

DOCTORAL THESES

Selective Separation of Cesium, Strontium and Technetium from Radioactive Waste Solutions

HIGH level liquid waste (HLLW) generated during reprocessing of spent fuel by PUREX (Plutonium Uranium Reductive Extraction) process retains majority of radio-toxicity of the original spent fuel. ^{137}Cs ($t_{1/2} = 30.1\text{ y}$) and ^{90}Sr ($t_{1/2} = 28.9\text{ y}$) are major heat emitting nuclides contributing largely on heat and radiation load of HLLW. ^{99}Tc , a beta emitting radionuclide ($t_{1/2} = 2.11 \times 10^5\text{ y}$) present in alkaline low level waste (LLW) as NaTcO_4 . Separation of these elements is necessary for safe waste management and also for their uses in societal applications. The present studies are focused on development of macrocyclic extractants of the class calix-crown-6 and crown ethers for selective separation of Cs, Sr and Tc from high salt content radioactive waste solutions.

The extractants developed are 1,3-dioctylcalix[4]arene-crown-6 (CC6) and 1,3-bis(2-ethylhexyloxy)calix[4]arene-crown-6 (branched calix-crown-6) for selective separation of Cs^+ from HLLW, 4,4(5)-[di-tert-butylidicyclohexano]-18-crown-6 (DtBuCH18C6) for selective separation of Sr^{2+} from HLLW and 4,4(5)-[di-tert-butylidibenzo]-18-crown-6 (DtBuDB18C6) for selective separation of $\text{Na}^+\text{TcO}_4^-$ from LLW and are dissolved in a new diluents system, a mixture of isodecyl alcohol and n-dodecane for extraction studies. ^{137}Cs and ^{90}Sr removal from HLLW were more than 99.5% in a counter-current continuous extraction system. Fig.1 shows pictorial representation of extraction of $\text{Na}^+\text{TcO}_4^-$ from LLW using 0.2 M DtBuDB18C6 +50% IDA/n-dodecane and stripping of $\text{Na}^+\text{TcO}_4^-$ from loaded solvent with DM water. Radiolytic and hydrolytic degradation studies indicated high stability of solvents.

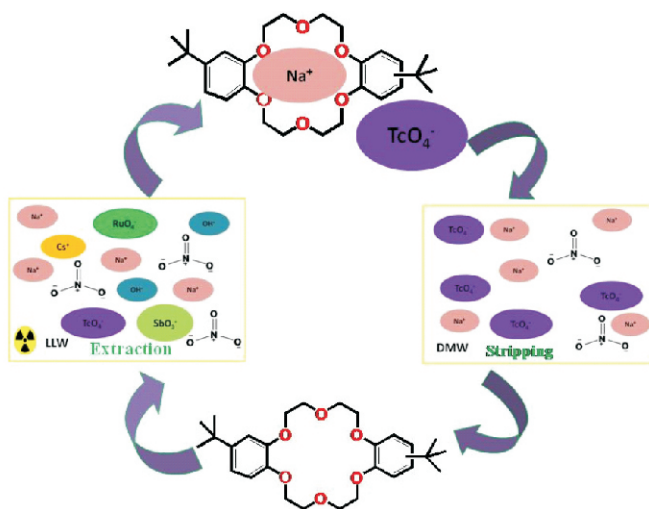


Fig.1: Extraction and stripping of $\text{Na}^+\text{TcO}_4^-$ from low level waste DtBuDB18C6 and demineralised water.

Highlights of the work carried out by **Joti Nath Sharma** under the supervision of **Dr. Tessa Vincent** (guide) as a part of his doctoral thesis work. He was awarded a Ph.D. degree from Homi Bhabha National Institute in Chemical Sciences in 2020.

