistance of dyes; limitations such as adsorbent regeneration and disposal; sludge formation, membrane fouling, tedious process, sophisticated facilities, high power consumption, high process cost, scale up issues etc. [1, 3, 4]. The selection of decolourization method depends upon various factors such as composition of effluent, industrial suitability, ease of process, economy, energy utilization, efficiency, environmental sustainability etc. [5].

In the current study, the dual functional role of gum kondagogu was utilized for the phytogetic green production of silver and palladium nanoparticles at optimal conditions employing a domestic pressure cooker as a hydrothermal vessel. The fabricated nanoparticles were studied with UV–visible absorption spectroscopy, X-ray diffraction, scanning electron microscopy coupled to energy dispersive X-ray spectroscopy, transmission electron microscopy and zetasizer. The catalytic activity of the produced nanoparticles was utilized towards borohydride reduction of model synthetic dyes, rhodamine B and methylene blue.

2 Experimental Section

2.1 Materials

Gum kondagogu (Telangana State Girijan Cooperative Corporation, Hyderabad, India), silver nitrate (AgNO_3) (Merck, Mumbai, India), palladium chloride (PdCl_2), sodium borohydride (NaBH_4) (Sigma-Aldrich, Bengaluru, India), rhodamine B (RB) (SD Fine, Mumbai, India), methylene blue (MB) (Qualigens, Pune, India) and ultrapure water (Elga, High Wycombe, England) were used.

2.2 Synthesis and Characterization of Nanoparticles

The silver nanoparticles (Ag NP) were produced at optimal concentrations of 0.5% gum kondagogu, 1 mM of AgNO_3 by autoclaving for 60 min in a domestic pressure cooker, by changing the concentration of gum (0.1–0.5%), AgNO_3 (1–5 mM) and reaction time (10–60 min) [16–18]. Similarly, palladium nanoparticles (Pd NP) were generated at standardized reaction conditions of 0.5% gum kondagogu, 1 mM of PdCl_2 by autoclaving for 30 min in a domestic pressure cooker, by varying the concentration of gum (0.1–1%), PdCl_2 (0.25–2.5 mM) and reaction time (10–30 min) [20]. The concentration of silver and palladium in the produced NP solution was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Horiba, France). The generated NP were characterized for surface plasmon resonance with UV–visible (UV–vis) absorption spectroscopy (Analytik Jena AG, Germany), crystal structure with X-ray diffraction (XRD) (Rigaku, Japan), morphology and elemental analysis with scanning electron microscopy (SEM) (Carl Zeiss, Germany) coupled to energy dispersive X-ray spectroscopy (EDS) (Oxford, UK), size and shape with transmission electron microscopy (TEM) (FEI, Netherlands) and zeta potential with zetasizer (Malvern, UK) [21]. The stability of generated NP were monitored at variable temperatures (30, 40, 60, 80, 100 °C), pH (5, 6, 7, 8, 9), sodium chloride concentrations (25, 50, 75, 100 mM) and storage time (as synthesized, 6 months) by measuring the UV–vis spectra [20, 22].

2.3 Dye Decolourization

The dye decolourization of synthetic dyes, including rhodamine B (RB) and methylene blue (MB) with sodium borohydride (NaBH_4) (475 µg/mL) was investigated by utilizing Ag NP and Pd NP as catalysts [4, 13, 22]. The effect of variables such as concentration levels of Ag NP (0.5–5 µg/mL), Pd NP (0.025–0.3 µg/mL) and RB (2.5–7.5 µg/mL) and MB (5–15 µg/mL); and reaction time (1–8 min/0.25–2 min)





OPEN Plasma copolymerized oxazoline and fluoro monomer based amphiphilic coatings for antibacterial and antifouling applications

Nilanjana Misra^{1,2,✉}, Swarnima Rawat^{1,2}, Sweetie R. Kanatt^{2,3}, Shubhangi A. Shelkar¹, Anitta Thomas², Ankita Pathak⁴, Sanjay Kumar⁵, Manish Singh⁶ & Virendra Kumar^{1,2,✉}

Incorporation of antibacterial and antibiofouling properties into commercial fabrics is an attractive proposition considering its multifold applications in the health industry. However poor bacterial anti adhesion and low shelf-life limit their widespread applicability. Moreover, while antifouling at the liquid-solid can be addressed by hydrophilic properties, that at the air-solid interface demands hydrophobicity. This work reports the use of an indigenously developed low pressure plasma set-up to deposit amphiphilic coatings through simultaneous deposition of poly(2-ethyl-2-oxazoline) (2E2O) and 1 H,1 H,2 H,2 H-perfluorodecyl acrylate (PFDA). Plasma parameters: deposition time, power, gas and monomer flow rates were optimized and the samples characterized using FTIR, XPS, SEM-EDX, AFM and Contact Angle (CA) measurement techniques. Samples were observed to inhibit biofilm formation from the viable cell enumeration method, while their biocidal efficacy was also established through antibacterial tests performed as per ISO 22196:2011. These hybrid coatings have potential applications in the healthcare sector as efficient antibacterial and antibiofouling surfaces.

Keywords Plasma-enhanced CVD (PECVD) (deposition), Polymerization, Biofilm, X-ray photoelectron spectroscopy (XPS), Scanning electron microscopy (SEM)

In the health industry, non-specific adhesion of bacteria to solid surfaces and subsequent biofilm formation are a severe deterrent to the performance of many devices (contact lenses, catheter tubes, blood contacting devices, implants, surfaces for cell culture, biosensors, drug delivery systems, etc.) and pose serious problems to public health^{1–3}. Infections resulting from bacterial colonization are responsible for a majority of all healthcare associated infections (HAI)⁴. One of the most effective routes to avoid such contamination is the coating of surfaces with materials that can impart antibiofouling/antibacterial properties. The two main coating strategies adopted to prevent fouling involves biocidal and nonbiocidal surfaces^{5–7}. While biocidal coatings directly eliminate bacteria to prevent surface adherence, nonbiocidal (or biopassive) coatings prevent adhesion of cells and proteins by virtue of their inherent surface properties. This eliminates the problem at its root and is not limited by the disadvantages of purely biocidal surfaces, such as fouling, leaching or gradual inactivation of the functionally active groups. As a result, biopassive surfaces have garnered special interest in the recent past because of its immense applicability in the field of healthcare.

The most common polymer used in biopassive coatings is the hydrophilic poly(ethylene) glycol (PEG) and its copolymers^{8,9}, although the poor stability of these PEG based surface coatings, besides susceptibility to hydrolysis, oxidative and microbial degradation and poor long term performance, remains a roadblock in their widespread applicability^{10,11}. Moreover, the extensive application of PEG and the continuous exposure to PEG-containing products has led to the development of anti-PEG antibodies in certain patients, leading to faster

¹Radiation Technology Development Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India.

²Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India. ³Food Technology Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India. ⁴Technical Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India. ⁵Material Science Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India. ⁶Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India. ✉email: nilanjana@barc.gov.in; vkumar@barc.gov.in

elimination from the body, reduced therapeutic efficacy and even allergic reactions. PEGs have also been shown to undergo oxidative degradation generating by-products that are toxic to humans and leading to limited long-term efficiency for antifouling applications¹².

Alternatively, hydrophobic polymers, such as 1 H,1 H,2 H,2 H-perfluorodecyl acrylate (PFDA) are also frequently used to impart antifouling properties to surfaces, owing to their beneficial properties, such as high thermal stability, excellent chemical resistance, low friction coefficient, superior weatherability, etc^{13,14}. These extraordinary properties arise from the unique chemical structure imparted by the polymer chains of the perfluorocarbon. However, it has also been reported that amphiphilic coatings, i.e., surfaces containing pockets of both hydrophilic and hydrophobic zones offer enhanced performance compared to coatings with unidimensional properties^{15–17}. This quality probably arises from the fact that proteins contain both hydrophobic and hydrophilic segments, and can tune their condition and structure to match the surface energy of the adsorbing surface. Amphiphilic coatings essentially are an unwelcome terrain for bacterial adhesion owing to their heterogeneous surface energy domains and ability to offer an ambiguous surface that deters adhesion.

The limitations of PEG based coatings has led to a search for stable alternatives, and one such alternative of considerable interest is polyoxazolines (POx)¹⁸. POx coatings have been reported for their potential biomedical applications and better stability compared to their PEG counterparts^{19,20}. The conventional approaches for POx film formation include living-cationic ring opening polymerization, photocoupling, and grafting, all of which suffer from limitations, such as being slow and complex multistep processes involving the use of organic solvents. Under the circumstances, plasma deposition has emerged as a novel approach to overcome these disadvantages to generate even nanometre thin polyoxazoline coatings, without the necessity for any substrate surface preparation or the use of toxic organic solvents²¹. Plasma polymerization also allows production of homogeneous, pinhole-free coatings and offers facile control over the reaction parameters, making it an ideal candidate for numerous biomaterial coating applications. Many of the oxazoline ring containing compounds, such as 2-methyl-2-oxazoline (2M2O) and 2-ethyl-2-oxazoline (2E2O), are low molecular weight liquids with substantial vapour pressure, and thus facilitate plasma polymerization. Although plasma polymerization too suffers from limitations such as high operational costs due to complex, expensive vacuum equipment, challenging process control and the occasional unsaturation causing colouration in coatings, the benefits offered by the approach still outweigh these factors to make it highly attractive for novel coatings design. Cavallaro et al.²² have demonstrated that plasma deposited polyoxazolines, being a mild functionalization approach, allow the POx coatings to retain their chemical reactivity and exhibit excellent biocompatibility and low biofouling. Plasma-enhanced chemical vapor deposition (PECVD) methods have been employed to deposit 2M2O and 2E2O in low-pressure radio frequency (RF) discharge²³. But, the possibility of combining the advantages of hydrophilic oxazolines with those of hydrophobic PFDA in the form of an amphiphilic coating with properties superior to either system individually has not been explored thus far. Of even greater interest is the potential application of this methodology to functionalize the surface of non-woven fabrics. Nonwovens are extensively used in products, such as filtration media, wipes, baby diapers, garment interlinings, etc. Most of these application areas are critical in the sense that there is a high chance of microbial contamination and infection arising from the use of these materials, especially in high humid regions like India. PECVD mediated surface modification is an exciting proposition to make value addition to these fabrics and ensure minimum proliferation of infection by incorporating antifouling/antibacterial properties.

This work presents, to the best of our knowledge, the first reported PECVD mediated co-deposition of stable 2E2O-PFDA amphiphilic polymer coatings to impart antibiofouling and antibacterial properties, synergistically blending hydrophilic and hydrophobic properties for potentially superior performances. The sample hydrophilicity and roughness were observed to be regulated by the composition of the two monomers deposited simultaneously on the substrate. Antibacterial and antifouling properties of samples containing different compositions of 2E2O and PFDA and deposited for different durations were tested against gram positive (*S. aureus*) and gram negative (*E. coli*) bacteria. The stability of the coatings was evident from the retention of biocidal properties even after multiple washing cycles, exhibiting distinct advantages over previously reported PEG and DEGVE (Di (ethylene glycol) vinyl ether) based amphiphilic coatings.

Results and discussion

FTIR and XPS analysis

The PET control film (Fig. 1a(i)) displayed characteristic peaks corresponding to aromatic rings (846, 870 and 968 cm^{-1}), methylene group (bending mode at 1460 cm^{-1}), vibrations of the ester CO bond (C = O stretching mode at 1715 cm^{-1} and C-O stretching at 1245 cm^{-1}), O-C-C stretching (1100 cm^{-1}), bending and wagging vibrational modes of the ethylene glycol segment (1339, 1409 and 1458 cm^{-1}), vibrations of aromatic skeleton with stretching of C = C (1505 and 1580 cm^{-1}), and the broad axial symmetrical deformation of CO_2 (~ 2200 cm^{-1})²⁴. The PFDA deposited PET films (Fig. 1a(ii)) were recognizable by the appearance of CF_2 and CF_3 end group vibrations at 1155 cm^{-1} , besides the CF symmetric and asymmetric stretching modes at 1200 cm^{-1} . The weak absorption band at 1338 cm^{-1} was assigned to C-F stretching vibration in the $-\text{CF}_2\text{CF}_3$ group. The absence of an ester group peak could be attributed to the fragmentation of the same during the plasma polymerization process. The electrons generated in the plasma can induce cleavage of the ester bonds, either homolytically or heterolytically, to form smaller fragments that finally form the fluorocarbon coating. 2E2O coating on PET (Fig. 1a (iii)) displayed bands corresponding to C = O stretching (1730 cm^{-1}), CC stretching (1202 cm^{-1}), NH stretching (1540 cm^{-1}), and CO of the tertiary amide (1659 cm^{-1}). These amide groups are probably formed during post deposition reactions in the film²⁴. The bands between 1463 and 1350 cm^{-1} are typical of the bending vibrations of CH_3 and CH_2 groups. The small but broad peak at 2160 cm^{-1} arises from the nitrile $\text{C} \equiv \text{N}$ groups formed during the plasma polymerization process through fragmentation and recombination of the oxazoline monomers in the plasma. 2E2O-PFDA amphiphilic coatings (Fig. 1a(iv)) presented strong CC stretching



Scan the QR Code or Click for full text



European Journal of Clinical Microbiology & Infectious Diseases (2025) 44:2645–2654
<https://doi.org/10.1007/s10096-025-05221-6>

RESEARCH



Rapid screening of mutations for second-line-drug-resistant genes in *Mycobacterium tuberculosis* culture isolates by in-house developed DNA bio-chip

Bharti Jain^{1,2} · Savita Kulkarni^{1,2} · Nawab Singh Baghel¹

Received: 3 March 2025 / Accepted: 15 July 2025 / Published online: 29 July 2025
 © The Author(s) 2025

Abstract

Background The rate of multidrug-resistant (MDR) and extensively drug-resistant (XDR) tuberculosis (TB) has been steadily increasing and is a major setback to TB control in India. The availability of quick and reliable methods for detecting second-line drug resistance (SLDR) is vital to managing patients satisfactorily. A rapid molecular technique to detect SLDR in *Mycobacterium tuberculosis* (*M. tuberculosis*) has been developed using DNA biochip.

Methods Specific probes containing wild-type region or specific mutations were designed for immobilization on DNA bio-chip. DNA bio-chip was developed in-house on polycarbonate track-etched membranes (PC-TEM). DNA bio-chip allows the identification of mutations in *gyrA* gene for fluoroquinolone (FQ) resistance, in *rrs* gene and the *eis* promoter region for resistance to second-line injectable drugs (SLID). An asymmetric multiplex PCR was standardized for *gyrA*, *rrs* and *eis* genes. A chemiluminescence based biochip assay was optimized. Bio-chip was tested on 112 *M. tuberculosis* clinical isolates with different resistance spectra.

Results Isolates analyzed using bio-chip shows that 61 (61%) samples were wild-type. Twelve samples show mutations in *gyrA* gene, 11 samples in *rrs* gene, 12 samples in *eis* gene and 4 samples show double mutation in *rrs* and *eis* genes. The sensitivity and specificity of bio-chip for detection of FQ resistance ranged from 75 to 100% and 96.7%–100%, respectively. The sensitivity and specificity of SLID detection ranged from 90.9 to 100% and 96.7–100% respectively. The analytical sensitivity of the bio-chip was ~250 genome copies per assay.

Conclusion The biochip has high sensitivity and specificity and could be useful for clinical microbiology studies and epidemiological surveillance of drug resistant (DR) *M. tuberculosis*. It is a highly accurate tool for screening for SLDR, significantly reducing the time for phenotypic drug susceptibility test (DST) results from weeks to a single day.

