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BARC
ATOMS IN THE SERVICE OF THE NATION

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75 आज़ादी का अमृत महोत्सव

Reprocessing and Waste Management

editorial
MESSAGE

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TECHNOLOGIES FOR
NEW INDIA@75
आज़ादी का अमृत महोत्सव

Waste 2 WEALTH

During the last decade, a quantum leap has been achieved in the technological advancement in back-end of nuclear fuel cycle, especially in the field of spent fuel reprocessing and radioactive waste management. Right from the inception of BARC, Nuclear Recycle Group is contributing towards the expansion of Indian Nuclear Power Programme (INPP) envisioned by Dr Homi J. Bhabha. The journey started from 1965 when India's first reprocessing plant, i.e., Plutonium Plant at Trombay was commissioned for reprocessing of Spent Nuclear Fuel (SNF) of research reactor origin. Since then, efforts were continued for development of advanced technologies for reprocessing of SNF from each stage of power programme as well as ensuring safe and efficient management of radioactive waste including extracting valuable radionuclides from waste for societal applications to realise the concept of *'Wealth from Waste'*.

India follows *'closed fuel cycle'* and spent fuel reprocessing acts as a bridge to integrate various stages of INPP adapted for enabling optimum use of available nuclear fuel resources in our country. This will catalyse transition towards thorium-based technology to provide self-sustained solution for country's long term energy needs. Over the past decades, progressive advancement has been made in reprocessing flow sheet to continuously enhance the overall product purity and separation efficiency. The head-end systems of reprocessing plants were mechanised & automated for increased throughput with reduced radiation exposure to plant personnel while operating and maintaining the systems.

As a result, technological maturity has been achieved by reprocessing of spent fuel from thermal neutron based research reactor and power reactors. R&D was also focussed to achieve the goal of tapping power from Thorium for nuclear energy security. As a part of this, irradiated Thoria fuel bundles in CIRUS and PHWRs were reprocessed in UTSF and PRTRF respectively, to demonstrate the engineering capabilities of Thoria-based fuel reprocessing flow sheet on industrial scale. This has helped in establishing a steadfast scientific and technological foundation.

Management of radioactive waste has always been the thrust area for developing scientific concepts and translating the same into innovative technologies. Emphasis has been towards environment friendly green solutions and diverting recovered radionuclides for healthcare applications. There has been distinctly visible improvements in its treatment, conditioning, transport and disposal technologies. An efficient and safe waste management practices in congruence with evolving global approaches has been given vital priority in INPP. The same has been recognised as a very important component of National Policy on Radioactive Waste Management (RWM). India has made a phenomenal progress in technological advances towards development of novel extractants and separation technologies for recovery of valuable radio-isotopes from high level radioactive liquid waste and their utilisation for societal benefit like medicine and cancer treatment. This has altered the public perception in the otherwise complicated issues pertaining to waste management. The radioactive wastes are gradually turning into the material of resource thereby, establishing *'Waste to Wealth'* philosophy.

It is felt necessary to bring out a gamut of scientific and technological aspect about advanced fuel cycle so that effective and state-of-the-art technologies can be implemented at various stages especially in view of the sense of fear in general public associated with radioactive wastes and their long-term radiological characteristics.

This issue features twelve articles on industrial experience of reprocessing and radioactive waste management and four articles on technological advancements towards healthcare applications. Nine articles are pertaining to R&D activities involving process and matrix development along with spinoff applications. Finally, News Corner and Synopsis sections are also included to highlight the outcome of diversified scientific and academia efforts towards technological development for spent fuel reprocessing and radioactive waste management.

The front cover of this issue carries an iconic picture of Plutonium Plant, first milestone to India's progressive journey of back-end fuel cycle, glimpses of back-end activities and view of future melter technology. The back cover of the issue is highlighted with Waste Immobilisation Plant at Trombay presently under operation for management of HLW and equipped with associated systems to demonstrate the concept of *'Wealth from Waste'*.

I take this opportunity to congratulate all the authors for their precious contributions to enhance the elegance of scientific and technological contents published in this issue. Finally, I acknowledge the untiring efforts and sincere hard work of Editorial Team members for their time-bound compilation of all the articles to bring out the special issue of BARC Newsletter on activities pertaining to back-end of nuclear fuel cycle.

Table of Contents

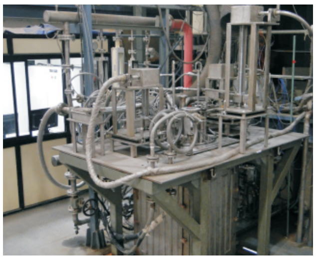
Inside view of hot cell

ASM slave arm

Tile Hole Battery

@BARC Photo

On Cover
Plutonium Plant
in BARC, Trombay



Cold Crucible Induction Melter

Cut-end Rod Handling System

Prussian Blue capsules

RESEARCH & DEVELOPMENT

NEWS DIGEST

SNAPSHOTS OF DOCTORAL THESES

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EDITORIAL COMMITTEE

SPECIAL FEATURE

CLOSED FUEL CYCLE

For Sustainable Growth of Nuclear Power Program in India

C. P. Kaushik and K. V. Ravi

ABSTRACT

Energy availability is an enabler for growth, progress and prosperity. Indeed, energy availability and progress feedback positively to each other. The Indian growth story means higher energy demand, which will further fuel growth in a virtuous cycle. However, India has not been blessed with an abundance of fossil fuel reserves, which in turn places an emphasis on the judicious management of available energy resources to allow sustainable growth. While renewable energy is the new rage and is growing increasingly popular, harnessing the power of the atom was the original "low pollution energy" idea dating back to the 1960s in India.

Recognizing with acute foresight that India would have to tap her abundant Thorium reserves and not depend upon imported Uranium, Dr. Homi J. Bhabha, the founder of the Indian Atomic Energy Programme conceptualized a three stage nuclear power programme. Indeed, the three stage nuclear fuel programme necessitates a closed fuel cycle with reprocessing of spent fuel. In addition to long-term energy security, and optimum utilization of Uranium resources, reprocessing promises reduced radio-toxicity and a smaller waste volume for final disposal in a repository. Additionally, reprocessing opens new avenues for the recovery of valuable radionuclides from radioactive wastes for various societal applications, reinforcing our view that nuclear waste is an abundant resource for national wealth.

The status and recent advancements of back end fuel cycle activities to realize the closed fuel cycle for each stage of the Indian nuclear power program along with achievements in the field of radioactive waste management in India are presented in this article.

KEYWORDS: Fuel cycle options, Closed fuel cycle, Reprocessing, spent nuclear fuel, High level waste, Radioactive waste management, Wealth from waste, Geological disposal facility.

THE INDIAN economy is growing fast leading to an increase in prosperity, quality of life, purchasing power and an insatiable appetite for energy. By 2036–37, electricity utilization is expected to double [1]. Meeting this demand by the conventional fossil fuelled route is unsustainable economically and especially environmentally. Various sources of energy including renewable sources such as solar, wind, hydroelectricity, geothermal, tidal etc. have emerged as promising alternates for fossil fuels. However, these energy sources are not reliably available at all time, necessitating a base driver. This role can be appreciably filled by nuclear energy thereby permitting an energy mix with an optimal utilization of available energy resources to ensure growth of the country.

The vision of nuclear energy utilization in India was first nurtured and brought to realization by Dr. Homi J. Bhabha in the early 1960s. He was acutely aware that India possessed only limited resources of Uranium but abundant reserves of Thorium. Therefore, Dr. Bhabha advocated the three stage nuclear fuel programme intended to bring long-term energy security to India and minimize dependence on imported Uranium. As part of this programme, natural uranium fuelled pressurized heavy water reactors (PHWRs) would be used to generate electricity and plutonium. The latter would be utilized in preparation of mixed oxide (MOX) fuel for Fast Breeder Reactor (FBR) in the second stage to generate electricity and enable breeding uranium-233 (^{233}U) from thorium. In the third stage, ^{232}Th - ^{233}U will be used as fuel in advanced reactors for energy extraction from abundant thorium reserves and thereby achieve long-term energy security [2,3,4].

Indeed, the vision of a three stage Indian nuclear power program (INPP), cannot be fructified without adoption of a closed fuel cycle considering spent nuclear fuel (SNF) as a resource. For all the stages of INPP, reprocessing of SNF is essential for extracting the fuel and to recycle them in next generation reactors.

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Fuel Cycle Options

The fuel cycle can be open or closed depending upon the management philosophy for SNF. In case of the former, the SNF is classified as a waste, slated for direct disposal in a geological disposal facility (GDF). The latter entails chemical treatment of the SNF to recover fissile and fertile materials for reuse. The merits and limitations of each philosophy have been widely debated and both have their proponents and opponents. Of course, there is no one-size-fits-all in terms of selection of a suitable fuel cycle option. This must be selected based upon a variety of factors including the demand for energy, size of the nuclear power program, availability of resources, technology knowhow, public perception, long term strategy etc. Countries adopting the open fuel cycle generally utilize thermal neutron reactors for extraction of energy from the fission of enriched uranium-235 (^{235}U). Such a scheme obviates the need for complex reprocessing and waste management strategies. In contrast, the adoption of a closed fuel cycle is technologically more challenging requiring the chemical treatment of SNF for reprocessing and deployment of an FBR for breeding fertile material. Despite this, the closed fuel cycle significantly reduces decay heat load in the waste, reduces waste volume and mitigates radio-toxicity.

India's closed fuel cycle option is based on multi recycling of plutonium in FBRs with recovery of plutonium from SNF of MOX fuel of each cycle for its use in the next reactor for energy production. This results in maximum utilization of fertile uranium by converting it into fissile plutonium.

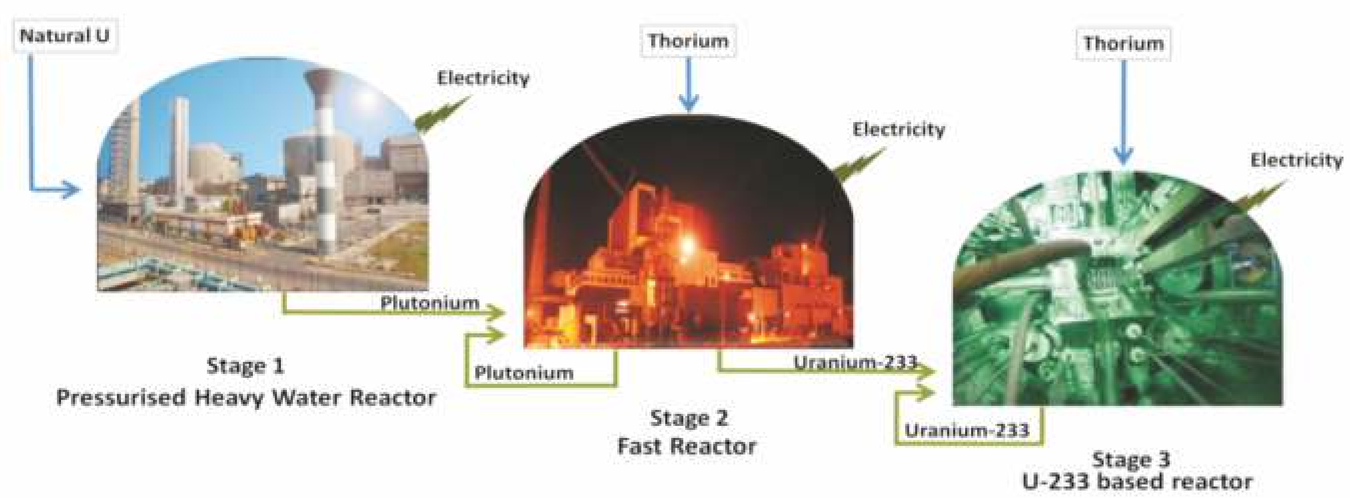

Fig.1: Closed fuel cycle based three stage nuclear power program.

Another area where the two approaches differ is in terms of economics. The largest cost associated with an open fuel cycle is the cost of construction and supervision of a GDF. Since the open cycle is technologically modest, upfront costs for disposal are lower. However, delays in GDF construction and operation can lead to rapid cost increases driven by the need for extending long term storage of SNF, augmentation of additional storage capacities, repacking of SNF etc. Available information estimates the cost of a GDF at hundreds of billions of dollars over a period of 100–150 years.

The closed fuel cycle entails higher upfront costs for investments associated with cost of recycling facilities and fast reactors. However, significant cost saving can be realized in the GDF due to reduction in decay heat, waste volume and radio-toxicity. Hence, the open-cycle has lower short-term costs but uncertainties around long term costs and waste hazards increase with time. In comparison, closed cycle options having higher short- to mid-term costs but the characteristics of the waste limit the long-term hazard, thus reducing future uncertainties [5].

Unlike open fuel cycle, the closed fuel cycle largely depends on back end facilities including reprocessing plants, high level waste management plants among others for achieving its goals.

Closed fuel cycle offers different options such as mono recycling of plutonium or multi recycling of plutonium. For example, France follows the mono recycling option based on the two stage cycle. In this scheme, SNF discharged from the first stage of uranium fuelled reactors is reprocessed to recover plutonium and uranium. MOX fuel consisting of recovered plutonium along with depleted uranium is fuelled to a reactor in the next stage. SNF of MOX fuel of second stage reactor is not reprocessed but considered a waste for disposal. This option helps in saving of 75% fresh fuel as well as reducing the waste volume requiring disposal in the repository [5]. Besides this, it also bypasses the need for Fast Breeder Reactor technology. In contrast, India's closed fuel cycle option is based on multi recycling of plutonium in FBRs with recovery of plutonium from SNF of MOX fuel of each cycle for its use in the next reactor for energy production. This results in maximum utilization of fertile uranium by converting it into fissile plutonium. This leads to a significant reduction in overall requirement of fresh uranium fuel for a given electricity generated as compared to an open fuel cycle as well or a closed fuel cycle with mono recycling of plutonium.

Closed Fuel Cycle - India's Option

India has adopted the closed fuel cycle to meet the goals of the three stage INPP, to allow optimum utilization of available uranium resources, while extracting maximum utility from abundant deposits of thorium. Multi recycling of plutonium is envisaged for maximum utilization of fertile uranium by placing MOX (mixed oxides of plutonium and depleted uranium) in Fast Breeder reactors to breed the fissile plutonium from fertile uranium, for its utilization in similar reactors. There also are plans to place thorium in Fast Breeder reactors as a blanket material at a later stage to breed ^{233}U for fuelling advanced reactors of the third stage (Fig.1).

In addition to ensuring optimal utilization of fuel, the closed fuel cycle also helps in reducing long term radio-toxicity associated with high level waste. For example, the radio-toxicity of SNF, disposed directly from an open fuel cycle, will decay to that of natural uranium in about 200,000 years. On the contrary, SNF discharged from a closed cycle scheme will have its radio-toxicity decay to that of natural uranium is about 10,000 years [6]. Besides this, close fuel cycle option recovers and, hence, removes almost all of the uranium and plutonium in SNF, which would end up in GDF in case of an open fuel cycle. Most advantageously, the final waste volume needing disposal in GDF will be reduced significantly in case of a closed cycle. This is emphasized by the fact that the volume of resulting vitrified waste after reprocessing of SNF generated from Indian PHWR is about five times lesser than volume of SNF if disposed directly. Besides this, it opens up new ways of partitioning of high level waste for transmutation of long lived minor actinides and also for recovery of valuable radionuclide for societal applications. Separation of heat generating fission products from long lived minor actinides further reduces the volume and decay heat associated with the final waste volume needed to be disposed in GDF.

A closed fuel cycle utilizing multi-recycle option helps in minimization of waste volume, thereby reducing concerns of long term radio-toxicity, while a reduction in the decay heat load helps reduction in space and time for geological isolation with beneficial impact on GDF cost.

Back end facilities including reprocessing of SNF plays a vital role in the power program conceptualized on the basis of a closed fuel cycle by providing fuel for same as well as next stage reactors. Unlike open fuel cycle, the closed fuel cycle largely depends on back end facilities including reprocessing plants, high level waste management plants etc. for achieving its goals.

Fig.2: Reprocessing Plant, Trombay.

Fig.3: PREFRE-I, Tarapur.

Fig.4: KARP, Kalpakkam.

Reprocessing of Spent Nuclear Fuel

By the time reprocessing was taken up by India, it was a relatively mature process and the best technological choice was the PUREX process, which is a solvent extraction process using 30% TBP in pure n-dodecane, for reprocessing of spent nuclear fuel (SNF). It may be mentioned here that the PUREX process is the workhorse of reprocessing and no process before or since can match its versatility.

Based on same, India has a wealth of experience in the reprocessing of SNF spanning more than five decades. The first reprocessing plant, i.e. Plutonium Plant, was commissioned in the year 1965 at Trombay and the same is still under operation, reprocessing the SNF from Trombay reactors (Fig.2). Based on experience obtained from the plant, reprocessing of Power Reactor (PHWR) fuel was initiated in the early seventies by building and operating the Power Reactor Fuel Reprocessing Plant (PREFRE-I) at Tarapur (Fig.3). Subsequently, one reprocessing plant at Kalpakkam, KARP, and one more reprocessing plant at Tarapur, PREFRE-II, were constructed and are presently under operation for reprocessing of PHWR Fuel (Fig.4). Recently, an additional plant KARP-II has been commissioned for PHWR Fuel reprocessing at Kalpakkam. Out of these, PREFRE-I has been shut down after successfully completing its operating life while the rest of the plants are in operation. India has mastered the technology of reprocessing of SNF of thermal neutron based research as well as power reactors such as PHWRs. The plutonium thus recovered has been utilized for fabrication of MOX fuel for upcoming Prototype Fast Breeder Reactor (PFBR), thus closing the fuel cycle of first stage of INPP. The management of high level waste generated from reprocessing is carried out safely and effectively as described in the subsequent section.

Concerted R&D efforts are underway in the field of HLLW portioning, which will enable a reduction in waste volume and mitigate the necessity for a GDF in the near future.

Over the period, indigenous developments resulted in various improvisations in the process flow sheet to improve recovery, separation efficiency and thus product quality of U and Pu. Recent developments have been carried out in the field of head end systems along with a desired state of automation to provide better availability of system, enhanced throughput and minimize personnel exposure. As a result, some of the reprocessing facilities have delivered better than rated capacity. As the nuclear energy based power capacity is likely to be increased multi-fold, the need for reprocessing SNF will also increase concomitantly. Utilising the vast experience in the field of spent fuel reprocessing, large capacity Integrated Nuclear Recycle Plant (INRP) is under construction at Tarapur to increase multifold the reprocessing capacity of the country.

Reprocessing of spent fuel generated from Fast Breeder Test Reactor has also been demonstrated in the CORAL facility at Kalpakkam. Similarly, capability in reprocessing of Thoria fuel has also been shown successfully at BARC, Trombay demonstrating the technology needed for third stage of INPP. Thoria fuels irradiated at CIRUS and at PHWR were successfully reprocessed for recovery of ^{233}U as well as thorium at UTSF and PRTRF of Trombay respectively [7,8,9,10].

Radioactive Waste Management

The management of radioactive waste is an important aspect for the widespread acceptability of nuclear power while ensuring sustainability of the programme. Consequently, the safe management of radioactive waste has been an important consideration since the inception of our nuclear power program. Waste volume minimization and near zero discharge of radioactivity have always been the central principles of radioactive waste management. The implementation of the nuclear waste management plan hinges on the following broad concepts: delay and decay; dilute and disperse; recycle and reuse and concentrate and contain.

As mentioned earlier, an important advantage of the closed cycle is the reduction in the volume and radio-toxicity of the waste requiring internment in the GDF. However, safe and effective management of High Level Liquid Waste (HLLW), generated during the reprocessing of SNF, is an important and decisive aspect motivating the selection of the closed fuel cycle. HLLW contains more than 99% of radioactivity present in SNF. Conventionally, HLLW is immobilized in an inert glass matrix by vitrification process to reduce the waste volume and to isolate the radionuclides from the environment. Vitrified HLLW is stored in a passive air cooled vault for removal of decay heat for a few decades followed by planned disposal in a GDF sited in stable granitic host rock about a few hundred meters below the surface.

The first vitrification facility for HLLW, Waste Immoblisation Plant (WIP), was built in the early 1990's at Tarapur based on an Induction Heated Metallic Melter (IHMM) for converting HLLW, generated from PREFRE-I, into a vitreous waste product (VWP). Based on the experience gained from WIP, Tarapur, another IHMM based vitrification plant was commissioned at Trombay in 2002, which remains under operation to treat HLLW generated from reprocessing research reactor SNF (Fig.5). The Joule Heated Ceramic Melter (JHCM) was developed to overcome the throughput limitation of IHMM thereby catering to a higher capacity of HLLW immobilization. This melter was successfully deployed at the Advanced Vitrification System (AVS), Tarapur (Fig.6). WIP, Kalpakkam has been commissioned for management of HLLW using JHCM in the year 2017 (Fig.7). Combining all these

Fig.5: WIP, Trombay.

Fig.6: AVS, Tarapur.

Fig.7: WIP, Kalpakkam.

plants, more than 500 vitrification operations were carried out safely showcasing the capabilities of the country in the field of vitrification of HLLW. India is among very few countries of the world, which have gained proficiency in the vitrification technology at an industrial scale.

The first facility for the interim storage of vitrified HLLW in an air cooled vault, Solid Storage Surveillance Facility (SSSF), Tarapur was commissioned and remains in operation. More recently, the Vitrified Waste Storage Facility (VWSF), Kalpakkam was also commissioned in 2020 for the interim storage of vitrified HLLW.

For GDF, R&D with respect to finalization of the site selection criteria, characterization of backfill materials, modeling of radionuclide migration in the geosphere, thermal-hydraulic studies, conceptualization of design etc. are underway. National as well as international collaborative works with various academic and other research institutes of the country and across the globe are being pursued for converging expeditiously on an optimal solution for such the complex problem of a GDF. At present, there are no operational GDFs anywhere in the world.

Concerted R&D efforts are underway in the field of HLLW portioning, which will enable a reduction in waste volume and mitigate the necessity for a GDF in the near future. Further, consistent efforts directed towards novel extractants has led to the successful commissioning of solvent extraction based Actinide Separation Demonstration Facility (ASDF), Tarapur in year 2014 aiming to partition of minor actinides from HLLW. ASDF, Tarapur has been the first and only engineering scale facility in the world for partitioning of minor actinides from HLLW treating few tens of thousands of liters of HLLW. Based on successful operation of ASDF, Tarapur, another engineering scale solvent extraction based partitioning system at WIP; Trombay was built and commissioned in the year 2015 for the separation of radioactive components from inactive components.

Utilising this solvent extraction system, recovery of many valuable fission products such as ^{137}Cs, ^{90}Sr, ^{106}Ru etc. could be demonstrated on a bulk scale from HLLW at WIP, Trombay for various societal applications. Besides recovery of useful radionuclides, partitioning process could also demonstrate multifold reduction in final vitrified waste volume greatly reducing space demand in the GDF. Considering the advantages of partitioning of HLLW prior to vitrification and the technological knowhow accrued, the same is being implemented at High Level Waste Management plant engaged in management of HLLW from reprocessing of power reactor spent nuclear fuel.

Besides management of HLLW, Intermediate Level Liquid Waste (ILLW) generated from reprocessing facilities is also treated effectively using radionuclide specific ion exchange resins at waste management facilities of Trombay, Tarapur and Kalpakkam. Low Level Liquid Waste (LLLW), generated from all the fuel cycle facilities, are treated intensely prior to discharge to the environment. Chemical treatment is the oldest process under operation at various radioactive waste management sites for getting good decontamination factors for bulk removal of radioactivity prior to discharge of effluent to the environment. R&D is ongoing for the development of membrane based novel technologies for treatment of large volume of LLLW to achieve superior decontamination factors and to discharge minimal radioactivity, thereby realizing the concept of 'near zero discharge of radioactivity'.

Low and intermediate level radioactive solid waste are generated from all the fuel cycle facilities. Various treatment methodologies such as compaction, incineration and melt-densification have been deployed based on the nature of radioactive solid waste to reduce the volume prior to their disposal in Near Surface Disposal Facility (NSDF). Recently, plasma based incineration system has been developed at Trombay to treat large quantities of polymeric waste for achieving augmented volume reduction factor without generation of toxic gases. This radioactive solid waste is finally disposed in a suitable engineered barrier, based on their nature and category of waste, in NSDF, which have been designed based on a multi-barrier concept to retard the migration of radionuclide to the environment. Presently, about eight NSDFs are under operation in the country for disposal of low and intermediate level radioactive solid waste after suitable treatment, if required. The NSDFs will have surveillance for 300 years after closure to monitor the migration of radionuclides, if any. More than 60 years of experience of disposal of solid waste in NSDF enhances the confidence on its design and construction for safe disposal of radioactive solid waste. For example, the NSDF site of BARC, Trombay commenced operations for the disposal of wastes since the 1960's and no noteworthy migration of radionuclides from the disposal site has been observed till date.

Wealth from Waste

HLLW contains many valuable radionuclide such as ^{137}Cs, ^{90}Sr, ^{106}Ru etc. which are potentially useful in many societal applications. Solvent extraction system of WIP, Trombay could demonstrate the recovery of ^{137}Cs, ^{90}Sr and ^{106}Ru for their societal applications. Recovered ^{137}Cs is converted into non-dispersive sealed source of Cs glass pencil for application in blood irradiation. India is the first country to

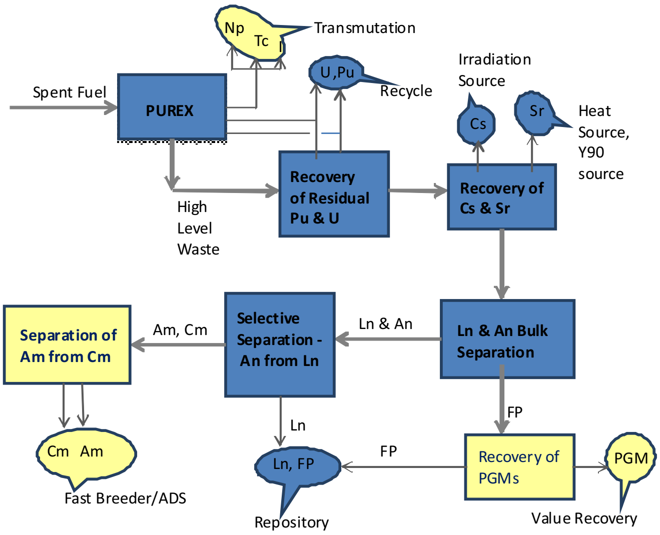

Fig.8: Evolving fuel cycle.

deploy ^{137}Cs in non-dispersive glass form for irradiation application. ^{90}Sr is recovered and purified for milking of clinical grade ^{90}Y for radiopharmaceutical applications. ^{106}Ru based eye plaques, RuBy, has been indigenously developed of different configurations from recovered ^{106}Ru from radioactive waste for affordable eye cancer treatment. Thus recovery of valuable radio-nuclide for deployment in social applications is an important contribution of the reprocessing scheme.

Evolving Fuel Cycle

Development of technologies for novel extractants and partitioning processes have paved new avenues at the back end of the fuel cycle. Closed fuel cycle can be further evolved to separate various radionuclide at different stages of the fuel cycle for their optimum management, as well as societal applications, if needed. A glimpse of the evolving fuel cycle is illustrated in Fig.8.

Future Activities

To reduce the fuel cycle costs, continued R&D efforts are required in the PHWR reprocessing program to further optimize consumption of chemicals, water, energy, manpower, dose etc. Further improvements in processes are needed to reduce the generation of secondary wastes as well as further volume reduction of solid wastes like hull, Coolant tubes etc. Process intensification (larger columns, compact layout, automation, etc.) also need to be evolved to achieve larger throughput in plants with smaller footprints.

As the Indian Nuclear Power program also has BWRs, PWRs, FBRs and it is also planned to establish AHWR, MSR and Research reactors with different types of fuels, continued R&D on back end technologies required for each type of fuel needs to be pursued with vigor to be prepared for future programs which are promising. Keeping in view the reactors operated using imported fuel, robust technological solutions are required for addressing the safe guard aspects. Methodology for disposal of decommissioned wastes from power plants also needs to be evolved.

Acknowledgements

Authors acknowledge the guidance & support extended as well as efforts to pave the path of back end fuel cycle by previous Group Directors, Heads of Divisions and all Senior Colleagues of Nuclear Recycle Group and Nuclear Recycle Board. The authors also acknowledge the dedicated efforts put by scientific and technical team of Nuclear Recycle Group and Nuclear Recycle Board for realizing the technological breakthroughs in the field of reprocessing and radioactive waste management. The authors wish to convey their special thanks to Darshit Mehta and G. Sugilal for compiling this article.

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INDUSTRIAL EXPERIENCE

RECYCLING PERSPECTIVES
Indian Experiences and Road Ahead

Smitha Manohar and S. Pradhan

INDIA is committed to the closed fuel cycle (Fig.1) and perceives spent fuel as a source of energy. Although the Pressurized Heavy Water Reactors (PHWRs) are the main stay of nuclear power generation in India, Light Water Reactors (LWRs) and other reactors are also being adopted for meeting the growing energy demands of the country. The recovered Plutonium from PHWR spent fuel reprocessing is to be utilized in sodium cooled Fast Breeder Reactors (FBRs) along with recovered Uranium as MOX fuel as part of a multi-recycling concept enabling maximum utilization of fuel for electricity generation (Fig.2) .This strategy not only enables recycling of fissile and fertile elements into the nuclear reactor, but also presents us with an opportunity to reduce the radiotoxicity of the final waste for disposal. Recent developmental activities have helped in the evolution of the partition strategy that not only helps to reduce the radiotoxicity of the high-level waste but also enable the separation of useful radionuclides for societal benefits. In line with the abundant natural reserves of Thorium in our country, a thorium utilization program is also being pursued which encompasses reprocessing of irradiated thorium to recover U^{233} for its use in future reactors.

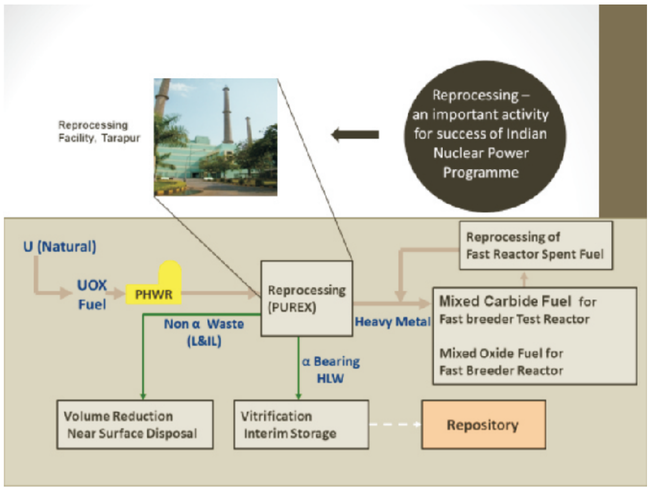

Fig.1: Indian Nuclear Fuel Cycle.

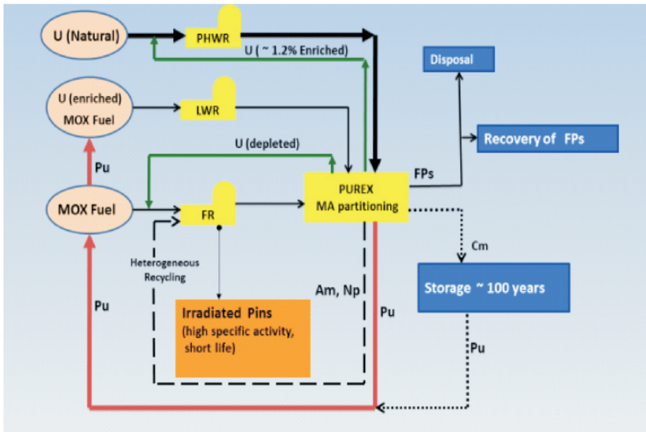

Fig.2: Evolving Nuclear Fuel Cycle.

Lessons Learnt

More than five decades of operational experience of back-end fuel cycle facilities have established a safe operating culture in India. Adopting good practices and incorporation of improved technologies have resulted in sustained higher through puts, increased separation efficiencies and higher decontamination factors resulting in acceptable product quality. This has also resulted in reduced man-rem consumption, improved safety, reduced environmental discharges and reduction in secondary wastes volumes for disposal. The challenging activities with regard to spent fuel handling, head-end operations, dissolution, solvent extraction cycles and final conversions are all carried out in conformity with internationally laid out safety regulations. Such indigenous, industrially matured technology is being now extended to set up an integrated nuclear recycle project with a name plate capacity of 600 T/year. This article will not only highlight the lessons learned during these five decades of operation but will also highlight the overall design perspectives of such plants for the future.

Recent developmental activities have helped in the evolution of the partition strategy that not only helps to reduce the radiotoxicity of the high-level waste but also enable the separation of useful radionuclides for societal benefits.

The entire reprocessing operations can broadly be listed as a) head-end operations, b) solvent extraction cycles for obtaining pure product solutions and c) precipitation and calcination of product streams.

Head-end Operations

These operations entail receipt of spent fuel from the reactor facility, followed by safe storage in the spent fuel storage pool at the reprocessing facility. Since these sufficiently cooled fuels are to be taken up for reprocessing operations, under-water storage is deemed convenient and is widely practiced. The reprocessing plants are situated advantageously relative to operational nuclear reactors to facilitate easy movement of spent fuel from reactor site to the plants. The casks that carry spent fuel during transport are appropriately designed to not only provide the necessary shielding at all times but are also designed to remain intact during off-normal situations including impact, fire etc.

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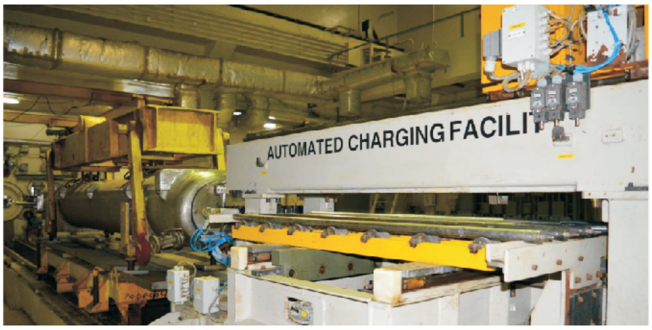

Fig.3: Automated fuel charging facility, Trombay.

Fig.4: Gang chopper.