Separation of Cesium from High Level Liquid Waste

RECOVERY of radio-caesium from high-level liquid waste (HLLW) is one of the challenging tasks at the back end of nuclear fuel cycle. This has been attempted in the present thesis through solvent extraction and membrane-based techniques using Calix-crown-6 ligands in phenyl trifluoromethyl sulphone (PTMS) diluent. Among the different Calix crown-6 ligands (Fig.1) investigated, CBC (Calix-[4]arene-bis-benzo-crown-6) is found to possess the highest Cs(I) extraction efficiency. Further, the Cs(I) extraction efficiency of the Calix-crown-6 ligands is found out to be: $\text{CBC} > \text{CNC} > \text{CMC} > \text{CC}$, which was attributed to trends of their partition coefficients. Further studies using CBC have shown its efficacy for selective recovery of radio-caesium from uranium depleted HLLW. Solvent extraction parameters were optimized for the quantitative extraction and stripping of Cs from nitric acid medium and 10 m Ciradiocesium was recovered from actual HLLW solutions at laboratory scale.

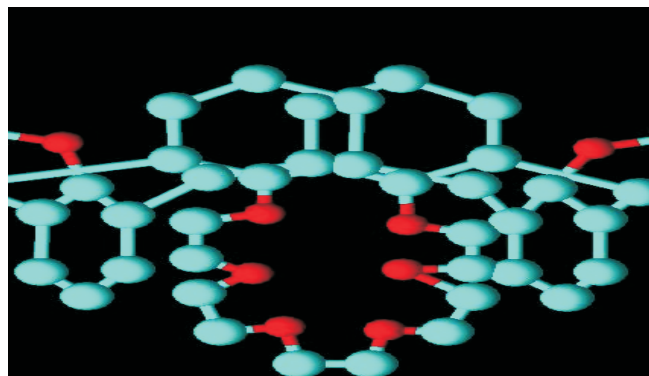


Fig.1: Structural formula CC, CBC, CNC & CMC.

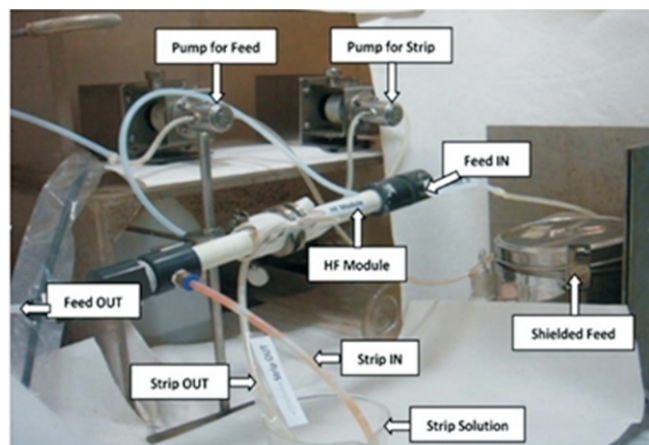


Fig.2: Photograph of the hollow fiber contractor set up used in the present study.

Encouraged by the solvent extraction results, further studies were carried out using supported liquid membrane-based separation. However, CBC in PTMS was not the suitable solvent for the membrane separation studies, and CMC (calix[4]arene-mono-crown-6) in a mixture of n-dodecane and iso-decanol was found to be more efficient with excellent membrane stability. Efficient transport of Cs from actual HLLW solutions has been demonstrated using CMC (0.01M in 40% iso-decanol + 60% n-dodecane). The optimized conditions were used to recover Cs using a hollow fibre contactor. Recovery >90% are achieved in ~20 h, which was reproduced even after a long period of 50 days. These results will find application for large scale recovery of Cs from acidic waste solution.

Highlights of the work carried out by **Poonam P. Jagasia** under the supervision of **Prof. P. K. Mohapatra** and **Prof. P. S. Dhami** (co-guide) as a part of her doctoral thesis work. She is awarded PhD degree from Homi Bhabha National Institute in Chemical Sciences in 2017.