Keywords Second-line drug resistance · Extensively drug resistance TB · TB · *Mycobacterium tuberculosis* · DNA bio-chip

Introduction

Tuberculosis (TB), caused by *Mycobacterium tuberculosis* (*M. tuberculosis*), is a major global health issue, causing an estimated 10.8 million new cases and 1.25 million

deaths in 2023 [1]. Despite being preventable and curable, TB remains one of the top ten causes of death worldwide, primarily affecting low- and middle-income countries where healthcare resources are limited [2]. The advent of antibiotic therapy in the mid-20th century marked a turning point in TB management, drastically reducing the incidence and prevalence of the disease. However, improper use, such as inadequate dosing, poor patient adherence, and incomplete treatment courses, has led to the development of drug-resistant (DR) TB strains. The emergence of DR-TB strains has posed a substantial threat to TB control programs, complicating treatment regimens and worsening patient outcomes. Multidrug-resistant TB (MDR-TB), is *M.*

✉ Bharti Jain
 bharti.jain09@gmail.com

¹ Radiation Medicine Centre, Bhabha Atomic Research Centre, Parel, Mumbai, Maharashtra, India

² Homi Bhabha National Institute, Mumbai, Maharashtra, India

tuberculosis resistant to at least isoniazid and rifampicin, the two most potent first-line anti-TB drugs, and extensively drug-resistant TB (XDR-TB), is MDR-TB resistant to any fluoroquinolone (FQ) and at least one of the three second-line injectable drugs (SLID) viz. amikacin (AMI), kanamycin (KAN), or capreomycin (CAP). Second-line drugs are critical for the treatment of MDR-TB, making the emergence of resistance to second-line drugs particularly alarming. Despite a 23% decrease in TB mortality from 2015 to 2023, the prevalence rates of multidrug-resistant TB (MDR-TB) and extensively drug-resistant TB (XDR-TB) continue to rise among both new and previously treated TB cases [1]. Also, the COVID-19 pandemic has reversed years of gains in TB detection, notification, and treatment [3]. It is estimated that nearly 6.2% of all MDR-TB cases have XDR-TB [4]. As per systematic review by Diriba G, the pooled proportions of XDR-TB among new patients with MDR-TB were 3% and 6% in previously treated patients. The pooled proportions of pre-XDR-TB (MDR TB resistant to any FQ or any SLID) among new patients with MDR-TB were 9% and 13% among previously treated patients. The overall pooled proportion of pre-XDR was 26%, whereas the proportion of XDR-TB was 9% among patients diagnosed with MDR-TB [5].

The emergence of XDR-TB indirectly indicates programmatic failure to diagnose and treat MDR-TB effectively. The management of second-line drug-resistant (SLDR) TB is complex and necessitates a multilayered approach, including the development of new drugs, the implementation of robust diagnostic methods, and the use of personalized treatment regimens based on drug susceptibility testing (DST) [6]. The diagnosis of DR for first-line antitubercular drugs is easy due to the availability of WHO-endorsed molecular tests like Xpert MTB/RIF and line probe assays (LPAs). The SLDR detection is challenging due to limited WHO-endorsed tests. The most reliable test for SLDR is phenotypic DST in liquid culture, which is laborious and time-consuming [7]. Genotype MTBDRsl Ver 2.0, LPA for FQ and second-line injectable drugs (SLID) resistance detection based on reverse hybridization technology, was endorsed by WHO for rapid detection of SLDR [8]. Broader availability of rapid second-line DST that performs reliably and economically in resource-limited settings is needed to stop the spread of resistant strains and deaths due to XDR-TB.

The mutations leading to resistance to anti-TB drugs and molecular mechanisms of resistance was identified by many researchers. Resistance to FQ is most frequently associated with mutations in *gyrA* and *gyrB* genes. Studies have demonstrated that targeting mutations in codons 90, 91, and 94 in *gyrA* can accurately predict approximately 70 to 90% of all FQ resistance [9–13]. Similarly, mutations in the *rrs*

gene, particularly the hotspot region from nucleotides 1401 to 1484, can accurately predict resistance to second-line aminoglycosides [14–17]. The aim of analyzing a maximum number of mutations in drug resistance-determining regions led to the development of highly multiplex tests like LPA and array-based assay. Genotype MTBDRsl Ver 2.0 assay is a frontline test for second-line resistance detection in MDR TB/RR TB or isoniazid-resistant TB in India [18]. Both LPA and array-based analysis of *M. tuberculosis* complex provides important information on the mechanism of DR, the identity of the species or strain, and gene expression [19]. Compared to LPA, array analysis is economical on sample and reagents due to its miniaturization. However, there are few reports on the development of DNA array/bio-chip to detect SLDR [20, 21]. We report the development of DNA bio-chip for detecting SLDR mutations since DNA bio-chip can detect multiple mutations in multiple genes involved in SLDR. Our DNA bio-chip was developed on polycarbonate track-etched membrane (PC-TEM) as its high porosity allows for the immobilization of a higher amount of probe as compared to planar surfaces. Using PC-TEM, we had previously developed a multianalyte immunoassay for the quantification of thyroid hormones [22–24]. We had also developed DNA bio-chip for the detection of DR to first line drugs and MDR in *M. tuberculosis* [25, 26]. We herein developed DNA bio-chip that can detect SLDR by designing probes to identify gene mutations conferring *gyrA*, *rrs* and *eis* resistance. Multiplexed PCR for relevant genes and bio-chip assay was designed and optimized for SLDR detection. Using DNA bio-chip for SLDR, developed in this study and a previously developed MDR bio-chip, XDR *M. tuberculosis* can be detected in a single day.

Materials and methods

Clinical isolates and DNA isolation

For the present study, 112 *M. tuberculosis* clinical isolates were chosen. The isolates were obtained from clinical samples (sputum, biopsy, bronchioalveolar lavage) collected from pulmonary TB patients at TB hospital, Sewari, Mumbai, India. The clinical isolates were obtained from samples collected retrospectively by our laboratory for a different purpose. *M. tuberculosis* strain H37Rv was used as a control for the genetic tests. The clinical samples were processed according to the international guidelines using the N-acetyl-L-cysteine-NaOH decontamination procedure (final NaOH concentration: 1%). DNA extraction from clinical isolates was performed using DNA extraction method described by Soilingen et al. [27]. The DNA concentrations





RESEARCH



Realistic simulation of molecular emission spectra: an advancement in direct calibration-free isotopic analysis

Anandhu Mohan^{1,2} · Anannya Banerjee² · Rajesh V. Pai^{1,2} · Arnab Sarkar^{1,2}

Received: 11 August 2025 / Accepted: 30 September 2025 / Published online: 22 October 2025
 © The Author(s) 2025

Abstract

This study employs Calibration-Free Laser Ablation Molecular Isotopic Spectrometry (CF-LAMIS), enhanced by the Molecular spectrA simulator under Born–Oppenheimer Approximation and Boltzmann Equilibrium environment (MAHADEV) algorithm and its AWGN (Additive White Gaussian Noise) incorporated variant to directly analyse boron isotopes in natural boric acid samples and nuclear-grade boron carbide (B_4C) samples. The boric acid samples yielded accuracy and precision consistent with previous studies. Initial analyses of B_4C samples were challenged by the atomic and ionic interference lines. However, the BO:B-X (0–1) ro-vibrational band (RVB) was found to have fewer interferences, providing a clearer analytical window at longer acquisition delay times ($t_d = 22 \mu s$). This approach achieved reasonable accuracy and precision levels comparable to those obtained from pure boric acid samples, demonstrating the effectiveness of the CF-LAMIS method in handling complex matrices. The application of the AWGN–MAHADEV algorithm provided isotopic composition with significant ($\sim 50\%$) improvement in precision while maintaining comparable accuracy. Boric acid samples achieved an accuracy and precision of 0.3% and 0.8% respectively, while natural and ^{10}B -enriched B_4C samples achieved an accuracy of 0.7% and 0.2% and a precision of 0.9% and 0.6% respectively. This study highlights the potential of noise integration in calibration-free methods to achieve more precise and accurate results.

1 Introduction

Isotopic analysis plays a crucial role in various domains of science and industry, ranging from geochemistry [1, 2], environmental monitoring [3], nuclear technology and materials science [4, 5]. Isotopic abundance measurements can provide valuable information regarding the origin, history, natural interactions, and engineered processes like fluid migration and nuclear reactor operations [6, 7]. Precise and accurate isotopic abundance measurements are of utmost importance due to its high significance in various fields, and even a minute change can result in a cataclysmic event.

Although many sophisticated methods, such as inductively coupled plasma mass spectrometry (ICP-MS) [8], thermal ionization mass spectrometry (TIMS) [9], secondary

ion mass spectrometry (SIMS) [10], glow discharge mass spectrometry (GDMS) [11], multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) [12], etc., are prevalent for superior analytical results with respect to isotopic analysis, these methods suffer certain drawbacks such as the limited capability for direct sample analysis and remote operation. Laser-Induced Breakdown Spectroscopy (LIBS) [13–15] and Laser Ablation Molecular Isotopic Spectrometry (LAMIS) [16–18] overcome these drawbacks and deliver acceptable analytical results. Traditional LIBS or LAMIS requires calibration with standard samples to establish a relationship between spectral intensity and elemental concentration. However, this requirement limits many applications where reference materials are not readily available. Calibration-free methodologies have emerged as a solution to these challenges by allowing direct compositional analysis without the need for calibration curves [19, 20]. As a result, calibration-free techniques for isotopic composition determination are gaining interest.

Calibration-free LAMIS (CF-LAMIS) is a laser-based spectroscopic technique which has recently emerged as a promising analytical method for direct isotopic analysis. This technique eliminates the need for external calibration,

✉ Arnab Sarkar
arnab@barc.gov.in; asarkar@ymail.com

¹ Homi Bhabha National Institute, Anushakti Nagar, Mumbai 400 094, India

² Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

enabling the direct quantification of isotope ratios by fitting the emission spectra generated during laser ablation with a mathematically simulated spectrum [19, 20]. By eliminating the need for sample preparation and minimising matrix effects, CF-LAMIS offers significant advantages in terms of portability, speed, cost-effectiveness, and applicability to a wide range of solid materials [19, 21]. By utilising mathematical models that describe the physical states of laser-induced plasmas (LIP), CF-LAMIS can achieve accurate elemental as well as isotopic composition determinations even in complex matrices. This capability is particularly valuable in the nuclear industry, where the accurate isotopic composition is of paramount importance [14, 22, 23].

Our group has recently developed a CF-LAMIS methodology utilising an algorithm named MAHADEV (Molecular spectra simulator under Born–Oppenheimer Approximation and Boltzmann Equilibrium Environment) [20]. The methodology was able to directly analyse crystalline boric acid samples without any sample preparation or external calibration. This technique has demonstrated promising results in determining the isotopic composition of pure boric acid samples [20]. One of the main challenges in implementing CF-LAMIS with MAHADEV algorithm was the influence of the inherent random noises associated with the recorded molecular spectra. These noises are associated with the detector and introduce random error in the real system [24] which is absent in the mathematical simulated spectra, resulting in a high spectral residue after fitting. While these factors can influence both accuracy and precision, they predominantly compromise the precision of isotopic measurements. Accuracy ensures that the measured isotopic abundances reflect the true values; however, achieving high accuracy alone is insufficient for isotopes, where the variations in desired isotopic composition are often extremely small. In such cases, high precision is essential to detect the subtle differences between samples and ensuring reproducible, meaningful measurements. To address this issue, the integration of random noise in the simulated spectrum is crucial. Additive White Gaussian Noise (AWGN) [25–28] serves as a useful model for simulating random noise encountered in real-world measurements, allowing the generation of better simulated spectra to imitate the real conditions.

This work explores the applicability of introducing simulated white random noise to the MAHADEV algorithm for improved boron isotopic composition calculation using the CF-LAMIS methodology. Photon Transfer (PT) was used to profile noise sources in the iCCD detector–spectrograph system. The MAHADEV algorithm was modified by incorporating the AWGN model based on the PT curve, and boron isotopic compositions were calculated. The performance of this methodology was statistically evaluated to assess

improvements over the previous version of the algorithm. Additionally, the algorithms were tested on various samples with varying chemical compositions and enrichment levels to evaluate the effectiveness.

2 Experimental section

2.1 CF-LAMIS system and spectral measurements

The experimental setup is described in detail elsewhere [20]. In summary, the ablation source was a Q-switched Nd-YAG laser (Brilliant B, Quantel). The pulse energy of the laser was monitored using a pyroelectric energy meter (Ophir Photonics) over 100 shots, and exhibited a minimal variation of $\pm 1.5\%$. The laser beam was directed using reflecting mirrors and focused through a microscopic lens ($f=10$ mm). Emitted light from the plasma was collected by an in-house developed collimator. The sample was placed on a computer-controlled XYZ translation stage. Optical connectivity between the collimator and a Czerny–Turner spectrometer (Shamrock SR750, Andor, 2400 lines/mm, $\Delta\lambda=25$ pm, bandpass ~ 6 nm), was established using an optic fibre bundle.

The boric acid pellets (S1) were prepared using natural boric acid crystals (Chemco Fine Chemicals, 99.5%). Approximately 1 g of boric acid was pelletised using a pressure of 50 kg/cm² to prepare a pellet of 10 mm diameter. The natural ¹⁰B isotopic composition of boric acid crystals was verified to be 19.67% using TIMS analysis. Two B₄C pellet samples, one natural (S2) and one enriched (S3), were acquired from Heavy Water Board (HWB), Mumbai. The purity of the ¹⁰B isotope of these standard samples was determined by TIMS analysis, where other elemental composition values were measured by various methods such as the titrimetric method (for B), CHNS analyser (for C) and Atomic Absorption Spectrometry (AAS) for the rest of the elements. The ¹⁰B isotopic purity and the elemental composition of the pellets are given in Table 1.

The spectra of both boric acid and B₄C samples were recorded in ambient atmosphere conditions with a new surface for every new spectrum. The experimental conditions required for spectral recording, such as wavelength range and acquisition delay time (t_d), were optimised by the methods adopted from our previous study [20]. The energy of the laser pulse was optimised to be 90 mJ. The spectra were recorded by accumulating 200 laser shots in digging mode under ambient atmospheric air conditions with a gain level of 1000. In the present study, the sample pellets were directly analysed, and the isotopic composition determination was carried out.





OPEN Redox investigation of L-A9 peptide and evaluation of its binding with double stranded DNA

Preeti Dwivedi^{1,2}, Sudipa Manna¹, Drishti Satpati^{3,5}, Amit Das^{4,5}, Suresh Shendage² & Ashis Kumar Satpati^{1,5}✉

L-A9 is one of the important short peptides having biomedical applications in relation to its affinity towards HER2 receptors. The peptide has been synthesised using manual solid phase synthesis protocol and the redox property has been investigated using the voltammetric techniques. The oxidation peak of the peptide has shown strong pH dependency, revealed the 1 e and 2 proton transfer process. Electroanalytical method is developed with limit of detection of 1.17×10^{-7} M. The modulation of the redox property has been monitored to investigate the binding of the peptide with dsDNA, with binding constant of 1.8×10^5 M⁻¹. Spectroscopic measurements of the peptide revealed the pH dependent electronic transition and the binding constant with dsDNA of 1.4×10^4 M⁻¹. The needle like assembly of L-A9 peptide has been indicated from the SEM measurements with coil kind of morphology of dsDNA has been observed when the L-A9 peptide and dsDNA interacted with each other. The electrochemical and spectroscopic investigations indicated that the acidic functional groups of L-A9 interacts with the major groove of dsDNA through the modifications of 3 hydrogen bonds between the strands, whereas the basic functional groups of L-A9 binds externally with dsDNA by formation of bonds with O atoms of the phosphodiester groups, which has been supported from the molecular docking investigations.

Keywords L-A9 peptide, Redox property, Spectroscopic investigation, Surface charge, DNA, Binding property

The development of peptides-based drugs and pharmaceuticals have made significant progress in last few decades due to the advancement in the synthesis, purification and analytical methods of their characterisation. Additionally, the improvised delivery strategy of the peptide-based drugs overcomes the challenges of the therapeutic usage of peptides. Insulin has been the most popular and important peptide-based drug dominated the market for over 90 years, which is now replaced by the recombinant insulin^{1,2}. Smaller sized drugs have the advantages as it is easy to administer which has enhanced patient compliance and penetration^{3,4}.

Additionally, the short peptides are mostly used due to their biological activities in immune reactions, in brain functions, blood pressure normalization and controlling the vascular tone. Short peptides are present in all tissues, and they are usually treated as “fragments” of functional proteins and having complex functions in biological systems⁵. The short peptides generally considered to have up to 100 amino acids, have the advantage of easy penetration through the cell membranes⁶. Importantly the short peptides can interact with DNA^{7–9,10}. The gene expression has strong influence on the controlled combination of DNA-binding proteins, which also has influence of the presence of metals¹¹. Metal ions play important role in modulating the interaction of the peptides with DNA, which influence important biological functions¹². Monoclonal antibodies were considered as the potential magic bullet for cancer treatment because of their antigen specific binding to the neoplastic cells. In the view of challenges posed by their high molecular weight, low penetration, risk of allergic reactions and long half-life¹³, researchers turned to antibody fragments as they retain the specific antigen binding capability while having more tailored half-life and better membrane penetration¹⁴. Antibody fragments offers several simultaneous benefits as they can be perfect drug carriers due to their specific antigen binding while it induces tumour cell apoptosis by interfering with signalling and manipulating immune system. More tailored treatment

¹Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India. ²Department of Chemistry, KET's Vinayak Ganesh Vaze College of Arts, Science and Commerce (Autonomous), Mulund (E), Mumbai 400081, India. ³Radiopharmaceutical Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India. ⁴Protein Crystallography Section, Bioscience Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India. ⁵Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India. ✉email: asatpati@barc.gov.in

or imaging can be achieved by small peptide chains which are the principal antigen binding moieties in these antibody fragments. In the field of targeted cancer therapy, these tumour targeting peptides are emerging as appealing choice due to their small molecular weight, cost-effective synthesis, easy modification along with fewer off-target toxicity, high membrane penetration, low immunogenicity, specificity and high action potency^{15,16}.