While the research reactor reprocessing entails chemical decladding followed by dissolution of fuel, the PHWR spent fuel bundles are chopped into ~50 mm long pieces and dropped into a basket before being taken up for dissolution. The challenging aspects of head-end operation encompassing spent fuel charging and chopping have been successfully addressed by the deployment of an automatic fuel charger (Fig.3) and gang chopper (Fig.4). The hulls from PHWR reprocessing are further rinsed and assayed for activity before being stored, pending disposal.

Solvent Extraction Cycles

The dissolved solution containing uranium and plutonium along with all the fission products in nitrate form are subjected to solvent extraction cycles based on well-established PUREX process, resulting in relatively pure solutions with very low fission product contamination. The Co-decontamination and partitioning step ensures separation of Pu and U from all the other unwanted components of spent fuel and further separation of U and Pu product streams. The products thus separated, namely uranium and plutonium streams are further subjected to purification cycles to meet product specifications. Although the present plants employ uranus as the partitioning agent, focused R&D efforts are on to identify suitable and tailor-made agents for reprocessing of advanced reactors fuels including ^{229}Th-^{233}U systems.

The management of nuclear waste has been accorded high priority in the near term as it is well recognized that this can lead to a substantial impact on our nuclear energy programme.

Design and setting up of such operational facilities call for deployment of robust hot cell technology and appropriate remotisation of engineering system to operate safely and reliably in a high radiation environment. While the hot cells are primarily designed with appropriate shielding for processing such wastes, they also have to be equipped with remotely operated, O&M friendly material handling devices like EOT cranes, power manipulators, master slave manipulators, trolleys etc. Hot cells are also provided with shielding windows for viewing and suitably designed access areas for removal of used components and putting them into shielded casks for further management. Another most important aspect of hot cells is the design of appropriate penetration in hot cells serving as an interface between the inside active areas and the outside inactive areas of the plant.

In-cell transfer systems are designed with adequate stand by provisions and redundancies to ensure high system-availability. In this regard, air lifts, pumps and steam ejectors are used as maintenance-free transfer devices. An elaborate ventilation and off-gas system is put in place ensuring the required air changes in the various designated areas of the plant and also to ensure that the environmental discharges from such facilities are well below regulatory limits. Remote process sampling and automated sample transfer systems are very important aspect for efficient and safe operation of such radiochemical facilities. Fig.5 gives the inside view of such a hotcell showing an elaborate and complex piping system.

Reconversion Operations

The purified product solutions from solvent extraction cycles are further taken up for precipitation and calcination yielding their respective solid product in the oxide forms. While the uranyl nitrate is processed by the ADU route, the plutonium is processed by the oxalate precipitation route.

Utility & Services

The reprocessing operations are ably supported by vast utility and services that include ventilation and off-gas handling, common utilities like steam, water and compressed air. Radiological safety is ensured by radiation zoning of plant

Fig.5: Inside view of a hot cell.

Fig.6: Service distribution system.

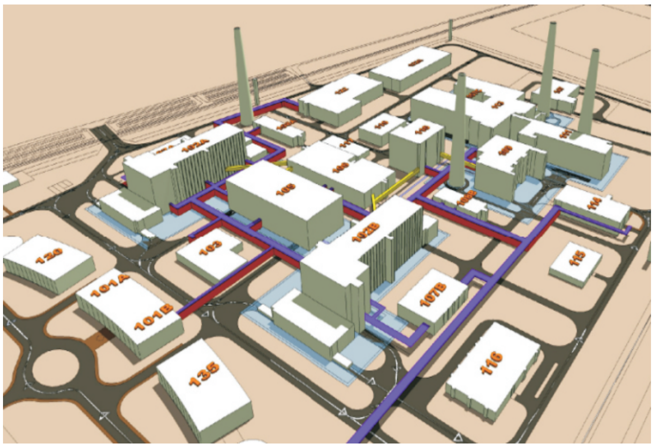

Fig.7: Integrated Nuclear Recycle Facility.

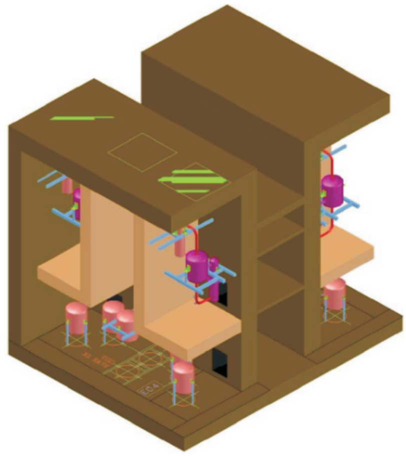

Fig.8: Sectional image of INRP.

areas and maintaining proper air flow pattern to these areas as per the radiation zoning. The industrial safety and security of such radiochemical facilities are accorded high importance and are therefore, ensured both by way of active as well as passive measures. A typical service distribution system is shown in Fig.6.

Instrumentation and control systems form a very important sub-system of reprocessing facilities, since all operations must be executed remotely inside radiological cells having concrete shielding structures of thickness ranging from 1-1.5 meters. Remote sensing of parameters like level, density, interphase, temperature, pressure etc. are done by various techniques and are made available to the control room. The present plants are all PLC-based SCADA systems, facilitating complete remote operation of such systems.

The electrical sub-systems of the reprocessing facilities essentially comprise of appropriate distribution systems along with the rated transformers. The DG sets sized in line with the safety requirements are set up and maintained as per regulations.

Safety Systems

All concerns with regard to safety of reprocessing facilities including criticality and red oil explosion are addressed right from the design stages to ensure that such situations are precluded during plant operations. While criticality is avoided by means of restricting mass, concentration, size and geometry, red oil formation is avoided by ensuring that the aqueous solutions going for evaporation are devoid of entrained organics.

The steam pressure and temperature along with vent sizing of evaporators are also some of the considerations for avoiding unsafe situations.

Waste Management

The management of nuclear waste has been accorded high priority in the near term as it is well recognized that this can lead to a substantial impact on our nuclear energy programme. In this regard, the partitioning program has been accorded high priority leading to setting up and operation of a first of its kind partitioning facilities at both Tarapur and Trombay. While the plant at Tarapur demonstrated the partitioning of minor actinides from HLW, the plant at Trombay has established fission product partitioning and the use of these radionuclides for societal benefits. Non-high level wastes are subsequently treated and managed appropriately with a focus on waste volume reduction and minimizing discharges to the environment.

The Concept of INRP

The concept of Integrated Nuclear Recycle Facility (Figs. 7 & 8) has stemmed from holding the concept of recycling as the main tenet for back-end processing. Recognizing the need for such activities, especially with regard to shared services and solution transfers, the next facility has been designed and is being set up at Tarapur for a name plate capacity of 600 T HM/year. The valuable experiences and lessons learnt have been incorporated in designing this project which is in advanced stages of construction.

Acknowledgements

The authors very humbly acknowledge not only the large and dedicated workforce of today who are contributing to this cause, but also the doyens of back-end who have led indigenous development of such a challenging technology in our country way back in 1964 when the first spent fuel rod was charged in the Trombay facility and all those who have contributed in improving and sustaining these activities.

IRRADIATED THORIA-BASED FUEL

Experiences in Reprocessing

Sanjay Kumar and Smitha Manohar

ABSTRACT

With superior neutronic and material properties along with advantage of lower production of long-lived actinides, Th^{233}-U^{233} fuel has attracted the world towards its utilization for nuclear energy. The Indian three-stage nuclear power programme envisages a large-scale utilization of thorium due to its abundant availability, while uranium resources in India are limited. For a complete understanding of the Thorium cycle, laboratory studies were carried out to establish processing of irradiated thorium to recover U^{233} and Th^{232} and recycle these to the reactor. Thoria rods irradiated in a research reactor were successfully processed at the Uranium Thorium Separation Facility (UTSF). With know-how gained from the UTSF operating experience, processing of Thoria bundles irradiated in power reactors (PHWRs) was successfully demonstrated at Power Reactor Thoria Reprocessing Facility (PRTRF). The challenges like inertness of sintered Thoria for chemical dissolution, radiological hazards due to presence of ^{232}U contamination in ^{233}U, safe handling of highly dispersive gaseous decay product Radon-220 (^{220}Rn) during processing and increasing dose of ^{228}Th containing raffinate during its interim storage were successfully addressed at PRTRF.

Further, R&D activities were also carried out to process Advanced Heavy Water Reactor (AHWR) spent fuel. Three-component flow sheet for processing of AHWR (Th-U) fuel pins was successfully established after extensive studies on laboratory scale. The article gives a glimpse of the valuable experience gained while addressing the challenges encountered during the reprocessing of irradiated Thoria.

KEYWORDS: Reprocessing of thoria fuel, Radon-220, Uranium-232, Sintered thoria pellets, Three-component flowsheet, THOREX, UTSF, PRTRF.

IN INDIAN context, thorium is perceived as a long-term source of energy due to its abundant availability, which will ensure sustainable energy security. Thorium based fuels have better in-core performance as well as inherent proliferation resistance. Their superior neutronic and material properties, along with advantage of lower production of long-lived actinides in the ^{232}Th-^{233}U fuel, have attracted the world towards its utilization for nuclear energy. The feasibility of the thorium cycle has been demonstrated worldwide in a wide variety of reactors over the years. During irradiation in the reactor, ^{232}Th absorbs a neutron to transmute to ^{233}U, a naturally non-occurring fissile uranium isotope which has superior fission fuel properties in comparison to ^{239}Pu and ^{235}U. Reprocessing of irradiated Thoria fuel is necessary to recover ^{233}U for its utilization as fuel in a nuclear reactor.

R&D Activities for Irradiated Thoria Fuel Reprocessing

Initial R&D activities for developing a flow sheet for processing of irradiated Thoria fuel were limited to recovery of ^{233}U. With the well proven solvent, Tri Butyl Phosphate (TBP), used in PUREX process, ^{233}U recovery was successfully established. Pilot plant scale studies on the recovery of ^{233}U alone were taken up in India in the 1970s. Later the studies were extended to establish recovery of uranium as well as thorium. With single valence state of thorium, separation of U and Th could be achieved by varying TBP concentrations in two separate cycles. The reprocessing process flowsheet for irradiated Thoria fuel (THOREX) was successfully developed at FRD laboratory for U and Th recovery. ^{233}U is recovered in the first cycle using 3% TBP in n-dodecane and ^{232}Th is aimed to be recovered in second cycle with 38% TBP in n-dodecane.

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Demonstration of Irradiated Thoria Fuel Reprocessing at UTSF

Thoria fuel rods cladded with aluminium were irradiated in research reactor CIRUS (J rods) up to a burn up of about 1000 MWD/Te. Processing of these rods was demonstrated successfully at UTSF. Processing consists of following steps:

A. Chemical decladding of the fuel to remove aluminium cladding using sodium hydroxide along with sodium nitrate solutions and subsequently dissolution of Thorium in concentrated nitric acid in presence of sodium fluoride catalyst along with aluminium nitrate as a complexing agent (to reduce corrosion effects of free fluoride in the system).

B. Separation of uranium using 3% TBP in n-dodecane in mixer settler, its final purification with cation exchange resin, concentration of uranium product by evaporation and final conversion of uranium product to oxide form using oxalate precipitation technique.

C. Processing of highly active raffinate stream (containing thorium as well as fission products) generated in the uranium recovery cycle, using 38% TBP in n-dodecanefor the recovery of thorium leaving behind the fission products in the raffinate. The Thorium-lean Raffinate (TLR) from the thorium recovery cycle was then transferred to a waste tank farm for interim storage. The management of TLR was successfully demonstrated following the vitrification of active components after necessary pre-treatment.

Thorium based fuels have better in-core performance as well as inherent proliferation resistance. Their superior neutronic and material properties, along with advantage of lower production of long-lived actinides in the Th^{232}-U^{233} fuel, have attracted the world towards its utilization for nuclear energy.

Since the level of contamination of ^{232}U in ^{233}U product in thoria fuel irradiated in research reactor is only 2–3 ppm, it did not pose any significant radiological problems during processing. Valuable experience could be generated at UTSF demonstrating the reprocessing of irradiated thoria of research reactor origin.

Demonstration of Power Reactor Irradiated Thoria Fuel Processing at PRTRF

With the experience gained at UTSF a new facility named PRTRF was designed and set up for processing of power reactor irradiated thoria fuel. It was planned to process thoria bundles, used for initial flux flattening of PHWRs, with an aim to establish the reprocessing flow sheet for irradiated thoria fuel bundles in PHWR. The PRTRF with two concrete shielded hot cells was utilized for the same.

The major differences between the thoria bundles processed during the campaign of UTSF and PRTRF are with respect to the clad material, burn up and contamination levels of ^{232}U in the ^{233}U product. The fuel irradiated in PHWR was a 19-pin bundle with zircaloy cladding and having burn up of about 10000–12000 MWD/Te HM, contained about 0.5-1.5% ^{233}U with significant ^{232}U content in the range 100-500 ppm calling for special radiological attention. The process involved the following major steps:

A. Operation of Head-end system involving

- Dismantling of the fuel bundles to separate the fuel pins and cutting the individual pins into small pieces using a laser chopper
- Dissolution of the chopped pieces in concentrated nitric acid using sodium fluoride catalyst along with aluminium nitrate as a complexing agent to avoid corrosion due to free fluoride ions
- Filtration of zircaloy fines using air ejector assisted vacuum filtration system with polypropylene cloth as filter media
- Off-gas treatment using specially designed cleaning system for safe handling of the Rn-220 containing gases, generated during processing

B. Separation of uranium using 5% TBP in n-dodecane in mixer settler, its final purification with cation exchange resin, concentration of uranium product by evaporation and final conversion of uranium product to oxide form using oxalate precipitation technique

C. Interim storage of thorium-bearing highly active raffinate solution containing 99% of the fission products in waste tank farm before taking up its final management.

Challenges in Reprocessing of Thoria Based Irradiated Fuels

Radiation level in the recovered ^{233}U as well as thorium product increased due to the associated decay products of ^{232}U. Besides, dissolution of inert ThO_2 and management of highly dispersible gaseous ^{220}Rn pose major challenges during dissolution of Thoria fuel. Attempts were made to address these challenges during the processing campaigns at UTSF and PRTRF and same are summarized below:

- Extreme chemical inertness of ThO_2

Sintered thoria pellets are extremely inert towards chemical interactions making the dissolution a difficult task. Use of sodium fluoride catalyst along with aluminium nitrate as a complexing agent for free fluoride ions helped to overcome this challenge. With the addition of required concentration of aluminium nitrate, corrosion rate could be mitigated in the SS 304L dissolver.

- The radiological hazards due to presence of ^{232}U in ^{233}U

The ^{233}U produced in the reactor is always contaminated with ^{232}U ($T_{1/2}$ = 68.9 y) and its immediate decay product ^{228}Th ($T_{1/2}$=1.98 y) (Fig.1). The level of contamination depends upon the isotopic composition of uranium in the initial fuel, the burn up and neutron spectrum encountered in the reactor.

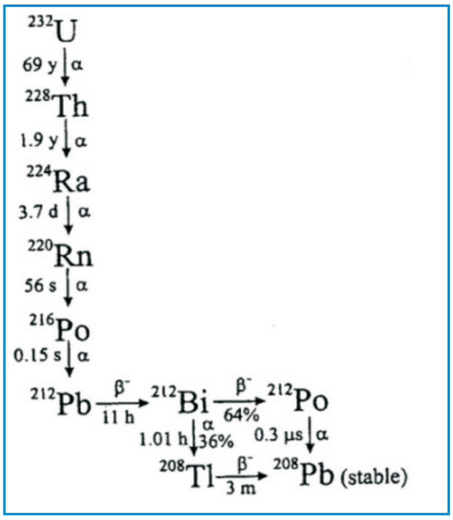

Fig.1: Decay chain of ^{232}U.

Daughter products of contaminants ^{232}U, ^{228}Th, viz: ^{212}Bi and ^{208}Tl, emit high energy gamma radiations during their decay. Hence, ^{233}U product pose very high radiation field due to presence of ^{212}Bi and ^{208}Tl. The high radiation field associated with handling ^{233}U, the , necessitates the provision of heavy shielding as well as remote handling systems for spent fuel transportation, reprocessing and fuel fabrication. Immediately after extraction from irradiated fuel, the radiation dose associated with ^{233}U is low for a few days driven by the lower concentrations of ^{228}Th and its daughter products (like ^{212}Bi and ^{208}Tl). It is well understood that a limited window period with lower radiation dose is available for easy handling of ^{233}U product (Fig.1). It is safe to handle ^{233}U product for fuel fabrication in shielded glove boxes within 28 days of extraction and purification of ^{233}U product stream.

- Increasing dose of Thorium product

Due to presence ^{228}Th along with their hard gamma emitter daughter products, ^{212}Bi and ^{208}Tl, in the purified stream of recovered Thorium from irradiated fuel, its handling

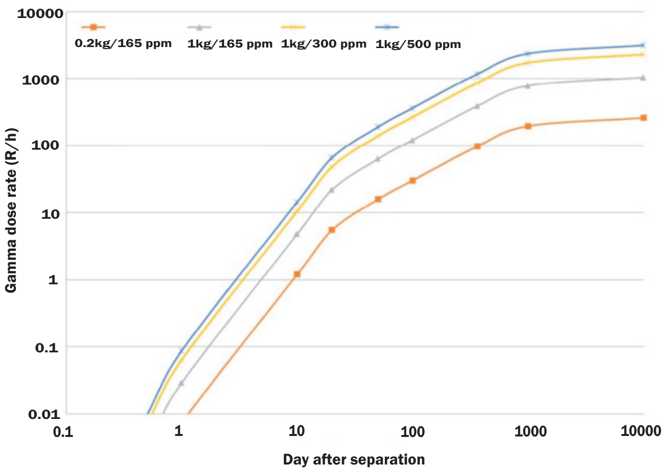

Fig.2: Radiation dose rate build up trend for ^{233}U with ^{232}U contamination.

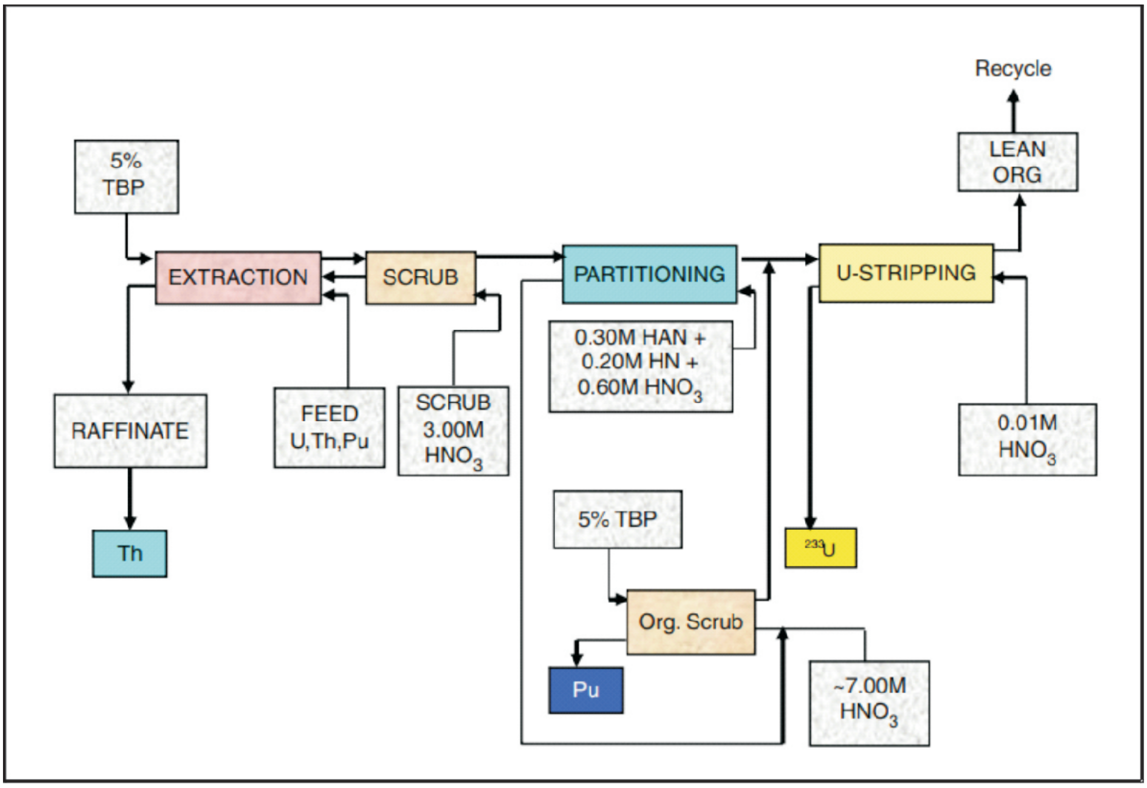

Fig.3: Three-component process flow sheet for AHWR spent fuel reprocessing.

is highly challenging after a short cooling period. A cooling period of approximately 20 years is required to bring down the gamma dose associated with the thorium product, which necessitated adequate storage facility for same.

- Special feature for off gas filtration system:

^{220}Rn (220-Radon), the noble gas & one of the decay products in the ^{232}U decay chain, can pass through the High Efficiency Particulate Air (HEPA) filters and then further decay into solid particles of ^{212}Bi and ^{208}Tl, which are hard gamma emitters. Following considerations were given while designing the head-end as well as off-gas systems to handle highly diffusive ^{220}Rn, released during chopping and dissolution of the fuel:

- Minimum carrier gases were used in the system
- Hold up time of 10 minutes was provided in the off-gas system
- Charcoal bed filter was used for delay and decay of ^{220}Rn
- Areas were provided with higher air changes to avoid back diffusion of ^{220}Rn into working areas.

An efficient off gas system was provided with important features like double HEPA filters and a hold up volume (to give a delay of about 10 min to the off gas) in between to hold the Radon gas till it decays to solid material. The first HEPA filter collects the solids generated prior to ^{220}Rn decay, while the second HEPA filter removes the solid decay products of ^{220}Rn from the off gases. The high radiation level not only calls for gamma shielding for these off gas system components but also its remote maintenance.

Processing of AHWR Fuel

As no fissile isotope is present in thorium, the initial production of ^{233}U requires a source of neutrons in reactors using other fissile elements like ^{235}U or ^{239}Pu as fuel. As the fuel for AHWR is expected to be a combination of Pu-Th, the discharged fuel after irradiation is expected to have three components U, Pu and Th, calling for specially designed reprocessing flow sheet for recovery of all the three components[2].

The extensive R&D work on various aspects of ^{232}Th-^{233}U based fuel along with our expertise on the PUREX process over five decades resulted in formulating a conceptual process flow sheet for three-component reprocessing of long cooled AHWR fuel on laboratory scale (Fig.2).

Considering the high radioactive field while handling the off-gas system filters as well as the ^{228}Th and ^{233}U product, remote handling mechanism is inevitable in the reprocessing and fuel fabrication facility.

TBP in n-dodecane as a solvent with different concentrations along with Hydroxyl Amine Nitrate (HAN) plays important roles in separation and purification of U, Pu and Th products. The number of purification cycles for U, Pu and Th would depend on the desired extent of products purity.

For taking care of radiological hazard, chemical separation of ^{233}U containing 1000-2000 ppm of ^{232}U from ^{228}Th can be carried out just before delivery of ^{233}U to the fuel fabrication facility. Provision can be made at the reprocessing plant to store ^{233}U solution in shielded cells. Final purification of ^{233}U can be taken up as per the schedule of ^{233}U requirement from fuel fabrication plant.

Considering the high radioactive field while handling the off-gas system filters as well as the ^{228}Th and ^{233}U product, remote handling mechanism is inevitable in the reprocessing and fuel fabrication facility.

Conclusions

Exploration of Thorium fuel cycle is inevitable for India for its self-sustained nuclear energy program. Thorium utilization calls for addressing significant technological challenges right from fuel chopping to product storage in the ^{233}Th-^{232}U fuel cycle, essentially arising out of the associated radiological hazards and also due to extreme chemical inertness of ThO_2. Extensive laboratory studies were carried out to address the challenges and the processing was demonstrated successfully. Three-component process flow sheet for AHWR spent fuel reprocessing was formulated on the basis of the experience gained during UTSF and PRTRF processing campaigns. Higher levels of contamination of ^{232}U in the product pose major challenges in handling the Thoria-based fuel during reprocessing as well as fuel fabrication calling for co-locating fuel fabrication and reprocessing facility as well as meticulous planning of the reprocessing activities as per the fuel fabrication activities.

Acknowledgements

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INDIAN EXPERIENCE

Vitrification of High Level Liquid Waste

D. B. Mehta, Gattu Suneel, D. Anirudhha, Sangam Gupta and J. K. Gayen

ABSTRACT

Characteristics of radioactive waste generated in the back-end of a closed nuclear fuel cycle depends upon the type of reactor, fuel, burn-up, off-reactor cooling period, and reprocessing flow sheet adopted. Source of radioactivity in the waste is mainly from the fission and activation products. Greater than 98% of radioactivity associated with the spent fuel is present in High Level Liquid Waste (HLLW). Immobilisation of HLLW in an inert glass matrix is carried out by employing equipment like Induction Heated Metallic Melter (IHMT), Joule Heated Ceramic Melter (JHCM) and Cold Crucible Induction Melter (CCIM). All these technologies are developed indigenously and their deployment is guided by the waste characteristic, processing temperature, and throughput. India has demonstrated excellent safety record in vitrifying about 30 million Curie of HLLW generated in different reprocessing plants. This article briefly presents the Indian experience of vitrification of HLLW gained using IHMM and JHCM.

KEYWORDS: High Level Liquid Waste, Vitrification, Metallic Melter, Joule Heated Ceramic Melter, Cold Crucible Induction Melter.

ONE of the factors limiting the worldwide adoption of nuclear power is the concern regarding the management of nuclear waste generated from nuclear fuel cycle facilities [1,2]. Nuclear waste poses a special risk to the human health and environment as it cannot be disposed in a manner generally followed for their non-radioactive counterparts. Since nuclear wastes can remain radioactive for thousands of years, the radioactive isotopes in the waste have to be suitably contained and isolated from the biosphere for relatively longer periods of time. In view of the large amount of spent fuel being progressively added to the cumulative nuclear waste inventory of the world, the significance of spent fuel management will continue to grow. Therefore, the management of radioactive waste in a safe and economical manner is necessary for large scale adoption of nuclear energy as an alternative to the available conventional sources. The perceived lack of progress towards successful waste disposal stands as one of the primary obstacles to the expansion of nuclear power around the world.

The management of HLLW is one of the most challenging problems faced by the nuclear industry. Storage of HLLW in stainless steel (SS) tanks cannot be a long term management strategy due to the long half-lives of radioactive isotopes and the susceptibility of the vessels to failure due to corrosion. The leaking of tanks meant for storage of HLLW at the Hanford site in Washington is a case in point[3]. Therefore, the preferred technological approach should be to dispose the waste in repositories constructed in rock formations hundreds of meters below the earth's surface in a form which is not prone to leaching in case of any contact with water or other leaching agents. Typically, a three-step strategy for management of HLLW involving immobilisation of HLLW, interim storage and disposal in repository has been adopted by countries like India, France, and Russia. India has achieved significant proficiency in both the vitrification technology and the interim storage of vitrified waste form under surveillance and passive cooling.

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Management of High Level Liquid Waste

The HLLW originating from reprocessing of spent fuel using PUREX process contains more than 98% of the radioactivity associated with the spent fuel. The high specific activity and high acid concentration in the waste streams together with the elevated glass processing temperature makes the choice of material and equipment extremely challenging. Besides, the off-gases generated during the process contain many volatile radioactive components that demand an elaborate off-gas cleaning system. Ingenious planning and design of equipment/system can make a large impact on the overall treatment efficacy and waste volume reduction for the management of HLLW.

Vitrification of HLLW

Internationally glass has been considered as desired matrix for immobilization of HLLW due to its inert chemical nature, adequate life, ability to incorporate wide range of elements present in HLLW, desired thermal and radiation stability, and associated techno-economic feasibility. Immobilization of HLLW comprises of feeding metered quantity of HLLW along with desired amount of glass forming additives and heating in specially designed melters in order to incorporate the radionuclides in the glass matrix. Vitrification is a complex process involving six major steps: evaporation of volatile water and nitric acid, drying of salts, thermal decomposition of salts to respective oxides, fusion of waste oxides with oxides of glass making additives, soaking of glass for homogenization of glass structure and draining of vitrified waste into stainless steel container called canister. Most of these steps are endothermic, requiring energy/heat and occurs at definite temperature ranges. For example, evaporation occurs between 100- 150°C, drying of salts at 150- 300°C, calcination between 350- 700°C, Fusion at 700- 900°C, draining of glass at 925- 950°C for the sodium borosilicate glass matrix adopted at WIP, Trombay. Out of all these steps, evaporation requires highest heat input.

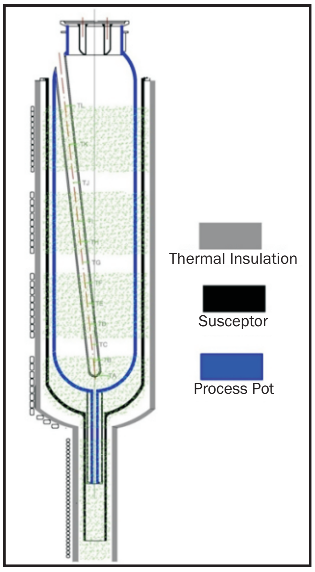

Fig.1: Schematic of IHMM.

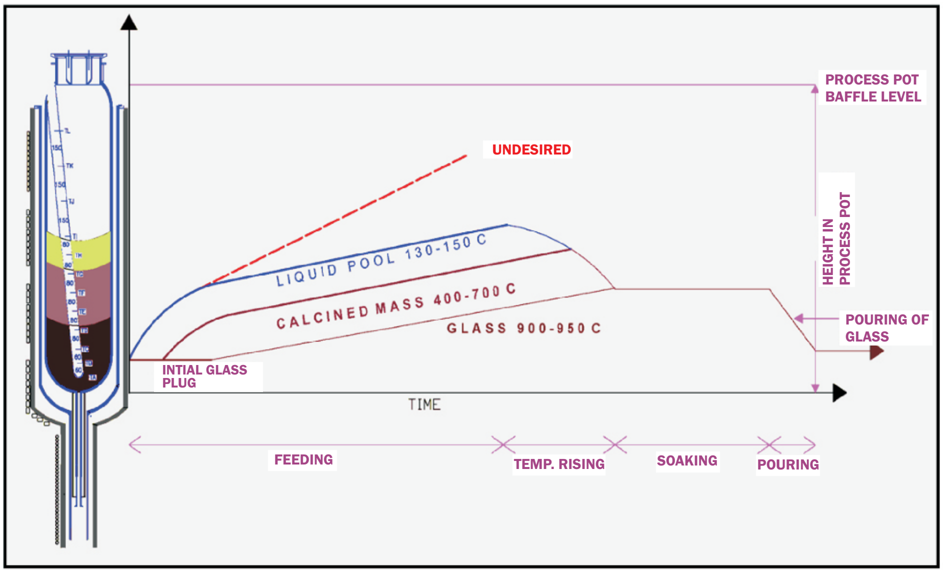

Fig.2: Temperature profile inside process pot of IHMM.

Melter Technologies for Vitrification

The melter is the most important component of any vitrification system. Therefore, development of melter technologies is crucial for successful and effective deployment of vitrification of HLLW. India has expertise and technical knowhow of designing and operating three different types of melters for vitrification: Induction Heated Metallic Melter (IHMM), Joule Heated Ceramic Melter (JHCM) and Cold Crucible Induction Melter (CCIM). IHMM is operational at BARC, Trombay to vitrify the HLLW and JHCM is operational at Tarapur and Kalpakkam facilities of BARC. Industrial scale demonstration of CCIM operation has been completed for its plant adoption.

IHMM is simple and compact, though it has low throughput due to limited diameter and short melter life as a result of high temperature glass corrosion. JHCM was developed to overcome these limitations. CCIM offers additional benefits such as high temperature availability with longer melter life and higher processing capacity.

Induction Heated Metallic Melter

IHMM utilises about 2-3 kHz alternating current for providing heat as needed for vitrification process. Oscillating magnetic field, generated due to alternating current in the copper coil, couples with the susceptor and heats it to about 1050°C. Heat required for vitrification in the process pot is obtained through thermal radiation from the hot susceptor. The prime reason for selection of high Nickel- Chromium alloy as the material of construction is its high temperature corrosion resistance. Entire melter is divided in to multiple zones and each zone is equipped with separate coil for better control of the overall process (Fig.1). Thermal insulation is provided between susceptor and coil to reduce loss of heat from susceptor to coil.

IHMM is usually operated in semi batch mode with continuous feeding of waste as well as glass forming additives in predetermined quantity to suit the given batch size. Batch size of vitrified waste is determined considering the HLLW characteristics, glass matrix composition and safe free board space requirement to overcome operational problems such as excessive frothing and swelling of the mass. After completing the feeding, calcination of entire mass is ensured and glass is soaked for 8 hours. The vitrified waste is finally drained into stainless a steel canister. The process pot is provided with a vent of suitable size to route off-gases generated from vitrification process through the off-gas cleaning system.

Different zones exist inside the process pot during the vitrification process. In the topmost zone, the incoming liquid waste forms a boiling pool below which a drying zone exists. The salts at the bottom of the drying zone undergo calcination. As the operation continues, calcined mass gradually converts to molten glass which forms the bottom most zone. Adequate care needs to be taken during the operation to maintain the heights of these zones. Increase in the thickness of the calcined mass, dry salts and liquid pool can result in uncontrolled swelling of the mass and makes the process unstable. Various process parameters such as feed rate, input power, intermittent soaking and batch size are optimized in such a way to ensure the ‘rising glass level pot vitrification’ with adequate freeboard to overcome any undesired swelling of the mass. Fig.2 depicts a typical temperature profile inside process pot for a batch of vitrification operation using IHMM. Batch size and process parameters are optimized to avoid the undesired condition as marked with red line. Knowledge of temperatures at different elevations inside process pot plays an important role to understand the operation stage and to identify the problems like swelling/frothing of mass at an early stage to control with appropriate measures like lowering the heat input etc. Trained operators and well defined procedures have been the key components to overcome such problems and ensure safe operations.

Limitations with respect to processing capacity and operating temperature of process pot (less than 1000°C) are the main drawbacks of IHMM technology. Keeping apart these drawbacks, IHMM offers many advantages including flexibility in operation, capability to adopt the variations of glass matrix, ease of decommissioning, better decontamination factor, remote operations and maintenance, etc. IHMM is best suited for the facilities handling multiple waste streams with moderate generation rate such as WIP, Trombay.