Specific Extractants for Separation Processes in Back-end of Fuel Cycle

DEVELOPMENT of a process for isolating ^{106}Ru from acidic waste is one of the successful accomplishments of this doctoral thesis work. Notably, Ruthenium is the most troublesome element present in nuclear waste, and it is attributed to the presence of aquatic complexes involving nitrosyl ruthenium species. The process developed (Fig.1) envisages oxidation of nitrosyl ruthenium species to RuO_4 (g) followed by extraction of generated RuO_4 in chlorinated CCl_4

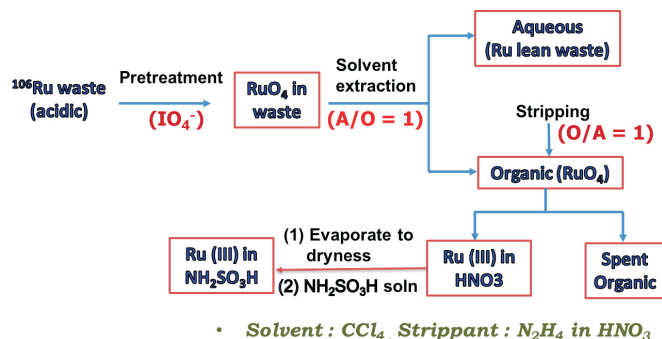


Fig.1: Process for Ruthenium separation.

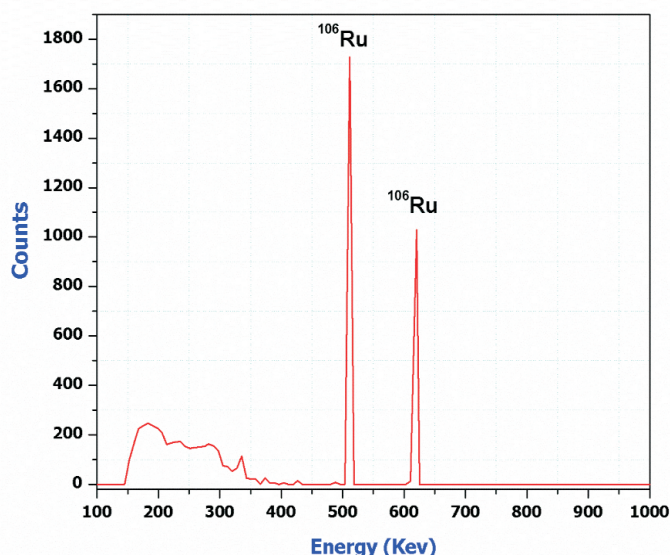


Fig.2: MCA spectrum of Ru product.

and finally recovery of the Ru isotopes as Ru(III) by reductive stripping using acidic hydrazine solution. The study was extended towards the evaluation of RuO_4 generation and volatilization kinetics under varying process conditions. The scientific understanding developed from RuO_4 volatilization studies was helpful in the optimization of the process parameters for the production of purified ^{106}Ru solution. The optimized process has been demonstrated with a real waste solution of reprocessing plant origin with the successful production of radiochemically pure ^{106}Ru (Fig.2).

The utility of the research findings can be noted with the realization of Ruthenium Brachytherapy (RuBy) plaque sources useful in eye cancer treatment. The process is now routinely adopted to produce radiochemically pure ^{106}Ru and subsequent fabrication of RuBy plaques. Presently, fifteen RuBy plaques are used in eye cancer treatment at seven hospitals in India.

The reported work by **Dr. Prithwish Sinharoy** is a highlight of his Doctoral thesis work. He has carried out the work under the supervision of **Dr. C. P. Kaushik**, Professor, HBNI and **Dr. D. Banerjee** (Co-guide). He was awarded a PhD degree from Homi Bhabha National Institute in Chemical Sciences in 2021.

Ligand Functionalized Solid Support in Nuclear Waste Management

SOLID-PHASE extraction draws attention from separation scientists due to its several advantages over conventional extraction techniques such as simplicity, speed, convenience, easy operation, cost-effectiveness and low secondary waste generation. Additionally, ligands with pre-organized conformation would be highly advantageous for coordination with the metal ions.

This has conclusively been established during the doctoral thesis work under the titled topic, with the successful development of several functionalized solid-phase extractants. One of the synthesized sorbents, Dipicolinic acid functionalized anatase (Fig.1), formed through amino ethoxy silane bridge, showed highly efficient sorption of Am^{3+} and Eu^{3+} from aqueous acidic medium through chemical interaction. The hard base oxo donor from DPA moieties showed preferential interaction with trivalent lanthanide compared to trivalent actinide.