In cancer cells, the mutation or alteration in normal functioning gene or proto-oncogenes results in overexpression of its protein product. Receptors found in these overexpressed neoplastic tissues are chosen as targets. In wide varieties of cancer e.g. breast, ovarian, lung, gastric, oropharynx, ovarian, colorectal and bladder, the human epidermal growth factor receptor 2 (HER2), a transmembrane receptor is found to be overexpressed in both primary as well as metastasized organs. Hence, HER2 targeting antibodies or peptides are of importance while developing new cancer drugs¹⁷. In this regard, A9 peptide, 9 amino acid peptide chain, represents a minimal sequence, derived from Herceptin antibody fragment and rationally designed from biomolecular HER2-Herceptin antigen-binding fragment (Fab). L-A9 specifically bind to extracellular domain IV of HER2 receptor^{18–22}.

There have been studies relating to the efficacy of A9 in targeted cancer therapy and imaging. When A9 is conjugated to antineoplastic drug like doxorubicin, the cellular internalization and cytotoxicity was improved²³. Diethylenetriamine pentaacetate conjugated A9 peptide radiolabelled with ¹¹¹In has shown nanomolar affinity to HER2 overexpressed cells. However, the problem with ordinary peptides lies in their vulnerability towards enzymatic degradation and subsequent rapid renal clearance resulting in lower bioavailability and lower target accumulation which limits their clinical applicability. Hence, many researchers devise methods such as PEGylation, cyclization, retro-peptide synthesis etc. to confer metabolic stability²⁴.

Amino acids in small peptides that contain charges at the side chain, have the ability to bind to double stranded DNA (dsDNA), the strong electrostatic binding modify the double helical structure of the dsDNA. It has been reported that the Glu, Asp weaken the H-bonds between DNA strands, whereas amino acids, Arg and Lys, which are basic in nature are known to strengthen the interaction between the strands. The interactions of peptides and proteins with DNA are generally similar, which are essentially driven by the compositions of the amino acids in them. The peptide containing the Asp and Glu, which are negatively charged binds with DNA in major groove of double helix. Through such binding the double helix structure becomes more fragile and results in the separation of strands. These flexible strands of DNA initiate the genetic transcription and replication²⁵. The mechanisms of intermolecular interactions between amino acids and individual nucleic bases are through the hydrogen bonds²⁶. Thus, any probing of such interactions has the essence of the peptide and DNA binding. Therefore, the electrochemical techniques which has the capability to probe the interactions due to the difference in the electrostatic charges could be applied in evaluating the interactions between the peptides and dsDNA. For the redox active peptides, it would open new avenues while the evaluating the electrostatic interactions, groove binding or the intercalative bindings of the peptides with the dsDNA strands. Molecular docking investigation were carried to support the experimental findings on the sites of interactions between the peptide and dsDNA. There are no such investigations has been reported evaluating the interactions between the L-A9 peptides with dsDNA using the electrochemical probing.

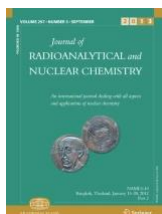
The peptide L-A9 that has been used in the investigation is a nine-amino acid peptide which specifically binds to the HER2 receptor at the extracellular domain IV. The A9 sequence essentially is the minimal sequence derived from Herceptin Fab. The dissociation constant has been reasonably good. The bioactive A9 peptide is tagged with the ionic 7-sulfo benzofurazan as the fluorescent tag for the investigation in biological binding and migration^{27–29}. The design, synthesis, and validation of this peptide was previously described, as well as its application as a radiolabelled tracer for molecular imaging of HER2^{18–20,30}. Presently, the peptide was synthesized with the synthesis procedure as described in our previous publication^{31,32}. The electrochemical response of L-A9 peptide over the commercially available electrode is not significant for their investigation and developing method of analytical determination. In order to enhance the electrochemical response, glassy carbon (GC) electrode is modified with gold nano particles (AuNPs) and the AuNPs modified GC electrode has shown enhanced response, which is used to develop method of determination of the L-A9 peptide. The enhanced electrochemical signal was also utilised for the investigation of the interaction between the peptide and dsDNA. Electrochemical measurements are also supported by the UV-Vis spectral measurements and also from the FTIR and Raman measurements. The investigation thus provided comprehensive electrochemical information of the L-A9 peptide, developing the analytical method of its determination and exploring its interactions with dsDNA.

Experimental Materials

The peptide, A9 was synthesized manually by Fmoc solid-phase peptide synthesis. The protected peptide sequence Gln(Trt)-Asp(OtBu)-Val-Asn(Trt)-Thr(tBu)-Ala-Val-Ala-Trp(Boc)-NH₂ was constructed on NovaSyn TGR resin. Amino acid couplings were performed by activation of Fmoc-amino acids (3 eq.) with *O*-(7-azabenzotriazol-1-yl)-*N,N,N',N'*-tetramethyluroniumhexafluorophosphate (HATU) (3 eq.) and *N,N'*-diisopropylethylamine (DIPEA) (6 eq.) in dimethylformamide (DMF) followed by gentle rotation for 120 min. Fmoc-deprotection was carried out with 20% piperidine in DMF (v/v, 2 × 10 min). Coupling reactions were monitored by the colorimetric trinitrobenzenesulphonic acid (TNBS) test. The chelator was incorporated at N-terminus by coupling of DOTA-tris (t-Bu) ester (3 eq.) in presence of HATU and DIPEA. The peptide was finally cleaved from the resin with a cocktail mixture of trifluoroacetic acid (TFA)/triisopropylsilane (TIPS)/H₂O (95/2.5/2.5, v/v) wherein protecting groups were also removed. The crude peptide was precipitated by addition of diethyl ether. The precipitate as obtained was dissolved in water and washed with ether for three times. The crude peptide as obtained was purified using semi-preparative HPLC and then lyophilized to obtain white fluffy powder. MALDI-TOF (DOTA-A9); calculated for C₆₀H₉₃N₁₇O₂₁, 1388.48; found, 1388.517. Double-stranded DNA from calf thymus was also sourced from Sigma Aldrich, with 98% purity verified by SDS-PAGE



Scan the QR Code or Click for full text



Journal of Radioanalytical and Nuclear Chemistry (2026) 335:1513–1520
<https://doi.org/10.1007/s10967-025-10449-9>



Residence time distribution studies in rotating packed bed (RPB) reactor for improving its hydrodynamics and design validation using radiotracer

Sunil Goswami¹ · Jayashree Biswal¹ · J. S. Samantray¹ · Vijay K. Sharma¹

Received: 19 June 2025 / Accepted: 3 October 2025 / Published online: 17 October 2025
 © The Author(s) 2025

Abstract

Rotating packed beds (RPBs) utilizes high centrifugal force to enhance mass transfer, making them ideal for intensified processes such as gas–liquid stripping, absorption, and reactive separations. This study investigates the liquid-phase hydrodynamics of two reactor designs of RPB i.e. base and modified—using radiotracer-based residence time distribution (RTD) measurements. Technetium-99m was used as a radiotracer to measure RTD under varying liquid flow rates, gas flow rates, and rotational speeds. The base design exhibited significant flow path malfunctions, particularly under gas flow, leading to reduced process efficiency and degradation of packing material. In contrast, the modified RPB design eliminated flow path malfunctions by improving design of liquid distributor. Two different combination of plug flow and tank in series model were used to simulate RTD curves. The present study provides experimental data and validated models for the design validation and scale-up of intensified processes using RPB reactors.

Keywords Rotating packed bed reactor · Residence time distribution · Based and modified design · Technetium-99m · Tank in series · Channelling

Introduction

The rotating packed bed (RPB) reactor, also known as a HiGee (High Gravity) reactor, is an intensified reactor design that enhances mass transfer, heat transfer and reaction rates by using centrifugal force. These reactors are now days widely used for process intensification in chemical, biological and environmental engineering. RPBs have ability to significantly improve absorption / desorption processes like CO₂ capture with amines, SO₂ scrubbing, H₂S removal by providing higher interfacial area, deaeration of water using nitrogen (N₂) as a stripping media [1]. For liquid–liquid extraction, RPBs enables efficient separation of compounds such as rare earth metals and pharmaceuticals with reduced solvent usage and high mass transfer coefficients [2]. They also intensify reactive distillation processes—e.g., esterification—by integrating reaction and separation in a compact

unit. In wastewater treatment, RPBs are used to strip ammonia, phenols, and volatile organic compounds (VOCs) more efficiently than conventional towers [3, 4]. In bioprocessing, they offer a low-shear environment with high oxygen transfer, suitable for fermentation and enzyme-catalysed reactions [3, 4]. For crystallization, especially in nanoparticle or pharmaceutical synthesis, RPBs promote uniform particle formation through controlled supersaturation [5]. Additionally, they enhance polymerization reactions such as emulsion polymerization by enabling better thermal control and reactant mixing [6]. Finally, RPBs facilitate oxidative desulfurization of fuels by accelerating reaction rates and reducing reactor volume, aligning with goals in cleaner fuel production. However, the real flow dynamics inside the RPB, which is responsible for process intensification is still not understood clear and topic of research for engineers and scientists worldwide [7].

Experimental Residence Time Distribution (RTD) studies in RPB reactors are crucial for understanding and optimizing their performance. RPBs operate under high centrifugal forces, leading to complex flow patterns that can deviate from ideal plug flow. The RTD experiments help identify such deviations, detect dead zones or channelling

✉ Sunil Goswami
 gsunil@barc.gov.in

¹ Isotope and Radiation Application Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

and evaluate the extent of back-mixing, all of which can significantly affect product quality and reaction efficiency [6, 7]. These studies are essential for reactor design and scale-up, as they provide data necessary for designing appropriate reactor geometries, predicting performance when scaling up from lab to pilot to industrial scale and ensuring that reaction time matches with residence time, which is vital for achieving desired chemical or environmental conversion [7]. Additionally, RTD studies also help to quantify, how well reactants are distributed across the packed bed, ensuring effective utilization of the catalyst packing [8]. They also provide experimental data for the validation of computational fluid dynamics (CFD) models or residence time models and calibration of kinetic models used for simulating complex systems [9]. In essence, experimental RTD studies are crucial for developing, optimizing and scaling RPB reactors, especially for sensitive and complex reactions like polymerization, bridging the gap between theoretical design and practical performance. The measurement of the RTD of the fluid flow in a process reactor is generally carried out using stimulus–response technique using tracers such as coloured dyes detection via UV–visible spectroscopy, salts detection by conductivity measurements, helium gas detection via thermal conductivity detectors, anhydrous calcium diphosphate solution detection via on-line near infrared spectroscopy, carbon ink detection via fast cameras and radiotracer detection via radiation sensitive detectors [10–18]. But only radiotracers provide practical means of the measurement of the RTD in pilot or large-scale reactors; whereas other techniques are widely used in small scale-laboratory systems [13–15]. The various advantages of the radiotracer over the conventional tracers such as online detection, high detection sensitivity, physico-chemical compatibility and availability in wide range tracer for most of the phases makes them a preferred choice for RTD measurements in large-scale and complex flow systems [13–18]. In the present study, RTD measurement using radiotracers was carried out to evaluate the performance of the two different base and modified design of RPB used to carry out deaeration reaction using N_2 as a stripping agent.

Experimental

Rotating packed reactor

The experimental setup (Fig. 1) of a Rotating Packed Bed (RPB) reactor consists of a cylindrical rotor, with a diameter approximately equal to 700 mm and a packing thickness of 150 mm. The rotor is packed with structured or random metallic foam packing to provide a large surface area for mass transfer and is mounted on a shaft connected to an electric motor. The motor, rated between 0.5 and 3 kW, is

equipped with a variable frequency drive (VFD), allowing precise control of the rotational speed in the range of 100 to 2000 revolutions per minute (RPM). The liquid feed is introduced at the centre of the rotor through a stationary liquid distributor, where the centrifugal force generated by high-speed rotation drives the liquid radially outward through the packing, forming thin liquid films that significantly enhance mass transfer. The gas phase (N_2) is introduced counter-current direction to the liquid phase in the RPB, enabling intensive gas–liquid contact within the rotating bed. After interaction, the processed liquid and gas streams exit the reactor through their respective outlets. The entire assembly is mounted on a sturdy support frame and enclosed within a safety casing to ensure mechanical stability and operator protection during high-speed operation. The system is instrumented with flow meters, pressure gauges, and temperature sensors for real-time monitoring and control of the process variables. This compact, high-efficiency setup enables process intensification, allowing substantial reduction in equipment size and operational time for applications such as absorption, stripping, and reactive separations. In the base design of the RPB, liquid is fed to RPB metal foam having through a distributor having 10 mm holes. However, in the modified design of the RPB, a wire mesh having 0.5 mm holes was installed on the liquid distributor to uniformly distribute the liquid over the metal foam in the RPB.

Residence time distribution measurement

A series of radiotracer experiments was carried out to measure RTD of the liquid phase in the RPB at different operating conditions i.e. liquid and air flow rate and rotation speed as given in Table 1 and 2. Prior to conducting a RTD run, the RPB was set to operate for a period of 15 min at desired operating conditions and allowed to attain steady state condition. In the present study, technetium-99m (^{99m}Tc) ($t_{1/2}$: 6 h, γ : 141 keV (87.8%)) as sodium pectechinate was selected and used as radiotracer [19]. The Tc-99m was eluted from a Molybdenum-Technetium generator supplied by Broad of Radiation and Nuclear Technology (BRIT), Mumbai, India using saline solution. Out of the eluted activity of ^{99m}Tc , about 7.4 MBq ($\sim 200 \mu Ci$ in 0.5 ml) was used as radiotracer in each run. The radiotracer was injected into the feed line located at the middle of the RPB as shown in Fig. 1. The passage of radiotracer in the column was monitoring at inlet and outlet of the RPB using collimated NaI(Tl) scintillation detectors [Size: 2.54 cm by 2.54 cm] D1 and D2 as shown in Fig. 1. The detectors were connected to a computer-controlled data acquisition system (DAS) set to record radiotracer concentration at an interval of 0.5 s. The acquired data was saved for further processing and analysis.

Since the radiotracer was injected as an impulse, the treated and normalized radiotracer concentration measured





RESEARCH

Open Access



Structural and functional insights into Ubl domain-mediated regulation of SARS-CoV-2 PLpro

Rimanshee Arya^{1,2}, Janani Ganesh^{1,2}, Vishal Prashar^{1,2*} and Mukesh Kumar^{1,2*}

Abstract

Background SARS-CoV-2 papain-like protease (PLpro) is essential for viral replication and immune evasion. It contains an N-terminal ubiquitin-like (Ubl) domain, whose involvement in enzymatic function remains poorly understood.

Results In this study, we investigated the role of the Ubl domain in modulating the structural dynamics and catalytic efficiency of PLpro. Using molecular dynamics (MD) simulations, inhibitor binding assays, and steady-state kinetic analyses, we found that the Ubl domain stabilizes critical structural elements, notably the ridge helix in the thumb subdomain. Removal of the Ubl domain altered substrate processing, reducing catalytic efficiency of the enzyme. Interestingly, free ubiquitin enhanced enzymatic activity, likely via non-canonical binding sites distinct from the SUB1 and SUB2 sites.

Conclusion These findings uncover a regulatory role for the Ubl domain in allosteric modulation of PLpro activity and reveal additional layers of enzymatic plasticity. Understanding these mechanisms could guide the design of future antiviral therapeutics targeting PLpro's regulatory or allosteric sites.