IHMM is operational since 2002 for vitrification of HLLW and high active product steams of pre-treatment facility at WIP, Trombay. 280 canisters of vitrified waste product have been produced using IHMM for treating nearly 150m^3 of HLLW. Two decades of successful operation of IHMM at WIP, Trombay resulted in the vast experience related to remote operation and maintenance of vitrification system and trouble shooting

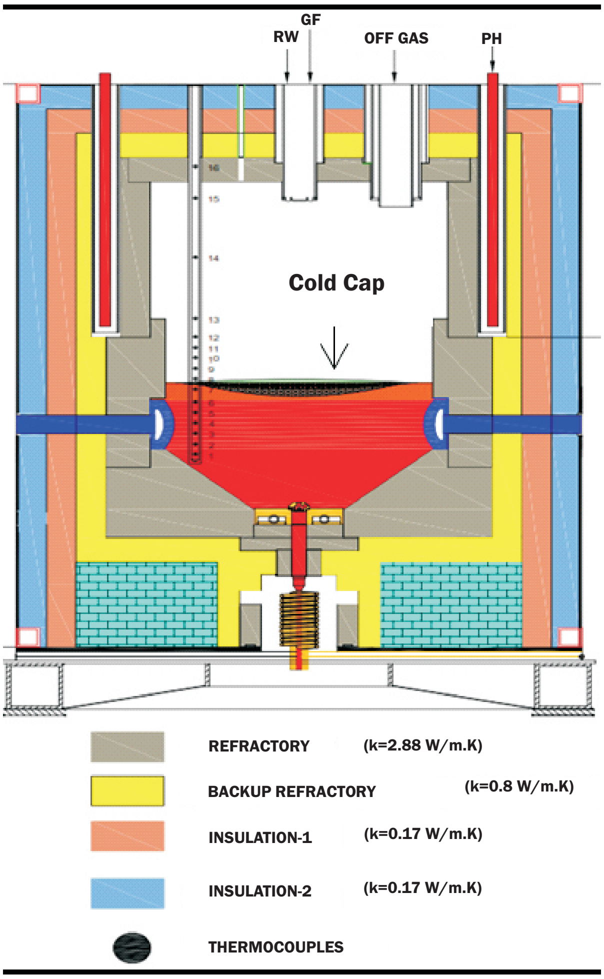

Fig.3: JHCM operational at INRP-Kalpakkam.

of various operational problems. Over this time period, operating procedures were improved based on operational feedback. Glass matrix was also modified to suit compositions of different HLLW streams. Each time, newly developed matrix is tested with corresponding simulated waste steams at plant scale melters for finalization of operating procedures and parameters customized to new matrix and thereafter, deployed for vitrification of actual waste streams.

Joule Heated Ceramic Melter

The schematic of a typical JHCM used for the vitrification of HLLW is shown in Fig.3. Alternating current (50 Hz) is pumped into the JHCM cavity using a system of submerged electrodes made of Inconel-690. The molten glass is contained within the cavity formed by refractory blocks. The glass contact refractory blocks are followed by back up refractory which is provided to supress glass migration. The thermal insulation of JHCM is designed to restrict its outer wall temperature to 70°C.

In JHCM, glass frits and HLLW are fed simultaneously from the top to produce a durable, vitreous waste form. Like in the IHHM, different zones exist in the JHCM also. In the first zone, at the top of the molten glass pool, evaporation of water and volatile components of HLLW takes place. Below this is drying zone, where moisture is removed and thermal decomposition of nitric acid occurs. In the calcination zone, the non-volatile components of HLLW thermally decompose to their corresponding oxides. The waste oxides from the calcination zone move into the glass-forming zone, where they react with molten glass and get embedded into the glass structure. The first, second and third zones are collectively known as the cold cap[5,6]. The heat generated in molten glass by passing current between submerged electrodes is transferred through the three zones in series. The glass conversion rate in the cold cap layer depends on efficient heat transfer from the molten glass pool to the cold cap.

To have a better control on glass pouring operation, induction heating is used for heating of freeze valve during product withdrawal operation. Bottom section of the freeze valve is heated by medium frequency induction heating system. The melter also has an off-gas nozzle which is meant for routing the off gases generated during vitrification towards an elaborated off gas treatment system.

The throughput of the melter depends upon a) the power fed to the electrodes b) operating temperature and c) the salt content of HLLW. The melter operating capacity is optimized between waste evaporation rate and glass assimilation rate. At higher salt loading, the glass assimilation rate is poor due to low heat transfer through porous media i.e., through the foam generated during calcination. The relationship between the throughput and salt content of waste for JHCM has also been established using numerical studies.

The molten glass pool surface has a certain heat flux beyond which the power supplied will result in an increase in the temperature of the molten glass. Hence, the power fed to the melter depends on the heat transfer to the cold cap. As the cold cap has multiple layers, accumulation of NO_x gases will reduce the heat flux to the boiling zone. Further raising power will lead to increase in operating temperature of glass pool beyond 1000°C instead of increasing the processing capacity. The throughput of the melter reduces in terms of waste volume at higher salt concentrations whereas the glass production rate increases due to decrease of evaporation load.

Melter Off-gas Treatment

The off-gas generated during the vitrification process in the melter is passed through an elaborate off-gas cleaning system which includes HEPA filters in the final stage. Large amount of radioactive inventory, process dynamics and high processing temperature give rise to radioactive aerosols, which frequently exhaust the HEPA filters. In order to minimize the secondary solid waste generation in the form of HEPA filters, the concepts of multiple scrubbing and washable filters were introduced to bring the majority of radioactivity in liquid phase which can be treated effectively with secondary waste streams. Decontamination factor of more than 10^8 is achieved resulting in minimum radioactivity discharge. Contamination of cell exhaust during draining of molten glass into canister is addressed by adopting a closed pouring system.

Melter Instrumentation

Measurement of glass pool temperature and level in an industrial furnace is essential for process control and safe operation of a system. Inclined thermowell inside process pot with twelve thermocouples at different elevations has been provided for IHMM, which has successfully provided the real time information of level of material and on-going various process steps inside the process pot. A novel level measurement technique, developed for level measurement for JHCM installed at WIP, Kalpakkam is shown in Fig.4. Measurement of level in a radioactive industrial vitrification furnace (JHCM) is developed using a non-contact, remotely placed real-time Radio-Detection and Ranging level measurement in a 1.5m concrete cell. A frequency of 25-30 GHz is suitable for this application. The system till date has been exposed to more than 540 MRads and successfully

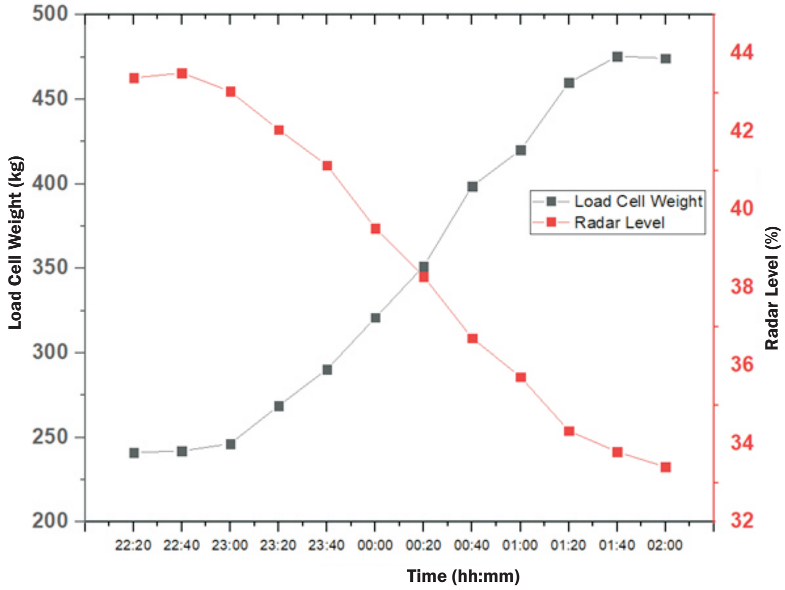

Fig.4: The RADAR level measurement system inside industrial scale JHCM and (b) RADAR Level against Load cell weight during pouring.

performed continuous monitoring of level in vitrification equipment. Measurement in a radioactive JHCM containing about 1 MCi was demonstrated and instrument functioned for 30000 h uninterruptedly without drift in the sensor.

Remote Handling and Maintenance

Vitrification process involves material handling inside the hot-cell and maintenance of melter and associated systems, which need to be carried out remotely in view of the presence of very high radiation field inside the hot-cell. Material handling operations involve movement of empty as well as vitrified waste filled canisters, welding of lid over the filled canisters, decontamination of external surface of canister/overpack etc. Vitrification hot-cells are employed with remote handling equipment including in-cell crane, servo/power manipulators, master-slave manipulators, remote welding machine, product transfer trolley etc. Advanced remote viewing systems are deployed enabling viewing of major parts of hot-cells to meet the need for remote handling and maintenance.

Conclusions

Vitrification has been extensively studied and applied for effective management of HLLW generated from spent nuclear fuel reprocessing. However, as more experience has been gained in vitrifying a range of HLLW, new challenges and opportunities for improvement have been identified. Development of most appropriate glass composition and process technology resulted in emptying out waste tank farms containing almost 20 MCi in each tank.

Great strides have been made in increasing the throughput and efficiency in waste vitrification plants as well as waste loadings in waste glasses. However, as more experience has been gained in vitrifying a range of different wastes, new challenges and opportunities for improvement have been identified and further improvements are likely through continued technology-development activities.

Acknowledgements

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PARTITIONING OF HIGH LEVEL LIQUID WASTE

Operational Experience and the Way Forward

Smitha Manohar and U. Dani

ABSTRACT

The Partitioning & Transmutation (P&T) strategy is perceived as a step in the direction of reducing the radio-toxicity associated with high level liquid waste for final disposal. In this regard, the partitioning step is well recognized as the first approach towards the goal of reduction in radio-toxicity. The first industrial experience in setting up and operation of a completely indigenous Actinide Partitioning Demonstration Facility (ASDF) at Tarapur in the year 2013 has paved the way for this strategy to be inducted into our back-end plants[1,2]. The second such facility was set up and commissioned in 2015 at Trombay, which has not only led to separation of radionuclides from the inactive content of HLLW but has also made it possible for the use of few of the radionuclides for societal applications. Important among them are ^{137}Cs, which is separated and converted to glass rods for its use as blood irradiators[3] and ^{90}Sr, which is purified further and milked for ^{90}Y, which is being used for therapeutic application as 90Y-acetate. Very recently, ^{106}Ru so separated from waste has also been used for preparation of eye plaques for treatment of eye-cancer with very positive feedback. The ^{241}Am separated from the ASDF demonstration trials, is presently being envisaged to be used for the transmutation experiments using fast neutron spectrum and alternatively, as a heat source/RTGs for the Indian space application. The smooth and uninterrupted operation of both these facilities have strengthened our knowledge base for extending such technologies to more of our plants including that at Kalpakkam in the near future. This article deals with the operational experiences and lessons learnt during setting up and operation of such facilities.

KEYWORDS: Partitioning, High Level Liquid Waste, Fission products.

HIGH Level Liquid Waste (HLLW), getting generated from reprocessing of spent nuclear fuel, is conventionally immobilized in glass matrix to isolate the radionuclide from human environment. The vitrified waste is stored in air-cooled vault for removal of decay heat for a few decades prior to their disposal in deep geological repository. HLLW mainly contains fission products, minor actinides, corrosion products as well as various inactive chemicals added during reprocessing. Out of which, minor actinides are major contributors towards high radiotoxicity associated with HLLW in the far time line of final disposal. Fission products like ^{137}Cs and ^{90}Sr are some of the main contributors to heat source for final disposal, which dictate the overall size and design of deep geological repository. Industrial adoption of partitioning technology has demonstrated technological feasibility of splitting HLLW into heat generating fission product stream and long lived alpha product stream impacting final repository design. Another advantage that has been exploited in the near time line, is that, by separation of the radionuclides from HLLW and then subjecting the separated stream to vitrification can lead to a substantial reduction in final waste volumes for final disposal. This is due to the presence of inactive salts which are contained in HLLW due to reprocessing steps involving additives. This approach has yielded substantial volume reduction in case of legacy high level waste stored at Trombay. Extending this scheme to some of the stored HLLW can also lead to a sizable volume reduction factors.

HLLW Partitioning Facilities in India

The ASDF facility (Fig.1) set up at SSSF, Tarapur, is meant for demonstration of 'Partitioning of Minor Actinide from HLLW'. Among the minor actinides, Americium is generally considered a prime candidate for partitioning and transmutation because it is present in relatively large amounts and is a major contributor to radiotoxicity. The three-cycle solvent extraction-based process was demonstrated with regard to bulk separation of actinides along with rare earths followed by separation of trivalent actinides from the lanthanides. Table 1 gives the details of solvents deployed for three different cycles of ASDF. The 241-Am rich solution so separated was subjected to appropriate polishing process, followed by a reconversion step leading to obtaining AmO_2 having acceptable level of β-Y contamination (of <3 mCi/g of product). Based on the successful demonstration of this facility, another such partitioning facility was designed incorporating the feedback of Tarapur experiences.

The Trombay flow sheet, three cycle based solvent extraction process, addressed separation of inactive

Table 1: Solvent systems deployed at ASDF, Tarapur.

Solvent Extraction	Objective	Solvent Deployed
Cycle 1	U separation	30% TBP in n-Dodecane
Cycle 2	Actinide + Rare Earthbulk separation	0.2 M TEHDGA in 30% IDA in n-Dodecane
Cycle 3	Actinide - Lanthanide separation	0.4 M D2EHPA in n-Dodecane

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Fig.1: Actinide separation demonstration facility, Tarapur.

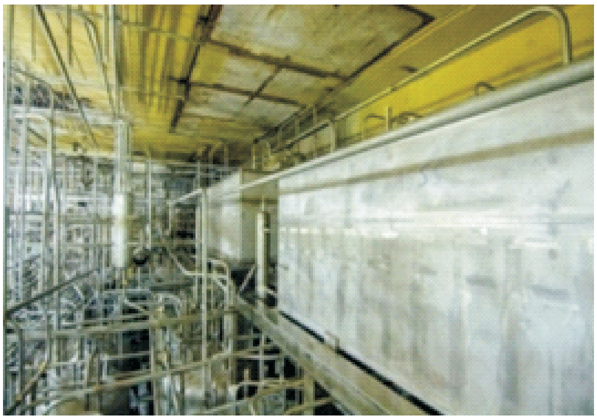

Fig.2: Solvent extraction system, Trombay.

components of waste from the radioactive elements, thereby precluding unwanted loading of vitrified glass with inactive components of waste, especially with regard to historic sulphate-bearing HLLW. In first cycle, residual Uranium and Plutonium are recovered from HLLW. While Cesium recovery is aimed in second cycle, Strontium-Actinide-Lanthanide combined separation is achieved in third cycle from HLLW. Table 2 gives the details of solvents deployed for three different cycles of solvent extraction system, Trombay. Fig.2 depicts the solvent extraction system installed at Trombay for pre-treatment of HLLW. The inherent composition of the waste stream resulted in only 250 L of waste being incorporated in 100 kg of glass matrix. By induction of the partitioning step, it is now possible to incorporate about 10,000 L of waste in 100 kg of vitrified product. As a spin-off of this program, it was also possible to recover a few fission products for direct use in societal application, namely ^{137}Cs, ^{90}Sr & ^{106}Ru. Fig.3 gives overall process schematic of solvent extraction process for treatment of sulphate-bearing Historic HLLW at Trombay.

Bulk Synthesis of Novel Extractant

The development of novel extractants, of desired quality, has been a key element for success of partitioning technologies in India. For example, selective recovery of cesium would not have been possible without the extractant named 'Calix Crown 6'. Similarly, extractants like TEHDGA and D2EHPA found necessary for separation of strontium, actinides & lanthanides from HLLW and partitioning of actinides from bulk of lanthanides respectively. Indigenous development of these extractants and its synthesis at large scale, to meet the requirement of engineering scale partitioning facilities, were the real challenge. Consistent R&D efforts in the field of development of extractants by nuclear chemists of BARC and participation of qualified vendors for its bulk synthesis with proper quality assurance program could realize the synthesis of these extractants at larger scale.

Air Lift Based Mixer Settler Unit

Air lift-based mixer settler units were selected as extraction equipment for the partitioning facilities as it imparts many benefits and better suits to desired applications. Air lift-based mixer settler unit gives flexibility in terms of number of stages for extraction, large range of organic to aqueous (O/A) ratios and flow rates, and also enable handling of varying densities of streams etc. Besides this, mixer settler unit does not require hot-cells having higher head room, as in case of air pulsed column, and helps in designing compact hot-cells. This further strengthens the selection of air lift-based mixer settler unit for said applications of extraction process. With the aim of eliminating all moving/maintainable parts of the mixer-settler, the agitator of conventional mixer-settler unit is replaced by an innovatively designed static mixing element CALMIX (**C**ombined **A**ir **L**ifting and **MIX**ing), which uses air to create high turbulence effecting the intimate contact of the two phases i.e., aqueous and organic. The CALMIX (Fig.4) has three identical square cross-section flow channel. One of them is the organic downcomer, which facilitates taking organic from top from previous settler irrespective of interface position. The other two flow channels are two identical annular flow path airlift created by locating airline at the center of flow channel. Both flow-channels get combined in the upper part of the mixing element which is similar to a vent pot with two inputs. This part is called mixing zone, where intense mixing takes place and the mixed phase along with air, are discharged through suitably sized holes provided in this region. As the energy for dispersion is supplied in the form of air, the liquid droplets do not experience shear and hence are easy to coalescence, resulting in a more compact settler design. The required contact time and the physical characteristics of the two phases form the design basis for the mixing element. The corresponding settlers are designed in a conventional manner. These units are provided with end-settlers to take care of any entrained phases in the terminal streams.

Table 2: Solvent Systems Deployed at Solvent Extraction System, Trombay.

Solvent Extraction	Objective	Solvent Deployed
Cycle 1	Uranium separation	30% TBP in n-Dodecane
Cycle 2	Cesium separation	0.03 M Calyx Crown(CC)6 in 50% IDA in n-Dodecane
Cycle 3	Strontium, Actinide & Lanthanide separation	0.4 M TEHDGA in 15% IDA in n-Dodecane

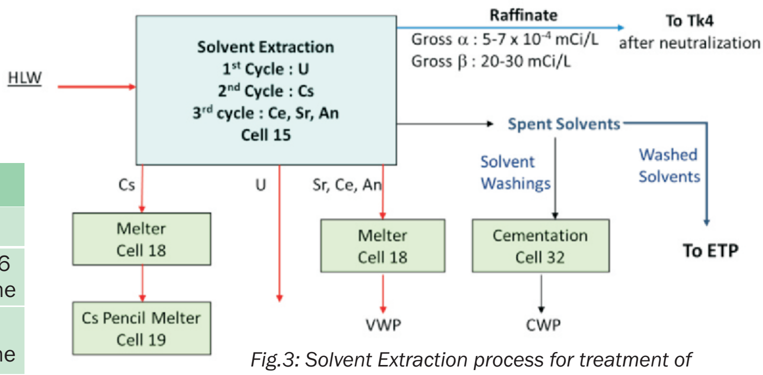

Fig.3: Solvent Extraction process for treatment of Sulphate bearing HHLW at Trombay.

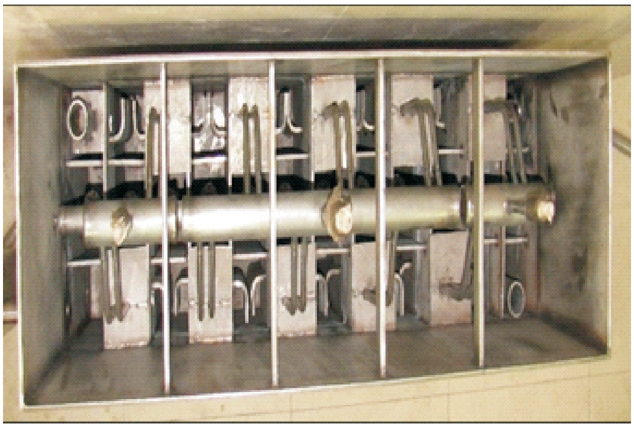

Fig.4: Combined Airlift based Mixer Settler Unit.

Design Considerations of Partitioning Facilities

Design & setting up of such operational facilities called for identification of robust engineering system to suit in-cell application and integration of such facilities to the vitrification plants. Setting up and operation of such facilities, being the first of its kind called for appropriate safety analysis and thorough documentation preceding a rigorous review process that culminated in obtaining regulatory clearances for these facilities.

In view of first time demonstration of partitioning technology, various features have been provided right from design stage to overcome unexpected challenges. Design provisions were made to address the uncertainties with regard to separation process. Recycle provisions were inbuilt in the system to ensure product purity with high decontamination factors. An elaborate solvent management provisions was worked out and incorporated leading to handling of multiple organic systems in the same cell. Focused attention was also given to secondary stream management including spent solvent streams.

Retrofitting of System in Existing Hot-cells

Both partitioning systems, of Trombay and Tarapur, have been retrofitted in existing hot-cells of facilities for demonstrating the technology of partitioning in the smallest possible time. Retrofitting of system with comprehensive design provisions in existing hot-cell is one of the major challenges. For example, three cycle solvent extraction based partitioning system is retrofitted in a hot-cell of WIP, Trombay having capacity to accommodate only one set of mixer settler units (one for extraction and one for stripper) and associated storage tanks. This necessitates use of single set of mixer units for three different solvent extraction cycles utilizing three different solvent system for recovery of varying radio-nuclide as mentioned above. The system needs to decontaminate effectively, to prevent cross contamination of radionuclide as well as solvents also, prior to change over to next cycle. Comprehensive design features and operating procedures are established to realize the desired decontamination of system. As a result, more than 100 m^3 of HLLW has been successfully treated for separation of radionuclides with desired purity fulfilling the objective of partitioning technology.

The Way Forward

Both the partitioning facilities have been operated successfully with actual HLLW demonstrating the partitioning technology at engineering scale. ASDF, Tarapur demonstrated the partitioning of minor actinides from HLLW by treating few tens of m^3 of HLLW for recovery of minor actinides of desire purity. Solvent extraction-based pre-treatment system at WIP, Trombay enabled effective treatment of more than 100 m^3 of HLLW with recovery of ~0.5 million Ci of Cs-137 and multi-fold reduction of vitrified waste volume to save precious repository space. Success of partitioning technology paves way for their deployment as pre-treatment step for facilities managing HLLW generated from reprocessing of power reactor spent nuclear fuel. Further focused efforts are also being directed towards secondary waste stream management including solvent management. Alternate and improved solvent systems are also being researched, especially for addressing the challenging task of An/Ln separation.

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MANAGEMENT OF INTERMEDIATE LEVEL LIQUID WASTE

Problems and Solutions

Kiran Kumar, Helen Jeyaraj, Suneel Gattu
Nilay J. Jasu, Aniruddha D. and Neelima S. Tomar

ABSTRACT

Intermediate Level Radioactive Liquid Waste (ILW) generated during reprocessing of spent fuel is stored for decades in underground tanks. The ILW is alkaline in nature and contains a high concentration of inactive salts, dissolved organics and ^{137}Cs as the major radioactivity contributors. This ILW is treated using a Cs-selective ion exchange process employing indigenously developed Resorcinol Formaldehyde (RF) resin. The process partitions the ILW into two streams, viz., a high-level caesium-rich eluate stream and a low-level effluent stream. The Cs-rich eluate is concentrated and immobilized in a vitreous matrix. The low-level effluents are managed by various treatment methodologies involving industrially usable precipitants. The process has been adopted for industrial scale treatment of legacy ILW, and more than 2000 m^3 of waste has been treated successfully. An ILW Treatment Plant has been established in Trombay. Based on this feedback, a similar facility is now commissioned at Kalpakkam for the effective management of ILW.

KEYWORDS: Intermediate level liquid waste, Cs-specific resin, Degraded solvent, Ion exchange.

THE Indian nuclear fuel cycle reprocesses spent fuel to recover valuable materials. The reprocessing plant generates various kinds of radioactive liquid wastes (Fig.1).

The major challenges associated with Indian historic ILW have been large volumes, high inactive salt loads, traces of other radio-contaminants, and problematic elements like aluminium. The radioactivity content is primarily contributed by Cs and traces of Ru, which depend on the decay period of spent fuels.

The acidic ILW emanating as the condensates of the evaporation of first cycle raffinates were neutralized and stored. This neutralization step was carried out to facilitate storage in carbon-steel tanks. In addition, Trombay had the unique problem of handling high aluminium concentrations in the ILW arising from the decladding activities. Components generated from degraded solvents of reprocessing also pose issues in treating ILW arising from PHWR spent fuels.

Process and Technology Development

During the initial phase of process selection, bituminization and cementation were considered for ILW treatment. Bituminization process has potential fire hazards and hence it was not explored further. Cementation process would have led to unacceptable consumption of limited Near Surface Disposal Facility (NSDF) space considering the voluminous inventory of legacy waste and factors leading to negative volume reduction. In contrast, the ion exchange offers a simple process for treating this ILW with high decontamination factor (DF) and appreciable volume reduction factor (VRF). Resorcinol Formaldehyde (RF) resin is known to be selective to Cs under these conditions, even in the presence of high concentrations of Na ions. This resin, as depicted in Fig.2, has an acceptable distribution coefficient yielding a good volume reduction factor, high selectivity producing necessary decontamination factor, regenerability allowing reduced secondary wastes generation and acceptable column usage properties enabling plant scale operation[1–2].

Using ion exchange process, ILW is partitioned into two streams, a Cs-rich eluate stream which is high level in nature and a low level effluent which qualifies for transfer to Effluent Treatment Plant (ETP)[3]. The process was deployed at plant scale initially at WIP, Tarapur. Later the process was also used at Trombay and Kalpakkam for the management of ILW.

Based on the above operational experience, a permanent facility named, Pump House Ion Exchange (PHIX) facility at Trombay, was designed for higher through puts. As an

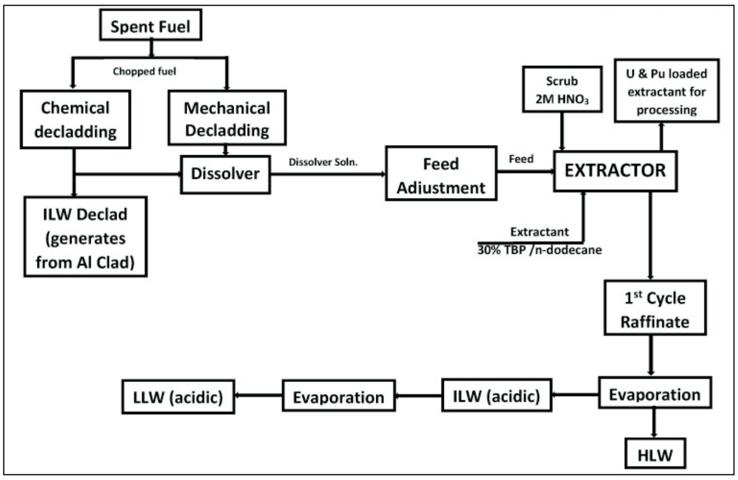

Fig.1: Typical flowscheme indicating the source of ILW.

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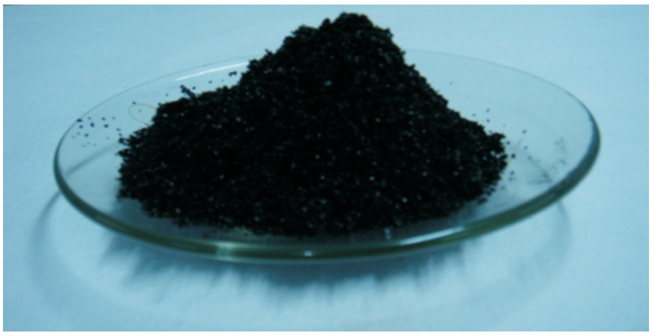

Fig.2: RFPR resin placed on a petridish.

improvement over the previous campaigns, the facility was extensively automated for remote process and column handling operations. Through a PLC-based system, the facility is controlled from a centralized control room. A typical process flowsheet followed for the campaign of ILW treatment and in-cell view of Ion Exchange System is shown in Fig.3 and Fig.4, respectively.

Presence of aluminium in declad waste has been a major challenge. The innovative step of managing downstream effluents containing aluminium was done by converting it into a stable, inert complex using a novel reagent. This addressed the challenges associated with Al- precipitation encountered during pH adjustments of downstream treatment and helped successfully manage Al-bearing legacy ILW.

Challenges in the Processing of ILW From PHWR Fuel Reprocessing

ILW generated during the reprocessing of PHWR fuel comprises two streams viz., the neutralized ILW arising from concentrating the second cycle raffinate stream and the Di Butyl Phosphate (DBP) bearing ILW generated during carbonate washes. These two streams are segregated at the source and stored in designated waste tank farms.

Organic-free ILW is subjected to mainly three processes *viz.* acidification, precipitation and settling, and ion-exchange. This process has a decontamination factor of 105-106.

The DBP-bearing ILW is generated due to radiolytic and hydrolytic damage of Tri Butyl Phosphate (TBP) deployed as a solvent in Plutonium Uranium Redox Extraction (PUREX) process. It has been proven that these degraded products have an affinity for specific metal ions like ^{95}Zr, ^{65}Nb and actinides.

At Kalpakkam & Tarapur, it has been observed that the presence of degradation products of TBP in ILW (5 g/L of DBP) create problem during carbonate killing step. DBP forms a sticky, difficult to handle yellow mass with uranyl ion during acidification. Some portion of the sticky mass tends to float on the solution surface while sticking to the wall of the reaction vessel[4]. This mass also picks up a significant portion of actinides and some amount of beta activity. Passing this type of waste through the present ILW treatment plant without destruction of DBP leads to choking of pre-filter & ion exchange columns, thereby affecting the processing capacity of the plant.

Oxidative degradation of DBP in the ILW stream using Advanced Oxidation Process (AOP) is presently being carried out with ozone and hydrogen peroxide prior to carbonate killing on an industrial scale. The destruction of DBP in the ILW stream makes the waste amenable to conventional treatment schemes.

Operating Experience and Improvement

At Trombay, the ILW treatment facility operates an average processing rate of 100-120 m^3 per month. The overall volume reduction factor of 85 was obtained with respect to eluate volume. This Cs-rich eluate is immobilized in a vitreous matrix yielding much higher overall VRF. Cs decontamination factor in the range of 1000-3000 is obtained. At all the sites, ILW processing adopting this general philosophy of partitioning using highly selective indigenously prepared organic resins with component-specific pre or post-treatment has enabled effective management of ILW.

Conclusions

A permanent facility has been established at the Pump House building of WIP Trombay to treat legacy ILW stored at the reprocessing plant. The robustness and reliability of the process and its systems have been demonstrated for remote operations. A high plant throughput, more than 100 m^3 per month, is achievable by these facilities. Ion exchange processes using these resins are also being implemented for the treatment of other alkaline waste streams.

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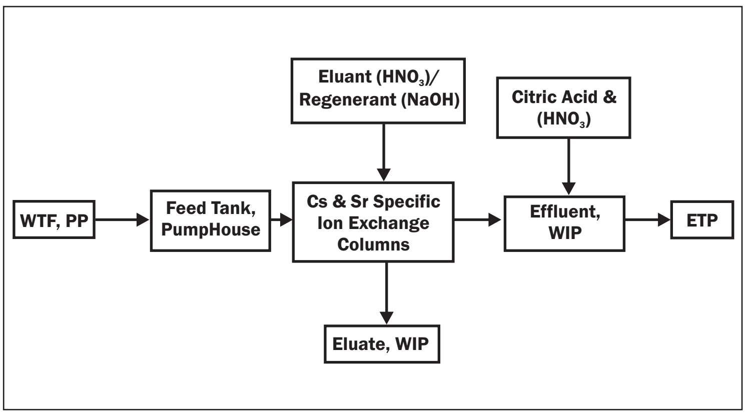

Fig.3: Typical flow scheme indicating the source of ILW.

Fig.4: Incell view of Ion Exchange system.

Banerjee, R. Guruprasad and S. Satheesh Kumar of WMD, BARC whose perseverance and dedication have led to the establishment of the facility. Above all, the authors acknowledge the effort of personnel in WIP in making the campaign a great success.

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PROGRESS IN RADIOACTIVE EFFLUENT MANAGEMENT

Hybrid Process Towards "ALARA"

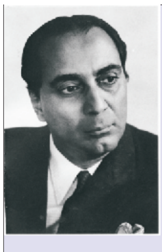
Anand Gangadharan

ABSTRACT

Management of radioactive effluents is vital to the success and acceptability of nuclear energy in public domain. Extensive research & development and five decades of operational experience at Trombay have resulted in standardization of the treatment methodologies. In order to follow ALARA philosophy, newer technologies like ion exchange and membrane processes have been evaluated in laboratory and pilot scale. A plant-scale ion exchange facility has been established. The use of membrane processes has also provided a firm foundation for demonstrating recycling of water recovered from LLW thus, proving the "Water Recycle" concept.

KEYWORDS: Radioactive effluent, Low level waste, Treatment, Ion exchange, Membrane.

THE safe management of nuclear waste has been a priority for this Research Centre from the early days of its inception. The importance placed on this area is evident from the extract of an order issued by our Founder-Director, Dr H. J. Bhabha.



"Radioactive materials and sources of radiation should be handled in the Atomic Energy Establishment in a manner which not only ensures that no harm can come to workers in the Establishment or anyone else, but also in an exemplary manner, so as to set a standard which other organisations in the country may be asked to emulate".

Feb.27,1960 ***-Homi Jehangir Bhabha***

Research and Development activities in radioactive waste management were initiated in parallel with ongoing research activities on Reactors and Nuclear Fuel Cycle. These activities eventually resulted in the commissioning of India's first plant for treatment of liquid radioactive waste *viz.*, Effluent Treatment Plant (ETP, then known as Waste Treatment Plant) at Trombay on July 26, 1966. The clarity of thought process is indicated from the fact that ETP was set out as facility to implement a "single discharge point" philosophy to control discharges, a model that is emulated even today. From the days of its commissioning, continuous endeavors for reduction of discharges to the environment were made. A quote from Dr. H. N. Sethna, second Director of this Research Centre, amply demonstrates this.

"...The radioactive waste management in the Indian Nuclear Programme has continued to ensure that man and environment are not endangered to release of radioactivity....While we have worked on the basis of 'as low a discharge as possible' as a practical reality, our current efforts are directed towards the concept of limiting discharge activity to the environment..."