The experimentally observed maximum adsorption capacity (Am^{3+} and Eu^{3+} are 67mg/g and 93 mg/g, respectively) was validated by the DFT calculated free energy of adsorption (Eu^{3+} and Am^{3+} ions are -135 kcal/mol and -129 kcal/mol, respectively). The interaction was seen to be ion-dipole type as revealed by the significant positive charge on the metal ions. Further, a small extra orbital population to the inner 's' and 'f' subshells and a considerable population in

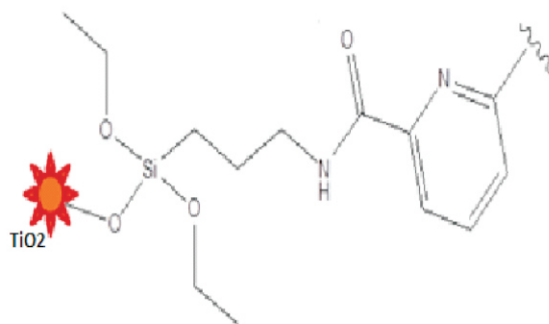


Fig.1: Dipicolinic acid functionalized.

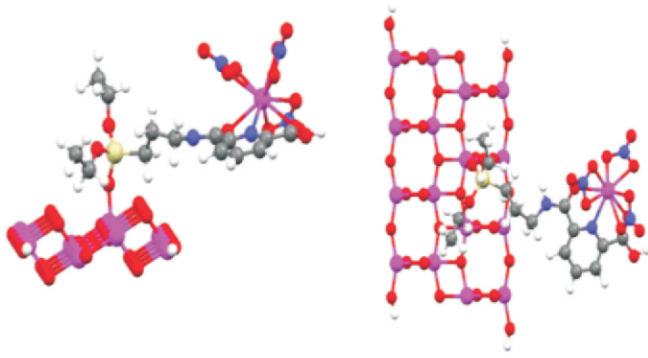


Fig.2: DFT complexation of the sorbent with Am³⁺ and Eu³⁺ .

the d subshells of the metal ion reveals a bit covalent nature of the bonding. Further, the significant shift of the Eu-4d peak (0.8 eV) in the XPS spectrum confirms strong absorption of Eu³⁺ by DPA functionalized TiO₂ .

Highlights of the work carried out by **Sumit Pahan** under the supervision of **Dr. C. P. Kaushik** (Guide) and **Dr. D. Banerjee** (Co-guide) as a part of his doctoral thesis work. He was awarded a Ph.D. degree from Homi Bhabha National Institute in Chemical Sciences in 2021.

Joule Heated Ceramic Melter

THE WASTE generated in spent fuel reprocessing facilities contains a significant quantity of high-level liquid waste (HLLW). This liquid waste is converted into a solid waste form by vitrifying in a stable borosilicate glass matrix. This process called “Vitrification” is carried out in Joule Heated Ceramic Melter (JHCM).

A holistic model of JHCM was developed by incorporating the physical and chemical phenomena occurring inside the melter. It is a realistic model that couples the batch melting and reactions in the glass, chemical equilibria and solubility data. Development of integrated melter model includes a model framework, incorporating properties of molten glass in the temperature range of 303 K to 1273 K, cold cap model and determination of heat and mass transfer rates using data generated from pilot plant and industrial scale melters. Studies were carried out to determine the reaction kinetics of the different reactions taking place during vitrification and the results were incorporated in the 3-D model. This integrated model predicts the parameters with an accuracy of 98% and lends flexibility to carry out optimization studies by varying different inputs.