Keywords SARS-CoV-2, Papain-like protease, Ubl domain, Ubiquitin, ISG15, Deubiquitination and deISGylation

Introduction

SARS-CoV-2, the causative agent of the COVID-19, relies on various structural, non-structural and accessory proteins for its replication and pathogenicity. Among the non-structural proteins, Nsp3 is the largest and the most complex protein, comprising multiple functional domains, including the papain-like protease (PLpro)

domain that hydrolyzes peptide and isopeptide bonds of viral and cellular substrates. PLpro cleaves viral polyproteins to release Nsp1, Nsp2, and Nsp3 which is essential for viral replication [1, 2]. In addition, PLpro removes ubiquitin (Ub) and interferon-stimulated gene product 15 (ISG15) from the cellular protein substrates- a process known as deubiquitination (DUB) and deISGylation, respectively [2–4]. By acting as both a deubiquitinase and a deISGylase, PLpro enables SARS-CoV-2 to evade host immune responses. It impairs the interferon signalling pathway by removing Ub and ISG15 from key signalling proteins, thereby disrupting innate immunity [5–7]. Furthermore, PLpro-mediated deISGylation of the viral nucleocapsid protein enhances viral replication [8].

*Correspondence:

Vishal Prashar
vishalp@barc.gov.in

Mukesh Kumar
mukeshk@barc.gov.in

¹Protein Crystallography Section, Bhabha Atomic Research Centre, Mumbai 400085, India

²Homi Bhabha National Institute, Anushakti Nagar, Mumbai 400094, India



© The Author(s) 2025. **Open Access** This article is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License, which permits any non-commercial use, sharing, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if you modified the licensed material. You do not have permission under this licence to share adapted material derived from this article or parts of it. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by-nc-nd/4.0/>.

SARS-CoV-2 PLpro comprises an N-terminal ubiquitin-like (Ubl) domain (residues 1–60) followed by a catalytic core domain (residues 61–314). While the function of catalytic domain is well-characterized, the role of Ubl domain in catalysis remains largely unexplored. The Ubl domain shares ~17% sequence identity with the ubiquitin and structural studies, including cryo-EM analysis of full-length Nsp3 [9], show that the Ubl domain is spatially separated from other functional domains of Nsp3. Moreover, crystal structures of PLpro bound to ubiquitin (PDB ID: 7RBR, 5E6J and 7UV5) and ISG15 (PDB ID: 7RBS, 6XA9 and 6YVA) reveal no direct interactions between the Ubl domain and these substrates [4, 10–12]. Interestingly, certain PLpro inhibitors have been observed to bind at the interface between the Ubl and catalytic domains [13], raising questions about how ligand binding at distal sites can modulate enzymatic activity. A set of engineered ubiquitin variants (UbVs) were also shown to bind at a distal allosteric site on PLpro, potentially inhibiting its enzymatic activity and reducing viral replication in cell culture [14]. Further, a single mutation near the Ubl domain (F69S) was shown to impair hydrolysis of K48-linked diUb-TAMRA and reduce cleavage efficiency of Ub-TAMRA substrate [12] suggesting a possible regulatory role for the Ubl domain in catalysis. It was also shown recently that the catalytic cysteine (C111) of SARS-CoV-2 PLpro is essential for suppressing NF- κ B signaling, while its Ubl domain is dispensable for interferon antagonism [5].

Previous studies on MERS-CoV PLpro suggest that its Ubl domain is dispensable for proteolytic, deubiquitinating or deISGylating functions [15, 16]. In contrast, deletion of Ubl domain in SARS-CoV PLpro leads to protein instability and a loss of enzymatic activity over time, indicating that this domain is critical for maintaining structural integrity in vitro [17]. The Ubl domain of SARS-CoV-2 PLpro shares 88% sequence identity and high structural similarity with SARS-CoV counterpart. In SARS-CoV-2, the significance of Ubl domain in proteolytic activity, substrate interaction, and inhibitor binding remains unclear.

Interestingly, parallels can be drawn from ubiquitin-specific proteases (USPs), a major subclass of deubiquitinases (DUBs), given their involvement in diverse processes such as ubiquitin homeostasis and protein regulation [18, 19]. Ubiquitin-like (Ubl) domains within USPs play pivotal roles in modulating their enzymatic activity. For example, the Ubl domain of USP14 promotes its association with the proteasome, thereby enhancing its catalytic performance [20, 21]. In contrast, USP4's Ubl domain functions as an autoinhibitory element, mimicking ubiquitin to suppress activity until it is removed or masked [22]. USP7 contains five Ubl domains, with the last two enhancing catalysis allosterically by inducing

favorable conformational changes [23]. These cases illustrate the diverse mechanisms through which Ubl domains regulate DUB activity ranging from inhibition to allosteric activation ensuring precise control over their cellular functions.

In this study, we investigate the structural and functional significance of the Ubl domain in SARS-CoV-2 PLpro. By characterizing a truncated variant lacking the Ubl domain (PLpro TR), we examine its effects on enzymatic activity, stability, and substrate/inhibitor interactions. Our findings reveal that the Ubl domain plays a critical role in maintaining the catalytic efficiency and structural integrity of PLpro, providing new mechanistic insights into its regulatory function.

Materials and methods

Cloning, expression, and purification of PLpro WT and TR

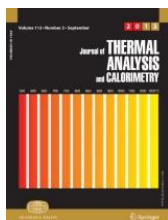
The gene encoding wild-type (WT) SARS-CoV-2 PLpro was available in our laboratory [24]. Genes for truncated version of PLpro (TR) lacking the N-terminal 60 residues, human ISG15 and Ubiquitin (based on NCBI reference sequences NP_005092.1 & 1UBQ_A, respectively) were codon-optimized and synthesized for expression in *Escherichia coli*. All constructs were cloned into the pET28a vector (Novagen) using NdeI and BamHI restriction sites. Each included an N-terminal hexahistidine tag for affinity purification. A thrombin cleavage site was introduced downstream of the His-tag for PLpro and ISG15 constructs, while a TEV protease site was used for the Ubiquitin construct. Recombinant plasmids were transformed into *E. coli* BL21 (DE3) cells. Cultures were grown in Luria-Bertani (LB) medium at 37 °C until the optical density at 600 nm (OD_{600}) reached 0.8–1.0. Protein expression was induced by adding IPTG to a final concentration of 0.5 mM, followed by overnight incubation at 18 °C. Cells were harvested by centrifugation at 6000 Xg, resuspended in lysis buffer (50 mM Tris-HCl, pH 7.5; 300 mM NaCl; 10 mM imidazole; 10 mM β -mercaptoethanol; 1 mg/mL lysozyme), and lysed by sonication. The lysate was clarified by centrifugation at 10,000 Xg for 30 min at 4 °C. The resulting supernatant was incubated with Ni-NTA agarose resin (Roche) for 90 min at 4 °C with gentle rocking. The resin was washed twice with wash buffer (50 mM Tris-HCl, pH 7.5; 300 mM NaCl; 20 mM imidazole; 10 mM β -mercaptoethanol), and the bound protein was eluted using elution buffer (50 mM Tris-HCl, pH 7.5; 300 mM NaCl; 250 mM imidazole; 10 mM β -mercaptoethanol). Eluted proteins were dialyzed overnight at 4 °C against dialysis buffer (30 mM Tris-HCl, pH 7.5; 150 mM NaCl; 5 mM DTT).

Enzymatic assays

All enzymatic assays were performed in black, flat-bottom, 96-well, non-treated plates (Corning, USA) using a



Scan the QR Code or Click for full text



Structural and thermal stability studies on irradiated magnesium potassium phosphates for back end nuclear fuel cycle applications

Rumu H. Banerjee¹ · Naina Raje^{2,3} · Kulwant Singh^{1,3} · Pranesh Sengupta^{1,3}

Received: 30 May 2025 / Accepted: 13 December 2025
 © The Author(s) 2026

Abstract

Magnesium potassium phosphate (MKP) cement has emerged as a potential eco-friendly alternative to Portland cement for nuclear waste encapsulation. Its superior resistance to sulfate attack, low permeability and mechanical strength makes it a promising material. This study investigates the thermal and radiation stability of MKP specimens prepared by gel crystallization, followed by heat treatment at 120, 400, 800 and 1000 °C and subsequent irradiation with 10 MeV electron beam to a dose of 20 MGy. MKP specimens prepared at room temperature ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$) partially lose their structural water upon irradiation forming an amorphous phase which coexists with the untransformed $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ phase. MKP heat-treated at 1000 °C (KMgPO_4 having monoclinic structure) exhibited high structural stability, minimal mass loss and negligible gas evolution under thermal and radiation conditions. A mechanism for radiation damage is proposed.

Keywords Magnesium potassium phosphate cement · Thermal stability · Phase transformation · Nuclear waste immobilization · Electron beam irradiation · Radiation resistance

Introduction

Magnesium potassium phosphate (MKP) ceramic, a synthetic analogue of the naturally occurring mineral K-struvite [1], has attracted considerable attention for its ability to stabilize heavy metal ions such as lead, arsenic, and iron from waste streams [2, 3]. In addition to its use in environmental remediation, MKP has potential applications as a bioceramic, a refractory material for high-temperature furnaces, and as a component in fire-resistant coatings [4–6]. As a cementitious material, it is also employed for the rapid repair of damaged civil structures [7]. Notably, magnesium potassium phosphate cement ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$, hereafter referred to as MKP) is emerging as a sustainable, high-performance alternative to Portland cement, particularly for addressing critical challenges in nuclear waste immobilization [8–10].

Currently, ordinary Portland cement (OPC) is extensively used for constructing protective structures in nuclear power plants, serving as matrices for the temporary storage and long-term disposal of radioactive wastes—including low- and intermediate-level wastes and spent fuel assemblies—and as shielding for radiation sources [11]. However, OPC production is energy-intensive and accounts for approximately 6–8% of global anthropogenic CO_2 emissions [12]. In the context of nuclear waste immobilization, OPC exhibits several limitations: (i) encapsulation of reactive metals (e.g., Al, Mg, U) can result in corrosion under high pH conditions [13]; (ii) such corrosion reactions (e.g., $\text{U} + 2\text{H}_2\text{O} \rightarrow \text{UO}_2 + \text{H}_2$) generate hydrogen gas, leading to pressurization, container distortion, potential fracture of the wasteform, and increased flammability risk [13, 14]; and (iii) OPC matrices have a limited waste loading capacity (7–10 mass%) for high salt-bearing liquid radioactive waste streams [11, 13, 14].

MKP is synthesized via an acid–base reaction between magnesium oxide and potassium dihydrogen phosphate, resulting in a material with superior mechanical strength, high resistance to sulfate attack, and compatibility across a broad pH range compared to Portland cement [11–14]. These properties, combined with low leachability and permeability, make MKP especially suitable for encapsulating

✉ Rumu H. Banerjee
 rumu@barc.gov.in

¹ Materials Science Division, Bhabha Atomic Research Centre, Mumbai 400085, India

² Analytical Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

³ Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

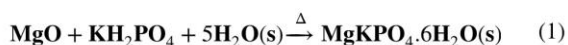
beta-emitting radionuclides such as ^{137}Cs and ^{90}Sr , which are major contributors to radioactive waste activity [4–14]. Unlike Portland cement, which is susceptible to structural degradation from radiolytic gas generation, chemical instability, and poor performance in high-salt environments, MKP offers enhanced chemical resilience and a lower leaching rate for cesium [11–14].

Owing to their possible use in various high-temperature applications, it is necessary to gain structural insights into the thermal and crystallographic aspects of these synthetic K-struvite ceramics. Furthermore, the application of MKP in nuclear waste management necessitates a detailed understanding of its behavior under radiation. Ionizing radiation, particularly from beta-emitting isotopes, can induce significant structural modifications, including defect generation, amorphization and radiolysis of bonded water molecules [11, 13, 14]. These effects, compounded by thermal stresses from decay heat, may lead to dehydration and phase transformations that could potentially compromise matrix integrity. This study systematically investigates the thermal and radiation stability of MKP, with a focus on the role of heat treatment in enhancing its structural and chemical durability.

Experimental study

Materials synthesis

The raw materials used for the preparation of magnesium potassium phosphate (MKP) cement samples were MgO , H_2KPO_4 , and demineralized water. The dry components— MgO (11.53 g), H_2KPO_4 (35.79 g), boric acid (as a retardant), and Al_2O_3 (as a sintering agent for subsequent heat treatment)—were first mixed in a fixed stoichiometric ratio of 1:1 ($\text{MgO}:\text{H}_2\text{KPO}_4$) using a Kenwood electric hand mixer. Demineralized water was then added (resulting in a $\text{MgO}:\text{H}_2\text{KPO}_4:\text{H}_2\text{O}$ ratio of 1:1:5), and the mixture was continuously stirred until its temperature increased from room temperature (25 °C) to between 60 and 80 °C, as measured by a Newport thermocouple, indicating the onset of exothermic acid–base reaction. The mixture was subsequently poured into cylindrical molds having diameter of 15 mm and height 5 mm, where gel crystallization continued until the temperature of the formed monolith returned to room temperature. The MKP samples were then cured at ambient conditions (25–5 °C) for 7–21 days, after which they were demolded and characterized. Approximately 100–200 g of each sample was prepared.



For the dehydration studies, the as-prepared MKP samples were heated in ambient atmosphere using a

programmable furnace with a linear heating rate was of $0.5\text{ }^\circ\text{C min}^{-1}$. The specimens were heated to 120, 400, 800, and 1000 °C, each with a dwell time of 120 min followed by furnace cooling ($10\text{ }^\circ\text{C min}^{-1}$). The samples are hereafter labelled as MKP-RT, MKP-120, MKP-400, MKP-800, and MKP-1000.



The density of the pellets was measured by Archimedes principle in water at ambient temperature.

Electron irradiation

The powdered samples were exposed to a 10 MeV electron beam (EB) at room temperature, receiving doses between 10 and 20 MGy at a rate of 1 MGy per hour. To avoid any loss of material, the powdered specimens were placed in uncovered nickel crucibles while the pellets were placed on steel plate and positioned on the irradiation stage. This dose was selected to examine the early stages of radiation-induced damage in the matrix. The 10 MeV beam was generated using an indigenously designed radio-frequency accelerator developed by the Bhabha Atomic Research Centre (BARC) housed at Kharghar, India [15]. The beam pulses were directed through a 1 m long titanium exit window and uniformly scanned over the MKP powder contained in nickel crucibles, which were maintained at room temperature under normal light conditions and ambient atmosphere. The various beam parameters used were 0.25 mA beam current, 2.4 kW beam power and electron flux— 1.6×10^{16} electrons $\text{cm}^{-2} \text{h}^{-1}$.

Structural and spectroscopic characterization

The as prepared specimens were characterized using a Jordan Valley EX-3600 M model energy-dispersive X-ray fluorescence (EDXRF) at room temperature. The EDXRF spectra were acquired under vacuum environment, applying a voltage of 5 kV and an emission current of 2000 μA . Rhodium was used as the secondary target, and the counting time was exceeded 50 s. The pre- and post-irradiation characteristics of the MKP samples were examined using X-ray diffraction (XRD) and spectroscopic techniques. These non-destructive, direct, and non-invasive techniques offer high sensitivity and detection limits, enabling the identification of minute structural and compositional changes. XRD measurements were performed using a Rigaku Miniflex600 system with $\text{CuK}\alpha$ radiation, scanned over a 2θ range of 15–75 deg at a scan rate of $0.2\text{ }^\circ \text{min}^{-1}$.

In addition, Thermogravimetric Analysis (TGA)-differential thermal analysis (DTA) was performed using a Netzsch STA 409 PC Luxx system to evaluate the thermal behavior





Structure, thermal stability and thermodynamics investigations on Na₂MnF₅

S. Narang^{1,2} · P. M. Aiswarya^{1,2} · Rimpi Dawar^{1,2} · Akanksha Samanta^{2,3} · R. Mishra^{1,2}

Received: 22 January 2025 / Accepted: 26 July 2025 / Published online: 9 September 2025
 © The Author(s) 2025

Abstract

In the present study, structural and thermodynamic investigations are performed on the ternary Na₂MnF₅(s) compound, which can be formed due to interaction of molten fluoride salts with structural materials of the molten salt reactor (MSR). The standard molar enthalpy of formation ($\Delta H_{f,298.15K}^{\circ}$) at 298.15 K of this compound was determined by room temperature solution calorimetry and the corresponding value is found to be -2318.84 ± 15.72 kJ mol⁻¹. Critical insights into the thermal stability of this compound were obtained by performing TG–DTA–MS analysis supported by parallel XRD measurements. At temperatures between 573 and 623 K, the compound was found to undergo thermal decomposition. A thorough decomposition mechanism for this compound is proposed based on the inference. Utilizing a combined approach of relaxation calorimetry and differential scanning calorimetry, molar heat capacity of this compound from 2 to 573 K is obtained. Using enthalpy of formation value at 298.15 K and molar heat capacity of this compound other thermodynamic functions are derived in the current investigation. The temperature dependence of the Gibbs energy, which reflects the thermodynamic stability, was determined using the thermodynamic parameters of Na₂MnF₅(s).