-***H. N. Sethna****, Chairman, AEC (1972-1983)*
Address at IAEA General Conference, 1975.

This division has not only continued to follow the strategy of "limiting discharge" but, has over past five decades, progressed to the philosophy of "as low as reasonably achievable". It has now expanded it for the demonstration of "Water Recycle" concept.

Early Years

Even before CIRUS Reactor went operational, detailed studies were undertaken and discharge limits finalized. The early years of R&D and plant operations were focused on meeting the prescribed discharge limits and mastering the technologies for the entire cycle of low level radioactive waste (LLW) treatment[1]. Initial R&D activities had resulted in selection of a robust treatment process *viz.*, chemical co-precipitation for achieving initial aim of meeting discharge limits[2]. Subsequently efforts were directed towards optimizing the upstream and downstream processes of chemical co-precipitation. An example of this is that the plant, in response to operational challenges, changed its chemical co-precipitation sludge concentration techniques from rotary vacuum drum filtration to solar evaporation and finally to use of dewatering centrifuge. An overview of the LLW processing scheme is illustrated in Fig.1.

Towards "ALARA"

With the commissioning of new nuclear facilities in Trombay over the years, the challenges involved in LLW management has increased. Even as processes at waste

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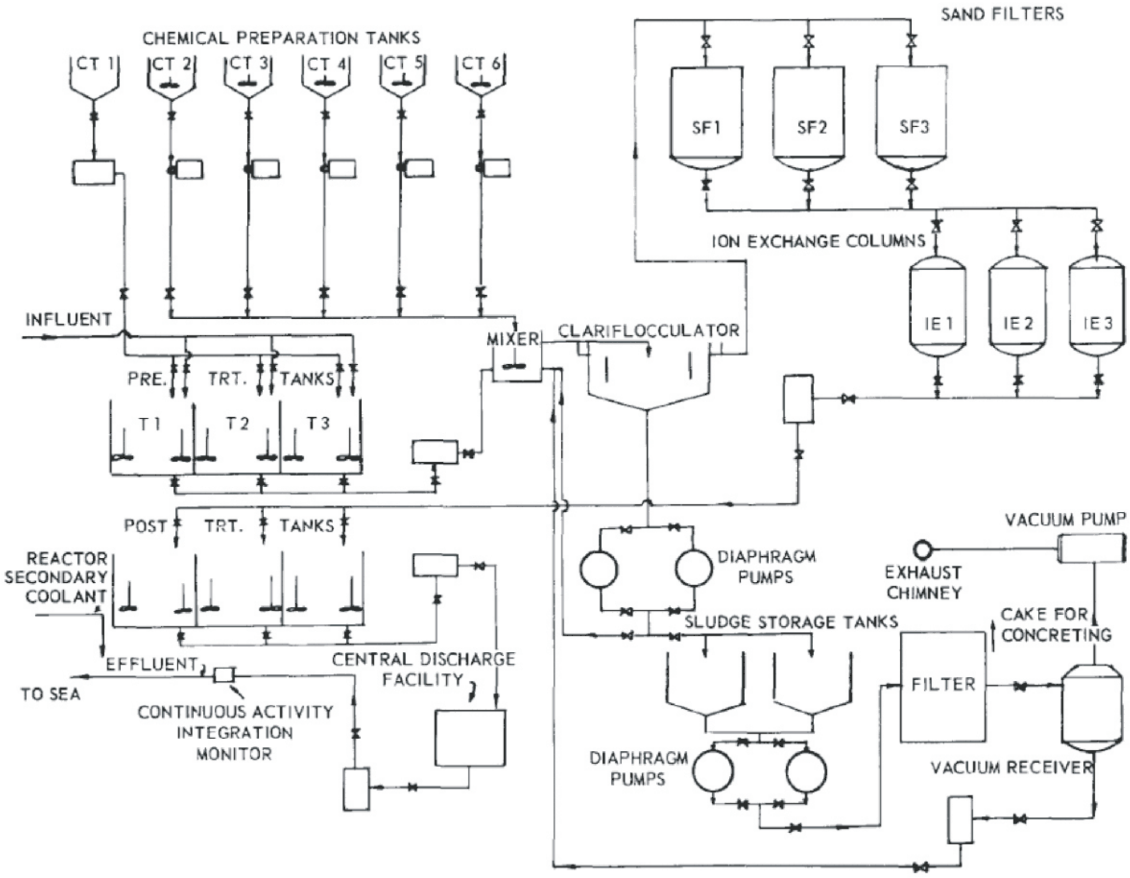

Fig.1: Process Flowsheet for Treatment of LLW.

generators improved, the overall quantum of LLW has increased along with the nature of wastes. The complexity of the LLW stream is highlighted by the fact that LLW is received from multiple facilities and even within a facility, widely differing streams ranging from process condensates, decontamination effluents, potentially active effluents, chemical wastes etc are generated. The broad characteristics of the LLW are given in Table 1.

For limiting the discharges, polishing of the supernate from chemical co-precipitation process was considered essential right from the design stage[3]. This was achieved by metering the supernate through ion exchange columns (Fig.2) filled with Cs-selective sorbent. The operating parameters of the column systems are also presented (left of Fig.2).

Due to the low loading capacity of the columns (500-800 bed volumes), the use of this sorbent was discontinued in the 1990s. Numerous laboratory scale studies were carried out to investigate possible high capacity sorbents as alternatives. Two classes of sorbents were explored and tested in laboratory and pilot plants. These were Synthetic Zeolites and Copper Ferrocyanide (CFC) impregnated on suitable substrates. Though CFC is a known high capacity Cs-selective material, due to its powdery form, it is not easily amenable to column operations. Impregnation on suitable substrates like anion exchange resins, polyurethane foam (PUF) and Zeolite 13X were explored over the years[4, 5, 6]. A 500 L scale ion exchange (IX) pilot plant using CFC-impregnated on anion exchanger was operated at WIP Trombay during the late 1990s for treatment of reprocessing effluents. Approximately 2400 bed volumes of LLW (1-5 x 10^{-4} mCi/lit) were passed through the column prior to its complete loading. Decontamination factor of 7-10 was obtained in the trial runs. The organic nature of substrate, non-regenerability and disposal considerations precluded use of this sorbent for regular operations. Pilot plants were also operated on 50 L scale for testing of CFC-PUF sorbents. Trial runs at Trombay indicated that 4000 bed volumes of LLW at 10 bed volume/hr were treatable with 10^{-4} mCi/lit as effluent quality. These sorbents, though promising, due to their low bulk density, would have resulted in large column sizes on plant scale considering the large processing rate requirement. CFC-Zeolite 13X and CFC-Zeolite 4A configuration were also tested on 50 L scale. Promising results were obtained with actual LLW. Loading of approximately 10,000 bed volumes at 10 bed volume/hr flow was obtained for few trials[7]. However due to non-reproducibility of results, further research is underway. Use of Zeolite 4A for selective separation of Sr was proven in

Table 1: Typical LLW Characteristics as received at ETP, Trombay.

Parameter	Value
Generation rate	50 to 1500 m^3/day
pH	8 - 10
Gross ß	10^{-5} to 2×10^{-2} mCi/L
Total Solids	Upto 1000 mg/lit

Overall Size: 1.82 m dia x 2.42 m ht	
Sorbent: Natural Vermiculite	
Type: Non-regenerative	
Size: -20 to +30 ASTM Mesh Size	
No. of Columns: 4	
Quantity of Sorbent: 4000 kg/Column	

Fig.2: Operating characterisitics of Cs-sorbent column (left) and a 1970s file photograph of the same (right).

Fig.3: Self-shielded Ion Exchange columns.

Fig.4: Valving station of Ion Exchange system.

laboratory scale earlier. However, the sorbent also shows selectivity for Cs too. When operated at 50 L scale, loading of minimum 7000 bed volumes was obtained consistently at 10 bed volume/hr flow. Thus, after trials involving approximately 2500 m^3 of LLW treatment, this sorbent was chosen as a primary material. In view of the simplicity of ion exchange process and large body of scientific work in this area, a plant (Figs.3 and 4) based on ion exchange process was installed at ETP. The process flowsheet is provided with sufficient flexibility to use improved sorbents in future.

Towards "Water Recycle"

An alternate process involving use of membranes showed significant promise in its use for LLW treatment on laboratory scale in early 2000s. With the commercial availability of reverse osmosis membranes on the rise, during the period from 2009–2015, thin-film composite reverse osmosis membranes in spiral-wound and disc-tube configurations were operated in three campaigns at Trombay in consultation with Desalination Division. Actual LLW was used in these pilot plants[8]. A total of 33,00,000 L of LLW was processed. These runs provided valuable insights into usability of the membrane process on plant scale. Throughout its operation, effluent specific activity of <1 Bq/ml was consistently obtained. This is three times lower than the effluent quality with ion exchange. The trial runs proved that efficient pre-treatment technique is vital to operation of RO plants especially when mixed effluents, as generated at Trombay, are encountered. Conventional pre-treatment techniques like sand & activated carbon filtration and two-stage microfiltration was found to be ineffective for Trombay effluents as it choked the membranes and rendered in unusable. Ultrafiltration was found to be the most promising pre-treatment technique for RO systems with mixed wastes as feed material. Effluent streams, which led to long life of the membranes, were identified and qualified in pilot plant runs. Polishing of this very low active stream by mixed bed resin rendered the effluent specific activity to below detectable levels. These observations indicated that LLW could be decontaminated to a level where its use as "process water" could be conceptualized. A pilot plant for "Water Recycle" has been installed at Trombay for "proof of concept" demonstration. This can eventually pave way for recovery and reuse of water from LLW for large nuclear facilities planned in the country. This will further strengthen and extend the philosophy of "Recycle & Reuse" being followed in Nuclear Recycle Programmes.

Conclusions

During the period from 1966 till date, mastery over the technologies for low level liquid radioactive waste treatment has been achieved leading to standardization of process flowsheet. Without relying on laurels, continuous efforts towards research and development to further reduce discharges are underway. An Ion Exchange Plant at ETP Trombay will be a test bed for some of these promising

Fig.5: Ultrafiltration Pilot Plant.

Fig.6: Spiral RO Pilot Plant.

Fig.7: Disc Tube RO Pilot Plant.

sorbents in the future. The R&D in membrane processes carried out over the years has provided confidence for demonstration of concept of “Water recycle” which will be the need of the hour in near future. India thus, can be world leader in emulating the philosophy of “Wealth from Waste”.

Acknowledgements

This article is the result of intensive and dedicated efforts of large number of scientists and engineers working over five decades in Waste Management Division and Process Development Division of Nuclear Recycle Group. I would like to thank C. P. Kaushik, Director, Nuclear Recycle Group for providing me an opportunity to learn and contribute to this important field in Radioactive Waste Management.

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VITRIFICATION

Advances in Remote Handling and Robotics

S. Wadhwa, Rahul Tripathi, Rohit Khokher, Pravind Kumar, B. N. Bhagywant, Jyoti Diwan and C. P. Kaushik

ABSTRACT

India has mastered the technology of vitrification of High Level Liquid Waste (HLLW) both by using metallic and ceramic melters for the management of HLLW generated from reprocessing of research as well as power reactor fuels. Interim storage and surveillance facility for Vitrified Waste Product (VWP) packages is operational and valuable experience has been gained in safe handling of these packages through the public domain during transportation as well as at the storage end. Remote handling plays an important role in the vitrification and in storage facility. Various remote handling tools and systems have been deployed in the vitrification facilities as per process requirements. Mechanical and electrical Master Slave Manipulators (MSM), Power Manipulators (PM), in-cell cranes, pneumatically and electrically driven trolleys and transfer systems, impact wrenches and various types of grapplers operated mechanically, electrically or pneumatically, are the major remote handling tools and systems utilized in the present facilities. Based on feedback of operational experience, new generation of remote handling equipment e.g. robots, advanced manipulators, sensors have been developed incorporating modern remote technologies. This has resulted in greater reliability, cost saving, minimum man-rem expenditure and downtime of systems in the vitrification facility. This paper discusses the past experience of remote handling in vitrification facility and advances made in remote handling including remote viewing for adoption in existing and upcoming facilities for better reliability, productivity and safety.

KEYWORDS: Vitrification, Remote handling, Remote viewing, MSM, In-cell crane, Remote welding.

IN INDIA, vitrification of High-level Liquid Waste (HLLW) generated in reprocessing plant is carried out in glass matrix in waste immobilization facilities located at Tromaby, Tarapur and Kalpakkam[1]. Work on the next facility, which will be an integrated reprocessing and waste management facility, is in progress at Tarapur. WIP Trombay employs Induction Heated Metallic Melter for HLW vitrification, while facilities in Tarapur and Kalpakkam utilize Joule heated Ceramic Melters. The major operation in vitrification of HLW consists of pouring of VWP inside a canister, capping, decontamination and over packing, which needs to be carried out remotely. Further handling of the over pack in a shielded cask for transportation, emplacing the same into interim storage/disposal facilities, liquid sampling and handling of filters etc. requires remote handling systems. These systems are also critical for dismantling of aged Melters. With development of advanced waste treatment processes & recovery of Cs-137 for production of Cs glass pencils demands precision remote handling for safe operation[2]. NRG has made necessary advancement and developed the requisite remote handling tools to meet remote handling and operation requirements of hot cell which are elaborated in subsequent sections.

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Remote Handling in Vitrification Facility, Trombay

The remote handling systems are the backbone of a waste management facility. The HL vitrification bay of WIP is equipped with three induction melters for production of vitrified glass products. The system is supported by various remote handling gadgets such as canister positioning system, transfer trolleys, self-actuated mechanical grapplers, advanced SERVO manipulators, three piece manipulators, in-cell crane, in-cell viewing system etc[3]. A 2 Te capacity in-cell crane (Fig.1) and trolleys are being utilised for material handling and movement of canisters and over-packs during vitrification operations. Self-actuated mechanical grapplers ensures failsafe gripping and handling of empty and glass filled canisters throughout its movement from inter cell trolleys to canister positioning system and then to the welding station for remote lid welding and over-packing as shown in Fig.2.

With technological advancement and waste separation techniques, WMD has been generating valuable products such as Cs-137 source pencils, Sr-90 and Ru-106 eye plaques which are milestones in the indigenous resource developments for medical treatment. These achievements are the results of robust remote handling facilities deployed. The Cs-137 source pencil production setup has been installed at area 19 of HL bay. The system consist of a scaled down induction re-melting furnace, pencil indexing arrangement with trolley and three piece manipulators for handling of pencils during operation shown in Fig.3. The challenge is to carry out pouring of predefined glass mass in small pencils of 23mm diameter precisely, sealing of the thin section pencils with quality welds that passes stringent quality checks set by

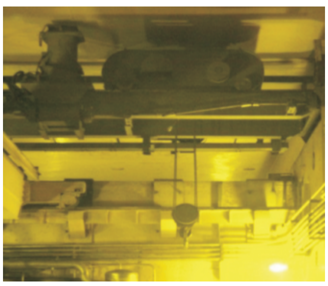

Fig.1: In-cell (2 T) crane in hot cell.

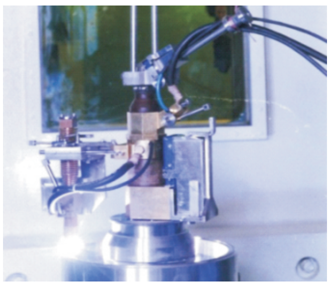

Fig.2: Remote welding of canister.

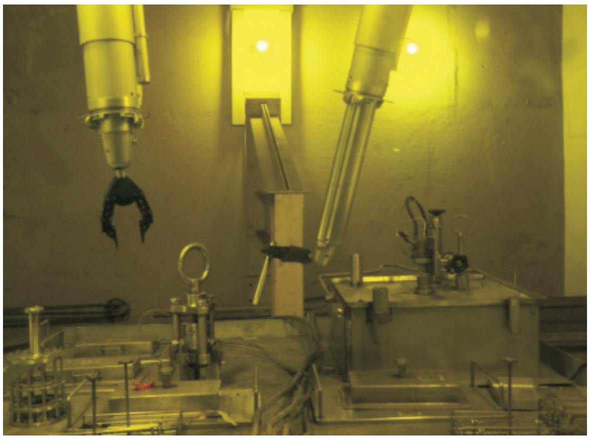

Fig.3: Cs-137 source pencils handling by TPM.

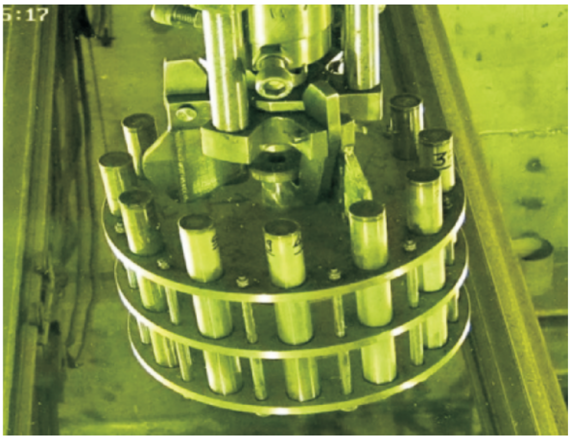

Fig.4: Cs-137 source pencils in cage.

regulatory agencies and handling of small but highly concentrated radioactive source. Since installation, more than 230 pencils have been produced and shipped to BRIT for deployment in blood irradiators depicted in Fig.4. The successful use of three piece manipulators with excellent operator skills has made it possible to achieve this target safely.

The advanced SERVO manipulator shown in Fig.5 is another value addition to remote handling operations playing a crucial role during maintenance activities[4]. The slave arm replicating the human hand movements with six degrees of freedom and 15 kg handling capacity, has approach to almost every corner of the melter cell (area-18) due to its mounting on a telescopic, movable carriage. The induction furnaces can be refurbished easily with the help of the SERVO Manipulator and In-cell crane, replacing its process pot/susceptor. Thus, plant operations can resume with minimum man-rem expenditure and downtime. Three piece manipulators as shown in Fig.6 installed in vitrfication bay (area-19 & area-21) have been a critical remote handling gadget in Cs source pencil fabrication. The precise handling with safety and reliability can be ensured with these manipulators over a sizeable approach area, for pencil handling into the indexing table for glass pouring, weighing, and transferring to cages for further processing. At the welding station, lid capping, welding and decontamination; and leak testing are crucial activities where operator skills and manipulator's finite movements comes into the picture. Key features are through the wall tube type, six degree of freedom, motion transmission from master to slave through many joints by a set of wire rope, metal tapes or other linkages & a payload of 22 kg. Articulated manipulator is another type used for radioactive sampling.

The in-cell viewing system is an equally important aspect of remote handling system. Six radiation shielding windows have been installed at different locations in HL bay area. The oil filled shielding windows provide equivalent radiation shielding of concrete wall with limited view of hot cell. The passive system has minimum maintenance requirement with a prolonged life of 30-40 years.

In addition, 10 CCTV cameras have been installed at various locations of different cells, depending on operational requirements, remote handling and remote maintenance of systems. The standard CCTV cameras have limited life span in highly radioactive areas. In order to enhance the camera life various fixtures and systems have been developed and deployed in hot cell.

Advances in Remote Handling & Robotics

With the experience gained in remote handling and with the availability of better electronics, improvements in remote handling equipments have been carried out. This enhances safe handling of highly radioactive materials. A new facility is being retrofitted at WIP Trombay named as Rad Waste Management Facility (RWMF) incorporating advanced system for increased reliability and higher productivity, resulting in reduced risk of radiation exposure to operators. Equipment design is modular in construction for easy remote maintenance using robotic devices, employing advanced materials with high radiation resistance for increased life.

Important design changes incorporated in RWMF are the process pot with mechanical plug (Fig.7), process pot coupling system, canister positioning system, closed pouring system, Cs glass pouring system (Fig.8). These changes potentially

Fig.5: ASM slave arm.

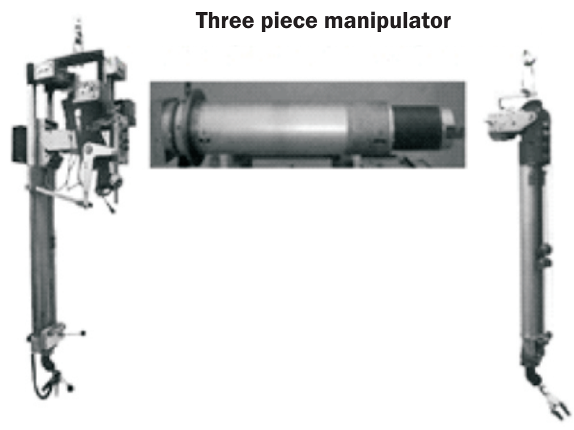

Fig.6: TPM for remote handling.

Fig.7: Process pot Assembly.

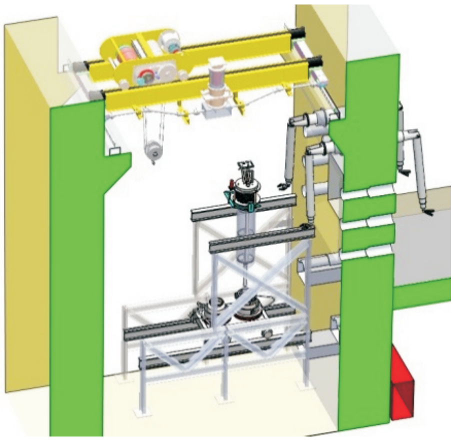

Fig.8: Vitrification system.

Fig.9: Mobile Robo for remote DC of hotcell.

reduce the maintenance of system and enhance the life of system. The major designs changes will be validated by setting up testing facility and simulate the modified system under real conditions.

Wireless decontamination mobile robot (Fig.9) has been developed in coordination with Electronics & Instrumentation Systems Division (EISD) for hot cell decontamination. The mobile robot comprises various features compatible with hot cell operations such as scrubbing action and remote replacement of scrubber, water and acid spray with remote refill, remote charging etc. The mobile robot can be brought out of the hot cell for completion of major maintenance. This mobile robot has three degrees of freedom, which allows coverage of nearly the entire hot-cell area. Individual wheels are provided with motor and power steering is programmed. Remote replaceable camera is mounted on the unit for remote viewing of the area.

Automatic miniature welding machine is another development for the precision welding of glass pencils. Vitrified Cs glass pencils made of a 23mm diameter inner tube and a 25.4 mm outer tube are seal welded on lids. Autogenous Pulse Tungsten Inert Gas (TIG) Welding shown in Fig.10 is used for seal welding of pencils having wall thickness of 0.4 mm at lid portion which has to be remotely carried out inside the hot cells. Precision operations in this miniature welding such as the positioning of the lid, placing weld head above the pencil lip, maintaining the gap and alignment between electrode tip and weld pool are carried out manually with the help of manipulators. This sometimes results in unsatisfactory welding. In order to overcome this, a fully automated version of the advanced welding machine has been developed. The key features of this welding machine is that it has three degrees of freedom, 2 translation motion on electrode and one rotational motion on collet. Further, it has provision of a Graphic User Interface (GUI) based system which can be operated remotely with precision of 5 micron in movements. Modular design helps in remote replacement of electrode and other components.

A remotely replaceable Internet Protocol (IP) based wireless camera system depicts in Fig.11 is recent development for existing in-cell crane mounted camera. The development would result in negligible man-rem expenditure as well as system downtime with its remote replace ability and auto latching connector design features.

Various advances in remote viewing have also been carried out to facilitate better vision while handling highly

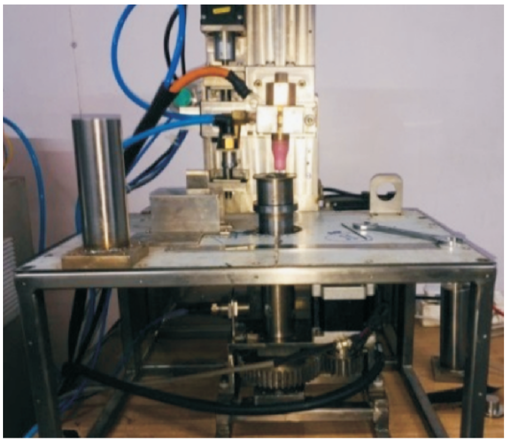

Fig.10: Automated Cs Pencil Welding.

radioactive materials inside hot cells. Development of a telescope mounted camera as shown in Fig.12 on a rotary swing arm has been designed and installed on partition wall of area-18 for viewing glass pouring and to aid remote handling operation during operation and maintenance activities. The swing arm can move the camera behind the shielding when not in use, thus reducing exposure time and prolonging camera life considerably.

Most of the cameras have been installed through wall Embedment Plug (EP). A pneumatic cylinder based retractable camera mounting has been designed and installed to optimise camera exposure. The advanced version of retractable mounting system can enhance camera life further by providing

Fig.11: Remotely replaceable wireless camera system.

Fig.12: Telescope -mounted camera.

Fig.13: EP Hot-cell Retractable camera.

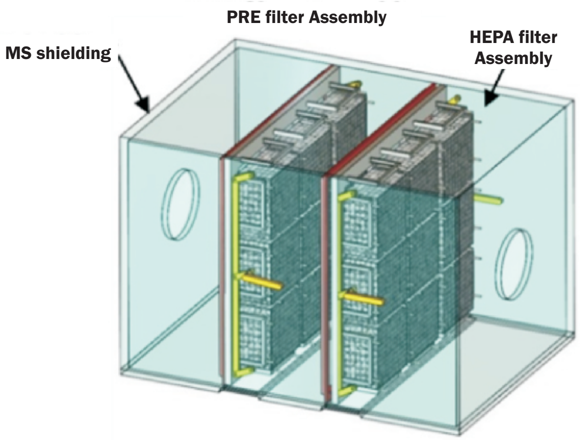

Fig.14: Series arrangement of Pre and HEPA filters.

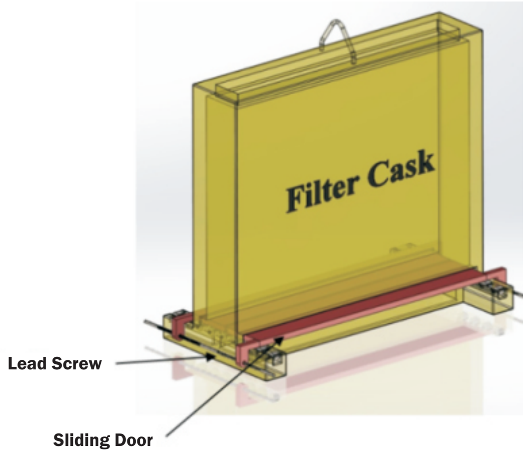

Fig.15: Filter cask for remote replacement of filter bank.

additional shielding on hot side with mechanical movements through lead screw mechanism as depicted in Fig.13. The newer technologies such as power line Ethernet transmission have been successfully implemented for replacement of existing camera systems in hard to reach hot cell areas, where additional cable laying is not possible.

Manual replacement of ventilation exhaust filters results in large man-rem expenditure and plant down time. Remote replacement of these filters in a cubicle concept has been adopted in an upcoming facility. Hot cell exhaust is routed through filtration cubicle to plant suction plenum before being discharge to stack. Filters along with frame will brought in the cask with the help of a crane for further disposal. Figs.14 and 15 shows the cubicle and cask for these systems.

A compact remote cutting machine, shown in Fig.16, has been developed to recover precious metals from disused sources. Low speed source cutting machine was developed for varying sizes of sources of 6mm dia. to 30 mm dia. in a glove box. Cutting speed was optimised to 50-70 rpm with varying dead weight controlled feed arrangement depending on source size. For Ru-106 eye plaque production, programmable pneumatically assisted resistance brazing machine with digital microcontroller (Fig.17) was developed in WIP, Trombay of BARC.

Conclusions

The continuous up-gradation of remote handling systems with plant specific requirements and evolving technological developments has made it possible to achieve goals of developing indigenous products for societal benefits besides safe management of radioactive waste. With advancement in remote engineering technology, waste management plants of BARC have achieved several milestones while generating several valuable products such as Cs-137 source pencils, Ru-106 eye plaques, Y-90 based treatment etc. Till now, more than 230 nos. of Cs-137 source pencils and more than 15 nos. of Ru-106 eye plaques have been produced for medical applications. These achievements have been made only because of safe, reliable and advanced remote handling systems.

Fig.16: Remote cutting machine for disused sources.

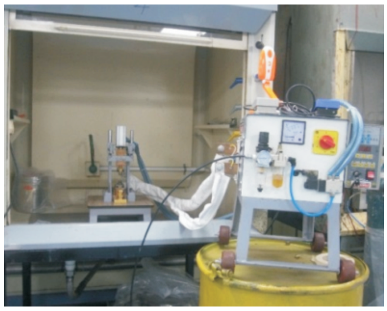

Fig.17: Remote resistance brazing machine.

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PRODUCTION OF CESIUM PENCILS

Challenges to Innovations

Jyoti Diwan, Aniruddha Dharashiokar, S. Wadhwa, Amar Kumar, Neelima S. Tomar and C. P. Kaushik

ABSTRACT

High Level Radioactive Liquid Waste (HLLW) contains many useful radio isotopes having several industrial as well as medical applications. Separation and recovery of useful isotopes from radioactive waste and their deployment for societal application make the waste a material of resource. Radioisotope of Cesium, ^{137}Cs, is one of the gamma emitting radionuclides which has immense potential for use as a sealed gamma source in radiation technology applications such as irradiation of blood and foodstuffs, sterilization of medical supplies and radiation processing of sewage sludge [2]. ^{137}Cs, one of the major constituent of the nuclear waste, is a suitable substitute for ^{60}Co as a radioactive source because of its longer life. Several challenges are faced during the extraction of ^{137}Cs from HLLW, immobilization of ^{137}Cs in glass matrix, production of Cesium glass pencils, their remote welding and quality assurance before transportation in shielded cask to BRIT for deployment in hospitals as blood irradiator .Challenges faced during each step and the innovative techniques adopted are discussed in the present article.

KEYWORDS: HLLW, Partitioning, ^{137}Cs, Immobilization, Remote viewing, Cs glass pencil.

INDIA has adopted a closed fuel cycle by reprocessing the spent fuel for energy security as envisaged by Dr. Homi J. Bhabha, the founder of Indian Nuclear Power Programme[1]. High level liquid waste originates from the spent fuel reprocessing plants. Over 90% of the radioactivity of this waste is contributed by fission generated Cesium and Strontium radioisotopes, making HLLW a source for Cs recovery. India has taken a conscious decision of deploying Cesium in a vitrified form as an irradiation source. India is the only country to have the technology of partitioning of High Level Liquid Waste (HLLW) and manufacturing ^{137}Cs in vitrified form. Waste Management Division of Nuclear Recycle Group has achieved a milestone in the production of radioactive Cesium glass pencil to be used towards societal benefits in the healthcare sector for blood irradiators. The preparation of ^{137}Cs based radiation sources involves processes like recovery of the radioelement from nuclear waste, immobilization of the recovered Cs in vitreous matrix, pouring of Cs glass in stainless steel pencils, remote encapsulation, leak testing and transportation (Fig.1).

Partitioning of High Level Liquid Waste

With the advent of new technologies based on partitioning of waste, long lived radioactive waste constituents are separated prior to immobilization in a glass matrix. HLLW contains many useful fission products such as ^{137}Cs, ^{90}Sr and ^{106}Ru. Separation and recovery of these fission products not only reduces the waste burden to the environment but also gives value addition to drive social impact[1]. Challenge lies in the recovery of cesium from radioactive waste stream which has the presence of other radioactive fission products, long lived minor actinides and inactive constituents added during reprocessing. To address the same, development of novel extractant and separation equipment to recover ^{137}Cs in pure form was done indigenously.

The plant scale facility at Waste Immobilization Plant, Trombay for recovery of Cesium from HLLW has been accomplished using solvent extraction process (Fig.2) after testing the efficacy of process on laboratory scale.

Immobilization of ^{137}Cs Solution in Vitrified Form

During vitrification, cesium nitrate is added to the melter as the feed solution along with other glass forming additives at a controlled rate. The vitrification is carried out in Induction

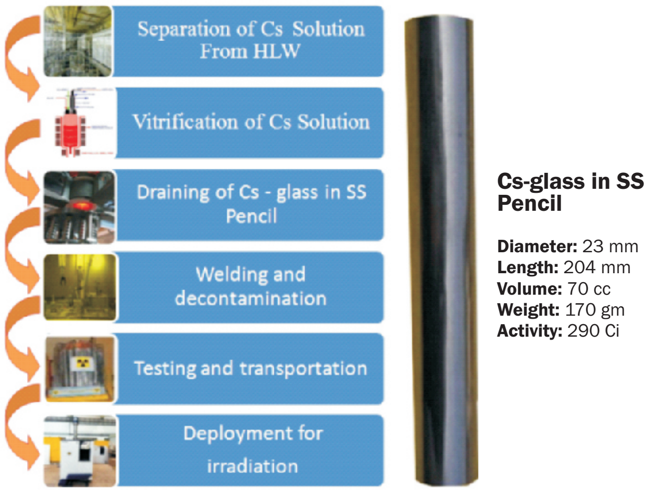
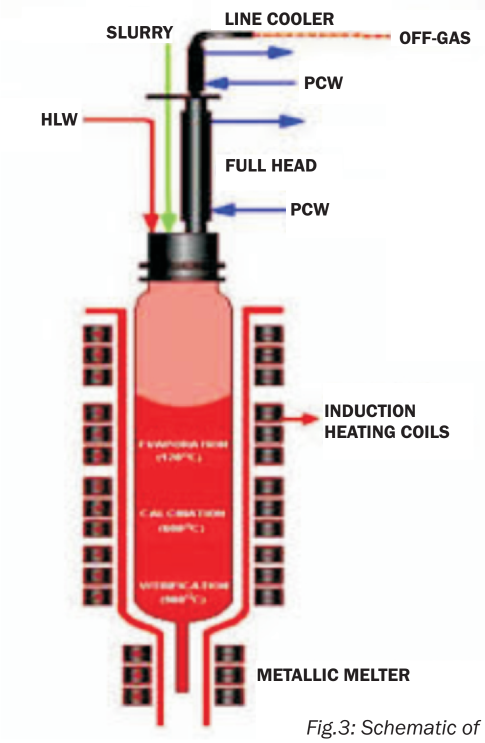


Fig.1: Overview of Cs pencil Making Process.

Fig.2: Partitioning of HLLW for selective extraction of ^{137}Cs in Hot cell.

The authors are from Waste Management Division, Bhabha Atomic Research Centre, Mumbai & Homi Bhabha National Institute, Mumbai.