The model is used for maximizing waste loading while improving the melting rate by using customized glass composition. The study helps in the design and development

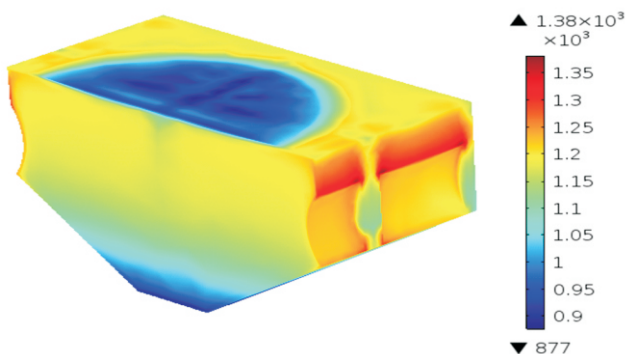


Fig.1: Temperature field inside the symmetric melter cavity (Temperature in Kelvin).

of a durable glass matrix for keeping the radioactive waste in isolation over an extended period.

The reported work by **Dr. G. Suneel** is a highlight of his Doctoral Thesis work. He has carried out the work under the supervision of **Dr. C. P. Kaushik**, Professor, HBNI. He was awarded a PhD degree from Homi Bhabha National Institute in Chemical Sciences in 2021.

Alternative Glass Forming Systems for Immobilization of Radioactive Wastes

HIGH-LEVEL Liquid Waste (HLW), containing over 90% of the activity generated in the fuel cycle, is vitrified for long term immobilization commonly in sodium borosilicate based glasses. HLW can contain elements which have limited solubility such as Cr (corrosion product), and Mo (fission product; both having solubility ~3% wt.) and Al (arising from Th fuel reprocessing). The aim of this thesis to study the effect of additives to increase the solubility of problematic species allowing enhanced waste loading, with attendant minimization of waste volumes. During the thesis work, the effect of Al₂O₃, MoO₃ and CrO₃ on structural and thermal properties of sodium and barium borosilicate glass was studied using XRD, DSC, XRF, LIBS etc. Thermal and chemical durability of glass samples were also evaluated.

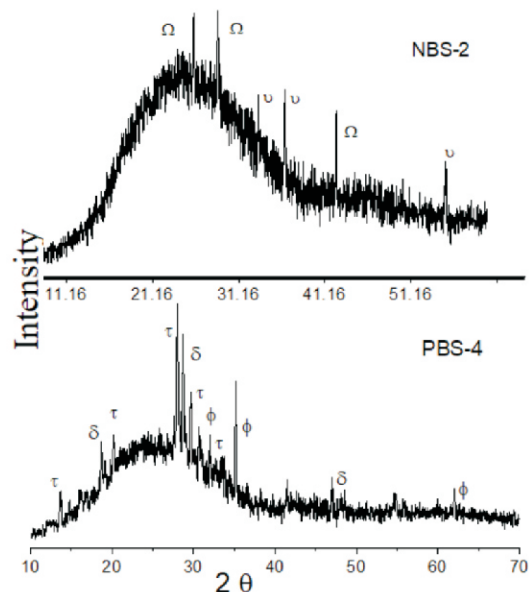


Fig.1: XRD patterns of product glass samples (Ω- BaCrO₄, ν-Cr₂O₃, τ- Pyroxene, δ-Powellite, φ-spinel).

An important finding arising from this thesis is that the incorporation of ~5 mol% P₂O₅ allowed an increase in Cr-rich waste loading from 27% wt. to 33% wt. before the formation of crystalline phases as evident in the XRD patterns of NBS-2 and PBS-4. The former, devoid of P₂O₅, exhibits reflections corresponding to BaCrO₄ and Cr₂O₃ crystalline phases on addition of 27% wt. waste oxide. The presence of 5 mol% P₂O₅ in the latter delayed the formation of crystalline phases till 33% wt. waste oxide loading when pyroxene, powellite and spinel crystalline phases emerge. These studies can inform strategies to increase waste loading and reduce the cost of waste management campaigns.

Highlights of the work carried out by **Amrita Dhara Prakash** under the supervision of guide: **Prof. C. P. Kaushik** and Co-guide: **Prof. A. K. Tyagi** as a part of her doctoral thesis work. She was awarded PhD degree from Homi Bhabha National Institute in Chemical Sciences in 2021.