Keywords Na₂MnF₅(s) · Molar heat capacity · Thermal stability · Solution calorimetry · Enthalpy of formation

Introduction

Molten salt reactor (MSR) is one among the most fascinating reactor concepts for futuristic nuclear energy program. It is one of the six novel reactor designs proposed by the Generation IV International Forum (GIF), having several noteworthy features, including enhanced sustainability, feasibility, safety, high thermal efficiency and proliferation resistance [1–5]. India has vast resources of thorium which can be effectively utilized using MSR technology [6]. In MSRs, fertile and fissile materials are dissolved in a molten

salt known as the fuel carrier salt that circulates in the primary circuit, acting as both the primary coolant and fuel for the fission process [7, 8]. The projected neutron energy regime for the reactor is one of the key variables that influence the composition of the reference fuel salt. Presently, 8.6 mass%UF₄ + 68.9 mass.%ThF₄ + 22.5 mass.% LiF is the proposed fuel salt composition for Indian Molten Salt Breeder Reactor (IMSBR). Alternative reactor designs have proposed the use of sodium fluoride (NaF) in the epithermal neutron energy range to take advantage of the benefits associated with a harder neutron spectrum such as improved breeding ratios and a more negative temperature coefficient of reactivity which contribute to enhanced safety and reactor performance. FLiNaK, the eutectic mixture of LiF, NaF and KF is proposed to be used as coolant salt in IMSRs [9–12]. Physico-chemical properties of these molten salts change during reactor operation due to the generation of fission products as a function of burn up. Due to the interaction of these molten salts with fission products and structural materials, there is a possibility of formation of multi-component fluoride compounds affecting the physical and chemical characteristics of the molten salts [13–15].

✉ Rimpi Dawar
rimpid@barc.gov.in

✉ R. Mishra
mishrar@barc.gov.in

¹ Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, Maharashtra 400085, India

² Homi Bhabha National Institute, Anushaktinagar, Mumbai, Maharashtra 400094, India

³ Post Irradiation Examination Division, Bhabha Atomic Research Centre, Trombay, Mumbai, Maharashtra 400085, India

To withstand the highly corrosive nature of fluoride salts used in molten salt reactors (MSRs), corrosion-resistant nickel-based alloys such as Hastelloy, INOR, and Inconel are commonly proposed as structural materials [16, 17]. Nickel-based alloys consist of base metal Ni (55–70%) with inclusions of elements like Cr, Mo, Fe, Ti, Nb, Al, C, P, Mn, Si, Co and W [18–20]. The inclusion of these various specified elements is solely determined by different experimental requirements, such as reactor operating temperature, corrosiveness, and reactivity of the handling materials [21, 22].

Generation of a comprehensive thermodynamic database for the pertinent compounds, which can be formed during MSR operation, is in progress at the author's laboratory. As an extension of this database, the current work involves thermodynamic investigation on the compounds which can be formed due to interaction of fuel or coolant salt with the clad material. The current study focuses on determining the thermodynamic stability of one of these fluorides, $\text{Na}_2\text{MnF}_5(\text{s})$, which can be formed due to interaction of molten fluoride salts with structural material (Hastelloy N). At present, there are no reports available on the thermochemistry of $\text{Na}_2\text{MnF}_5(\text{s})$ that the authors are aware of. Numerous studies have investigated the magnetic properties of this compound, as it belongs to the A_2MnF_5 fluoro-manganate family, which has attracted significant research interest due to its one-dimensional antiferromagnetic behavior [23–25]. Sodium manganese fluorides also have been studied for their use as a cathode material for Na-ion batteries [26].

Experimental

Table 1 provides the purities and specifications of the chemicals used in the current investigation. Due to hygroscopic nature of fluorides and chlorides, these chemicals were dried at 473 K for 48 h under the dynamic vacuum (10^{-6} mbar) to get rid of any moisture traces prior to their use in the current study.

Synthesis

The compound $\text{Na}_2\text{MnF}_5(\text{s})$, used in the present study was prepared by co-precipitation method in a similar way as reported in [27]. For this, 2.5719 g of $\text{NaF}(\text{s})$ (0.060 mol) and 2.4174 g of $\text{Mn}_2\text{O}_3(\text{s})$ (0.015 mol) were mixed in 30 mL of $\text{HF}(\text{l})$ in a Teflon beaker. The resultant mixture was then subjected to vigorous stirring until the complete dissolution of the precursors occurred. Afterwards, mild stirring was continued for another 6 h at room temperature. The light pink color solid was precipitated, which was then separated out by centrifugation. The separated solid was then washed with ethanol and then finally dried at 343 K in an oven for about 3 h. This solid was then used for further studies.

Structural characterization

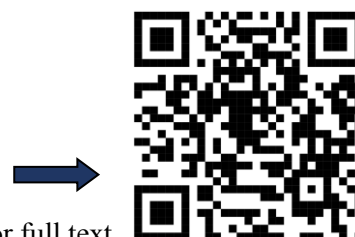
The synthesized $\text{Na}_2\text{MnF}_5(\text{s})$ sample was structurally characterized by powder X-ray diffraction (XRD) technique. The diffraction pattern was recorded using an X-ray diffractometer supplied by M/s Rigaku, Japan employing Ni filter and Cu K_α radiation ($\lambda = 1.541 \text{ \AA}$). The verification of the desired phase was carried out by comparing the experimental X-ray diffractogram with standard pattern provided in the ICDD-PDF-2 database. Further, Rietveld refinement of the experimental XRD pattern was carried out using Fullprof-2k software package [28]. The Pseudo-Voigt profile function was used to refine the peak profiles while the background of the recorded X-ray pattern was refined using the six order polynomial function. With the help of an Energy Dispersive X-ray fluorescence spectrometer coupled with a rhodium anode (Model No: EX 3600 SDD), supplied by M/s Xenometrix, Israel, the mass percentages of sodium and manganese in the synthesized sample were determined. Furthermore, Inductively Coupled Plasma-Optical Emission Spectrometry technique (ICP-OES) using an iCAP 6500 spectrometer fitted with a CCD detector, supplied by M/s Thermo Scientific,

Table 1 Specifications of chemicals used in the current investigation

S. No	Chemical name	Source	Mole fraction Purity/grade	Analysis method
1.	$\text{NaF}(\text{s})$	M/s Sigma Aldrich, USA	0.9999 on metal basis	Manufacturer assay
2.	$\text{Mn}_2\text{O}_3(\text{s})$	M/s Sigma Aldrich, USA	0.9990 on metal basis	Manufacturer assay
3.	$\text{MnF}_3(\text{s})$	M/s Sigma Aldrich, USA	0.9990 on metal basis	Manufacturer assay
4.	$\text{HF}(\text{l})$	M/s Sigma Aldrich, USA	0.40(w/w) in water [#]	Manufacturer assay
5.	$\text{KCl}(\text{s})$	M/s Sigma Aldrich, USA	0.9999 on metal basis	Manufacturer assay
6.	$\text{HCl}(\text{l})$	M/s Sigma Aldrich, USA	0.37(w/w) in water [*]	Manufacturer assay
7.	$\text{Na}_2\text{MnF}_5(\text{s})$	Prepared in the present study	0.995	XRD ^a , EDXRF ^b , ICP-OES ^c

^aX-ray powder diffraction, ^bEnergy dispersive X-Ray Fluorescence, ^cInductively Coupled Plasma-Optical Emission Spectroscopy

[#]Density of $\text{HF}(\text{l})$ used is 1.13 g cm^{-3} , ^{*}Density of $\text{HCl}(\text{l})$ used is 1.19 g cm^{-3}





Journal of Polymer Research (2025) 32:455
<https://doi.org/10.1007/s10965-025-04679-4>

ORIGINAL PAPER



The effect of composition and electron beam irradiation on the free volume and crystallinity of linear low-density polyethylene (LLDPE)/ethylene-octene copolymer (EOC) blends: a positron annihilation lifetime spectroscopic study

Manjeet Singh¹ · Rohini Agarwal¹ · Dhanadeep Dutta² · Subhendu Ray Chowdhury¹

Received: 17 June 2025 / Accepted: 12 November 2025 / Published online: 28 November 2025
 © The Author(s) 2025

Abstract

Blends of linear low-density polyethylene (LLDPE) and ethylene-octene copolymer (EOC) are prepared in various compositions by melt mixing, followed by electron beam (EB) irradiation at dose ranging from 50 to 250 kGy. The effects of blend composition and EB irradiation on the free volume of LLDPE/EOC blends are investigated using positron annihilation lifetime spectroscopy (PALS). Two ortho-positronium (o-Ps) lifetime components extracted from the PALS spectra indicate the presence of two distinct phases in the LLDPE/EOC blends. These components provide insights into the free volume properties of the crystalline and amorphous phases of the polymers. Analysis of the variation in o-Ps annihilation parameters (lifetime and intensity) in these phases confirms a significant increase in the crosslinked three-dimensional network with increasing irradiation dose up to 150 kGy for the LLEO82 blend (LLDPE/EOC: 80 wt%/20 wt%) and 200 kGy for the LLEO28 blend (LLDPE/EOC: 20 wt%/80 wt%). The increase in crosslinking density with EB irradiation is further supported by gel fraction measurements. The results from PALS, gel fraction and thermal analysis are consistent with each other. The study shows that o-Ps parameters are highly effective for determining the free volume hole size and relative fractional free volume in both unirradiated and irradiated LLDPE/EOC blends.

Keywords LLDPE · Ethylene-octene copolymer (EOC) · Electron beam irradiation · Crystalline phase · Amorphous phase · PALS · DSC · Gel fraction

Introduction

In recent years, polymers have been extensively used in a wide range of applications, thereby drawing significant research interest. One promising approach to advancing the field of polymer science and technology is the use of high-energy radiation to modify polymer properties. For polymer scientists aiming to tune polymer properties, electron beam (EB) and gamma radiation-assisted polymer modification have gained immense interest [1–3].

Radiation-induced crosslinking in polymers leads to an enhancement of the properties of the irradiated polymers. Moreover, blending polymers with distinct properties can significantly alter the characteristics of the resulting polymer blend system.

The final properties of irradiated polymer blends depend on both the radiation dose and the microscopic structure of the constituent polymers. Investigating the polymer structure at the microscopic level, both before and after irradiation, is one of the ways to optimize and control the irradiation dose and maximize benefits of the radiation-assisted polymer modification while avoiding degradation. Semicrystalline polymers consist of two distinct phases: crystalline and amorphous [4]. These phases respond differently with increasing doses of high-energy radiation. Determining the free volume holes in both crystalline and amorphous regions is very important for understanding the polymer behavior under irradiation [4, 5].

✉ Subhendu Ray Chowdhury
 rcsbhen@barc.gov.in; rcsbhen@gmail.com

¹ Radiation Technology Development Division, Bhabha Atomic Research Centre, Mumbai 400085, India

² Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

Positron annihilation lifetime spectroscopy (PALS) is one of the versatile and direct technique for determining free volume in polymeric materials [4–7]. It is highly sensitive to changes in free volume at the atomic scale [8]. In low electron density polymers, a fraction of thermalized positrons can form quasi-stable bound states—positronium (Ps)—with electrons from the medium. These Ps atoms preferentially localize in pre-existing free volume regions of the polymer [9]. Ps exists in two spin states: *singlet* para-positronium (*p*-Ps), which decays via two-photon emission with a short intrinsic lifetime of 0.125 ns (in vacuum), and *triplet* ortho-positronium (*o*-Ps), which decays via three-photon emission with a much longer lifetime of 142 ns (in vacuum). However, in matter, *o*-Ps often undergoes "pick-off" annihilation, where the positron interacts with an external electron of opposite spin, resulting in two-photon emission with a shortened lifetime of 1–10 ns. This pick-off component can be correlated with the average size and distribution of free volume, as well as the surface characteristics of these regions [10]. Therefore, the *o*-Ps pick-off component is highly useful for investigating free volume in polymers. The observed annihilation parameters—lifetime, intensity and fractional free volume can be quantitatively correlated with the size and concentration of free volume in polymeric materials [11–14].

Linear low-density polyethylene (LLDPE) is a widely used semicrystalline polymer with a typical crystallinity of ~39% [15, 16]. Ethylene-octene copolymer (EOC), another recently developed polymer (commercially known as Engage), is also employed in diverse applications due to its flexibility and enhanced processability. EOC is less crystalline (with crystallinity around 11–20%) and more amorphous than LLDPE [16–19]. EOC has advantages in improving the processability, filler incorporation capability and flexibility of polymer blends and composites [16, 20]. Because of its higher amorphous content, EOC generally achieves higher degree of crosslinking under high-energy radiation than LLDPE [2]. Therefore, blending EOC with LLDPE followed by EB irradiation is a promising strategy to create a material with intermediate crystallinity and tailored properties suitable for various applications.

In the present study, LLDPE/EOC blends with various compositions are prepared. These blends are analyzed to investigate the effect of composition on the free volume properties using the PALS technique. Two blend compositions—LLDPE/EOC: 80 wt%/20 wt% and 20 wt%/80 wt% are irradiated with different EB dose (50 to 250 kGy). Irradiated blends with various compositions are characterized using PALS to study changes in free volume. To assess the degree of crosslinking, gel content measurements are performed on EB irradiated LLDPE/EOC blends. Also, thermal

analysis is conducted to study the influence of blend composition and irradiation dose on crystallinity.

Experimental

Materials

The linear low-density polyethylene (LLDPE) used in this study is purchased from Reliance industry. LLDPE has density of 0.918 g/cc and melt flow index (MFI) of 1.0 g/10 min. Engage 8150, an ethylene octene copolymer (EOC), is purchased from DuPont-Dow Elastomers. It has density of 0.868 g/cc and MFI of 0.50 g/10 min. Xylene solvent is purchased from Sigma Adrich.

Preparation of LLDPE/EOC blends

Before preparation of blends, the pure polymers are dried in an oven at 85 °C for 4–5 h. LLDPE and EOC are mixed in various ratios and melt blended in a twin-screw extruder (Haake MiniLab mini extruder) at 170 °C and 40 rpm for 5 min. These extruded blends are compression moulded into 2 mm thick sheets at 170 °C and 5-ton pressure for 5 min.

The prepared blends are designated as LLEO82, LLEO64, LLEO46 and LLEO28 corresponding to LLDPE/EOC compositions of 80 wt%/20 wt%, 60 wt%/40 wt%, 40 wt%/60 wt% and 20 wt%/80 wt%, respectively.

Electron beam irradiation

Compression moulded LLEO82 and LLEO28 samples are irradiated using 3 MeV electron beam (EB) radiation at doses of 50, 100, 150, 200 and 250 kGy. Samples are placed 20 cm below the scan horn and irradiated at a beam current of 1 mA with a dose rate of 5 kGy/pass.

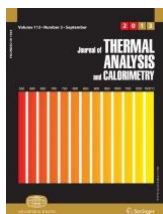
Characterization

Gel fraction measurements

Gel fraction analysis of EB irradiated polymers blends are carried out using the solvent etching technique with xylene as a solvent according to ASTM D 2765–16 standard [21–23].

Circular samples with a diameter of 10 mm and a thickness of 2 mm are first dried to a constant weight and then weighed. The samples are immersed in xylene and subjected to extraction at 120 °C for 24 h (Soxhlet and static reflux). After extraction, the swollen samples are carefully removed and dried in a vacuum oven at 90 °C until a constant weight is obtained. The samples were then reweighed to determine





Thermal study of *Bombyx mori* silk fibroin film obtained through degumming process for biomaterial application

Sanasam Yaiphabi^{1,2} · Sanjenbam Kabita¹ · Sorokhaibam Jibankumar Singh¹ · Shamjetshabam Babeeta Chanu¹ · Langlen Meinam¹ · Manoj Kumar Thota⁴ · R. Mishra^{2,3} · Senjam Sunil Singh¹ · Laishram Rupachandra Singh¹ · Sanjenbam Kunjeshwori Devi¹ · Raghumani Singh Ningthoujam^{2,3}

Received: 3 June 2025 / Accepted: 16 November 2025
 © The Author(s) 2025

Abstract

Silk fibroin of *Bombyx mori* cocoon has shown promising potential as a biomaterial for biomedical applications. In the present study, silk fibroin film was successfully fabricated from the regenerated silk fibroin solution prepared from the dissolution of degummed silk fiber in calcium nitrate solution. The degummed silk fiber exhibited markedly improved solubility in calcium nitrate solution. The thermal stability studies of raw cocoon shell, demineralized cocoon, degummed silk fiber and silk fibroin film were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Three main stages in thermogravimetric analysis curves were observed. The initial mass losses were observed at 70, 69, 58 and 83 °C in samples of raw cocoon shell, demineralized cocoon, degummed silk fiber and silk fibroin film, respectively, which is related to the loss of bound water molecules. Silk fibroin film has higher content of water molecules among other samples. The second stage showed the mass losses at 265, 245, 265 and 246 °C to above the respective samples, and third stage showed larger mass losses at around 350 °C. The differential scanning calorimetry (DSC) study exhibited the endothermic peaks in all four materials. The Fourier-transform infrared spectroscopy (FTIR) results revealed that all samples exhibited the presence of Amide I, Amide II and Amide III. Higher water content was found in the silk fibroin film as compared to other samples. An intricate surface morphology of the silk fibroin film was revealed using scanning electron microscope (SEM). Therefore, the present study will help in understanding the thermal stability of silk fibroin film for the potential utilization as a biomaterial for biomedical applications.