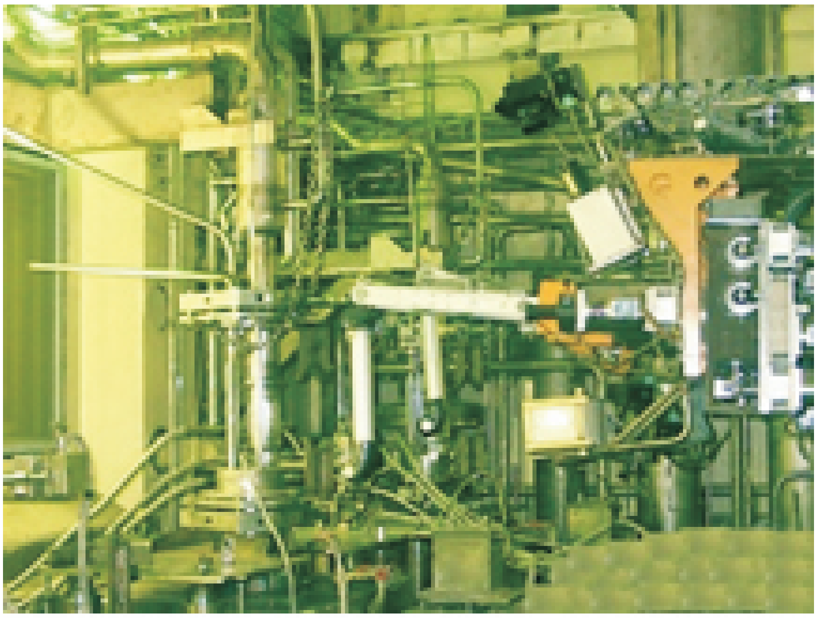


Fig.3: Schematic of Induction Heated Metallic Melter (left) and IHMM in operation (right).

Heated Metallic Melter (IHMM) as per the standard operating procedure with existing system based on predetermined temperature profile. For making Cesium pencils, a batch of 8 kg Cesium glass must be melted in the IHMM (Fig.3), completely drained in a small process pot, called the dispenser for its further remelting using custom designed IHMM and poured into small stainless steel pencils.

It was very challenging to prepare cesium glass in smaller batch size in the IHMM which was optimized for handling large volumes. This was negotiated with the modification in the operating practices based on expertise gained over decades in vitrification technology. Due to the volatile nature of cesium at high temperature, carryover of cesium in off-gas stream was an additional challenge. This was addressed by multiple scrubbing, modified operating procedures and elaborates off gas cleaning system. As opening of the dispenser process pot is lesser as compared to the canister ,special arrangement has been made to ensure safe draining of molten glass completely in the pot. A partially closed pouring system has been designed, installed and operated during Cs glass pouring to minimize carryover of volatile cesium towards the ventilation exhaust filter bank.

Production of Cesium Glass Pencils at Industrial Scale

Retrofitting of remelting furnace along with associated trolley arrangement (Fig.4) in an existing hot-cell was one of the major challenges. The same was very much important for remelting of cesium glass, pouring in a dispenser, and draining of a precise amount of cesium glass into SS pencils (Fig.5). As a result of dedicated team efforts, successful installation and commissioning of the system was carried out.

The available power supply for remelting and draining of glass was inadequate and the same was modified with enhanced capacity power supply to overcome the power transfer issue. Weighing system of the remelting furnace plays an important role as the molten Cesium glass has to be poured in small stainless steel pencils of 23 mm diameter and 204 mm length in a precise manner. Challenge with respect to precise weighing of the pencil glass pouring was resolved with industrial grade weighing system mounted on remotely replaceable cage. After pouring, pencil lid is placed remotely prior to remote welding and encapsulating (Fig.6).

Remote viewing system plays an important role in checking the weld quality and thus ,ensuring the quality of sealed source of Cs glass pencil. Improved viewing system with IP cameras was installed in welding cell which resulted in zero rejection of pencils. The produced pencils are subjected to various stringent quality assurance checks on par with international standards. The mechanisms involved in pencil welding system, leak detection test, surface decontamination system etc. have been in house developed at Waste Management Division.

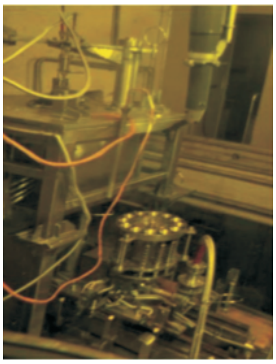


Fig.4: Remelting furnace.

Fig.5: Pouring of Cs glass.

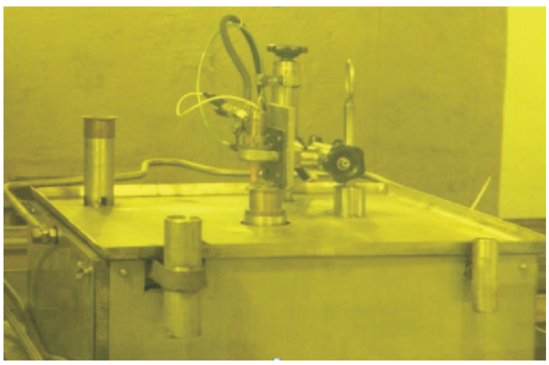


Fig.6: Welding of Cs glass pencil.

(a)

(b)

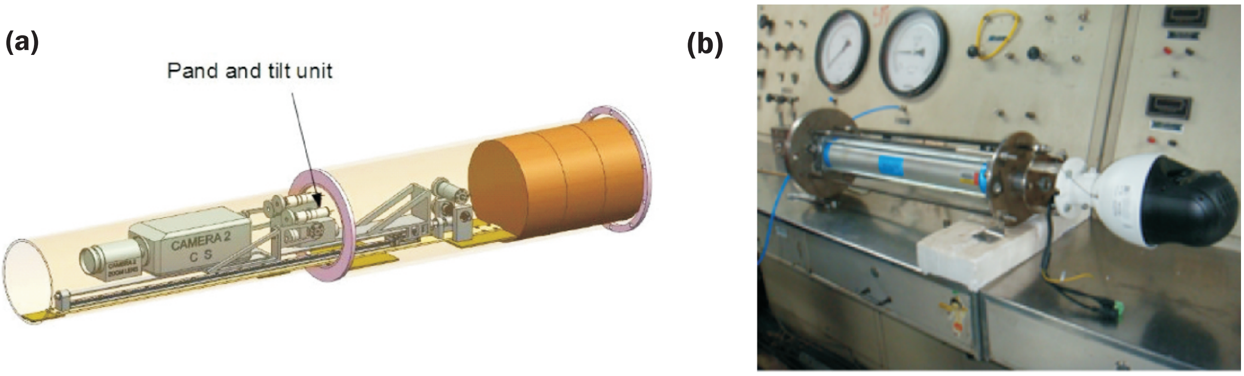


Fig.8: (a) Retractable Camera System for EP, (b) Retractable System with IP camera.

Fig.9: Radiation resistant camera.

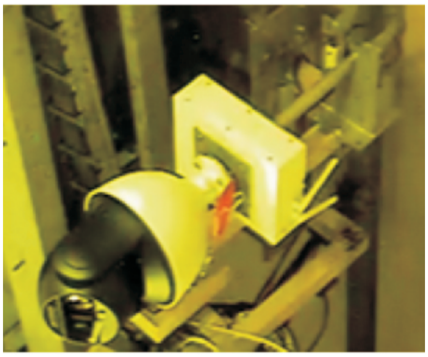


Fig.10: Wireless camera on cell crane.

Fig.11: Periscope based camera.

Fig.12: Telescope based camera.

As all the operations inside the hot-cell are done remotely, reliable remote viewing system is a must for safe and successful remote handling operations. Due to increase in radiation field inside the hot-cell during Cs pencil production, frequency of replacement of cameras of remote viewing system increased significantly. Various innovative developments have been carried out for increasing the usable life of the cameras. These include retractable design for EP cameras (Fig.8), Radiation Resistant (RR) camera system (Fig.9), wireless camera for in cell crane (Fig.10), periscope based camera on in cell crane and telescopic camera (Fig.12) for viewing pouring and material handling in the vitrification cell. Replacing CCD cameras with IP has shown encouraging results with respect to usable life enhancement in radiation field.

The Cs pencils are transported to BRIT in a lead shielded cask, from where these are subsequently transferred to blood irradiators for shipment to various hospitals. Ten such pencils containing radioactive cesium are used in each blood irradiator. The irradiation of blood is very much essential to prevent Transfusion Associated-Graft Versus Host Disease (TA-GVHD) particularly for immune-deficient patients.

Conclusions

With various innovative developments, the challenges in production of Cesium glass pencils at industrial scale were overcome. This resulted in production of 230 Nos. of Cs pencils of specific activity in the range of 1.4-4.5 Ci/gram which were handed over to BRIT. In the Indian context, as mentioned, HLLW is a wealth, since many isotopes present in this waste have societal application. With the present philosophy of recovery and reuse, we stand in the position to recover and supply ^{137}Cs to serve humanity at large. Various qualities of Cesium such as longer half-life, lower shielding requirement and amenability to be used in non-dispersive glass form make it a more suitable irradiation source. India is a forerunner in this technology for selectively partitioning of Cesium from HLLW, immobilizing in vitreous matrix and thereby deploying in blood irradiator.

Acknowledgements

The details of the work presented in this article are the ultimate results of dedicated and tireless efforts of large number of professionals including scientists and engineers of Nuclear Recycle Group which are heartily acknowledged by the authors. The authors are also thankful to the present and past officials of NRG who were involved during the industrial production of Cesium glass pencils.

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CIVIL STRUCTURES FOR BACK-END FUEL CYCLE FACILITIES

Design, Construction and Ageing Management

Somya Khare, Ajay Shirole, R. B. Sastry, R. R. Rakesh and P. D. Maniyar

ABSTRACT

Nuclear Recycle Group deals with back-end activities of the Nuclear Fuel Cycle aiming at recovery of useful materials by reprocessing of spent fuel and management of radioactive waste generated. Safe operation of these activities requires well designed structures, systems and components to ensure shielding, containment, strength, functionality, and longer service life. Various facilities are operational and are also under planning and construction for carrying the activities related to spent fuel reprocessing, extraction of useful radioisotopes for societal benefits and finally storing/disposing of the processed radioactive waste as per regulatory guidelines. Upkeep of old plants and buildings by assessing their condition periodically and health restoration by undertaking structural repair is also an important activity. This article presents an overview of various aspects of design, construction as well as ageing management of such facilities.

KEYWORDS: Reinforced cement concrete, Radiation shielding, Structural analysis, Condition assessment, NDT techniques, Structural repair, Structural health restoration.

A NUCLEAR facility involves engineering structures, systems and components (SSCs) which collectively ensure its safe and reliable operation. Civil structures play an important role in safety performance of these facilities. Nuclear Recycle Group (NRG), Trombay is entrusted with the responsibility of the back end fuel cycle activities which are of utmost importance under the three stage Indian nuclear power programme. Civil structures in NRG comprise fuel reprocessing facilities, High Level Waste (HLW) immobilization plant, HLW transfer ducts/trench, Low-level Liquid Waste (LLW) treatment & discharge facilities, solid waste storage and Near Surface Disposal Facilities (NSDF). Civil structures for these facilities have been designed and constructed to fulfill the requirements of shielding, containment, strength, functionality and longer service life.

Design of Structures

There are features which are unique to NRG facilities, e.g., irregular shape of civil structures which may require an in-depth study of torsional effects, high degree of confinement, provision of multiple barriers to contain radioactivity, shielding considerations resulting in heavy structures, associated corrosion, ageing problems under toxic and radiation environments, associated chemical and fire hazards and importance of long-term structural integrity[1].

"Defense-in-depth" approach is being adopted in design of the structures to prevent significant failures which could release activity in the environment. This can be achieved by:

i. Robust design and high quality in construction to prevent failures in normal and abnormal events

ii. Multiple engineered barriers

iii. Provision of protection which prevent the breach of any barrier or mitigate the consequences of the breach

Siting is an important aspect of safety which has significant impact on design of structures and has implications of safety with respect to mitigation of consequence of any breach. A suitable site limits the stringent design requirements, release of radioactivity to environment and limits the radiological consequences for the public in accidental scenarios including conditions that may lead to mitigatory actions being taken[2].

Function of multiple engineered barriers is to prevent activity migration and to design such containment, structure that shall perform up to desired strength and serviceability during normal and abnormal events (external events of earthquake, wind and flood). Serviceability criteria of design, limits the excessive deflections and crack-width in RCC members, to ensure prevention of breach of containment and functionality.

For a robust design and to prevent failure in normal and abnormal events, evaluation of external events (EE) exceedance frequency is of prime importance. Considering the hazard potential, a "graded approach" has been adopted for EE categorization of these facilities. The aim of such approach is that, a simplified seismic methodology and optimized return periods of external events could be used for facilities with low inventory or with lower unmitigated hazard consequences. This approach results in radiological hazard criteria categorizing facilities based on their hazard levels as presented in Table 1.

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Table 1: Mean annual frequency of major natural events for different hazard categories of nuclear Facilities (Graded according to hazard potential) [3].

Category	General Characteristics	Mean Annual Frequency of Exceedance		
		Earthquake Ground Motion	Flood/ Rain	Wind
I	Potential for off-site radiological impact	SSE:~1E -4 OBE(NPPs): 1E-2	1E -4	1E-4
II	Potential for on-site radiological impact	4E-4	1E -3	2E-3
III(a)	Potential for radiological impact within plant boundary	DBE using IS-1893(Part-4) with I=1.5 and R'=0.67 x Response reduction factor defined in IS:1893 for structure without any special provision for seismic resistance	1E-2	1E-2
III(b)	Potential for radiological impact within plant boundary and off-site chemical Hazard	MCE using IS-1893(Part-4) with I=1.5 and R'=0.67 x Response reduction factor defined in IS:1893 for structure without any special provision for seismic resistance	1E-2	1E-2
General	Conventional or industrial buildings	DBE using IS-1893(Part-4) with I=1.0 and R'=0.67 x Response reduction factor defined in IS:1893 for structure without any special provision for seismic resistance	1E -2	1E-2

Back-end fuel cycle facilities fall in category-II, III considering "onsite" and "with in plant boundary" radiological hazards. Analysis and design of structures for nuclear facilities are governed by AERB codes and standards[4,5] for category I & II structures. For hazard category-III, facilities are designed according to Indian standards[6,7].

The building structure comprising of beams, columns, walls and slabs along with the foundation is modelled as finite elements (FE) such as beam and shell elements. Soil is modelled as spring elements and subsequently structural FE analysis is performed considering soil structure interaction (SSI) for static and dynamic loads. Static analysis is carried out for self-weight, equipment loads, live loads, thermal loads, earth pressure, wind loads etc. and dynamic analysis is performed for seismic loads. Response of soil-structure system is evaluated in terms of deflections, forces, moments, bearing pressure below foundation and foundation uplift.

Design is carried out for worst combinations of these loads to satisfy strength, serviceability and stability criteria as per governing codes and standards.

Construction

Nuclear safety related structures require some special features during construction. Mass concreting is involved wherever shielding requirement using concrete is to be provided. Mass concreting work necessitates (i) providing adequate reinforcement for the stresses induced in the concrete due to heat of hydration, (ii) designing the concrete mix by using suitable pozzolanic ingredient and ice flakes to limit the temperature of concrete (iii) sequencing of the concrete pours to facilitate dissipation of heat and to avoid cold joints (iv) adequate design of shuttering/scaffolding to bear the wet concrete load.

Radiation streaming and leak tightness is another aspect that needs to be taken care of during the execution stage. This involves (i) leak tight joint formation at the interface of any two structures (ii) prevention of cold joint formation during concrete pouring, (iii) providing leak tight construction joint by using bonding agent, water bar etc., (iv) tie rod provision in the shuttering should be made with proper precautions so as not to create any direct path for radiation streaming afterwards, and (v) ensuring leak tightness of the structure/joints by either hydro testing or smoke test.

Industrial safety and quality are maintained at the site with due diligence. Additionally, handling contaminated soil, construction debris and work in areas having radiation field are carried out with strict adherence to radiation protections rules and regulations.

Some of the major civil construction works by NRG Projects at BARC Trombay are described below:

Above Ground RCC HLW Transfer Duct: An above ground duct as shown in Fig.1 has been constructed for transferring high level radioactive waste between AWTF & WIP Pump-house. It has been designed for earthquake load as well as thermal load imposed due to the environmental conditions.

Special Pot type PTFE bearings have been provided between the RCC duct and columns supporting the duct to allow longitudinal movement of the duct due to thermal expansion.

Fig.1: Above ground RCC HLW Transfer Duct from AWTF to WIP Pump House.

RCC Dyke for Disposing Solid Waste: An RCC dyke shown in Fig.2 has been constructed at RSMS, Trombay encircling the old used earthen trenches leading to effective utilisation of NSDF land. It is having an area of 60m x 60m, height of 3.5m and it is adequate for 6-7 years of disposal needs. This dyke has facilitated disposal of odd shaped and big sized consignments as well.

Fig.2: RCC dyke at RSMS Trombay.

Multitier Reinforced Concrete Disposal Module (MRDM): This is 22.6m x 17.5m x 8m deep (5m underground) RCC structure shown in Fig.3 constructed at RSMS, Trombay. The design of this MRDM is first of its kind over the conventional design followed so far and has enhanced land utilisation factor from 1.9 cum/sqm to 5 cum/sqm. This is a nuclear safety related structure, designed for seismic loads and uncracked section to have leak tightness during its service time. Water fill test has been carried out to ensure leak tightness. One unit of MRDM will serve for solid waste disposal needs for about 7 years.

Fig.3: Multitier Reinforced Concrete Disposal Module at RSMS, Trombay.

Tile Holes (TH): Tile Holes are special type of modules which are used in NSDF for disposal of higher surface dose rate (>50R/hr) solid waste. Tile holes are wire wrapped MS cylindrical units coated with 25mm thick cement mortar on outside as well as inside surface to protect it from corrosion. These units are installed in RCC vault with waterproofing on external surface of THs and vault.

Recently a TH battery comprising of 80 Nos. of TH of 710mm ID and 14 Nos. of THs of 950 mm ID has been constructed in RSMS and is shown in Fig.4.

Fig.4: Tile Hole Battery at RSMS, Trombay.

Low Level Liquid Waste (LLW) Transfer Line: Low-level Liquid Waste transfer pipelines (150 mm NB, carbon steel) from Reprocessing Plant to Effluent Treatment Plant (ETP) have been laid along the Security Road of BARC covering a total distance of 2.7km connecting various facilities en-route. All pipelines are covered by RCC precast half round cover (shroud) on top and precast slabs from bottom. These shrouds, bottom precast slabs and waste transfer pipelines are supported on RCC pedestals having 3-meter c/c spacing. These pipelines crossed difficult terrain and are laid underground at various locations, while at few other locations, they have been bridged over drains and nallahs.

Ageing Management

Condition Assessment: Assessment of the structural condition and necessary rectifications/retrofitting of the existing old RCC structures of NRG was carried out as a part of ageing management. Various standard Non-Destructive Techniques (NDT) have been utilised without affecting the safety and functionality of these structures. The NDT methods employed for condition assessment are visual inspection[8], Rebound Hammer Test[9], Ultrasonic Pulse Velocity Test[10], Half Cell Potential Test/Corrosion probability test[11], Core Extraction and Testing[12], Chemical analysis of concrete dust samples for Chloride and sulphate content determination, carbonation depth test, Concrete Cover test and Resistivity test. Various structures such as Stack, water tank, LLW tanks, chimney foundations, Material Handling Equipment (MHE) support structures, Office buildings etc. have been condition assessed as shown in Fig.5.

Rebound Hammer Test | *Corrosion Probability Test at Chimney foundation* | *Electrical resistivity test*

Ultrasonic Pulse Velocity test | *Collection of concrete dust samples for chemical tests* | *NDT & Repair of 135m high RCC chimney*

Fig.5: NDTs of different structures in NRG facilities.

Structure Health Restoration: Based on the findings of condition assessment, structural health restoration carried out is briefly described below:

i. 135 m High Stack: The 135 m stack of FRD plant was nearly 50 years old at the time of its restoration. The structure was showing signs of distress due to ageing as shown in Fig.6(a). To carry out the condition assessment and repair of 135m high stack, special scaffolding erection and its dismantling arrangements were made. The scaffolding design was carried out and vetted by the experts in the field. Structural repair was carried out using special repair mortar, replenishing exposed/corroded reinforcements, injecting low viscous grout for repairing cracks in concrete and finally an UV resistant anti-carbonation coating was applied on the complete outer stack surface. Personnel qualified with rigorous health checks ascertaining their capability for working at higher elevations were only deployed for carrying out this work. The restoration work was accomplished successfully without any safety related incidence.

ii. Underground Water Tank: This is a circular tank with annular partition having a tank inside tank (12m Ø internal tank and 18m Ø outer tank) having two openings of 600mm Ø in each tank. Spalling concrete and exposed reinforcement were observed during its condition assessment as shown in Fig.6(b). Outer tank repair in restricted annular space of 3m width with humid environment inside resulted in tough working conditions. Continuous seepage of groundwater from the walls and floor of the tank necessitated grouting the cracks in the wall with polyurethane for ensuring leak tightness of the

Fig.6: (a) 135m high stack. *(b) Underground water tank.* *(c) LLW Tanks.*

structure during repair work. Micro-concrete was used for filling the pits in the concrete slab. Crystalline coating was applied on the inner surface of the tank to increase its leak tightness. Finishing coat of food grade epoxy coating was provided on the inner surfaces as this tank stores potable water. The tank was repaired successfully and is functional now.

iii. LLW Tanks: MS lined RCC underground LLW treatment tanks at ETP are more than 60 years old. Condition assessment of 02 Nos. of LLW tanks revealed that these structures are in distressed condition. These structures have been restored by removing MS lining, structural repairs, grouting and increasing RCC wall & raft thickness by providing layer of RCC as shown in Fig.6c. New and old RCC members were connected by using shear connectors. SS lining has been provided on internal surface of the tanks. With this restoration, the tank life has been enhanced for uninterrupted operations of the LLW treatment.

Conclusions

Back-end fuel cycle civil structures assure safe environment to all the systems, equipment, components during their service life. To achieve such level of safety assurance, systematic & methodical approach during all the stages i.e. design, construction, periodic condition assessment and remedial measures are exercised. To ensure the performance of the structure up to expected level of strength and serviceability during normal and abnormal events, severest of all the load combinations of operational loads, wind loads, seismic loads, thermal effects and structure specific internal environmental exposure and shielding requirements are considered. During construction stage, rigorous quality assurance followed to ensure that the structure satisfy design intents. Under aging management, condition assessment & restoration is practiced for existing civil structures to ensure safe and continued operation of the facilities. Satisfactory performance of the newly designed and constructed structures as well as old structures of NRG strengthens this approach and drives towards continuous upgradation of latest know how and technologies in the field of civil engineering.

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BACK-END NUCLEAR FUEL CYCLE FACILITIES

Fabrication and Quality Assurance for Process Equipment

Deep Gupta, Jitendra Kumar, Yogendra Singh, Ramakant and P. D. Maniyar

ABSTRACT

India has adopted the three stage nuclear power programme with recycling of spent fuel forming an integral part of the scheme. Thus, reprocessing of spent fuel and management of radioactive nuclear waste are an essential part of the plan. Reprocessing plants and high level waste management facility are key components of the back-end of the nuclear fuel cycle besides management and disposal of low and intermediate level waste. Both of the above plants operate under highly aggressive process medium and necessitate the development and deployment of process equipment with highly stringent fabrication and quality assurance requirements. This article covers critical aspects of material, fabrication and QA requirements for process equipment for nuclear fuel recycle and waste management plants.

KEYWORDS: Stainless steel, NAG, Quality assurance, Metallurgical cleanliness, Inter granular corrosion, Grain size, Radiography, Ultrasonic examination, Dye penetrant test.

THE NUCLEAR Recycle Group (NRG) of the Bhabha Atomic Research Centre (BARC) is entrusted with the responsibility of back-end of nuclear fuel cycle activities at Trombay. These include design, engineering, construction and operation of spent fuel reprocessing plants and waste management plants. Besides, NRG is also responsible for R&D activities applicable for these plants and manufacturing of products utilizing radionuclides present in nuclear waste for societal benefits like Ru-106 eye plaques, Cesium-137 pencils, and Yttrium-90. These plants are basically chemical plants with nitric acid based processes, having very high level of radio-activities loaded in the process medium. The combination of a highly radioactive and acidic environment leads to enhanced corrosion in these environment. Indeed, proper care must be employed during fabrication of process equipment to avoid corrosion "hot-spots" that may then trigger wider corrosion issues in service. This is especially important as the equipment becomes inaccessible to future maintenance due to high background radiations and contamination. Thus, there is a need for careful selection of the materials for the construction and quality assurance requirements for fabrication to ensure equipment life meets performance criteria in real plant environments. Critical aspects of fabrication and QA requirements for process equipment of nuclear fuel recycle and waste management plants are addressed briefly in this article.

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Materials of Construction

The process medium is highly oxidizing in nature and for such environments, the performance of 304L grade Stainless Steel (SS) is well established, leading to its use in the construction of process equipment and piping components. However, the presence of corrosion promoters in process solutions arising at the back end of the fuel cycle makes SS of commercial purity (CP) grade 304L vulnerable to corrosion. Hence, there was a need to develop SS304L material with special requirements to suit the process environment prevailing in these plants. Accordingly, a special grade *viz.* SS304L Nitric Acid Grade (NAG) was evolved with stringent corrosion resistance in nitric acid process media. Table 1 indicates comparison of chemical composition of SS304L (CP) and SS304L (NAG).

Table 1: Comparison of SS304L (CP) and SS304L (NAG).

Wt . %	304 L (CP)	304 L (NAG)
C	0.03 max	0.02 max
Mn	2.00 max	1.8 max
Si	0.75 max	0.35 max
P	0.045 max	0.025 max
S	0.030 max	0.005 max
Cr	18-20	18 - 20
Ni	8.0-12	10 - 12
N	0.10 max	0.05 max

Table 2: Inclusion rating requirement

Type	Thin (max)	Heavy (max)
A	1	0.50
B	1	0.5
C	0	0
D	1.5	0.5
A+B+C+D	4.5	

Metallurgical cleanliness of the material is an important aspect for SS304L (NAG) and a strict criterion of the inclusion rating has been specified for the material. Table 2 gives information regarding the inclusion rating requirement measured as per ASTM E-45.

Quantification of the corrosion rates is required for identification and selection of suitable material using relevant corrosion test method. As ASTM A 262 IGC Pr C specifies the method to evaluate corrosion rates in boiling HNO_3 medium, simulating the process medium in the back end of the fuel cycle, the same is used to qualify the material for the application. Maximum permitted corrosion rates when tested to IGC Pr C is 10 mils per year (mpy) for all product forms *viz.* plates, pipes, tubes, rods etc. The equipment is of welded construction and the IGC Pr C is specified even for the welding consumables and weldments. Commercially available material generally does not meet the IGC Pr C requirements as specified above necessitating the manufacture of special heats and lots.

Materials for special Applications

a. Materials for High Temperature Application: High level waste management process involves use of glass matrix and the process requires very high temperatures (950-1000°C). For such aggressive process conditions, material with high nickel and chromium contents (Alloy 690) is employed. The high temperature requires good creep & oxidation resistance under corrosive glass environments and Alloy 690 exhibits excellent properties to sustain in such environments. Therefore, equipment subjected to high temperature glass environments are made using this alloy *viz.* Process Pot, Susceptor, Electrodes etc.

(b). Materials for treatment of Alpha Bearing Waste: Alpha bearing wastes are extremely challenging to manage and process. Ag (II) Mediated Electrolytic Dissolution process in 8 M nitric acid was used to manage such wastes in the Alpha Demonstration Facility (ADF) at WIP Trombay. The process medium is highly aggressive, and most metals will not survive the highly oxidizing environment of the process medium. Polyvinylidene Fluoride (PVDF) is a material which exhibits excellent corrosion resistance in such highly aggressive media and was tested in a simulated process environments. In the laboratory tests, the PVDF showed excellent performance and it was found to be unaffected in the process medium and was thus selected for the construction. Accordingly, process equipment (reactor and generators) with PVDF coting on SS304L material were designed, developed, and successfully deployed for the ADF. The performance of the material and equipment in the ADF has been satisfactory. Alternate materials for such process medium are Titanium or Zirconium alloys. PVDF is an economical option of material of construction for such process media.

Fabrication Aspects

Since the equipment, once hot commissioned, becomes inaccessible for any maintenance, utmost diligence is required during fabrication. The above requirement is adhered to by an elaborate Quality Assurance Plan (QAP) with constant monitoring at various stages during fabrication. Special attention is given to the orientation and technical briefings to the supplier engaged to enable an understanding of the specialized requirements. It is imperative that contamination from iron and chloride is prevented. Hence, fabrication is permitted only in clean and dust free shop floor dedicated for stainless steel works. In addition, cross contamination from other nearby carbon steel jobs either direct or indirect through tools and tackles must be prevented. At various stages, special test procedures are also performed to check and eliminate contaminants (iron and chloride).

Forming of the stainless steel material in various raw material product forms e.g. plates, pipes etc. must be carried out to obtain usable shapes like shell, dished ends, bends, coils etc. By design, it is ensured that the resultant strains in the components are minimized. In case of unavoidable excess strains, solution annealing operation is performed to eliminate the effects of the forming. Hardness survey is carried out on the formed components to ensure that the material has not suffered excessive strain hardening, which has detrimental effects on the corrosion resistance of the material.

The process equipment are in welded construction, hence, welding is an essential stage of the equipment during manufacturing. The process of welding must be qualified as per the provisions of the ASME Section IX codes and also for special requirements like delta ferrite and IGC Pr A & C. Gas Tungsten Arc Welding (GTAW) process is adopted owing to its cleanliness and better control. Argon gas of very high purity (min 99.995%) is used to reduce formation of defects in the weldments. The heat input to the job is also controlled by employing lower currents and by minimizing repairs. Local repairs for any spot are permitted only once to minimize Heat Affected Zones (HAZ). Welding consumables are also of special chemistry with controlled range of delta ferrite (4 to 10 FN) which ensures prevention of hot cracks and that the corrosion rates of the weldment is within acceptable range of 10 mpy.

Quality Assurance Aspects

Quality assurance is an essential part of the overall program. The program covers various stages starting from design, construction, installation & operation of all back end fuel cycle facilities to ensure that adequate levels of safety and reliability are achieved concurrent with the designed plant operating life. Accordingly, a well detailed Quality Assurance Plan (QAP) is devised enlisting stages of inspection, parameters, reference standards, acceptance norms and extent of examination. The QAP is the main stay of the fabrication process and is followed in letter and spirit. Experience of the QA engineer also plays a major role hence only experienced personnel are deployed for such critical jobs.

Non-Destructive Examination

Various NDE techniques are employed for implementing QA plan and are performed meeting the requirements of various codes and standards. All the weld joints appearing in the equipment are properly identified before manufacturing and non-destructive examination requirements are listed and defined. A check list of the joints and its completeness with regard to specified NDTs is always maintained. The defect acceptance criteria exceed the specifications in the governing codes. Following examinations are carried out for the equipment during fabrication:

a. ***Visual Examination***: Careful and complete visual inspection of weld joints and parent material is carried out during the inspection. Tools like fiberscope, magnifier, mirrors etc. are used to identify the possible surface defects like deep scratches, roll marks, die marks, dents etc. Inspection of the nozzles from inside is an important aspect because these are thin objects and often, burn through can occur if proper care is not taken during welding and weld-fit up stages.

b. ***Liquid Penetrant Examination***: Defects, that are open to the surface and extremely small in size, can be detected by LPE. Acceptance norms of LPE are very stringent e.g. no indications are permitted on surfaces which are in contact with process medium. While for other surfaces, acceptable indication can be maximum 0.8 mm. The LPE is specified for root weld, final weld, back chipped and refilled surface. The LPE is a specified requirement even for the bevel edges also to eliminate any chances of laminar type of defects.

c. ***Radiography Testing***: Only full penetration butt weld joints are permitted in the pressure boundary of the equipment and 100% radiography is a specified volumetric examination technique for the same. For the equipment, only X-ray is permitted which produces very high quality of radiographic images. Sensitivity requirements of the radiography are also stringent and Image Quality Indicators (IQI) as mentioned in ASME section III Div I NC or NB are selected.

d. ***Ultrasonic Examination***: The through penetrating nozzle joints and corner welds are also checked by ultrasonic testing to stringent acceptance criteria. Ultrasonic examination is performed on the raw material (plate, pipe, tubes etc) to ensure that the raw materials are also free from unacceptable discontinuities.

e. ***Helium Leak Testing***: Heat exchangers, cooling/heating coils and thermowells are some of the most critical components, through which the radioactive contents may come to the inactive areas of plant due to failures. Such components are given special care while manufacturing and are tested by helium leak testing methods.

f. ***Contamination Check Tests***: All equipment are thoroughly pickled and passivated as per approved procedure before closure and contamination check tests are performed. The equipment are checked for contaminations of iron and chloride which are detrimental to stainless steel.

Conclusions

Back end of the fuel cycle facilities deal with high level of radioactivity in a highly corrosive process medium. The equipment is not accessible for maintenance after the hot commissioning of a facility. As such, it is essential to design and fabricate the equipment maintaining strict quality assurance requirements. The raw materials employed for such critical applications must be checked to maintain stringent quality requirements and it is equally important to maintain proper checks during the fabrication stages through an elaborate Quality Assurance Plan. Further, control of contamination is also a very important aspect to protect the equipment from detrimental effects of the contaminants. As a result, process equipment, thus fabricated and deployed in back-end facilities, have quite good track records with satisfactory performance as intended in design.

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MEDICAL APPLICATIONS

RADIOISOTOPES FOR AFFORDABLE HEALTHCARE

Recovery of Valuable Radionuclides from High Level Waste

C. P. Kaushik

Utilization of the radioisotopes in medical applications is one of the prime objectives of the Indian nuclear program. Towards this, radioisotopes have been produced in nuclear reactors through the activation route. Of late, with the development of advanced separation techniques, it is possible to recover the radioisotopes from high level nuclear waste for medical applications. The high level waste generated from reprocessing the spent fuel contains many radioisotopes in significant quantities as produced during the fission of ^{235}U.

Table 1 lists some useful fission products present in the high level waste. Successful recovery and utilization of these isotopes in medical applications have led to the concept of treating nuclear waste as a source of wealth[1].

Towards utilization of radioisotopes, India has taken the lead role for their bulk scale recovery from high level waste. Further, the recovered isotopes are purified in a radio-chemically pure form meeting stringent regulatory limits.