Glasses for Immobilization of High-Level Radioactive Waste

THE PRESENT work focused on the chemical durability assessment of borosilicate glasses used to immobilize high-level nuclear radioactive waste. Suitable borosilicate glass formulations were developed to immobilize waste streams generated from the reprocessing of PHWR spent fuel and thorium irradiated rods were used. Chemical durability assessment of the glasses was studied by conducting different types of static leach tests, including characterization of altered phases. The results were compared with natural analogues of basalt glass (Fig.1). Understanding the leaching mechanism and kinetics of corrosion products associated with



Fig.1: Naturally leached basalt glass collected from hot water springs located in Vajreshwari at Bhivandi Taluka of District Thane in Maharashtra State, India.

borosilicate glasses, leaching studies were also done at high temperatures (200°C) and pressures (16bar). It was evident that the alteration products, sodium aluminium silicate (natrolite) $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{H}_2\text{O})_2$ zeolite phase, formed both in laboratory autoclave leaching studies and with hot springs leaching. These phases have been stable for millions of years.

The zeolite phases were formed in nuclear waste glasses under aggressive hydrothermal leach test conditions within short test durations. Extrapolating these test conditions to long term leach durations, it is concluded that the chemical durability of the selected waste glasses by and large are comparable and are suitable for the immobilization of high-level radioactive waste.

Highlights of the work carried out by **Vidya Thorat** under the supervision of **Dr. C. P. Kaushik** (guide) and **Dr. A. K. Tyagi** (Co-guide) as a part of his doctoral thesis work. She was awarded a Ph.D. degree from Homi Bhabha National Institute in Chemical Sciences (Enrolment No.: CHEM01201204018) in 2020.

X-Ray Fluorescence Spectrometric Characterization of Mixed Oxide Fuel during Fabrication

THE PRESENT work reports the development of Wavelength-Dispersive X-Ray Fluorescence (WDXRF) Spectrometric based methods for characterization of primary heavy metal (U, Pu and Th) contents and traces constituents in Oxide and Mixed Oxide (MOX) fuel during their industrial level fabrication process. The systematic studies have been performed to optimize instrumental parameters, prepare calibration standards, measure their WDXRF spectra, and make calibration plots for U, Pu and Th determination using WDXRF.

For direct determination of U and Pu content in the fabricated sintered pellets of DDUO_2 and $(\text{U}_{1-y}\text{Pu}_y)\text{O}_2$; ($y = 0.21$ & 0.28) MOX fuel, a special collet of Stainless Steel-304 (SS-304) material were designed and fabricated in-house (Fig.1). The RSD (relative standard deviation) for the measurement of U and Pu using WDXRF in annular MOX sintered pellets were found to be $\pm 0.13\%$ and $\pm 0.31\%$, respectively. In addition, clean rejected oxide powders were also analyzed for Pu content using the WDXRF methodology.

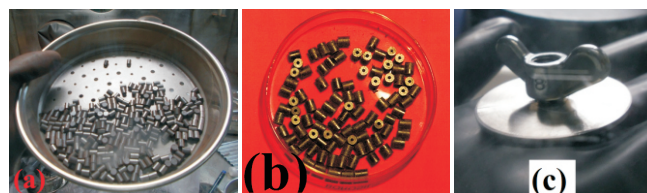


Fig.1: Portion of a batch of sintered (a) DDUO_2 , (b) $(\text{U}, \text{Pu})\text{O}_2$ Pellets and (c) Stainless Steel Collet.

The methods developed have resulted in saving precious U, Pu and Th from wastage and at the same time reduced radiation exposure to the analyst. Compared to conventional wet chemical analysis, the adaptation of the non-destructive analysis technique saved producing about 45 litre of alpha active liquid waste containing about 1.6 Kg of precious U and Pu.

Highlights of the work carried out by **Ashish Pandey** under the supervision of **Dr. Pradeep Kumar** as a part of his doctoral thesis work. He is awarded PhD degree from Homi Bhabha National Institute in Chemical Sciences in 2021.