Keywords Degummed silk fiber · Silk fibroin film · DSC · Thermogravimetric analysis

Introduction

Silk fibroin, derived from the cocoons of *Bombyx mori*, is a promising biomaterial for biomedical applications due to its biocompatibility, biodegradability, mechanical strength and thermal stability [1–3]. It can be processed into the films

[4, 5], hydrogels [6–8], sponges and nanoparticles [3] using regenerated silk fibroin solutions. The continuous silk filament of *Bombyx mori* cocoon is made up of two main silk proteins, fibroin and sericin [9]. Silk fibroin is considered the major protein of the silk fiber which helps in maintaining the structural integrity, constituting about 75–80% [3]. The silk fibroin is formed by two fibroin brins forming a continuous silk filament, held together by the gummy sericin protein [10]. Recently, silk fibroin has gained significant attention as a potential biomaterial for the various biomedical applications including corneal regeneration, bone engineering, drug delivery, wound healing and tissue engineering [11–13]. Degumming is an important and crucial process to effectively remove the sericin protein without damaging the structural integrity of silk fibroin [1]. The sericin-free degummed silk fiber is obtained after degumming using suitable dissolving methods. Previous studies commonly

✉ Raghumani Singh Ningthoujam
 rsn@barc.gov.in

¹ Department of Biochemistry, Manipur University, Canchipur, Imphal 795003, India

² Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

³ Homi Bhabha National Institute, Mumbai 400094, India

⁴ Mechanical Metallurgy Division, Bhabha Atomic Research Centre, Mumbai 400085, India

dissolved the degummed silk fiber in lithium bromide [5, 14–16], lithium thiocyanate [17, 18] and ternary system of calcium chloride/water/ethanol solutions [19] to prepare the regenerated silk fibroin solution for the fabrication of the silk fibroin film, but an improvement in the dissolution methods is needed to enhance biomaterial properties of the fabricated silk fibroin film. The solubility of degummed silk fiber depends upon the concentration of the dissolving solution and specific experimental temperature. Previous investigations had reported that dissolution of degummed silk fiber used highly concentrated solution systems [5]. *Bombyx mori* degummed silk fiber has been reported to dissolve in 9 M lithium thiocyanate or 9.3 M lithium bromide to prepare regenerated silk fibroin solution for fabrication of silk fibroin film [5]. Further studies had reported that silk fibroin film prepared using lithium-based dissolving systems, such as lithium thiocyanate or lithium bromide, shows a smooth film surface [20]. Such silk fibroin film having smooth surface is considered less suitable as a biomaterial due to poor cell attachment and proliferation for biomedical applications such as wound healing, bone regeneration and tissue engineering [21, 22]. The use of lithium solution systems exhibits more toxicity as compared to that of calcium-based solution for biomedical applications. To mitigate the limitations associated with lithium-based solutions, studies on the dissolution of degummed silk fiber in calcium nitrate solution at lower concentrations can offer a potentially safer alternative for biomedical applications. In addition, calcium nitrate is more cost-effective alternative compared to lithium thiocyanate and lithium bromide, which are considerably

more expensive. Previous studies have also shown that the residual calcium ions remaining after dialysis were insufficient to alter the secondary structural conformation of the fabricated silk fibroin film [20]. Moreover, reports indicate that silk fibroin films prepared using different calcium solutions exhibit improved hemostatic properties, by shortening thrombin and plasma recalcification times compared to films fabricated using lithium bromide [23]. These findings highlighted the potential biomedical advantage of using calcium nitrate solutions in silk fibroin processing for wound healing applications. Moreover, differences in the dissolution behavior and solubility of degummed silk fiber are expected to significantly influence the thermal stability of the resulting materials. Therefore, the thermal behavior of the raw cocoon shell, demineralized cocoon, degummed silk fiber and silk fibroin film need to be understood.

To address the thermal behavioral change, systematic thermal stability studies of the raw cocoon shell, demineralized cocoon, degummed silk fiber and silk fibroin film using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are carried out in this work. Functional groups present in material are studied using Fourier-transform infrared spectroscopy (FTIR). The substantial morphological changes in the microstructure of raw cocoon shell, demineralized cocoon, degummed silk fiber and silk fibroin film are confirmed using scanning electron microscope (SEM). In this study, calcium nitrate tetrahydrate is used as a solution for the dissolution of the degummed silk fiber to prepare a regenerated silk fibroin solution for fabrication of silk fibroin film.

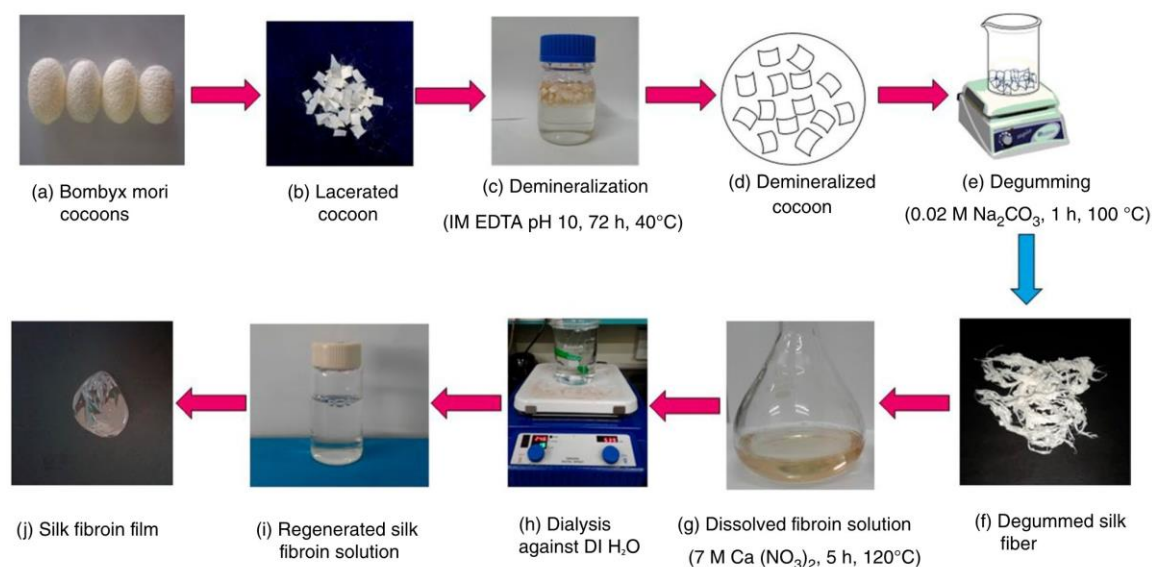


Fig. 1 Schematic diagram illustrating the sequential steps for fabrication of silk fibroin film from regenerated silk fibroin solution obtained from various processes (raw cocoon shell to demineralized cocoon to degummed silk fiber to regenerated silk fibroin solution)





CELEBRATING
40
YEARS

jmr Journal of
MATERIALS RESEARCH

70

Article

DOI:10.1557/s43578-025-01687-4



Twin formation through repeated dislocation impingement on phase boundary in Ni-based superalloys using atomistic simulations

Sagar Chandra^{1,a)}, Mahendra K. Samal², Vivek M. Chavan¹

¹ Reactor Technology Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

² Reactor Safety Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

^{a)} Address all correspondence to this author. e-mail: sagarc@barc.gov.in

Received: 1 June 2025; accepted: 21 August 2025; published online: 9 September 2025

Formation of stacking faults and deformation twins in the matrix as well as precipitate phase of Ni-based superalloys governs their proficiency in high-temperature service. In view of this phenomena, the present work reports a qualitatively different pathway for the formation of twins in γ' phase during plastic deformation. The involved mechanism relies on the prevalence of multiple matrix dislocations on adjacent slip planes in the vicinity of $\gamma - \gamma'$ interface along with sufficient magnitude of glide stress and temperature. An attempt is also made to compare the results with experiments available in the literature. It is envisioned that this work shall open up novel avenues for probing other deformation pathways also that may lead to formation of twins in γ' phase of Ni-based superalloys. This may ultimately lead to an advanced understanding of deformation mechanisms in Ni-based superalloys at high temperatures.

Introduction

Interfaces are an ubiquitous trademark of microstructures in crystalline metals and alloys. In pure polycrystalline metals, they prevail in the form of grain boundaries existing between mis-oriented grains. In alloys like precipitation hardened Ni-based superalloys, they may also exist in the form of phase boundaries between the γ matrix (Ni) and γ' (Ni_3Al) precipitates. Indeed, interfaces are an inevitable part of a materials microstructure and affect the deformation behavior by acting as sources, sinks, and barriers to dislocations [1, 2]. The interaction of dislocations with these interfaces is one of the primary mechanisms of plastic deformation in crystalline metals and alloys [3, 4].

However, dislocation glide and subsequent interactions with interfaces, although fundamental, are not the only mode through which metals deform plastically. In addition to dislocation slip, twinning is another conspicuous feature of plastic deformation. Investigations on relative contributions from slip and twinning to metal plasticity offer key insights into the dominant mode of deformation under a given condition of loading. Recognition of this aspect has led to the emergence of a number of seminal works focusing on the interplay of dislocation slip and twinning and their inherent mechanistic competition in various metals

and alloys [5–9]. Owing to their excellent mechanical properties, particularly at high temperatures, various studies have investigated the deformation behavior in precipitation-strengthened Ni-based superalloys also [10–14]. These unique properties are attributed to the presence of γ' precipitates (L_{12} structure) embedded coherently in the γ (FCC structure) Ni matrix. The presence of these precipitates in the γ matrix induces several strengthening mechanisms inhibiting dislocation glide like precipitation strengthening, solute strengthening, and stacking fault strengthening [15]. Interactions of matrix dislocations with the $\gamma - \gamma'$ interface under different loading conditions result in a variety of deformation mechanisms involving various planar defects like superlattice intrinsic/extrinsic stacking faults (SISF/SESF), anti-phase boundaries (APB), and twins in the γ' phase [15, 16]. These faults may either appear isolated in the γ' phase or may appear as extended bands traversing through both the γ matrix and the precipitate [17, 18].

Within the γ matrix, perfect dislocations split into Shockley partials bounding the intrinsic stacking fault [19]. These stacking faults may either lie completely within the matrix traversing few atomic distances (depending upon the stacking fault energy of the matrix) or may extend to large atomic distances if the trailing partial is pinned by an interface [4, 20]. In the γ'

phase, glide of a perfect matrix dislocation leads to the formation of APB which is restored back to the original $L1_2$ structure by another perfect trailing dislocation. Given the high cost of energetics involved with this process, deformation in γ' may also occur via formation of complex stacking faults (CSF) and superlattice stacking faults [15]. Another competing deformation mechanism in the γ' phase is the formation of twins [21, 22] at intermediate and high temperatures which are formed by the concomitant glide of Shockley partials on adjacent glide planes. This is somewhat interesting since twinning in FCC type packed crystals is considered to be a thermally activated phenomena observed generally at low temperatures and/or high strain rates [23].

The prevalence of aforementioned deformation mechanisms in Ni-based superalloys depends on applied stress and temperature. Extended APBs due to glide of $1/2(110)$ dislocations are observed at temperatures $\approx 900^\circ\text{C}$ [24, 25]. At intermediate temperatures of 600°C - 800°C , APBs coupled with superlattice stacking faults are also observed due to shearing through $1/6(112)$ and $1/3(112)$ partial dislocations [26, 27]. At temperatures greater than 900°C , precipitate shearing via passage of (110) and (100) dislocations has also been reported in single crystal Ni-based superalloys during tensile creep [28, 29]. Shearing of γ' precipitates by twins and isolated superlattice stacking faults [30–33] has also been reported during tensile and creep tests at intermediate temperatures of $\approx 600^\circ\text{C}$. The present work is focused on this intermediate temperature range wherein twinning is a competing deformation mechanism to dislocation slip in γ' -strengthened Ni-based superalloys.

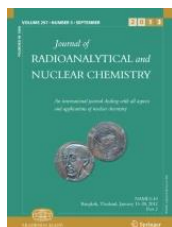
While the theory for deformation twinning in regular FCC lattices is well developed [23, 34], the mechanisms involved in twin formation in Ni-based superalloys are still debatable. Unocic et al. [18] and Kovarik et al. [35] provide an extensive review of the existing theories postulating twin formation in Ni-based superalloys. These theories include the mechanisms proposed by Kear et al. [36], Knowles and Chen [37], Kolbe et al. [21, 38], and Decamps et al. [39, 40]. According to the mechanism proposed by Kear et al. [36], the interactions of (110) superdislocations on two different slip systems lead to the formation of (112) dislocations which shear the γ' precipitate via formation of SISFs and SESFs [18, 35]. However, this mechanism requires a high symmetry orientation of the loading axis so that two slip systems become operative and experience high shear stresses [18]. The mechanism proposed by Knowles and Chen [37] relies on the formation of SESFs in the γ' phase by glide of two different $1/3(112)$ partials on adjacent $\{111\}$ planes. While the first partial will form SESF, the second partial will form a twin [35]. These partials are supposed to form through the classical pole mechanism [34] via interaction of two identical $1/2(110)$ dislocations in the matrix. This mechanism requires shearing of $\{111\}$ glide planes in directions which

possess small value of Schmid factor and is, therefore, conservative in nature [18, 35]. The mechanisms proposed by Decamps et al. [39, 40] rely on the formation of APB in the precipitate by the passage of $1/2(110)$ matrix dislocations. Due to high energy of this planar fault, the subsequent Shockley partial glides on adjacent $\{111\}$ plane that transforms this high-energy APB to a low-energy SESF via the formation of composite $1/3(112)$ partial. The mechanism by Kolbe et al. [21, 38] relies on vacancy mediated atomic reordering in the wake of $1/6(112)$ partials in the precipitate phase. Specifically, atomic diffusion is required to transform the CSF to SESF through local atomic rearrangements in the $L1_2$ lattice. Further diffusion at high temperatures then converts the planar fault to a twin. The temperature dependence of this thermally activated phenomena arises from the temperature dependence of atomic reordering process [18, 35]. Formation of SESFs and eventual twinning via glide of $1/6(112)$ partials on $\{111\}$ planes can also be assisted by elemental segregation ahead of these faults, which minimizes the CSF energy and facilitates twin formation [41, 42].

Given such diverse nature of twin formation mechanisms in precipitation-strengthened Ni-based superalloys, the aforementioned observations suggest that some other mechanisms of twin formation are also possible. It can be seen that all the above mechanisms require either the prevalence of multiple active slip systems [18, 36], activation of slip systems with lower Schmid factor [18, 37], special atomic reordering or rearrangements to convert the CSF to SESF [38, 40] or presence of solute segregation elements [32, 41, 42] that assist twin formation. However, experimental evidences do exist that suggest the existence of other possible alternative twin formation mechanisms in the γ' phase of Ni-based superalloys. For instance, transmission electron microscopy (TEM) investigation into plastic deformation behavior of γ' -strengthened Ni-based superalloy Rene-104 crept at 724 MPa and 677°C by Unocic et al. [43] revealed the existence of extended faults in γ matrix preceding the onset of twinning in γ' phase. Specifically, Unocic et al. [43] hypothesized that under appropriate shear loading, the leading partial of $1/2(110)$ dissociated matrix dislocation percolates the $\gamma - \gamma'$ interface and lays out large areas of ISFs. With the arrival of second matrix dislocation, the pair of identical partials traverse the γ' phase resulting in the removal of Shockley partial loops around the precipitate and formation of SESF in the sheared γ' particles, a precursor to twin formation. Very recently, Zhang et al. [44] revealed underlying deformation mechanisms in turbine disk superalloy GH4720Li deformed under hot compression at 900°C and 0.01 s^{-1} strain rate. The authors revealed the aggregation of $1/2(110)$ matrix dislocations on the γ side of the $\gamma - \gamma'$ interface preceding the onset of twinning in γ' phase.