Recovery of ^{137}Cs is accomplished through a novel solvent extraction-based process utilizing 1, 3-di-n-octyloxy Calix[4] arene-Crown-6 (CC6) in isodecyl alcohol (IDA)-dodacane solvent system. Stripping of Cs from the loaded organic phase is carried out using dilute nitric acid. The cesium rich product stream is further concentrated and used to make Cs glass pencils for gamma irradiation applications.

^{90}Y ($t_{½}$=64 h), produced from the beta decay of ^{90}Sr ($t_{½}$=30 y), has unique application as a radiopharmaceutical in treating liver cancer and neuroendocrine tumours. A series of separation processes has evolved towards isolation of the radioisotope to meet stringent purity requirements for nuclear medicine. The bulk separation of ^{90}Sr from Cs-lean HLW is carried out by solvent extraction using Tetra Ethyl Hexyl Di-Glyco Amide (TEHDGA) in IDA-Dodecane. It is to be noted that TEHDGA is used for the co-extraction of actinides (An) and Lanthanides(Ln) along with Strontium(Sr) from high active acidic streams. The stripping of the radionuclides from the loaded TEHDGA phase is carried out using dilute HNO_3(0.01 M).The product, Sr-An-Ln rich, is further concentrated and used for recovery of bulk amount of Strontium. Multi-step separation processes for the purification of Sr deployed involving solvent extraction by CMPO followed by chemical precipitation. The recovered Strontium product is used for milking out Yttrium-90 (^{90}Y).

^{106}Ru is in secular equilibrium with its daughter ^{106}Rh. It is a source of high energy beta radiation emitted from the decay of 106Rh to stable Pd and is useful for brachytherapy applications, particularly for eye cancer treatment. Separation of ^{106}Ru is carried out from post TEHDGA cycle raffinate as discussed above. The process utilizes oxidation of Runitrosyl nitrate to RuO_4 by KIO_4 followed by extraction of RuO_4 in chlorinated CCl_4. Finally, the extracted Ru is stripped from CCl_4 using acidic hydrazine solution. Preparation of brachytherapy source from purified ^{106}Ru solution includes electro-deposition of ^{106}Ru on a silver substrate followed by the production of sealed sources in the form of a plaque.

Subsequent articles of this segment highlight the medical applications of these three fission products.

Table 1: A list of valuable radionuclides present in the HLW

Radioisotopes	Half - life	Radiation type	Energy (MeV)	The primary area of applications
Cesium ^{137}Cs	30 y	Gamma (after emitting a Beta radiation)	0.66	Blood irradiation
Strontium/Yttrium $^{90}Sr/^{90}Y$	28 y/64 d	Beta	0.5 and 2.28	90Y used as a Radio-pharmaceutical for treatment of liver cancer, bone pain palliation
Ruthenium ^{106}Ru	365 d	Beta	3.54	Eye cancer (Brachytherapy)

Cesium-137 Glass Pencil Source for Blood Irradiators

C. P. Kaushik

Production of ^{137}Cs based blood irradiators is one of the examples of the successful deployment of radioisotopes recovered from High-Level Radioactive Waste (HLW) in medical industry. With this development, India has become the first country in the world to deploy ^{137}Cs in non-dispersible glassy form as the source in blood irradiators. This development will eventually replace the existing 60Co based blood irradiators in the country and abroad. The use of ^{137}Cs in blood irradiators is advantageous due to the its longer half-life, which reduces source replenishment frequency and man-rem consumption. Further, it is possible to build compact irradiators due to lower shielding requirement. Irradiation of blood to prevent Transfusion Associated–Graft Vs Host Disease (TA-GVHD) has to be done just before its transfusion to immuno-deficient patients like newborn babies, patients undergoing heart or bone-marrow transplant and immune-competent patients who have 1st degree relation with donor. This necessitates placement of irradiator within the hospital premises. The smaller footprint for housing the blood irradiator will, thus, be beneficial especially to small hospitals.

Production of ^{137}Cs-glass source for blood irradiator envisages industrial scale recovery of this radio element from high-level radioactive waste and its subsequent immobilization into a specially formulated glass matrix. Such non-dispersive glassy form of caesium is then metered into the small-sized stainless-steel pencils and sealed by remote welding. Post sealing, pencils are subjected to over packing, surface decontamination and stringent quality assurance checks, at par with international standards (Fig.1). Each pencil contains about 200 g of Cs-glass, amounting to about 300 Ci of ^{137}Cs. More than 200 numbers of Cs-glass pencils have been produced successfully till date

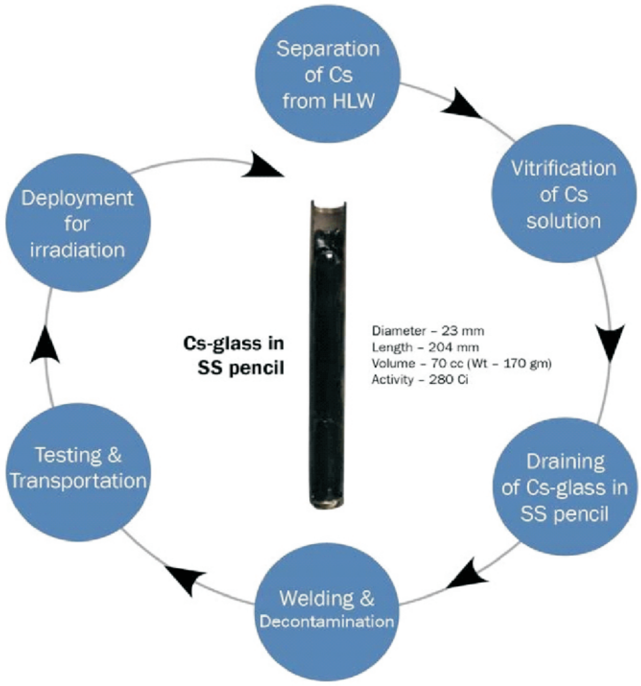

Fig.1: A thumbnail view of ^{137}Cs glass-pencil making process.

Fig.2: Stock image of ^{137}Cs based Blood Irradiators (BI-2000).

Qualified Cs-pencils are transported to BRIT for deployment in blood irradiators and subsequent supply to different hospitals. Each blood irradiator houses ten such pencils in a circular cage. This provides a dose-rate of about 11 Gy/minute, suitable for irradiating a standard blood bag within 3 minutes, with an estimated absorbed dose of about 30 Gy. Fig.2 shows the photograph of the ^{137}Cs based irradiator (BI-2000). At present, more than fifteen such irradiators are in use at leading hospitals of the country.

Clinical Grade ^{90}Y-acetate from Ultra-pure ^{90}Sr

C. P. Kaushik

Yttrium-90, a pure β-emitter (E_{max}=2.28MeV, $T_{½}$ = 64.1h) formed by β- decay of ^{90}Sr,is a potential therapeutic radionuclide. It is widely used in the treatment of hepatocellular carcinoma (HCC), leukaemia, lymphoma, and a range of tumours. Application of ^{90}Y is dependent on the supply of carrier-free, clinical-grade ^{90}Y, which can be separated from highly pure ^{90}Sr.

Ultra-pure ^{90}Sr is being separated from the product streams generated during the partitioning process of HLLW employing a multi-step separation technique using solvent extraction, extraction chromatography, radiochemical precipitation and membrane separation. An indigenously developed two-stage SLM based ^{90}Sr-^{90}Y generator system is utilized for milking carrier-free ^{90}Y [Fig. 1]. The radionuclide impurity of the separated ^{90}Y-acetate product has a β-content of ^{90}Sr less than 10^{-6}Ci/ Ci of ^{90}Y and gross α-activity less than 10^{-9}Ci/Ci of ^{90}Y,which is well within the permissible limit as per the European Pharmacopia. The separated clinical-grade carrier-free ^{90}Y is supplied to Radiation Medicine Centre (RMC), Parel, for cancer therapy.

Fig.1: ^{90}Sr-^{90}Y generator.

Extensive studies were undertaken to optimize various parameters for the transport rate and purity of ^{90}Y products in the generator system. Based on these studies, clinical-grade ^{90}Y-acetate in lots of ~140 mCi are regularly (about 15 lots per year) separated and transported to RMC, Parel, following BSC approved transport guidelines, for therapeutic applications. The feedback received from RMC on the purity and effectiveness of the separated ^{90}Y was excellent. Developmental studies for scaling up are under progress to meet the rising demand for ^{90}Y supply.

RuBy plaque and Simulation Software for Eye Cancer Treatment

C. P. Kaushik

Nuclear Recycle Group of Bhabha Atomic Research Centre has indigenously developed Ruthenium Brachytherapy (RuBy) Plaque for the treatment of eye cancers. RuBy plaque contains Ruthenium-106 radioisotope. The unique radiochemical characteristics of the radioisotope such as emission of high energy beta radiation (3.54 MeV) and rapid beta radiation dose rate fall off make it useful for selective killing of cancer cells without damaging the healthy organs of the eye.

RuBy plaques of two different configurations (round and notched) have been successfully deployed for the treatment of eye cancers. Round plaque is used commonly whereas notched configuration is suitable for the treatment of eye cancers located adjacent to the optic nerve. The first use of the indigenous plaque was carried out on 21st August 2019 by Dr. Santosh Honavar at the Centre for Sight Hospital, Hyderabad for treating a patient with ocular surface squamous neoplasia and the results were very encouraging with no evidence of local tumor recurrence, well-maintained and complete vision. Presently, RuBy plaques are being used at seven hospitals in the country (see Table 1) and more than fifty patients have been treated. All post-treatment results are highly satisfactory, confirming the fact that RuBy plaques have gained the trust of doctors and patients alike. More hospitals are progressively adopting RuBy plaques for better and cost-effective treatment of eye cancer.

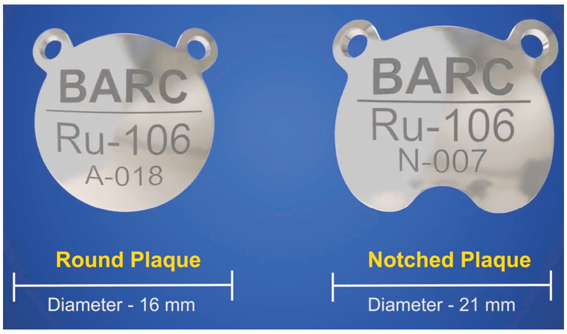

Fig.1: RuBy plaques for the treatment of eye cancers.

Table 1: List of hospitals using RuBy plaques

1	Centre for Sight Hospital, Hyderabad
2	Sankara Eye Hospital, Bangalore
3	RP Centre, AIIMS, Delhi
4	Army Hospital, Delhi
5	Ramakrishna Eye Hospital, Coimbatore
6	Hinduja Hospital, Mumbai
7	Fortis Hospital, Haryana

Complementing the RuBy plaques, NRG, BARC has also developed Plaque Simulation software to assist doctors with optimal treatment planning. The software provides an easy-to-use interface for calibration and dose rate distribution of the RuBy plaques. Fig.2 shows software predicted dose-rate distribution for a given tumor irradiated by a RuBy plaque. It predicts treatment duration and dose received by other healthy parts of the eye. This information is useful for the convenient and optimal planning of treatment for eye cancer.

Indigenous development of RuBy plaques and the Plaque Simulator are breakthroughs in the area of AtmaNirbhar healthcare and providing affordable treatment to eye cancer patients in India. RuBy plaques are marketed by the Board of Radiation & Isotope Technology (BRIT). Detailed information about the products is available at *"www.britatom.gov.in"*.

Input parameters	
Plaque ID	: A59 (Round plaque)
Activity	: 31.5 MBq as on Jan 27, 2021
Tumor radial dimension	: 8 mm
Tumor thickness	: 6 mm
Results	
Date of implant	: Sep 5, 2021
Ave dose rate	: 148 mGy/min
Apex point dose	: 100 Gy
Implant duration	: 35 h
Foveola point dose	: 26 Gy

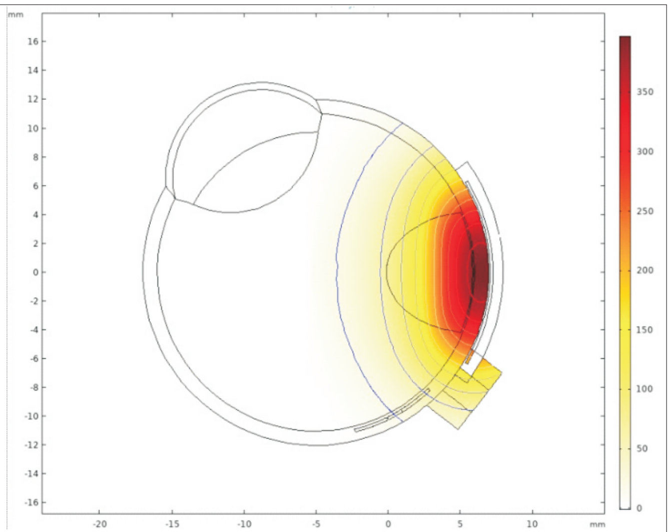

Fig.2: A typical results generated from RuBy Plaque simulator for a given tumor treatmnet by a RuBy plaque.

RESEARCH AND DEVELOPMENT

Advanced Treatment Process

Process Development in Back-end of Fuel Cycle

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Alpha Demonstration Facility in Waste Immobilisation Plant in Trombay

ABSTRACT

The activities in the back-end of nuclear fuel cycle demand sustained process development for meeting various challenges faced during spent fuel reprocessing and radioactive waste management. Adaptation of innovative process schemes and novel solvents has not only simplified the management of HLLW but also opened up a new dimension towards the beneficial applications of many of these radioactive isotopes in various medical and industrial radiation technology applications in concurrence with our mission of serving the nation and society through peaceful uses of nuclear energy. This article highlights some of the recent developments in the back-end of nuclear fuel cycle.

KEYWORDS: *Pyrolysis, Incineration, Advanced oxidation, Decontamination, Novel solvents, Functionalized resin.*

Introduction

The back-end of the Indian nuclear fuel cycle involves essentially spent fuel reprocessing and associated waste management activities. Process development in the back-end assumes greater importance to meet evolving requirements of higher productivity, improved product quality and enhanced safety. The reprocessing technology in the country has reached maturity at the industrial level with a very high recovery rate. Safe and economically efficient back-end operations that can further minimize waste generation and environmental impact are essential to the sustainable development of nuclear energy programmes. Sufficient scope exists to improvise processes and technologies with innovative approaches for significant reduction in radio-toxicity and hazard posed by radioactive substances to humans and the environment.

Process Development for the Management of Alpha-Contaminated Waste

Various types of cellulosic, polymeric and metallic wastes are generated during the glove box operations at fuel fabrication as well as at the back-end facilities. These wastes are currently stored at interim storage facilities pending treatment. Recovery of valuables and reduction in the waste volume are quite challenging while developing suitable treatment methods. Significant efforts have been geared towards process development for the treatment of aged cellulosic waste. To make the decontamination process more energy-efficient for treating polymeric and cellulosic waste, pyrolysis-incineration is envisaged prior to the decontamination step. Glove box adaptable modules for the pre-treatment step consisting of shredding, homogenizing and conveying of non-metallic waste in a continuous mode to the pyrolyzer and incinerator followed by combustion of off-gas in an afterburner. Performance of these modules have been demonstrated by feeding the shredded waste comprising 10% cellulose, 35% rubber and 55% PVC to a pyrolyzer followed by an incinerator to produce ash with an overall volume reduction factor of 25 (Fig. 1).

Process Development for Combined Removal of Ruthenium and Antimony

The philosophy followed for the management of waste streams containing short-lived fission products like Ruthenium (^{106}Ru) and Antimony (^{125}Sb) is either delay and decay by storage or dilute and disperse by discharging to water bodies meeting the regulatory criteria. A chemical precipitation process was developed for simultaneous removal of Ruthenium and Antimony with a DF > 300 for the acidic Intermediate Level Waste (ILW) generated during high-level waste management at Trombay. An international patent has been applied for the developed process. The same process was tried for Low Level Waste (LLW) generated from DHRUVA. Experiments carried out using declad waste containing citrate showed Ru removal of 50%, while declad waste without citrate resulted in ~95% removal.

Ozone-based Treatment of DBP-bearing Simulated Carbonate Waste

Ozone-based advanced oxidation processes use ozone to destroy a variety of organic compounds mainly to CO_2 and H_2O [1]. These processes offer a salt-free treatment of a given waste stream, thus minimizing the secondary waste volumes. One such process has been developed for pre-treatment of di-butyl-phosphate (DBP) bearing carbonate waste and is demonstrated on a 50 L scale. Ozone generated from air is used to destruct the DBP content of simulated waste from 4.3 to 0.3 g/L in 14 hours as shown in Fig. 2. A slight decrease in pH during the treatment was also observed, which could be attributed to the formation of equimolar quantities of H_3PO_4 during ozonation.

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 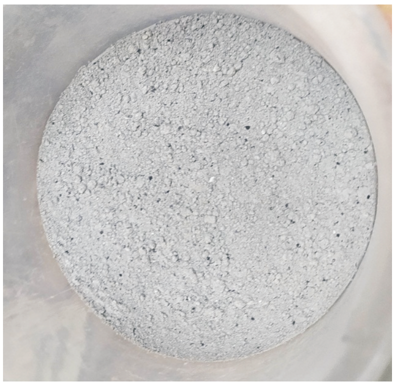

Fig.1: Pyrolysis-incineration process for management of GB waste.
(Left: Shredded feed to pyrolyzer and Right: Ash product from incinerator)

Sequestration Process for Tc Removal from LLW

It is well known that TcO_4^- removal from the LLW is difficult and challenging due to the presence of other monovalent anions like, NO_3^- and OH^-, which competes with TcO_4^- during separation processes. In this regard, a novel process for Tc sequestration by in-situ formed corrosion products of mild steel was developed and patented [2]. Based on the encouraging results on active and inactive studies at BARC, engineering scale studies were carried out at LWTP, Tarapur jointly by NRG & NRB. Tc sequestration process was demonstrated on a plant scale with 90-95% ^{99}Tc removal. After carrying out a few runs for fine-tuning, DF of 200 was obtained for ^{99}Tc. Decant activity after sequestration treatment was found to be in the order of 10^{-4} mCi/L.

Electro-Brush Method for Removal of Fixed Contamination

Removal of fixed alpha contamination on metal surfaces requires aggressive chemical/mechanical techniques. Secondary waste generated by these methods is difficult to manage by conventional routes [3]. To address this issue, an inherently safe electrolytic decontamination method using a movable cathode (electro-brush) was developed. By this method, effective decontamination was obtained with minimal secondary waste generation. Initial inactive trials were carried out using various nitric acid concentrations and current densities. The optimum corrosion rate was observed at 4M HNO_3 concentration and 200 mA/cm^2 current density. Active trials were performed with alpha planchets having fixed contamination, and up to 99% decontamination was recorded in 10-20 min. Based on these, active decontamination studies were jointly carried out between NRG & NRB. Stainless Steel surfaces were successfully decontaminated by removing all loose & fixed contaminations to a level of alpha activity < 0.037 Bq/cm^2.

Chemical precipitation process developed for simultaneous removal of Ruthenium and Antimony can be effectively used for the management of acidic Intermediate Level Waste.

Development of New Solvents and Resins with Chemically-bonded Ligands

Development of novel solvents and their successful deployment at the back end of the nuclear fuel cycle established an innovative strategy for managing high-level liquid waste (HLLW). The use of such highly specific solvents was aimed at better waste management, and the recovery of some radioactive isotopes deemed beneficial for societal applications. The current radionuclide partitioning process followed in India is based on the application of two crucial solvents, *viz.*, (i) 1,3-dioctyloxycalix[4]arene-18-crown-6 (Calix-Crown-6) for the recovery of ^{137}Cs and (ii) Tetra-2-Ethylhexyl-Diglycolamide (T2EHDGA) for bulk separation of trivalent actinides and lanthanides [4, 5]. Further, the separation between trivalent actinides and lanthanides from TEHDGA strip products is carried out by an improved TALSPEAK process for obtaining pure actinide products.

Consequent to the successful deployment of the above two solvents, recent R&D has been focused on the development of newer solvents with the objectives of process simplification and recovery of valuable radioisotopes with better product purity. Towards this, work has been taken up for the commercial synthesis of 4',4"(5")-di-tertiary-butyl-dicyclohexano-18-crown-6 (DtBuDCH18C6). DtBuDCH18C6 is a solvent that is highly selective for Strontium [6]. Laboratory scale evaluation of the solvent has conclusively confirmed that DtBuDCH18C6 extracts ^{90}Sr directly from HLLW. This ^{90}Sr is used to generate ^{90}Y, which has tremendous applications as radiopharmaceuticals for cancer treatment. In a similar approach, a new solvent Camphor Bistriazinyl Pyridine (CA-BTP), has been investigated for trivalent lanthanide-actinide group separation. Process evaluation utilizing CA-BTP has shown very high separation factors (~90) for trivalent lanthanide-actinide group separation. The synthesis and purification of this solvent have been carried out in-house, and the procedures for its scale-up have been optimized.

A functionalized resin has been synthesized with ligand chemically bonded upon a supporting material. The resin has been tested in batch mode. It shows a very high uptake for trivalent (Am^{3+} , Eu^{3+} & Y^{3+}), tetravalent (Pu^{4+}) and to some extent, hexavalent (UO_2^{2+}) metal ions but almost

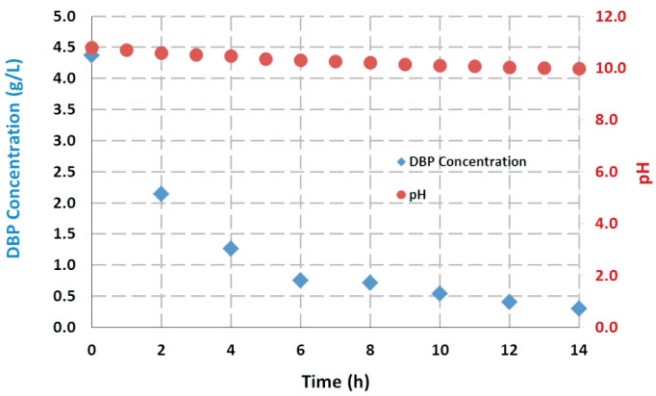

Fig.2: Di-butyl-phosphate (DBP) concentration. pH versus time plot.

negligible uptake for divalent metal ion (Sr^{2+}) from a feed acidity of 4.0 M nitric acid. The K_d values for the resin is in the range of ~3500 - 4000 mL/g for Am & Eu, Y and ~8 – 10 mL/g for Sr. Elution of Eu-loaded resin has also been carried out at pH~2 and 60% was eluted in 1st contact. Cumulative stripping of 98% was obtained in three successive contacts. The stability of the resin in the nitric acid medium was assessed by keeping the resin in nitric acid for 10 days continuously and was found to hold the same initial texture, colour and mass. The initial screening of the resin with respect to the extraction & elution behaviour of different metal ions shows potential for separation of Sr from TEHDGA-strip solution and for milking of ^{90}Y, from recovered ^{90}Sr from HLLW.

Conclusions

Process development is a continuous activity to meet the evolving requirements in the back-end of nuclear fuel cycle. Pyrolysis and incineration system has been developed for effective treatment of alpha contaminated polymeric and cellulosic wastes. Engineering scale demonstrations of ozone-based treatment process and Technetium sequestration process confirm their amenability for industrial deployment.

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Development of Head-end Equipments for High Throughput Plant

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Continuous Rotary Dissolver

Hull Rinser

ABSTRACT

India has gained sufficient experience and maturity in all aspects of spent fuel reprocessing required for closing the fuel cycle. Nuclear Recycle Group (NRG) has undertaken developmental efforts for improved equipment, which are required for a higher throughput plant in order to meet the rising demands in spent fuel reprocessing. A brief account of these developmental efforts related to head-end equipment namely Spent Fuel Chopper, Continuous Rotary Dissolver, Centrifugal Clarifier and Hull Rinser is presented in this article.

KEYWORDS: *Reprocessing, Head-end, Spent fuel, Shearing, Dissolution, Rinsing.*

Introduction

Spent fuel reprocessing is an important step in the closed fuel cycle adopted in the three-stage nuclear power programme of India. Closing the fuel cycle enables recovery of plutonium and unused uranium. The technology for reprocessing was developed and established indigenously, consisting of head-end operations, solvent extraction followed by purification and reconversion. After gaining sufficient knowhow of spent fuel reprocessing, efforts were taken up by NRG to develop improved equipment to meet the requirements of high throughput reprocessing plants. This article describes the efforts undertaken for the development of high throughput head-end equipment and the present status.

Head-end Operation

Head-end operation constitutes the first stage of spent fuel reprocessing. It involves operations such as fuel receipt and storage outside the hot-cell and fuel charging, spent fuel chopping, dissolution, feed clarification and hull management operations inside the hot-cell. The design of equipment for hot-cell operation is challenging due to highly acidic and radioactive environment. Amenability for remote handling and maintenance is also an important feature of hot-cell equipment.

Spent Fuel Chopper based on Gang Chopping

Spent Fuel Chopper (SFC) is used for shearing the fuel bundle or pins into small pieces thereby ,exposing it to leach acid for dissolution. The spent fuel chopper in PREFRE-I and KARP was based on a concept of progressive feeding, clamping and cutting of fuel with a single shear blade. Valuable experience was gained through operation and maintenance of these SFC's over the years. These experiences have helped in conceiving a novel SFC based on a new gang chopping concept[1].

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The SFC (Fig.1) comprises of fuel feed system, fuel shearing system, fuel positioning system, distribution system and hydraulics. The feed system is designed to house 10 Nos. of 220 MW PHWR fuel bundle. The fuel pushing is done with a chain pusher actuated by a hydraulic drive unit. The fuel shearing unit consists of a single shear module with a set of moving blades and fixed blades. The moving blades are mounted on carrier plates actuated by a pusher ram. The fuel positioning unit is designed to receive and position the complete fuel bundle between the cutting tools. The hydraulic unit consists of single hydraulic cylinder assembly with moving cylinder and stationary piston arrangement. The moving cylinder transmits the force to moving tool assembly via a pusher ram. The fuel distribution system controls flow of the cut pieces of fuel to dissolver-1 or dissolver-2. All the components within the hot-cell , like the shear module components, transfer system, pneumatic cylinders for distributor system, etc have been designed for remote handling using aids like in-cell crane, master slave manipulator, power manipulator etc. The hydraulic actuators and power packs, PLC and control panel are located in operating area freely accessible for maintenance. The system is provided with necessary PLC based controls with safety interlocks based on the feedback from the field sensors like reed switches and limit switches.

Fig.1: Spent Fuel Chopper Assembly.

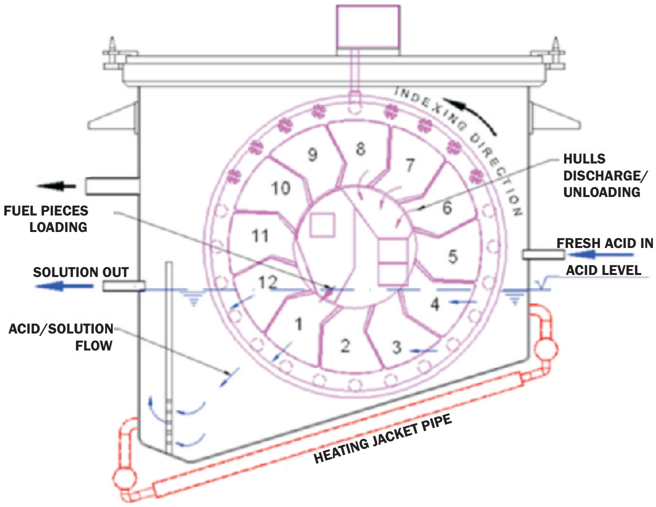

Fig.2: Schematic of Continuous Rotary Dissolver.

Fig.3: Continuous Rotary Dissolver

The SFC based on the gang chopping concept was installed in PREFRE-2, Tarapur and KARP-2 Kalpakkam. This has significantly enhanced the throughput of the present operating plant. The modular design of internals has reduced maintenance down time considerably.

Continuous Rotary Dissolver

Reprocessing plants in India presently employ batch dissolution process. In the batch mode of operation, sheared fuel pieces are received into a perforated basket within the dissolver limb. The core of the fuel segments gets dissolved when it comes in contact with the leach acid. The dissolved solution is subsequently transferred for further processing while the basket containing the hulls is handled remotely for its interim storage. While the process is simple and reliable, there are a few disadvantages with respect to large throughput plants *viz.*, poor utilization of dissolver during heating and cooling cycles of each batch, large chunk of stagnant fuel pieces resulting in longer duration for dissolution, unsteady off gas production and design of equipment managing the off gas for maximum rate. To address these drawbacks and to meet the requirement of future high throughput plants, NRG has initiated the development of continuous dissolver[2].

The Continuous Rotary Dissolver (CRD) developed by NRG is based on periodically indexing bucket wheel assembly (containing cut fuel pieces) within a slab tank partially filled with leach acid (nitric acid). The cut pieces of fuel are fed to a perforated bucket in loading position which undergoes dissolution in the acid bath while the buckets are immersed in acid. The hulls are discharged when buckets emerge out of the acid bath and attains unloading position as the wheel indexes (Fig.2). The central portion of the wheel assembly consists of a chute, which directs the cut pieces towards the bucket in loading position and discharges the hull from the buckets in unloading position.

A prototype CRD with processing capacity of 400 T/y was designed, manufactured and installed at CDCFT, WIP. The unit (Fig.3) was designed to meet the requirements of remote operation and maintenance. The maintenance prone components are part of a removable assembly which is amenable for remote handling. The removable assembly consists of bucket wheel, top lid and central chute assembly. The fixed part of equipment consists of main vessel (slab tank) and connected process & instrumentation piping. The drive mechanism is designed to have the major components out of the cell connected with the equipment through a remote coupling.

Mechanical loading trials, thermal-hydraulic studies, mathematical modelling of dissolution in continuous mode and remote handling trials were carried out. Based on the operational feedbacks, modified roller, hybrid air lift for management of fines[3] etc. were developed. A scaled down model of CRD has been manufactured for carrying out process evaluation with depleted uranium. NRG has gained sufficient knowhow and experience to design and deploy continuous rotary dissolver in upcoming plants.

Centrifugal Clarifier

The solution resulting from dissolution of spent fuel contains Zircaloy fines (resulting from chopping), insoluble residues of fission products such as of Mo, Tc, Ru, Pd etc., and crud introduced with fuel assembly. Feed clarification practised in the present plants is by means of vacuum assisted filtration using disposable filter elements. The filter element needs to be replaced after every batch of ~1.2 T of HM and thereby, results in large amount of secondary waste for high throughput plant. Frequent replacement of filter element also increases remote handling operations. Development of centrifugal clarifier for feed clarification application was taken up by NRG[4] to address these concerns. Centrifugal separation is a mechanical means of separating the components of a two-phase system by accelerating the material in a centrifugal field. The Centrifugal Clarifier comprises of a solid cylindrical bowl rotating at high speed. Slurry of liquid and suspended solids is fed to a fixed position within the bowl, and is accelerated outward to join the pool of liquid held on the bowl wall by the centrifugal force. This same force then causes the suspended solids to settle, and accumulate at the bowl wall. The clarified liquid then flows along the bowl, to leave at one end of it, over a weir which sets the level of the liquid surface in the bowl. An engineering scale

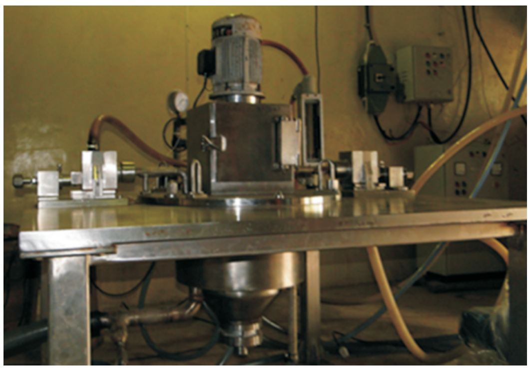

Fig.4: Centrifugal Clarifier.

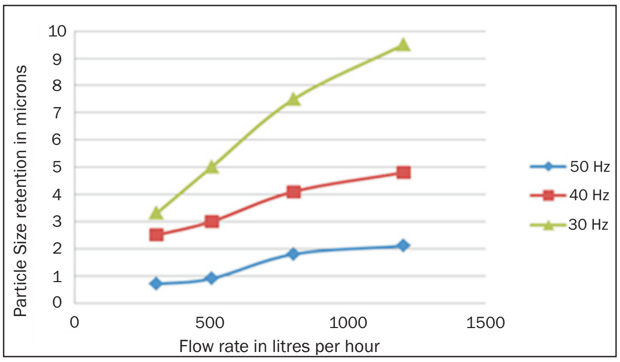

Fig.5: Particle retention characteristics.

prototype was designed, manufactured and installed at CDCFT building (Fig.4). The performance evaluation of system was carried out with simulated feed solution in a test loop. The samples of clarified solution were collected and analyzed for particulates present using DLS and SEM analysis. The results are shown in Fig.5. Remote handling trails were also carried out to check the amenability for remote maintenance.

Based on the trials carried out and experience gained, it can be concluded that system is capable of separating particulates of 2 micron at feed rate of 1200 LPH when operated at 50 Hz. At lower flow rates better clarification can be achieved. The prototype has a dirt holding capacity of 4 kg and the self-cleaning feature of the clarifier performed as intended.

Hull Rinser

Future reprocessing plants with automated head-end process will require automated hull rinsing equipment. The equipment shall receive the hulls from continuous rotary dissolver without disturbing the negative pressure atmosphere, rinse it to remove any loose particulate sticking and discharge it into drum which can be sent for disposal or interim storage. This will eliminate all the manual remote handling operation practiced in the present operating scheme.

NRG has under taken the development of Hull Rinser[5] based on the concept of movement of hulls upward along a helical path in a rinsing medium. The motive force for this upward movement is directional vibration achieved by means of a vibratory motor. The system consists of helical trays made of structural material, a pair of vibratory motors mounted diametrically opposite to central base cylinder, parallel but with 90°phase difference. During operation one of the motor rotates clockwise while the other in anti-clockwise direction. This creates a vibration which assists the movement of vibrating hulls in the desired direction. As the hulls are transferred due to vibration while immersed in rinsing liquid, the dual purpose of transfer of hulls as well as rinsing could be achieved simultaneously. An engineering scale prototype of Hull Rinser was manufactured and installed at Engineering Hall of CDCFT building (Fig.6). The performance evaluation of the system was carried out with simulated hulls and observations were recorded. Based on the performance evaluation carried out, it can be concluded that the operation time, rinsing effectiveness and amenability to remote operation and maintenance makes it suitable for automation of head-end operation for a large throughput plant. Valuable feedback was obtained during manufacturing and trials of the prototype which will aid in finalizing the design as per cell layout.