The existence of stacking faults in the γ phase [43] and the aggregation of matrix dislocations on the γ side of the $\gamma - \gamma'$ interface [44] preceding twinning in the precipitate suggests that





Journal of Radioanalytical and Nuclear Chemistry (2025) 334:5489–5498
<https://doi.org/10.1007/s10967-025-10276-y>



Application of low specific activity ^{90}Y produced in a medium flux research reactor in the preparation of radioactive patch for the treatment of skin ailments

K. V. Vimalnath¹ · A. Rajeswari¹ · Sai Kishore² · Nandini Pandit² · Sudipta Chakraborty^{1,3}

Received: 24 March 2025 / Accepted: 8 July 2025 / Published online: 2 August 2025
 © The Author(s) 2025

Abstract

The article discusses the application of low-specific-activity ^{90}Y [$T_{1/2} = 64.1$ h, $E_{\beta}(\text{max}) = 2.28$ MeV] in the preparation of radioactive patch sources for the treatment of superficial skin conditions, particularly keloids. Yttrium-90 was produced with 688 $\pm$ 41 MBq/mg specific activity and > 99.9% radionuclide purity in a medium flux research reactor. A simple and reproducible method was established to prepare radioactive patch sources, incorporating 92 $\pm$ 8 MBq of ^{90}Y in each source with uniform distribution of radioactivity, without any surface contamination and almost no leaching of radioactivity. Preliminary investigations with developed sources in recalcitrant keloids showed promising outcome.

Keywords ^{90}Y · Neutron activation · Patch sources · Keloids · Autoradiography

Introduction

Yttrium-90 [$T_{1/2} = 64.1$ h, $E_{\beta}(\text{max.}) = 2.28$ MeV] is a well-established radionuclide in nuclear medicine in the domain of targeted radionuclide therapy applications [1]. The therapeutic radionuclide obtained in no carrier added (NCA) form by regular radiochemical isolation from $^{90}\text{Sr}/^{90}\text{Y}$ radionuclide generator is used in the treatment of neuroendocrine originated tumors (NET) and several other malignancies [1–4]. However, one of the major challenges encountered in usage of NCA ^{90}Y sourced from this generator system is ^{90}Sr breakthrough in the eluate [1, 2]. Yttrium-90 used for radionuclide therapy should be of very high radionuclidic purity (> 99.998%), as the most probable contaminant ^{90}Sr is a bone seeker with a maximum permissible body burden of only 74 kBq (2 μCi). Consequently, ^{90}Sr contamination in the clinical grade NCA ^{90}Y for targeted radionuclide

therapy should be less than $2 \times 10^{-3}\%$ or 20 ppm [5]. Several commercial suppliers offer high-quality NCA ^{90}Y produced through the generator route suitable for clinical use. Although, the radiochemical separation of NCA ^{90}Y from $^{90}\text{Sr}/^{90}\text{Y}$ radionuclide generator poses certain technical challenges including conforming to stringent radionuclide purity requirements of ^{90}Y , it remains the preferred source of ^{90}Y for its clinical applications. Apart from $^{90}\text{Sr}/^{90}\text{Y}$ generator system, ^{90}Y could also be obtained in low specific activity (LSA) carrier added (CA) form by direct neutron activation of natural yttrium (mononuclidic in ^{89}Y). In this process, ^{89}Y is partly converted to ^{90}Y by $^{89}\text{Y}(n, \gamma)^{90}\text{Y}$ process [$\sigma_{\text{th}} = 1.28$ b] yielding LSA ^{90}Y . Yttrium-90 obtained by this route finds limited clinical utility except in the treatment of inoperable liver cancer, where ^{90}Y -glass microspheres produced by thermal neutron irradiation of yttria alumino silicate glass is used [6]. In recent years, our group has also successfully demonstrated utility of LSA ^{90}Y produced by (n, γ) route in radiation synovectomy (RSV) of knee joints affected by chronic inflammatory joint disease [7, 8]. A detailed comparison of [^{90}Y]YCl₃ availed from both routes i.e., both NCA and LSA grade is presented in Table 1. In the present work, we have explored the possible utility of LSA ^{90}Y produced by (n, γ) route in another therapeutic application, namely treatment of superficial skin ailments, such as keloids, using radioactive patch sources prepared using LSA ^{90}Y .

✉ Sudipta Chakraborty
 sudipta@barc.gov.in; sudiptac1273@gmail.com

¹ Radiopharmaceuticals Division, Bhabha Atomic Research Centre, Mumbai 400085, India

² Department of Nuclear Medicine, Jawaharlal Institute of Postgraduate Medical Education and Research, Puducherry 605006, India

³ Homi Bhabha National Institute, Mumbai 400094, India

Table 1 Detailed comparison of NCA ^{90}Y from $^{90}\text{Sr}/^{90}\text{Y}$ generator and LSA ^{90}Y from direct neutron activation and their suitability for different applications

Specifications	NCA ^{90}Y	LSA ^{90}Y
Radiochemical form	$[\text{}^{90}\text{Y}]\text{YCl}_3$	$[\text{}^{90}\text{Y}]\text{YCl}_3$
Source	Periodic elution from $^{90}\text{Sr}/^{90}\text{Y}$ generator	Neutron activation of Y_2O_3 target in nuclear reactor $[\text{}^{89}\text{Y}(\text{n},\gamma)\text{}^{90}\text{Y}]$ followed by radiochemical processing
Specific activity	No carrier added (theoretically $\sim 5\text{ TBq/mg}$)	500–1000 MBq/mg
Radiochemical purity	$> 95\%$	$> 95\%$
Radionuclide purity	$> 99.998\%$	$> 99.9\%$
Gross alpha content	$\leq 1 \times 10^{-7}\%$	Not applicable
Potential radionuclide impurity	^{90}Sr ($T_{1/2} = 28.9\text{ y}$)	^{89}Sr ($T_{1/2} = 50.53\text{ d}$), $^{90\text{m}}\text{Y}$ ($T_{1/2} = 3.19\text{ h}$)
Application	Suitable for preparation target-specific radiopharmaceuticals for cancer therapy	Limited clinical use in treatment of liver cancer, radiation synovectomy and superficial skin patch
Cost and availability in India	Expensive, import dependent availability	Can be made indigenously available as per requirement using medium flux research reactor at an affordable cost

Use of ionizing radiation by superficial application of radioactive patch sources of β^- particle emitting radionuclide with end point of energy of the particles $> 1.7\text{ MeV}$ have been well explored in the treatment of several types of external skin tumors and keloids and the modality is often termed as ‘mould brachytherapy’ [9–11]. Since the average tissue penetration range of β^- is only few mm, it imparts severe damage to tumor tissue or treat keloid by inhibiting scar hyperplasia without causing undesired radiation exposure to the neighboring healthy tissue [9–12].

Preparation of skin patches incorporating β^- emitters such as ^{32}P , ^{90}Y , ^{166}Ho and ^{188}Re and their evaluation in the treatment of superficial lesions in animal models and in some cases in human patients have been extensively reported [13–18]. All these radionuclides emit β^- with maximum energy in the range of 1.7–2.3 MeV but differ with each other in terms of half-life, other nuclear emissions and methods of production (Table 2). Consequently, each one has its own sets of merits and demerits. Among these, ^{90}Y is especially advantageous owing to its 2.28 MeV β^- emission without any concomitant gamma photon emission (only very insignificant percentage of 511 keV gamma photon due to very small positron emission component) and a convenient half-life of 64.1 h. Based on these, different groups have attempted preparation of superficial ^{90}Y -patch sources for

treatment of skin cancers and keloids using different types of substrates which can immobilize ^{90}Y activity and ensure its uniform distribution all over the source [15, 19–21]. While in almost all these attempts NCA ^{90}Y sourced from $^{90}\text{Sr}/^{90}\text{Y}$ have been used, only Pashazadeh et al. [21] have prepared the patch sources with ^{90}Y microspheres used in treatment of liver cancer. As mentioned earlier, although $^{90}\text{Sr}/^{90}\text{Y}$ generator system is the preferred source of ^{90}Y and high quality NCA ^{90}Y suitable for clinical use availed through generator route is commercially available, $^{90}\text{Sr}/^{90}\text{Y}$ generator technology could not be utilized to its full potential due to several reasons, including the requirement of handling of long-lived ^{90}Sr that necessitates additional regulatory approvals. As a matter of fact, only a few countries around the world such as United States of America, United Kingdom, Russian Federation and China have the capability of producing clinical grade NCA ^{90}Y using $^{90}\text{Sr}/^{90}\text{Y}$ generator. Consequently, availability of NCA ^{90}Y is import dependent and remains elusive in large number of nuclear medicine centres in populous developing countries like India. In this premise, we have attempted at developing a facile strategy for preparation of radioactive patch sources directly using LSA ^{90}Y produced by thermal neutron activation of yttrium oxide target. LSA ^{90}Y produced by this route can be made available as per the requirement using research reactors with medium

Table 2 Beta emitting radionuclides explored for treatment of superficial lesions in the form of skin patch

Radionuclide	Half-life (d)	E_β (max) (MeV)	E_γ (keV)	Maximum tissue penetration (mm)	Method of production
^{90}Y	2.67 d	2.28	–	11	^{90}Sr - ^{90}Y generator, $^{89}\text{Y}(\text{n}, \gamma)$
^{32}P	14.3 d	1.71	–	8	$^{32}\text{S}(\text{n}, \text{p})$ $^{31}\text{P}(\text{n}, \gamma)$
^{188}Re	17 h	2.12	155 (15%)	10	^{188}W - ^{188}Re generator, $^{187}\text{Re}(\text{n}, \gamma)$
^{166}Ho	26.8 h	1.85	81 (6.6%)	9	$^{165}\text{Ho}(\text{n}, \gamma)$





OPEN Whole genome sequencing reveals transcriptional and translational elements potentially regulating biotic and abiotic stress responses in cowpea

Dhanasekar Punniyamoorthy[✉] & Souframanien Jegadeesan

Cowpea (*Vigna unguiculata* (L.) Walp.) is a highly versatile and resilient crop, globally ranking as the third most pivotal grain legume. However, various biotic, abiotic, and physiological challenges, often hinder its productivity. Cowpea exhibits complex environmental adaptive responses regulated at the transcriptional and translational levels through mechanisms such as resistance genes (R-genes), transcription-associated proteins (TAPs), and protein kinases (PKs). A comprehensive study was conducted based on a whole-genome hybrid assembly (Illumina and Nanopore) in cowpea, revealing the identification of 2188 R-genes (29 classes), 5573 TAPs (118 families) and 1135 PKs (22 groups, 122 families). Among the R-genes, Kinases (KIN) and transmembrane proteins (RLKs and RLPs) were prominent, while CCHC (Zn), C2H2, MYB-HB-like, WD40-like, bHLH, and ERF families were notable among TAPs. The largest kinome group, RLK-Pelle, encompassed over three-fifths of the cowpea PKs (VuPKs), followed by CAMK and CMGC groups. Two and three novel families in TAPs (ABTB and CW-ZN-B3_VAL) and PKs (RLK-Pelle-URK-1, RLK-Pelle-URK-2, TKL-Cr-3), respectively, were identified along with two novel PK groups (NAK and TLK). Dispersed and tandem duplication events under purifying selection mainly contributed to kinome expansion, with chromosome 'Vu03' anchoring the maximum PKs. This investigation delves into the biological intricacies with manipulative potential to enhance cowpeas' resilience to environmental challenges without compromising yield.

Keywords R-genes, TAPs, Kinome, Climate resilience, Duplication, Purifying selection

Identification of climate resilient crops assumes prominence among the major research priorities for ensuring global food and nutritional security. Legumes are known to evince acclimatizing adaptation to an extensive range of ecological conditions from arid to temperate climates. Among the hardy legumes, cowpea (*Vigna unguiculata* (L.) Walp.) is a multifarious crop endowed with climate smart attributes and laden with inherent potential to mitigate the vagaries of climate change^{1,2}.

Globally, cowpea is the third most important grain legume crop in terms of area and production, next only to dry beans and chickpea. Cultivated over an estimated area of 15.19 Mha and production of 9.77 Mt³, the productivity of cowpea (643.5 kg/ha) is abysmally low compared to other legumes like chickpea and dry beans. Various biotic and abiotic stresses predominantly hinder cowpea productivity and augmentation of resistance against these factors is a research prerogative of eminence. Even though cowpeas are biologically resilient, the low productivity is essentially attributed to its cultivation under subsistence or marginal conditions with minimal inputs, limited access to improved varieties and largely grown as a mixed intercrop rather than sole crop⁴. From the genomics perspective, until recently, cowpea genetic improvement was on the backfoot unlike its counterparts like soybean, chickpea, and common bean. Cowpea is a diploid fabid with a chromosome number 2n = 22 and an estimated genome size of about 641 Mbp⁵. With next-generation sequencing becoming increasingly cost-effective and the various genomic tools and whole genome sequence of cowpea⁵ becoming readily accessible, the genetic improvement of cowpea has gathered momentum in recent times.

Like other plants, cowpea, when confronted with challenges imposed by various biotic and abiotic stresses, has a myriad of complex adaptive response mechanisms to thwart or minimize the negative impacts stemming

Nuclear Agriculture and Biotechnology Division, Bhabha Atomic Research Centre, Trombay, Mumbai, Maharashtra 400 085, India. ✉email: sekar@barc.gov.in

out of such situations. The rapid and efficient responses are moderated at the transcriptional or translational levels primarily through resistance genes (R-genes), transcription-associated proteins (TAPs) and protein kinases (PKs) among others. R-genes are largely involved in the response against biotic stresses, especially the disease-causing pathogens⁶. The disease resistance reaction of plants is the consequence of the interactions between the R-genes and pathogen specific effector molecules called avirulence proteins⁷. Upon recognizing the invading pathogen, the R-genes elicit defence response signalling cascades against it. These R-genes consist of well conserved domains and motifs such as the N-terminal transmembrane (TM), serine/threonine and tyrosine kinase (STTK), lysin motif (LysM), coiled-coil (CC) and Toll/Interleukin-1 receptor (TIR), central nucleotide binding site (NB-ARC), and the C-terminal leucine rich repeats (LRR)^{8,9}. These conserved structural features are utilized by various bioinformatic tools for mining the R-genes from the whole genome sequences. In plants, among the R-genes, the nucleotide-binding leucine-rich repeat (NLR) class of genes is most widely prevalent¹⁰. A collection of 481 NLRs have been validated through experimentation in 31 plant genera¹¹. These R-genes are known to play a pivotal role in disease resistance breeding and therefore, it is imperative to envisage the R-genes prevalent across the genome.

The developmental and resilient adaptive responses of plants to environmental variations are dynamically moderated primarily through the reprogramming of gene expressions by various transcriptional regulatory factors, apart from epigenetic and translational control. In plants, intricate systems of TAPs regulate the transcription of protein encoding genes^{12,13}. TAPs are primarily comprised of: (1) Transcription factors (TFs) that bind in a sequence-specific manner to cis-acting non-coding DNA regulatory regions; (2) Transcriptional regulators (TRs) that bring out regulation by non-specific DNA binding, protein-protein interactions or chromatin remodelling; and (3) Putative TAPs (PTs) with hitherto unknown roles¹⁴. Apart from these factors, a variety of other TAPs like RNA polymerases, mediator complexes, polyadenylation factors, transcription elongation and termination factors also work in a coordinated manner to regulate the transcription of genes, ensuring the accurate and controlled synthesis of RNA molecules in response to various cellular signals and environmental cues. As per an estimate, at least 5–7% of the genome encoded proteins in plants are tasked with transcriptional regulation^{15–17}. The fraction of TFs in the expressed genome is in positive consonance with the complexity of the organism¹⁸.

The third major family of proteins coordinating the signalling pathways in tandem with other regulatory factors are the PKs. Kinomes, the whole set of kinases present in the genome, constituting about 1–2% of functional proteome, usually present a conserved catalytic domain comprising 250–300 amino-acids¹⁹. The PKs primarily regulate the adaptive and cellular functions through reversible phosphorylation and post-translational modification of downstream target proteins influencing their activities, localization, inter-protein interactions, and other features²⁰. Activation of the proteins by appending phosphate moieties conjures a cascade of signal transductions eventually modulating the adaptive, developmental, metabolic, and stress-responsive cellular processes. PKs are documented as key elements in plant responses to biotic and abiotic stresses viz., water scarcity, high salinity, low temperature, and pathogen attack²⁰.