Fig.6: Hull Rinser

Conclusions

The development and deployment of Spent Fuel Chopper based on gang chopping concept is testimony to indigenous effort for improvement of system for higher throughput. The development of Continuous Rotary Dissolver, Centrifugal Clarifier and Hull rinser have been carried out with similar intension to meet the requirement of head-end operation for high throughput plant. Based on the experience gained after performance evaluation of these prototype equipment, NRG is in position to design and deploy plant adaptable units based on site requirements.

Acknowledgements

The development of head-end equipment would not have been possible without the motivation and guidance from S. D. Misra, Former Director, Nuclear Recycle Group, K. N. S. Nair, Former Head Technology Development Division, K. Banerjee Former Associate Director, Nuclear Recycle Group and D. A. S. Rao, Former General Manager, Nuclear Recycle Board. The fabrication and QA aspects for the equipment and control of quality during manufacturing activities was made possible with the support of P. D. Maniyar, Head Nuclear Recycle Group Projects and S. S. Khan, former Head Hot Cell Engineering Section, Technology Development Division, and we are thankful to them for the same. We would also like to thank Jyoti Jha, Shashi Kumar, M. H. Rao, Shakti Mishra, B. R. Meena, Partha Mazumdar, M. Dhoiphode, D. D. Pawar, V. G. Karande, Mahendra Wagh, Abhilasha Prajapati and Surekha Deolekar for their continuous cooperation and assistance during various stages of these developmental activities.

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Vitrification Technologies

Development and Demonstration of Cold Crucible Induction Melter

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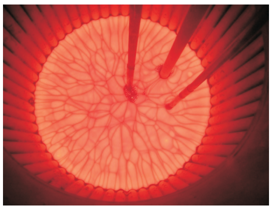
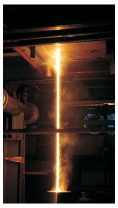


Molten glass pool inside Cold Crucible Induction Melter



Glass pouring

ABSTRACT

Indigenous development of cold crucible induction melter was taken up to address various limitations of induction-heated metallic melter and Joule-heated ceramic melter used for vitrification of high level liquid waste. Industrial scale prototype of cold crucible induction melter was developed based on the lab scale and bench scale experimental studies. Based on the operational feedbacks, a plant adaptable cold crucible induction melter was designed, fabricated and tested to demonstrate its remote operation and maintenance features for implementation in waste immobilization plant for vitrification of high level liquid waste.

KEYWORDS: *Cold crucible, Induction melter, Melter technology, Vitrification, High level waste.*

Introduction

Development of cold crucible induction melter (CCIM) technology for vitrification of radioactive liquid waste was pursued globally as it offers several advantages such as long melter life with high temperature availability and high waste loading compared to other melter technologies, *viz.*, induction-heated metallic melter (IHMM) and Joule-heated ceramic melter (JHCM)[1- 4]. In cold crucible induction melting, glass is directly heated by electromagnetic induction employing a segmented, water-cooled crucible. Internal water cooling of the segmented crucible produces a solidified glass layer, which prevents the metallic components from directly coming into contact with highly corrosive molten glass and thereby, provides long melter life. High processing temperature available with the CCIM results in high throughput per unit heat transfer area compared to IHMM and JHCM. By virtue of its structure and compactness, dismantling and decommissioning of CCIM is relatively easier compared to JHCM both in terms of remote operations involved and secondary waste generation. In view of the above mentioned advantages, indigenous development of CCIM technology was undertaken by NRG[5- 8].

Indigenous Development of CCIM Technology

Indigenous development of CCIM technology began with laboratory scale experimental studies to demonstrate the proof of concept and assess the overall thermal efficiency of the process. A segmented copper crucible with an inner diameter of 50mm and comprising 14 segments was employed for this purpose. Based on the experimental results, the overall efficiency of the cold crucible induction heating was observed to be ~17% [5]. Subsequent to the successful demonstration of the laboratory scale unit, a bench scale cold crucible induction melter of 200 mm inside diameter was developed and tested with regard to formation of solidified glass protective layer and glass pouring[5].

An industrial scale cold crucible induction melter with liquid feeding capability was developed to study its performance (Fig.1). The melter essentially has a segmented crucible formed by a circular array of 60 Nos. of SS 304 L tubes of one inch size. These stainless steel cooling tubes are arranged to hold a molten glass pool of 500mm diameter. A water-cooled mechanical plug assembly is used to drain molten glass from the melter. The plug seat protrudes into the melter in order to maintain a minimum amount of molten glass always inside the melter. The exterior of the vertical segments is provided with a 25mm thick casting of high temperature acid resistant refractory cement and a water impervious outermost layer.

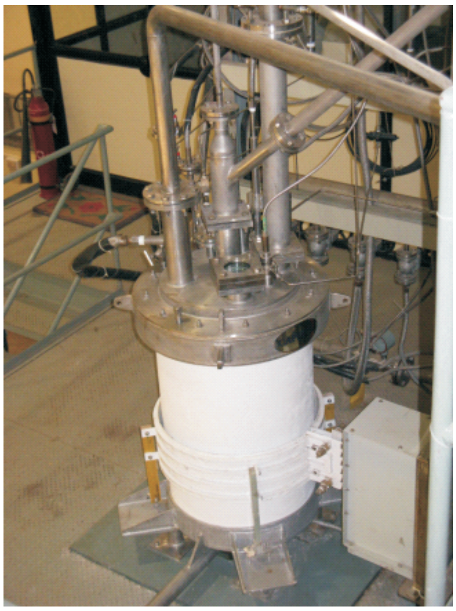


Fig.1: Industrial scale cold crucible induction melter.

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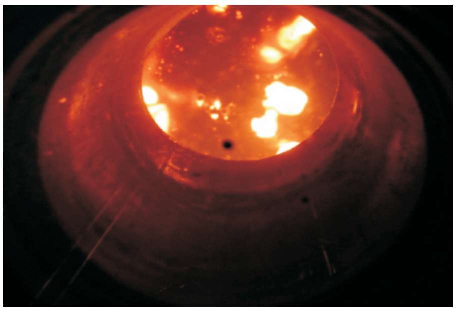
Start-up operation



Feeding operation

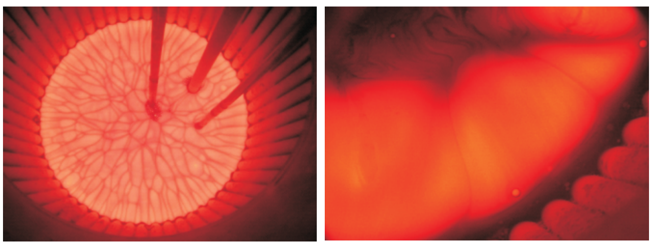
Pouring operation

Fig.2: Different stages of industrial scale CCIM operation.

The industrial scale CCIM was operated for more than 100 operations to assess its performance. The performance evaluation was carried out using sodium borosilicate glass having an electrical resistivity of ~5 Ohm cm at 1000°C. Industrially adaptable operating procedures for start-up, feeding and pouring operations were established (Fig.2). The overall melter efficiency, measured in terms of the ratio of thermal power output available for vitrification to electrical power input, was observed to vary with the glass level in the melter and found to be in the range of 10- 20% for the industrial scale CCIM.

A high temperature sodium borosilicate glass was used for the Cesium volatilization study. 1250 L of simulated waste as per the composition of ROP Tank-6 HLW was prepared with inactive cesium to simulate 20Ci/L activity of the waste stream. The industrial scale CCIM was operated at a temperature of 1250°C with a throughput of 25 lph. Off-gases from the melter plenum were bubbled through a cesium scrubber using a vacuum pump. Samples of cesium scrub solution were collected from the scrubber at different time intervals and analysed for Cs content. In order to compare the Cs volatilization with and without cold cap, liquid feeding was stopped at the end of ~50 hours of operation and heating was continued till melting of the cold cap was completed. The Cs scrub solution was analysed for the Cs content. Based on the experimental results, the cesium volatilization is ~5% when the CCIM was operated at 1250°C with a stable cold cap and ~ 20% without cold cap.

Industrial scale demonstration of CCIM was also demonstrated using high temperature glass containing zinc oxide, as a part of R&D efforts to establish waste form with improved radiation stability with high chemical durability. The melter was operated at 1250°C to achieve an average throughput of 25 LPH with a waste loading of 26%. Fig.3 compares the skull thickness observed for two different glasses–with and without ZnO. The skull thickness observed in the case of glass with ZnO is significantly higher than that of glass without ZnO. This effect is because of the increase in glass viscosity due to ZnO addition. The enhanced skull thickness provides better protection to the stainless steel fingers of the cold crucible.



(a) (b)

Fig.3: Comparison of skull thickness inside CCIM: (a) glass without ZnO (b) glass with ZnO.

Plant Adaptable Cold Crucible Induction Melter

Based on the operational feedbacks, a plant adaptable CCIM with additional features for remote operation and maintenance was developed and demonstrated. The salient features of the plant adaptable CCIM are presented in this section.

Secondary Metallic Enclosure: The plant adaptable CCIM has been provided with a metallic (SS 304L) enclosure for housing the segmented crucible. This secondary enclosure ensures the confinement of the radioactive waste in case of any abnormal operation or accidents. The square enclosure has an outer dimension of 800 x 800mm with its own cooling provision (Fig.4) .

Alumina Coated Metallic Components: As the melter start - up is achieved by remotely inserting a graphite ring into the meter, there exists a rare possibility of this ring coming in contact with the metallic components of the segmented crucible, resulting in an electric arcing. This has been addressed in the plant adaptable CCIM by providing the metallic cooling tubes and pour plug with an electrically-insulating alumina coating of 300- 350 microns and qualifying the insulation characteristics by holiday test for 1 kV (Fig.5).

Redundant Pouring Units: The plant adaptable CCIM has been provided with two pour ports for pouring (Fig.6). A monolith AZS block is provided to fill the dead volume between the base and two pour ports. One of the pour ports is raised by 50 mm as compared to other and is meant for regular pouring operation. This helps to maintain a pool of molten glass available for next batch of operation. The lower pour port is meant for completely emptying the melter at the end of its service life. However, the lower pour port can be used for normal pouring in case of non-availability of regular pour port.

Remotely Operable and Maintainable Pouring Mechanism: The pouring in industrial scale CCIM was achieved through actuation of mechanical pour plug using pneumatic actuator.

Fig.4: Secondary metallic enclosure.

Fig.5: Alumina cooling tubes.

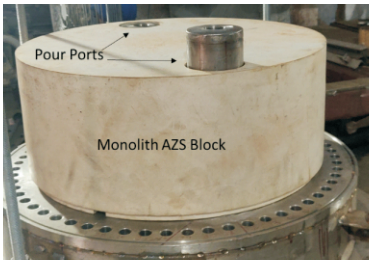


Fig.6: Redundant pour ports.

Fig.7: Pour plug actuator.

The pouring mechanism of the plant adaptable CCIM has now been modified by employing a ball screw actuated mechanism with power transmission through flexible shaft driven by remotely placed motor (Fig.7). The mechanism has enough flexibility for remote manual intervention and maintenance in case of failure of any component. Similar mechanism has been adopted for actuation of retractable thermocouple employed for temperature and level measurement.

Remote Connector for 50 NB Water Cooling Lines: A combination of customized three-jaw connector and block connector with an interconnecting flexible pipe spool has been used in the inlet and outlet of the main cooling water circuit connection to the plant adaptable CCIM (Fig.8). This has been employed considering the optimum utilization of in-cell space and remote operability and maintainability. The leak-tightness of these joints has been qualified through hydro-testing .

Quick Coupling for Smaller Water and Air Lines: Remotely operable stainless steel quick couplings (Fig.9) have been used for various smaller water and air lines connected to the plant adaptable CCIM. These coupling are amenable for actuation through master-slave manipulator employed in the hot-cell.

The plant adaptable CCIM has been installed in the engineering hall of CDCFT building at Trombay (Fig.10). It has been integrated with the existing high frequency (200 kHz) induction heating power supply system and operated to check the efficacy of all newly added features. Satisfactory commissioning of the system was carried out confirming high temperature operation (1250°C) and smooth pouring (Fig.11). Thus, the plant adaptable CCIM with all the remote operation and maintenance features is amenable for implementation in hot-cell for vitrification of high level liquid waste.

Conclusions

Cold crucible induction melter offers several advantages such as high temperature availability and high waste loading with long melter life. Other salient features such as compactness and ease of melter replacement with less secondary waste generation makes CCIM as a promising candidate for vitrification of high level liquid waste.

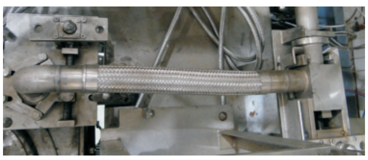


Fig.8: Three-Jaw connector & Block connector.

Fig.9: Quick couplings.

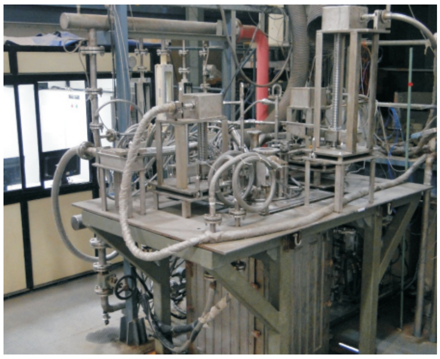


Fig.10: Plant adaptable CCIM.

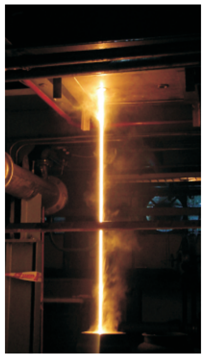


Fig.11: Glass pouring.

Development and demonstration of plant adaptable CCIM with remote operation and maintenance features pave the viable route for its implementation in Indian Waste Immobilization Plant for HLW vitrification.

Acknowledgements

The indigenous development of CCIM technology was possible only with the guidance and support from former senior colleagues of NRG. The authors thankfully acknowledge the invaluable contributions of former Directors of NRG - S. D. Misra, N. K. Bansal, P. K. Wattal, K. Banerjee and K. Agarwal; and former Heads of Divisions in NRG K. N. S. Nair, K. K. Prasad, Kanwar Raj, R. K. Gupta, P. B. Sengar and R. S. Sony. The authors gratefully acknowledge the constant support extended by C. P. Kaushik, Director, NRG for the development of the plant adaptable CCIM. The authors also acknowledge the support extended by NRB. Evolution of CCIM technology from lab scale to plant adaptable unit involved continuous and painstaking efforts of the CCIM team over decades. The authors appreciate the significant contributions of S. Sridhar, S. Satheesh Kumar, P. Abhilasha, W. Mahendra, D. D. Pawar, V. G. Karande, S. Deolekar, and N. Jadhav.

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Glass Matrix

Continuing Research for Improving Glass Matrix for Vitrification

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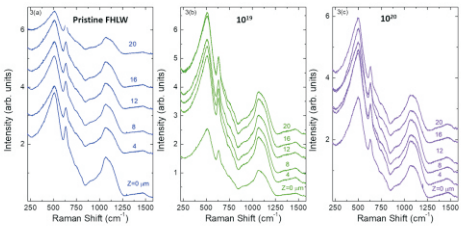

Raman spectra of NBS3 glasses

ABSTRACT

Vitrification forms an important part of the management of high level wastes (HLW). In this article the recent endeavours in the area of glass matrix development and optimization are highlighted. This paper presents recent work on the development of glasses capable of withstanding the alpha damage caused by high loading, which is important to minimize waste volume, and therefore eventual space utilization in the repository. The work presented here shows that even at a simulated α loading of 10^{20} αg^{-1}, there seems to be no detrimental effect on glass leaching.

KEYWORDS: *Glass, Alpha loading, Ion bombardment, Raman spectroscopy, Chemical durability.*

Introduction

The beneficial combination of excellent material properties including high chemical durability, resistance to crystallization/de-vitrification and the ability to accommodate a wide diversity of cations within its structure, combined with ease of handling borosilicate glasses in large scale, remotely handled facilities make them ideal candidates for HLW vitrification [1–3]. With the advent of partitioning, disposal of alpha-bearing wastes is envisaged as a future goal for waste management operations. Indeed, most minor actinides have a life of 10^6 years–10^7 years, during which time the vitreous matrix is likely to receive total alpha dose exceeding 10^{10} Gy. The recoiling daughter nucleus is also expected to create significant, albeit much shorter ranged, damage by initiating displacement cascades in the glass. A combination of these events can potentially cause alterations in the glass structure and lead to crystallization to the detriment of the waste form, with problems including formation of cracks and/or crystalline phases which in turn can increase the vulnerability of the waste form to aqueous attack[4, 5]. In this article, we discuss the role of ion bombardment[4] in actual sodium borosilicate waste glass compositions to simulate alpha loading, and achieve an insight into the structural reasons underlying radiation damage mechanisms. We also present studies of chemical durability to highlight the effect of radiation damage on chemical durability.

Simulation of High Alpha Loading Through Radiation Bombardment

A series of simplified ternary glasses and plant-based compositions with simulated waste loading were chosen for the studies. Table 1 summarizes the compositions used for the present study. The ternary compositions were chosen to

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Table 1: Compositions of glasses studied.

(NBS-1 and 3 represent ternary systems while FHLW simulates WIP Trombay glass)			
Oxide (Wt. %)	NBS1	NBS3	FHLW glass
SiO_2	52.90	50.89	34
B_2O_3	22.29	29.74	20
Na_2O	24.81	19.67	12
TiO_2	--	--	2
BaO	--	--	8
Waste Oxide	--	--	24

highlight the effect of radiation damage on simplified compositions.

The samples chosen were bombarded with He and Xe ions using irradiation conditions as summarized in Table 2. In all cases, alpha loading up to 1020 αg^{-1} has been simulated. Since ion bombardment causes damage on the surface of the sample, confocal Raman spectroscopy was the chosen technique to analyze the samples before and after irradiation. For brevity, we present the Raman spectra of glasses before and after Xe bombardment data in Figs. 1 to 3. Since Xe simulates the recoiling daughter nucleus, it is expected to be the major damage contributor.

The Raman band at ~528 cm^{-1} is attributed to bending and stretching modes of Si–O–Si linkages, and also the stretching modes of Reedmergnerite type structural units. All the glasses also show a sharp Raman peak at 630 cm^{-1}. This is attributed to tetrahedral B in danburite type (Si_2O_7–B_2O_7 rings) structural units. Additionally, the NBS-3 glasses exhibit a pronounced shoulder between 600 cm^{-1} and 800 cm^{-1}. These are attributed to vibration of boroxol rings and $B–O^-$ in

Table 2: Ion bombardment experiment parameters and the effective $\alpha\ g^{-1}$ simulated.

Ion	Charge State	Deck (kV)	Energy (keV)	Beam Current (A)	Flux (ions per cm^2s)	Total Fluence on Sample (ions/cm^2)	Exposure Time(h)	Effective ($\alpha\ g^{-1}$)
Xe	6	350	2100	10^{-9}	10^{10}	10^{15}	280	10^{19}
Xe	6	350	2100	10^{-9}	10^{10}	10^{16}	2800	10^{20}
He	2	350	750	10^{-6}	10^{12}	10^{15}	0.3	10^{19}
He	2	350	750	10^{-6}	10^{12}	10^{16}	3	10^{20}

Table 3: Normalised Na release rates

Glass Name	Normalized Na release (ppm cm^{-2})				
	Pristine	He-Bombarded		Xe-Bombarded	
		$10^{19}\alpha g^{-1}$	$10^{20}\alpha g^{-1}$	$10^{19}\alpha g^{-1}$	$10^{20}\alpha g^{-1}$
NBS1	4359	4065	4055	4211	4108
NBS3	881	874	880	1213	1336
FHLW	183	196	192	230	224

metaborate groups. The broad band between 900 cm^{-1} and 1200 cm^{-1} is a convolution of Q^n Si species [6–8].

In case of NBS1 glass, no significant change in the Raman spectra is evident. However, in case of NBS3, a sharp peak is observed in the Q^3 region at a depth of ~12 µm. It maybe mentioned here that the typical penetration depth of Xe into a glass is ~0.5 µm. Therefore, it is unclear how damage was created at such depth in the material. Clearly, further studies are essential to probe the same. It is likely that damage cascades may have deposited energy deep into the material or some heating may have resulted from bombardment, which could have altered the sample. However, it is clear that such a change is not observed in case of the FHLW multi-component system, where the irradiation effects are minimal.

Leaching Studies

Since the final consideration of the effect of radiation damage remains the chemical durability, samples were mounted in a suitable resin such that only the damaged surface remains exposed to the liquid. Short term degradation of one week was observed since the goal is to observe the leaching behaviour of the ion damaged layer only. The degradation experiments were carried out at a temperature of 90°C with the samples placed in sealed containers. A schematic diagram of the sample as mounted is presented in Fig.4. The leaching behaviour of the bombarded samples was compared with the pristine samples to obtain the Na^+ ion concentration in the leachate normalized to sample area exposed.

In terms of degradation behaviour, the initial samples obtained from He and Xe bombarded samples were compared and the results in terms of normalized Na^+ release rates are presented in Table 3.

As evident in Table 3, Na leach rate seems increased in case of the NBS3 samples under Xe bombardment. However, comprehensive investigation with further experiments is essential to confirm this finding. Confirming the absence of significant alteration observed in Raman spectroscopy measurements, FHLW glass does not seem to show a significant change in the normalized leach rate. This effect is most likely due to the multi-component nature of FHLW glasses.

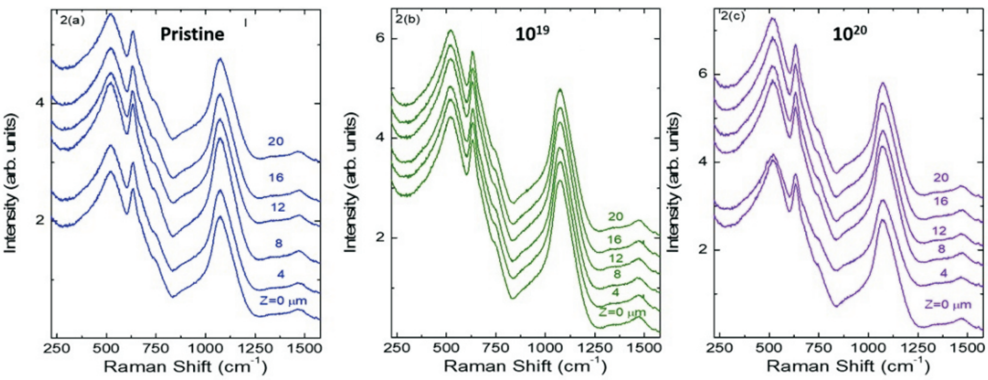

Fig.1: Raman spectra of NBS1 glasses-Pristine (left), $10^{19}\alpha g^{-1}$(middle) $10^{20}\ \alpha g^{-1}$ (bottom). The depth of the measured spectrum is indicated beside the relevant trace.

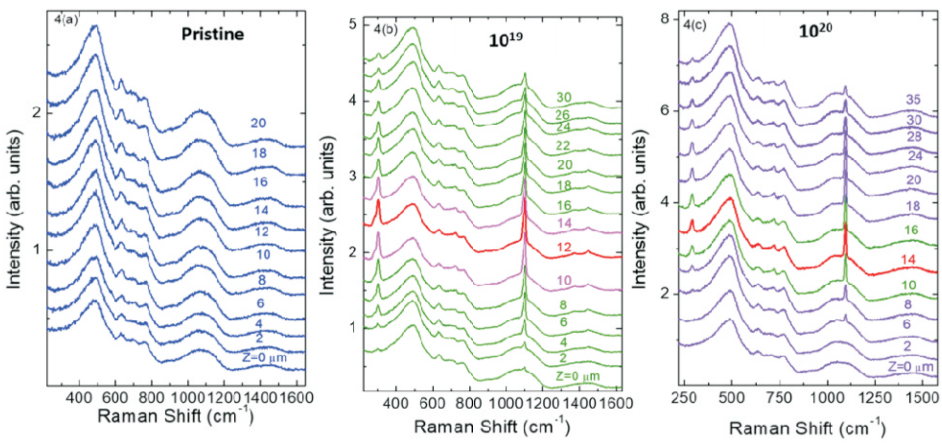

Fig.2: Raman spectra of NBS3 glasses-Pristine (left), $10^{19}\alpha g^{-1}$(middle)$10^{20}\ \alpha g^{-1}$(bottom). The depth of the measured spectrum is indicated beside the relevant trace. Note the emergence of a sharp peak indicating possible crystallization.

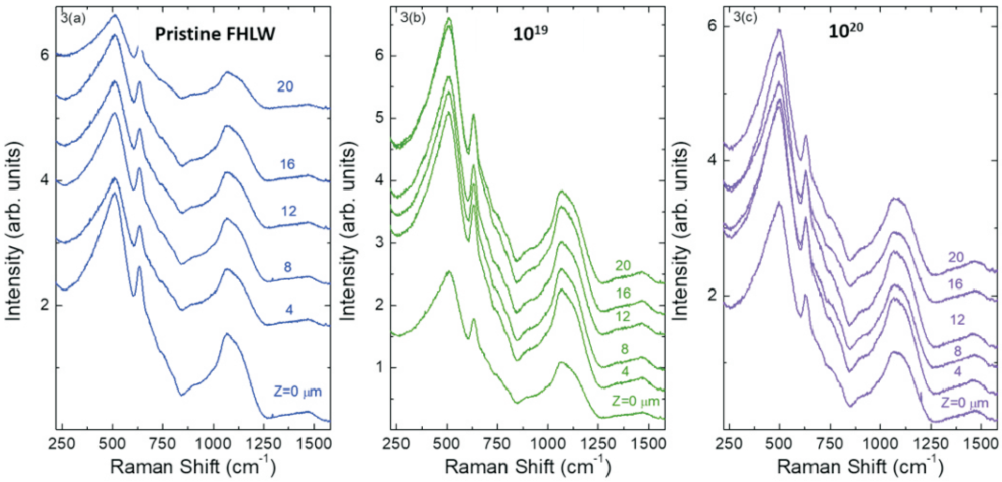

Fig.3: Raman spectra of FHLW glasses-Pristine (left), $10^{19}\alpha g^{-1}$(middle)10^{20} αg^{-1} (right). The depth of the measured spectrum is indicated beside the relevant trace.

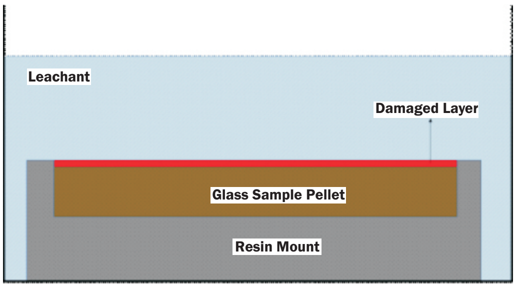

Fig.4: Schematic figure showing short term leaching test configuration to allow leaching of damaged layer.

Conclusions

- The studies presented confirmed that simplified glasses with a higher B_2O_3 percentage are susceptible to radiation damage from recoiling species. However, this effect is mitigated in multi-component glasses as typical in waste management applications
- Further studies into the effect of multi-component versus ternary systems will be required to fully understand this phenomenon
- Bombardment and characterization studies allied to degradation properties suggest that even at an α loading ~10^{20} $\alpha.g^{-1}$, no deleterious effects on leaching properties are evident.

Acknowledgements

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Solid Waste Processing and Disposal

Radioactive Solid Waste Management Practices and Advancements

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Near Surface Disposal Facility in Trombay

ABSTRACT

Radioactive solid wastes, generated from various stages of the closed nuclear fuel cycle of the country, need effective management. Segregation and categorization are important tools for management of these wastes. Low alpha content waste packages after amenable treatment are disposed in the engineered disposal modules of Near Surface Disposal Facility (NSDF). Management of Disused Sealed Radioactive Sources (DSRS) also pose a challenge for safe and secure disposal. Solid waste processing at once must address the challenge to optimize disposal land space of NSDF, while ensuring confinement of activity for prevention of migration to the environment. Technologies, like plasma incineration, spent resin fixation in cement matrix and futuristic disposal modules, like Multitier Reinforced concrete Disposal Modules (MRDM) with robust performance evaluation for meeting the regulatory authorized limits have been deployed.

KEYWORDS: *Radioactive solid wastes, Near surface disposal module, Dis-used sealed radioactive sources, Segregation, Plasma incineration, Resin fixation, Cementation, Multi-tier reinforced concrete disposal module.*

Introduction

Nuclear and radiological industries, during operation, maintenance and decommissioning, generate solid wastes with radioactive contents[1]. Plant protective gears like, lab coats, hand gloves, shoe covers, skull caps, boiler suits etc., which are organic in nature, contributes nearly 50-60% of the total waste volume generated from various industries and are potentially carry radioactive contamination[2]. The rest of the waste volume is contributed by decommissioned equipment and piping, cemented waste products, used process pots, used spent resins loaded with active isotopes etc. and are having low to high levels of radioactive contaminants. These wastes are mainly low in alpha contaminations and amenable for disposal in various engineered disposal modules of the Near Surface Disposal Facility (NSDF). Typical waste disposal modules are shown in Fig.1. Following the concept of *"Generator as First Waste Manager"*, waste minimization, segregation and R-3 concept (Reduce, Recycle & Reuse) are given utmost emphasis. Though R-3 concept is practiced meticulously, a good amount of potentially contaminated wastes generated needs effective management. Safe management of these wastes has been of priority since the inception of our nuclear energy and fuel cycle programme.

Waste Segregation and Categorization

Segregation is a very important tool to achieve the highest possible volume reduction and thereby minimize requirement of valuable land space for the disposal modules of NSDF. Solid wastes are segregated based on its physical nature, radioactivity content and applicable processing technologies as on date. Cellulosic waste contributes to about 15-20%, while rubber and plastic wastes contributes to 80-85% of the total treatable Category-I organic wastes[2,3]. Cellulosic wastes, marked as combustible, are packed in cardboard boxes. Rubber and plastic type of wastes, marked as compactable, are packed in 200 L standard Mild Steel drums. Metallic, cemented waste products, residue chemicals, contaminated soils and concrete debris etc. are segregated as non-treatable waste and packed separately in 200 L drums or specially designed packages. Table 1 gives a typical segregation of Category-I wastes based on processing needs.

Solid radioactive wastes are categorized based on beta-gamma activity, dose rate and alpha content. Category-IV wastes need to be stored in the interim storage facility or in retrievable storage in NSDF for its future management. Category-II and III wastes, contributing less than 15% of the total volume but having more than 90% of radioactivity of solid wastes, are disposed in Reinforced Concrete Trenches (RCT) or Tile holes, after applicable conditioning, depending on the contact dose criteria. Category-I waste contributing more than 85% of the waste volume, with less than 10% of contribution in total activity, is processed with applicable technologies for volume reduction and disposed, based on contact dose and potential activity contents, in Stone Lined Trenches (SLTs) or Above Ground RCC Dykes (Dyke) constructed above the closed SLTs[1].

Disused Sealed Radioactive Sources (DSRS) based on the radioactivity content are categorised in five categories. All categories of DSRS from the north, east and western regions

Table 1: Segregation and packaging of Category-I solid wastes conventional practices.

Type of Radioactive Waste	Segregation tag	Packaging
Cellulosic	Combustibles	Cardboard Boxes
Rubber and Plastics	Compactable	200 L Standard Mild Steel (MS) Drums
Others	Non-Treatable	200 L Standard MS Drums or Specific Containers

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Above ground dyke (Dyke)   Stone Lined Trench (SLT)   Reinforced Concrete Trench (RCT)

Tile hole (TH)   **Multi-Tier RCC Disposal Module (MRDM)**

Fig.1: Typical Engineered disposal modules of Near Surface Disposal Facility.

of the country are collected for safe management and disposal at the Trombay site. For southern regions DSRS are collected and managed at BARCF, Kalpakkam[1]. DSRS are transported safely by the generators, after regulatory authorization, till BARC facilities for further management, which are stored as per type of isotopes and category of DSRS.

Processing Technologies for Category-I Wastes and DSRS

In general, for cellulosic type of wastes, i.e. lab coats, boiler suits, cotton hand gloves, mops are treated by conventional incineration, where volume reduction factor (VRF) of more than 30 is achieved[1,2]. Rubber and plastics type of wastes, i.e. hand gloves, shoe covers, plastic sheets etc, are packed in standard 200 L barrel drums and compacted using high pressure hydraulic compactor achieving VRF of 3-5[1,2]. Non treatable wastes like metal scrapes, decommissioned equipment, cemented waste products, solid residues etc. are conditioned or packed in secondary containers and disposed in SLT or Dyke.

The DSRS are safely decasked, separated from inactive instruments and cemented in cement matrix. Cemented waste packages are managed based on solid waste categories and disposed to the applicable disposal modules of NSDF. Till date tens of thousands of DSRS of µCi to kCi range have been successfully and safely managed.

New Approaches in Processing Technologies and Advance Disposal Module

Conventional incineration of rubber and plastic wastes was hitherto limited by the low temperature (~1000K), as toxic gas formation including dioxins and furans at these temperatures was a significant concern. The availability of plasma incinerator (temperature > 1500K) now allows more rapid processing of all types of incinerable wastes.

Plasma pyrolysis and incineration system at WMD, Trombay (Fig.2)[3,4] has allowed processing of Category-I combustible wastes, including rubber and plastics, at a rate of 25 kg/hr. This setup has been retrofitted in the existing diesel fired incinerator system. Through the process more than 2500 kg of wastes (cellulosic, rubber and plastics) have been processed successfully achieving a VRF of more than 30 for each type of wastes[3]. Discharges from the system are measured using iso-kinetic sampling system and analyzed by in-house developed methodology. The values observed were well within the limits specified by the regulatory authority, i.e. dioxin and furans observed to be less than 0.1ng TEQ/m^3.