In cowpea, the meagre reports on R-genes, TAPs, and PKs encouraged the present study to comprehend these regulatory factors using the hybrid assembly (Illumina and Nanopore) of a whole genome sequence of cowpea cultivar 'CPD103'. The genome-wide identification and characterization of these regulatory factors will help not only understand the regulatory intricacies controlling the biological processes in legumes but also will pave the way for manipulating the processes to the relative advantage of mankind.

Materials and methods

Materials

The cowpea cultivar 'CPD103' is being used at our institute in cowpea mutation breeding programme for induction of resistance against cowpea aphid borne mosaic virus. To generate genomic resources, 'CPD103', also known as 'CDS', was subjected to de novo whole genome sequencing using Illumina and Nanopore sequencing techniques for hybrid assembly.

DNA extraction and quality control

Genomic DNA was extracted in duplicate from young leaves using Qiagen DNeasy Plant Mini kit as per the instructions contained in the kit and previously described²¹. Finally, DNA was eluted with 50 µl of 10 mM Tris-Cl (pH 8.0). The eluted genomic DNA was quantified and evaluated for quality using Nanodrop 2000 (Thermo Scientific, USA), Qubit (Thermo Scientific, USA), and agarose gel electrophoresis (samples with A260/A280 ratio 1.8–2.0, A260/A230 ratio > 1.8, Qubit concentration > 10–20 ng/µl for Illumina and > 50 ng/µl for Nanopore and those not showing smearing, degradation, RNA contamination or faint bands in gel electrophoresis were only used for sequencing).

Illumina and nanopore library preparation and sequencing

Library construction and sequencing was carried out at M/s Genotypic Technology, Bengaluru, India, as detailed previously²¹. Briefly, library preparation involved NEXTFLEX Rapid DNA-seq kit (BIOO Scientific, Inc. U.S.A.) for Illumina platform as per the manufacturer's directives. The Qubit quantified DNA (500 ng) was fragmented (200–250 bp) by sonication (Covaris S220, USA), purified, ligated to multiplex-barcoded adaptors, and prepared the sequencing library by PCR-amplification for 4 cycles using kit provided primers. The library was thereafter, purified, checked for quality, Qubit quantified, and analyzed for fragment size distribution (Agilent 2200 Tape Station). The paired-end sequencing of equimolar-normalized library post multiplexing was carried out on a HiSeq X Ten Illumina sequencer as per the instruction of the manufacturer (150 cycles). For Nanopore library preparation, the end-repaired (NEBNext ultra II end repair kit, New England Biolabs, MA, USA) and purified DNA (1.5 µg) were ligated with adapter (AMX) at room temperature (20 °C) for 20 min using NEB Quick T4



Alphabetical List of Journal of BARC Engaged in Open Access (OA) Publishing

WILEY

Sr. No.	Wiley Journal (July-Dec 2025)	Type of OA	No of publications	Impact Factor 2025
1	Advanced Energy and Sustainability Research	Fully OA	1	6.4
2	Advanced Photonics Research	Fully OA	1	4
3	Advances in Civil Engineering	Fully OA	1	1.8
4	Case Reports in Pathology	Fully OA	1	0.4
5	International Journal of RF and Microwave Computer-Aided Engineering	Fully OA	1	1.2
6	Journal of Food Processing and Preservation	Fully OA	1	3.1
7	APMIS	Hybrid OA	2	2.2
8	Chemistry - An Asian Journal	Hybrid OA	1	3.2
9	Chemphyschem	Hybrid OA	1	2.4
10	Energy Storage	Hybrid OA	1	4
11	Feddes Repertorium	Hybrid OA	2	0.9
12	International Journal of Quantum Chemistry	Hybrid OA	1	2.7
13	Journal of Applied Polymer Science	Hybrid OA	1	3.1
14	Journal of the American Ceramic Society	Hybrid OA	1	4.2
15	SMALL	Hybrid OA	1	11.8

Sr. No.	Springer Journal	Type of OA	No. of Publication	Impact Factor 2024
1	Biology Direct	Fully OA	1	4.9
2	BMC Plant Biology	Fully OA	1	4.8
3	npj 2D Materials and Applications	Fully OA	1	8.8
4	Scientific Reports	Fully OA	8	3.9
5	Applied Physics A	Hybrid OA	1	2.8
6	Applied Physics B	Hybrid OA	1	2
7	BioNanoScience	Hybrid OA	1	3.2
8	Current Genetics	Hybrid OA	1	1.6
9	Current Microbiology	Hybrid OA	1	2.6
10	Emergent Materials	Hybrid OA	1	4.1
11	European Journal of Clinical Microbiology & Infectious Diseases	Hybrid OA	1	3
12	Interactions	Hybrid OA	1	0.8
13	International Journal of System Assurance Engineering and Management	Hybrid OA	1	1.4
14	JOM	Hybrid OA	1	2.3
15	Journal of Cluster Science	Hybrid OA	1	3.6
16	Journal of Materials Engineering and Performance	Hybrid OA	1	2
17	Journal of Materials Research	Hybrid OA	1	2.9
18	Journal of Materials Science	Hybrid OA	2	3.9
19	Journal of Materials Science: Materials in Electronics	Hybrid OA	1	2.8
20	Journal of Polymer Research	Hybrid OA	1	2.8
21	Journal of Radioanalytical and Nuclear Chemistry	Hybrid OA	9	1.6
22	Journal of Thermal Analysis and Calorimetry	Hybrid OA	5	3.1
23	Lasers in Manufacturing and Materials Processing	Hybrid OA	1	3.2
24	MAPAN	Hybrid OA	1	1.3
25	Medical Oncology	Hybrid OA	1	3.5
26	Metallurgical and Materials Transactions A	Hybrid OA	1	2.5
27	Modeling Earth Systems and Environment	Hybrid OA	1	2.9
28	Molecular Biology Reports	Hybrid OA	1	2.8
29	MRS Communications	Hybrid OA	1	2.3
30	Radiation and Environmental Biophysics	Hybrid OA	2	2.3
31	Radiological Physics and Technology	Hybrid OA	1	1.5
32	The European Physical Journal A	Hybrid OA	1	2.8
33	The Journal of Obstetrics and Gynecology of India	Hybrid OA	1	0.6
34	Water, Air, & Soil Pollution	Hybrid OA	1	3

Alphabetical List of Division of BARC Engaged in Open Access (OA) Publishing

WILEY

- | | |
|--|--|
| 01. Accelerator & Pulse Power Division | 11. Human Resource Development Division |
| 02. Analytical Chemistry Division | 12. Mechanical Metallurgy Division |
| 03. Architectural and Structural Engineering Division | 13. Medical Division |
| 04. Atomic and Molecular Physics Division | 14. Molecular Biology Division |
| 05. Bio-Organic Division | 15. National Centre for Compositional Characterisation of Material |
| 06. Chemistry Division | 16. Radiation & Photochemistry Division |
| 07. Civil Engineering Division | 17. Radiation Technology Development Division |
| 08. Food Technology Division | 18. Radiochemistry Division |
| 09. Glass and Advanced Materials Division | 19. Solid State Physics Division |
| 10. High Pressure & Synchrotron Radiation Physics Division | |

SPRINGER NATURE

- | | |
|---|--|
| 01. Advanced Tunable Laser Applications Division | 21. Nuclear Agriculture and Biotechnology Division |
| 02. Analytical Chemistry Division | 22. Nuclear Physics Division |
| 03. Bio-Organic Division | 23. Post Irradiation Examination Division |
| 04. Chemical Engineering Division | 24. Protein Crystallography Section |
| 05. Chemistry Division | 25. Radiation Biology & Health Sciences Division |
| 06. Environmental Monitoring and Assessment Division | 26. Radiation Medicine Centre |
| 07. Food Technology Division | 27. Radiation Safety Systems Division |
| 08. Fuel Chemistry Division | 28. Radiation Technology Development Division |
| 09. Fuel Fabrication | 29. Radiochemistry Division |
| 10. Glass & Advanced Materials Division | 30. Radiological Physics & Advisory Division |
| 11. Health Physics Division | 31. Radiopharmaceutical Division |
| 12. Health Safety & Environment Group | 32. Reactor Safety Division |
| 13. Heavy Water Division | 33. Reactor Technology Division |
| 14. HRDD | 34. Scientific Information Resource Division |
| 15. Isotope and Radiation Application Division | 35. Solid State Physics Division |
| 16. Materials Processing & Corrosion Engineering Division | 36. Technical Physics Division |
| 17. Materials Science Division | 37. Technology Transfer and Collaboration Division |
| 18. Mechanical Metallurgy Division | 38. Uranium Extraction Division |
| 19. Medical Division | |
| 20. National Centre for Compositional Characterisation of Materials (NCCCM) | |

Alphabetical List of Authors of BARC Engaged in Open Access (OA) Publishing

WILEY

A	Deepak Kumar Baruah	Neha Mittal	Sonali Gupta
Abdulelah Alolayan	Dugeshwar Karley	Nidhi Chandrakar	Soumyaditya Mula
Afsal S. Shajahan	H	Nimai Pathak	Sruthi Thulaseedharan
Amarnath Marimuthu	Hirakendu Basu	P	Jayasree
Amitava Roy	Hussain A. Barbhuiya	Pallavi Chandwadkar	Subhadip Paul
Amol Thite	I	Prachi R. Gaddam	Subhash Sarkar
Ananda Guha Majumdar	Indu Pant	Puthusserickal A. Hassan	Subhendu Ray
Aruna Jyothi Kora	J	R	Chowdhury
Ashutosh Mohanty	Jatindra Sarma	Raji T. Naidu	Sudeshna Saha
Atanu Jha	Jayanta Das	Ratan K. Saha	Sudhir K. Shukla
B	K	Rishu Bhati	Susan Cherian
Bijaideep Dutta	Kanhu C. Barick	Rohit Singh Chauhan	T
Bikas Maji	Kapilesh Bhargava	Romesh Chandra	Thankan Jayasekharan
Brahmananda	Kawsar Ali	S	V
Chakraborty	M	Saha Dauji	Vanshika Adiani
C	Madhusudan Tyagi	Sandeep Singh	Veerendra K. Sharma
Celin Acharya	Mahesh Subramanian	Sangita D. Kumar	Venkata Balarama
Chandra Nath Patra	Manish Ramesh Shingole	Santanu Dey	Krishna Mullapudi
Chitaranjan Jadab	Mohammad Yunus	Sayali Gadre	Victoria García Sakai
D	N	Seemita Banerjee	Y
D. D. Sarma	Namrata Upadhyay	Shashidhar Ravindranath	Y. V. Nancharaiah
Deeksha Gupta	Nandakumar Kalarikkal	Shraddha SP Yadav	Yuanbing Mao

SPRINGER NATURE

A	Anjali Chauhan	Bhanu Partap Singh	Dimple P. Dutta
A. A. Sukumar	Anjana Goel	Bharti Jain	Dinesh K. Aswal
A. Baburajan	Ankita Pathak	Bhaskar Paul	Dipita Karmakar
A. Ghosh	Anu Ghosh	Bikas C. Maji	Drishty Satpati
A. Kumar	Anuj Shukla	Bikram K. Das	F
A. Mhatre	Anurag Bhate	C	Fariza Shaikh
A. P. Srivastava	Archana Sagdeo	C. Majumder	G
A. Rajeswari	Arghya Chattaraj	C. Rajesh	G. L. N. Reddy
A. Srivastava	Arijit Ghoshal	C. V. Singh	Gopika Vinod
A. Verma	Arijit Sengupta	D	Gotluru Kedarnath
A. Vinod Kumar	Arnab Sarkar	D. Arvindha Babu	H
Aditi Chakrabarty Patra	Arnomittra Chatterjee	D. H. Kumbhar	Harshada Tawade
Adityamani Nagar	Arpan Das	D. K. Aswal	I
Ajay Singh	Arshad Khan	D. V. Lakshmipathy	I. V. Saradhi
Akanksha Samanta	Aruna Jyothi Kora	Damu V. Rupnar	Indu Pant
Akhilesh C. Joshi	Ashis Kumar Satpati	Deepak Goyal	J
Amit Das	B	Deepak Sharma	J. B. Singh
Anandhu Mohan	B. K. Sahoo	Dhanadeep Dutta	J. J. Gaware
Anannya Banerjee	B. K. Sapra	Dhanasekar	J. S. Samantray
Aniruddha Kumar	B. Vishwanadh	Punniyamoorthy	J. V. Ramana
Anirudh Chandra	Babita Singh	Dharmendra Kumar	Janani Ganesh
Anitta Thomas	Balvinder K. Sapra	Maurya	Jayashree Biswal

Jitesh Singh Rathee
Jugal Kishor
K
K. Ramachandran
K. V. Vimalnath
Kapil B. Shirsath
Kulwant Singh
Kumar Abhinav Dubey
Kurva Jagannath

L
Laishram Rupachandra
Singh
Langlen Meinam
Laxya Gupta

M
M. Karri
M. P. Ratheesh
M. S. Pathan
Mahendra K. Samal
Manish Chopra
Manish Singh
Manjeet Singh
Meetu Bharti
Mukesh Kumar
Musharaf Ali Sheikh

N
Nachiket Keskar
Nagesh N. Bhat
Naina Raje
Nalini Bhat
Nancy Goyal
Nandini Pandit
Nawab Singh Baghel
Nilanjal Misra
Niranjan S. Ramgir
Nitin Gumber

P
P. D. Babu
P. Jha
P. M. Aiswarya
P. S. Ghosh
P. Sarawade

P. Sharma
P. Y. Nabhiraj
Pankaj Shrivastava
Parmeshwar K. Sahu
Pasupuleti Kalpana
Pooja Sahu
Pragati Patil
Pranesh Sengupta
Prasanta K. Mohapatra
Prasun Kumar
Mukherjee
Preeti Dwivedi
Probal Chaudhury

R
R. B. Oza
R. H. Gaikwad
R. Mishra
R. N. Singh
R. Tripathi
Raghumani Singh
Ningthoujam
Rahul Checker
Raj Kumar Mondal
Rajesh Kumar Chaurasia
Rajesh Kumar
Rajesh V. Pai
Ranjana S. Pathak
Ranjini Menon
Ranjit Kumar
Ravindra Bansal
Raviraj Singh Patel
Rimanshee Arya
Rimpi Dawar
Rishi Verma
Rohini Agarwal
Rumu H. Banerjee

S
S. Bhattacharya
S. D. Kanse
S. Gautam
S. H. Shinde
S. K. Jha

S. K. Satpati
S. K. Sharma
S. Kumar
S. M. Pradhan
S. Narang
S. Neogy
S. Patra
S. Samanta
S. Santra
S. V. Madge
Sachin N. Hajare
Sagar Chandra
Sai Kishore
Samim Molla
Samrath Baghel
Sanasam Yaiphabi
Sandip Mondal
Sanjay Kumar
Sanjay Saini
Sanjenbam Kabita
Sanjenbam Kunjeshwori
Devi
Sanjib Majumdar
Savita Kulkarni
Senjam Sunil Singh
Shamjetshabam Babeeta
Chanu
Shashidhar Ravindranath
Shruti Rane
Shubham Kumar
Shubhangi A. Shelkar
Sk Jayabun
Sk. Musharaf Ali
Sneha Chandrasekhar
Sonal Gupta
Sorokhaibam Jibankumar
Singh
Souframanien
Jegadeesan
Subhendu Ray
Chowdhury
Sudipa Manna

Sudipta Chakraborty
Suman K. Mishra
Suman Neogy
Sumitra Phanjoubam
Sunil Goswami
Sunil Kumar Sethy
Suresh Shendage
Susan Cherian
Suvendu Mondal
Swarnima Rawat
Sweetie R. Kanatt

T
T. N. Nag
T. Palani Selvam
Thota Manoj Kumar

U
U. K. Sahoo
U. R. Thakkar

V
V. B. Yadav
V. K. Sharma
V. K. Varakhedkar
V. M. Joshi
V. S. Srivastava
Vandana A. Pulhani
Vandana Shrivastava
Varshita Mehta
Vijay K. Sharma
Vinod S. Rawat
Vipul Garg
Virendra Kumar
Vishal Prashar
Vitthal T. Barvkar
Vivek Kant
Vivek M. Chavan

W
Willem Verboom
Y
Y. K. Bhardwaj
Y. Sunitha
Yerroju Sunitha