Spent resins from spent fuel storage bay were planned to be polymerized before disposal. Considering associated fire hazards, a novel cement (Mixed Slag + OPC) matrix has been investigated and in-drum cementation of loaded resins has been successfully demonstrated by retrofitting the modified cementation system in the polymerization system (Fig.3)[4]. The system has successfully demonstrated more than 10 cementation campaigns including nine actual spent resin

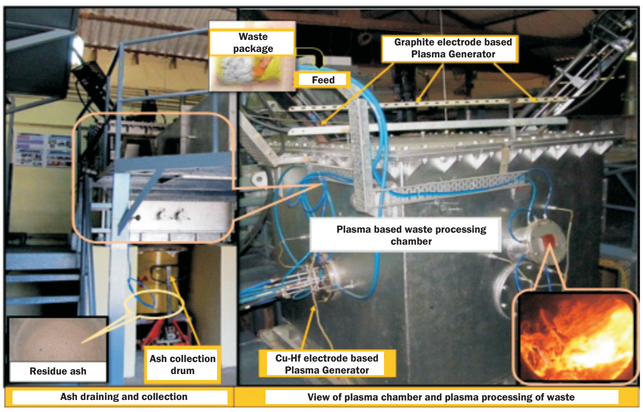

Fig.2: Plasma based incineration system and plasma processing of mixed wastes.

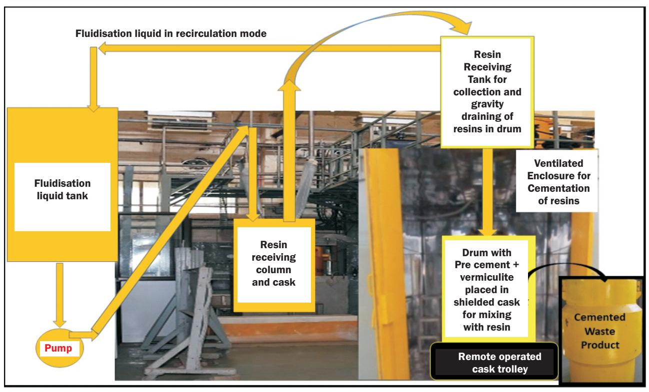

Fig.3: Facility for resin fluidization and fixation in cement matrix.

hopers from Dhruva, each was having about 50 Ci activity. Product quality has been confirmed where leaching rate less than 10^{-4} g/cm^2/day and compressive strength more than 50 kg/cm^2 could be achieved.

DSRS also have potential use after integrity check in other applications based on total left-over activity. Considering the same, before deciding for final disposal, recycle and reuse concept is introduced to minimize number of DSRS disposal frequency. Dismantling and disposal costs are also inducted. Repatriation of the sources to the country of origin is encouraged as far as possible. Safety and security of the general public has been accorded the highest priority during deciding the management of DSRS.

Towards requirement of optimum land space utilization and improvised disposal of radioactive solid waste, after amenable processing techniques, an advance disposal module, namely Multi-tier RCC Disposal Module (MRDM) has been designed and constructed (Fig.1). The module, 60 % below ground and 40% above ground, is expected to replace, Dyke, SLT and RCT in future with enhanced safety in waste disposal with optimum land space utilization factor[4].

Conclusions

Management of radioactive solid waste in India has progressed maturely and safely for all categories of wastes generated from entire nuclear fuel cycle including decommissioning activities as well as disused radioactive sources from applications like medicine, industry and research. Demonstration of plasma based processing using indigenously developed technologies has open up new field for effective volume reduction for all combustible waste forms. Based on the feedback of plasma incineration demonstration system, higher capacity plants are planned at Tarapur for radioactive as well as for municipal solid waste management. Immobilization in improvised cement composition has shown effective and safe management option for spent radioactive resins. Multitier disposal module has shown advantages for simplifying disposal for all categories of wastes in same disposal modules having improved engineering safety and optimal land space utilization factor. Department has also implemented a well-planned strategy and procedures for safe management of DSRS. Continuous efforts towards research and development to impart innovative and advance technologies have resulted in efficient and effective management of radioactive solid wastes in line with international practices.

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Decontamination System

Mechanization and Automation of DHRUVA Cut-end Rod Handling System

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Cut-end Rod Handling System in operation

ABSTRACT

Continued efforts are being made to upgrade the existing mechanical handling systems with automation features. Decontamination & recycle of the cut end of the fuel rods of research reactor is utmost important to ensure the minimum inventory of the components. For recycling operations, an automated Rod Handling System has been designed and deployed which is a major advancement over existing handling system. The system handles 5.7 m long cut-end rod in balanced condition and moves to different work stations for decontamination, cutting and dismantling operations. Deployment of the system has resulted in improved safety, reliability and reduction in collective dose with enhanced plant throughput.

KEYWORDS: *Mechanization, Automation, Man-rem consumption, Plant throughput.*

Introduction

Heavy Equipment Decontamination (HED) System in Decontamination Centre (DC) of WMD is mandated to decontaminate Dhruva cut-end rods leading to eventual recycling of the rods. The cut-end rod is a 5.7 m long composite Al-SS assembly weighing 70 kg. At HED, the rod is decontaminated and dismantled into three sections *viz.* Al shield (for recycle to AFD), Al cut piece (for disposal) and SS Plug (for recycle to AFD). The Al shield and SS plug are decontaminated using various DC baths before its recycle. For all these operations, an automated Rod Handling System has been deployed which is a major advancement over existing handling system. Since Dhruva, AFD and DC do not have any buffer storage capacity for these rods, HED system operations are continuous in nature and must be operated in tandem with Dhruva and AFD operations.

Earlier, a mechanical gripper system with limited long travel was installed in the facility for handling the cut end rods. However, due to the ventilation duct, crossing through the facility, the rod box was not accessible with the old mechanical gripper system. All the operations were then carried out manually, resulting in higher man-rem consumption and safety issues. The old system was unserviceable due to ageing effects. Therefore, it was necessary to design a new system to overcome the limitations of the old system and with provision of improved automation features.

System Design Features

The system is a custom designed special purpose electromechanical manipulator with four degrees of freedom. Out of these four degrees of freedom, three are in cartesian framework i.e. long travel (X) of 20 meter, cross travel of trolley (Y) of 6 meter, and vertical elbow hoist motion (Z) of 1.4 meter. Spatial positioning of the end gripper is achieved by actuation of the X, Y and Z movements. At the end of the elbow (Z), rotation of gripper assembly is provided. Payload capacity of the system in all positions is 70 kg. The 3-D schematic of the system is given in Fig.1.

The system is operated through a Programmable Logic Controller (PLC) based Supervisory Control and Data Acquisition (SCADA) Control Terminal. A radio operated push button pendant as an overriding operation feature has also been provided. Materials having high strength to weight ratio have been employed for structures like rails & CT girder for construction of the equipment.

The system can handle cut end rod having 60 mm diameter and unbalanced weight due to SS Plug at one end. The system is capable of picking the active cut end rod from the rod box in a horizontal balanced condition. The rod is then rotated through ± 90° depending on the plug position and moved it to the decontamination tank for lowering into it. The system is equipped with two Pan/Tilt/Zoom cameras to view the entire work volume during active operation from control room. Built-in safety features like triplex hoisting chain, hoist chain tension sensors, redundant hoist breaking system,

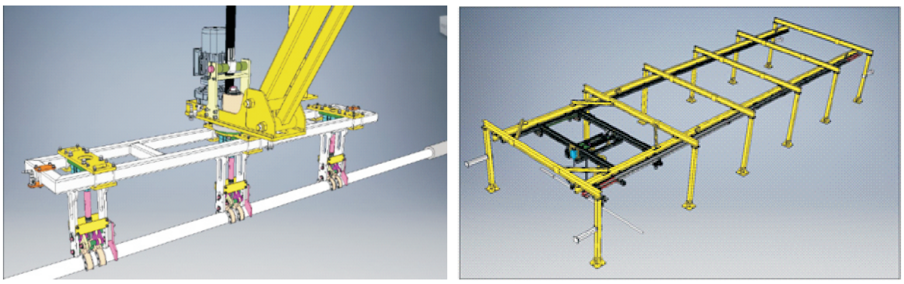

Fig.1: 3-D model of the Cut-end Rod Handling System.

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Fig.2: Cut-end Rod Handling System in operation.

provision for emergency release of load, proximity switches and LASER sensors for accurate detection of workstation positions & cut end rods are incorporated in the system. The system has three modes of operation *viz.* Auto Mode, Manual Mode & Bypass Mode. All routine operations are carried out in Auto Mode from the control room with minimum human intervention. Fig.2 shows actual cut-end rod handling system in operation at HED.

Installation, Testing & Commissioning

The system design mandate was the reduction of man-rem expenditure by incorporating automation features for decontamination of Dhruva cut end of fuel rod. Detailed planning was carried out for installation, testing and commissioning of the system so as not to affect Dhruva and AFD operations. A three-month time interval was available to complete the installation and testing requirements. Exhaustive and full-scale testing was carried out at manufacturing site prior to its installation to minimize time to restart facility operations. The old existing handling system, weighing 3.5 Te was dismantled. Relocation of process equipment was carried out for smooth operational flow & reduction in cycle time. The complete integration of system, testing & commissioning were carried out over a period of 3 months. After conducting multiple demonstration trials, the system has been deployed for regular active use. Till date, 180 Nos. of rods (12600 kg) have been processed successfully. The system has resulted in improved safety, reliability and reduction in collective dose with enhanced plant throughput.

Acknowledgements

During execution of all activities related to design, manufacturing and installation of the system, we acknowledge the enormous efforts of staff of Technology Development Division, Waste Management Division and M/s Fine Handling & Automation Pvt. Ltd., Pune. We also acknowledge the support extended by R. S. Bhatia, Former Head, Technology Development Division and C. P. Kaushik, Director, Nuclear Recycle Group for timely completion of this important activity.

Deep Geological Disposal

Swelling Clay based Buffer Component of Engineered Barrier System of Waste Disposal Facilities

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Barmer clays of Akli formation, Rajasthan

ABSTRACT

Swelling clays in general and Na-Smectite clays in particular have emerged as highly promising candidate material for use as buffer component of Engineered Barrier System (EBS) in deep as well as shallow radioactive waste disposal facilities due to their very low permeability, high retention of radionuclides, geochemical compatibility with host environment and high plasticity required for providing cushioning to disposed waste packages against rock movements. Such clays are under extensive characterization worldwide for assessment of their suitability for use as buffer material in waste disposal facilities. In the Indian context, a Deep Geological Disposal Facility (DGDF) with a capacity of accommodating 10000 waste canisters would require about 0.1 million tonnes of good quality swelling clays with a specific range of thermal-mechanical-hydraulic-radiological properties. Extensive experimental and numerical simulation based studies have been performed on promising Na-Smectite clays of Barmer district, Rajasthan to establish their suitability for the above purpose. The studies reveal that these clays possess adequate chemical, thermal and radiological properties on par with international reference clays MX-80 of the United States of America to serve as buffer material in Indian radioactive waste disposal facilities. It is also established that 25cm thick layer of Na-Smectite clay with high Smectite content (~80%) compacted to a dry density of 1.6gm/cc with inter-canister spacing of 2m can provide a stable thermal field around disposed waste canister by maintaining temperatures well below 100°C at any point of time with minimum possibility of building of thermal stresses and resultant micro-fracturing in EBS as well as in host rocks.

KEYWORDS: *Smectite, Geological disposal, Engineered Barrier System, Vitrified radioactive waste, Akli formation.*

Introduction

Disposal of solid radioactive wastes essentially requires their long term confinement and isolation from the accessible environment over varying extent of time span ranging from few hundreds of years to millions of years depending on half lives and concentrations of key radionuclide contained within such wastes. These objectives are achieved by disposing these wastes at varying depths underground. Low level solid wastes with short lived radionuclides like Cs-137, Sr-90 are thus disposed in engineered structures built within depth ranges of few tens of meters whereas vitrified high level waste with long lived radionuclides like isotopes of actinides, activation and fission products *viz.*, americium, neptunium, uranium, nickel, molybdenum, iodine, technetium, tin etc., become target wastes for disposal at >500m depth in specifically designed and excavated underground structures within suitable host rocks popularly known as Deep Geological Disposal Facilities (DGDF).

Sites for building these underground disposal facilities are selected based on very extensive evaluation of various parameters and earth processes that would eventually control the confinement of wastes over the desired period of time. Depth, geological stability of the site, low permeability & high strength of host rocks, high sorption capacity for radionuclides etc. are among important parameters that ensure long term isolation of wastes[1]. The long term safety offered by these disposal facilities are invariably provided by a combination of geological barrier (host rock) and Engineered Barrier System (EBS) represented by waste form, canister, over pack and additional layers of protection between the waste packages and the site soils/rocks in the form of admixtures of natural

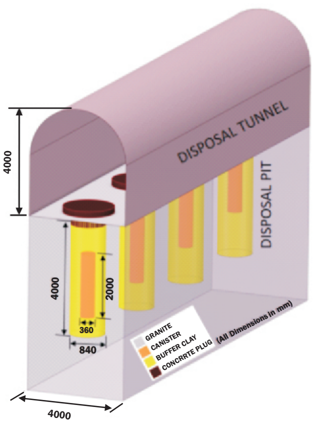

Fig.1: Layout of disposal concept adopted in India.

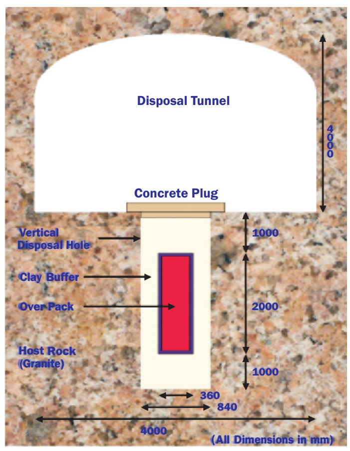

Fig.2: Schematic view of vertical disposal pit.

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Fig.3: Barmer clays of Akli (a village) formation in Rajasthan.

Table 1: Some important temperature-dependant geo-technical properties of Barmer clays

Sl. No.	Temp. (°C)	Specific Gravity (gm/cm^3)	Liquid limit (%)	Plastic limit (%)	Optimum moisture content (%)	Dry density (gm/cm^3)	Specific surface area (m^2/gm)	Free Swell index (%)
1	65	2.785	328.37	35.29	36.18	1.182	448	776
2	100	2.778	305.97	34.26	36.07	1.276	394	753
3	125	2.765	292.62	33.09	35.2	1.316	371	734
4	160	2.762	291.66	32.73	34.84	1.317	353	723

clays and sand, crushed rocks, crushed rocks and clay admixtures. These layers are referred as buffer material. A reference disposal system under consideration in India is shown in Fig.1 & Fig.2 [2]. Choice of the natural material is controlled by the site geochemical environment and groundwater conditions. In India, extensive works on clay-sand based EBS have been taken up in two decades[3, 4]. Studies have revealed that granite host rock based Indian Deep Geological Disposal Facility with a capacity of holding 10000 waste loaded canisters would require 0.1 million tonnes of high quality clays for use as buffer and backfill[5].

Waste loaded canisters at the time of their disposal in DGDF are characterised by continuous heat flux of the order of 500 W mainly produced by radioactive decay of fission products contained in the waste. As Clay based EBS lies in direct contact of the canister, their important functions include smooth dissipation of the heat from the waste into the surrounding rock, arrest the ingress of groundwater towards the waste package, protect the waste canister against rock movement, and retard the transport of radionuclide that may eventually release from the waste canister in the distant future. In India, scheme of deep disposal involves emplacement of vitrified high level radioactive waste contained in SS Canisters housed in 2m long metallic over pack at depth of 500 to 700m in a disposal pit of 4m depth and 840mm diameter with layers of swelling clay based EBS [2]. The Na-Smectite clay layers in a DGDF are expected to withstand about 15 MPa combined thermal and mechanical stresses coupled with a temperature of the order of 90°C [6].

In addition to these, they are also expected to witness varying geochemical condition like pH, Eh, changing groundwater compositions, oxygen fugacity etc.

Development of Clay Buffers of EBS

Large deposits of swelling clays chiefly composed of Na-Smectite, from the Barmer district of Rajasthan, known popularly as Bentonite, have been taken up for detailed evaluation. Samples of swelling clays used in this study were collected from the Akli mine located in the Akli village, Barmer district, Rajasthan, India. The Na-smectite rich clays in this area belong to the Akli Formation of Jagmal Group and are of Palaeocene age. The sampling was restricted to clay horizons with visible homogeneity in terms of texture, grain size, colour etc to avoid mineralogical variations that may result in wide scatter in parametric values. The samples were tested for their thermal, mechanical and hydraulic parameters following standard testing protocols mainly ASTM, ISRM and IS. Important characteristics of these clays are given in Table.1.

Limited decrease in moisture content (3.70%) and swelling index (6.82%) with increasing temperature make these clays highly suitable for use as buffer material in DGDF. Similarly, decrease in specific surface area and increase in dry density are also within desired limits. The UCS of these compacted clays varies from 2 to 3 MPa. The swelling pressure of these clays range from 2100-2200 kPa with a saturated hydraulic conductivity 1-5x10^{-15}cm/s. These parameters compare well with MX-80 clays of Wyoming Basin USA, which have emerged as the most suitable clays for use in DGDF[7, 8].

Mineralogy and Geochemistry

Chemical composition of these clays is characterized by 48-45% SiO_2, 15-20% Al_2O_3 and Fe_2O_3 3-6% with 3-4% MgO and 1-2% Na_2O and almost 4% organic impurities. XRD analysis of samples confirms presence of Na-Smectite as the major mineral (60-85%) accounting for higher SiO_2 and Al_2O_3. The Smectite content of these clays is adequate and at par with

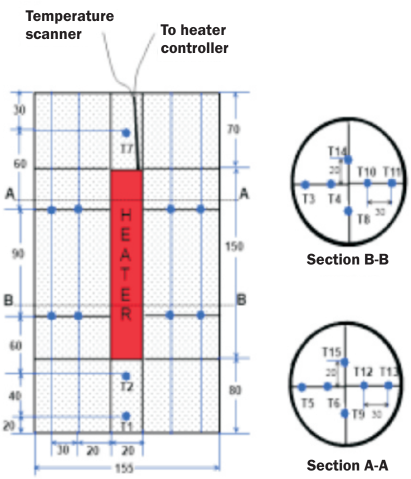

Fig.4: Layout of the TMH Experiment.

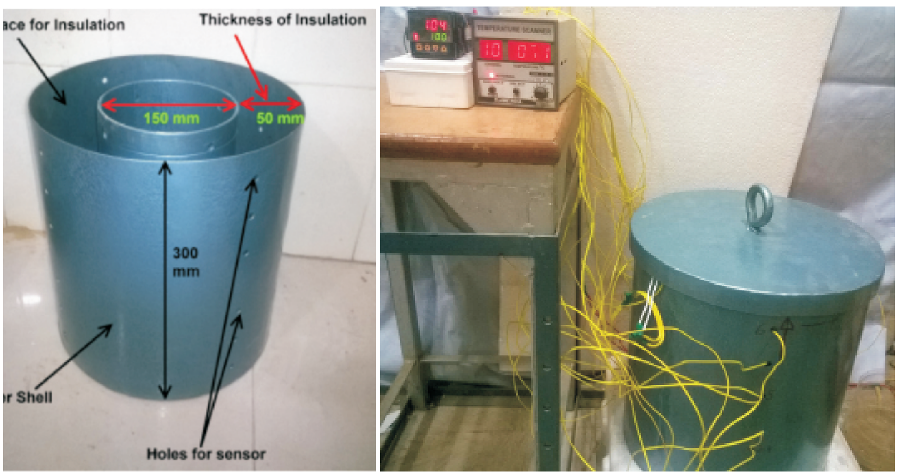

Fig.5: Components of Temperature-Moisture-Hydraulic (TMH) experiment.

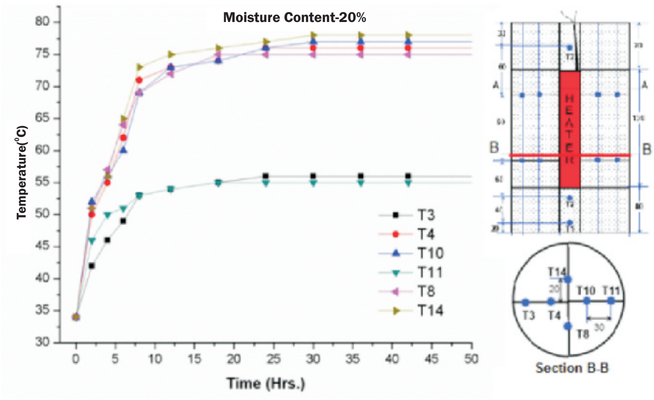

Fig.6: Radial temperature along section B-B within compacted buffer at moisture content 20% .

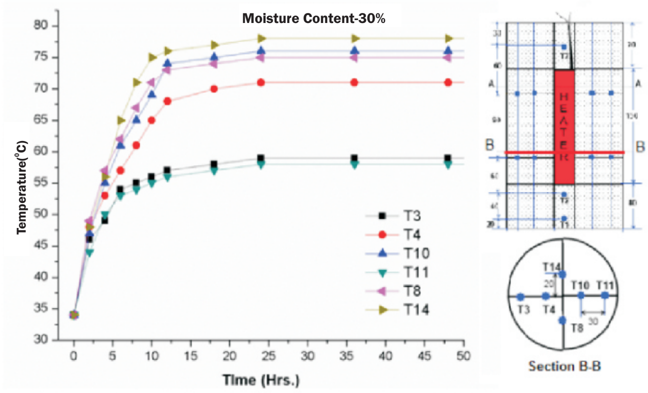

Fig.7: Radial temperature along section B-B within compacted buffer at moisture content of 30%.

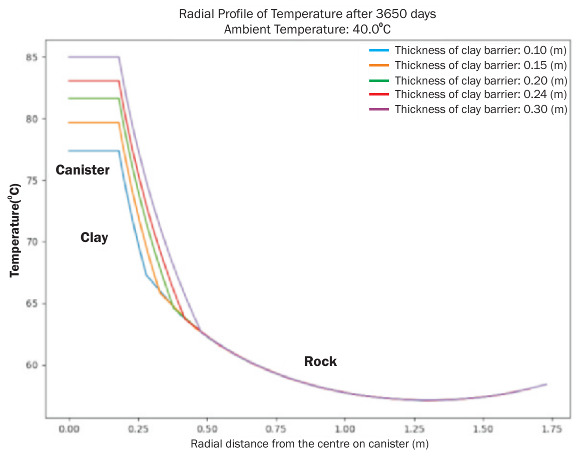

Fig.8: Radial profile of temperature at 5 different spacings of two disposal pits.

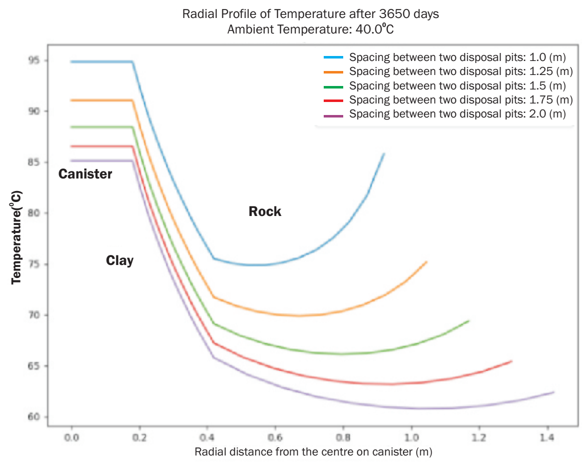

Fig.9: Radial profile of temperature at 5 different thicknesses of clay barrier.

Table 2: Thermal and physical properties of host rock (granite) & Barmer clay

Properties	Host rock (granite)	Barmer clay
Thermal conductivity (W/m/K)	3.3	1.27
Specific heat (J/Kg/K)	1000.0	870.0
Density (Kg/m^3)	2580.0	1600.0

MX-80. Temperature dependant variation in Cation Exchage Capacity (CEC) values reveals initial increase in the CEC from 54 to 59.52 up to temperature of 60°C which reduces to 55.36 at a temperature of 150°C. Experimental studies on sorption of americium on these clays have also been taken up. At lower pH values (2.5-3.5), the sorption of Am(III) increases slowly but rises sharply between the pH ranges of 4–8. Beyond a pH >8 the sorption of Am(III) remains nearly constant. The Kd value for Am(III) range of 111360-612023 mL/g at lower pH (2.5-4.0), 156828-918997 mL/g in intermediate pH range (4-8) and almost constant Kd (918997-926447 mL/g) at pH>8. These results indicate stability of clays in hyper alkaline environment that may eventually develop in disposal facilities due to the presence of concrete and cementeous material. In addition to this, this clay remains unaffected in the presence of anions like chlorine, sulphate and nitrate, typical of granite waters at higher pH values[9].

Experimental Evaluation

For experimental evaluation of the heat distribution within the clay layers of EBS, an experimental set up was developed. It includes a carbon steel cell of 300 mm length and 155mm diameter which was filled with Na-Smectite compacted to a dry density of 1.6 gm/cc with water saturation of 8.5%. The evolution of temperature in compacted bentonite depends on the dry density of clay and moisture content. A 150mm long and 20mm diameter heater with 500 watt output was used as heat source replicating the high level radioactive wastes. A total of 13 thermo couples were installed in the cell at locations shown in Figs. 4 & 5. The experimental dimension, heating system and hydraulic properties of clays were optimised through extensive sample scale testing as well as numerical simulation to optimise various components so that a reasonable replication of actual geological system is accomplished at experimental scale.

The heater remained on for 432 hours at a designated temperature and thereafter it was switched off after attaining steady state. Typical experimental results of temperature measurements with buffer zone measured for initial saturations are shown in the Figs. 6 & 7. The temperature evolution is highly influenced by the presence of moisture on the Na-Smectite clays and can be clearly observed from temperature profile obtained at different monitoring points for moisture content of 20% and 30% respectively. In case of 30% moisture, the temperature curves show larger spacing as compared to those for clays with 20% moisture. Larger movement of moisture is recorded in high temperature zone which also enhances the heat transfer and causes an increase in temperature. Slow evolution of temperature is due to the small temperature gradient. At all the locations within the clay buffer, the initial rate of heat transfer was comparatively high mainly due to the presence of moisture. This is mainly accomplished by evaporation near the heater contact and distribution of moisture in distant areas. Experiment reveals that temperature within the clay remains below 100°C under varying moisture content and hence establishing the capability in smoothly conducting the heat through them.

Modelling

One of the important parameter controlling suitability of these clays for their use as buffer material around disposed waste canisters is their heat dissipation capacity. Poor heat dissipation through clay buffer results in heat build up around disposed waste and may eventually lead to micro-cracking of barrier its self as well as surrounding host rock.

To model heat dissipation through a 25 cm radial thickness of buffer (Barmer Na-smectite) clay layer, a case involving three waste loaded canisters of 2m length and 30cm diameter with varying inter-canister spacing and buffer thickness was analysed. The material properties used in the modelling are shown in Table 2. The conductive heat transfer process is mathematically modeled using Fourier's Law. The governing heat diffusion equation is first solved for an instantaneous finite height vertical line heat source representing the actual canister using Laplace transformation technique. Since the governing equation of the heat transfer for a single canister is a linear partial differential equation, the temperature field for multi-canisters disposal in DGDF is calculated by superposing the solution of a number of single line heat sources.

A computer program is written for the closed form solution of temperature. The integration part of the solution is carried out numerically using the Gaussian quadrature integration technique. The graphical user interface (GUI) is developed using the Tkinter module of Python. The simulation was run for 5 different spacing between two disposal pits as 1.0m, 1.25m, 1.5m, 1.75m, 2.0m and 5 different values of radial thickness of Na-Smectite clay barrier as 0.1m, 0.15m, 0.2m, 0.24m, and 3.0m as shown in Figs. 8 & 9. The analysis reveals that a spacing of 1.0m between two disposal pits results in interaction of their thermal field with resultant temperature rising above 100°C. However, for spacing of >1m, Barmer Na-Smectite clay buffer provided adequate heat dissipation to maintain temperatures within recommended limit of 100°C. The variation of thickness of clay barrier does not have impact on the temperature of the rock but it increases the canister surface temperature.

Conclusions

Extensive laboratory based sample testing of swelling Na-Smectite clays of Barmer, Rajasthan for their TMH parameters, their performance under heat-hydraulic load in meter scale experiment and field scale numerical simulations of heat field around disposed waste canisters surrounded by clay based EBS has demonstrated suitability of these clays for use in Deep Geological Disposal Facility for ultimate disposal of heat emitting vitrified high level waste. These clays with almost 80% Smectite and adequate physicochemical and geotechnical parameters are comparable with those of MX-80 clays from the Wyoming Basin USA, an internationally recognised buffer clay. The studies establish the adequacy of 25cm radial thickness of these clay buffers and 2m inter-canister spacing for ensuring temperature limits within 100°C in any part of the waste disposal facility.

Acknowledgements

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Decorporation of Cesium

Prussian Blue Capsules for Decorporation of Cesium from Human Body

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Prussian Blue capsules

ABSTRACT

This paper reports indigenous development of a process for synthesizing high purity, insoluble Prussian blue (PB) powder. The purity of the product has been established using techniques like Mossbauer spectroscopy, SEM-EDS and XRD. It is confirmed that the synthesized PB powder has very high cesium uptake (K_d = 5.2 x 10^4) performance from a wide range of simulated solutions generated from different parts of the human digestive system. A comparison with literature data shows that the synthesized PB capsule is a suitable drug for the decorporation of radioactive cesium from the human body.

KEYWORDS: *Prussian blue capsules, Cesium, Decorporation, Remediation, bio-hazard.*

Introduction

Insoluble Prussian blue (PB), having chemical formula $Fe_4^{III}[Fe^{II}(CN)_6]_3$, is a well-known agent for decorporation of Cesium and Thallium contamination from the human body[1-3]. This has been used as a counter-measure for treating internal cesium contamination in several nuclear accidents like the Chernobyl reactor accident, the Goiânia tragedy[4] and in the comparatively recent Fukushima disaster. Radioactive cesium released from nuclear accidents or radiological bombs (dirty bombs), can enter the human body through ingestion or the food chain. Within the human body, it follows the path of potassium, gets absorbed through the intestine wall and is distributed in all soft tissues via blood. PB capsule is administered as an immediate medical intervention. The insoluble PB binds cesium during its passage through the digestive system and excretes it from the body. The rapid decorporation of Cs by PB helps in reducing the detrimental effect of radiation on human health. It is to be noted that PB capsule is a USFDA approved drug for Cs decorporation from the human body and is available in the international market in the trade name of *"Radiogardase"*.

This article reports a novel approach towards indigenous development of PB capsules and its evaluation towards removing cesium from the human body under simulated conditions.

Experimental Section

PB powder was synthesized by two methods *viz.* i) reacting K_4FeCN_6 with $FeCl_3$ (Code: PB-10B) and ii) reacting H_4FeCN_6 and $FeCl_3$ (Code: PB-6) utilizing AR grade chemicals. The final precipitate obtained from both processes were washed thoroughly with 0.01 M HCl, water followed by Ethanol. After drying under a vacuum at room temperature, the product was filled in zero size empty gelatine capsules and stored in a well-capped glass bottle. Purity of the product was assessed using techniques like x-ray diffraction (XRD), Mössbauer and SEM-EDS. Cesium uptake performance was evaluated by conducting batch equilibration tests using 0.1 g powder (particle size: 175 to 250 micron) and 10 mL water spiked with ^{137}Cs radiotracer. Cesium activity in the solutions before and after equilibration was measured using a NaI/Tl scintillation detector, and the results were used to calculate Cs uptake performance.

Results and Discussion

The optimized procedure for the synthesis of PB (PB-6) is summarised in Fig.1. $H_4Fe(CN)_6$ was prepared from K_4FeCN_6 using a cation exchange column and reacted with $FeCl_3$. In addition, a batch of PB was prepared as per conventional procedure (PB-10). Several factors like pH, temperature, stirring speed, and mode of addition were optimized for better product quality.

XRD spectra of the synthesized PB products are shown in Fig.2. The compounds synthesized by two routes (PB 6 and PB 10B) have identical XRD patterns. The major peaks at ~18°, 24°, 35°, and 39° (2θ) can be assigned to (200), (220), (400), and (420) planes of the PB crystal lattices, respectively. These peaks confirm a face centred cubic lattice structure and space group Fm_3m [Space group No.: 225] of PB crystal lattice.

Fig.3 shows the room temperature Mössbauer spectra of the synthesized PB samples. Mössbauer spectra are fitted with three symmetric doublets (A, B and C)[5]. For PB-6, the doublet (B) with low isomer shift (IS_B = - 0.158 mm/s), quadrupole splitting (QS_B = 0.141 mm/s), and relative area

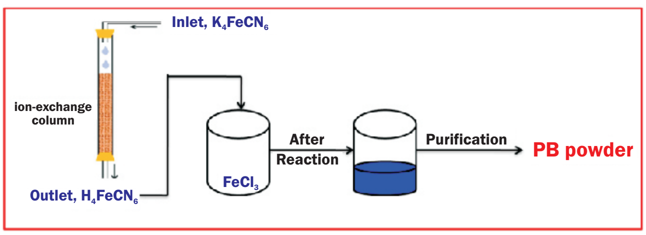

Fig.1: Procedure for synthesis of Insoluble PB powder.

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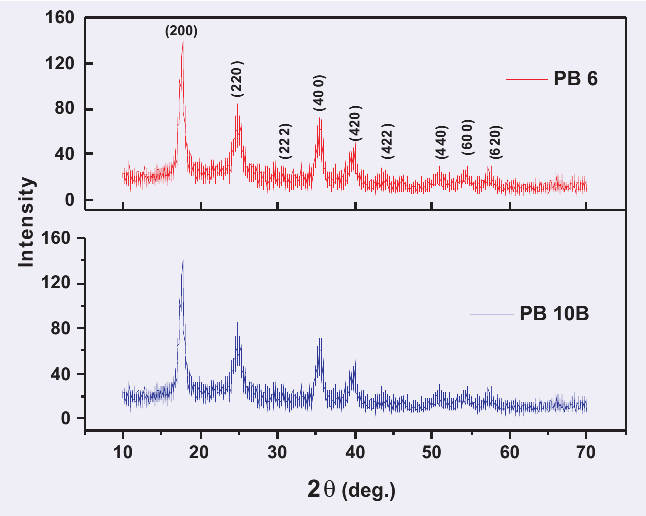

Fig.2: XRD spectra of synthesized Prussian Blue samples.

Table 1: Cs uptake performance of PB samples under in vitro conditions

Sr. No.	Initial pH	[K+] solution (ppm)	[Fe] solution (ppm)	Kd (mL/g) [^{137}Cs]
1	1.36	0.48	1.3	$4.2*10^3$
2	3.16	0.26	BDL#	$2.3*10^4$
3	5.36	0.15	BDL	$5.1*10^4$
4	6.57	0.39	BDL	$5.2*10^4$
5	8.56	0.26	BDL	$3.0*10^4$

 # MDA for iron analysis is 1 ppm (spectrophotometric method)

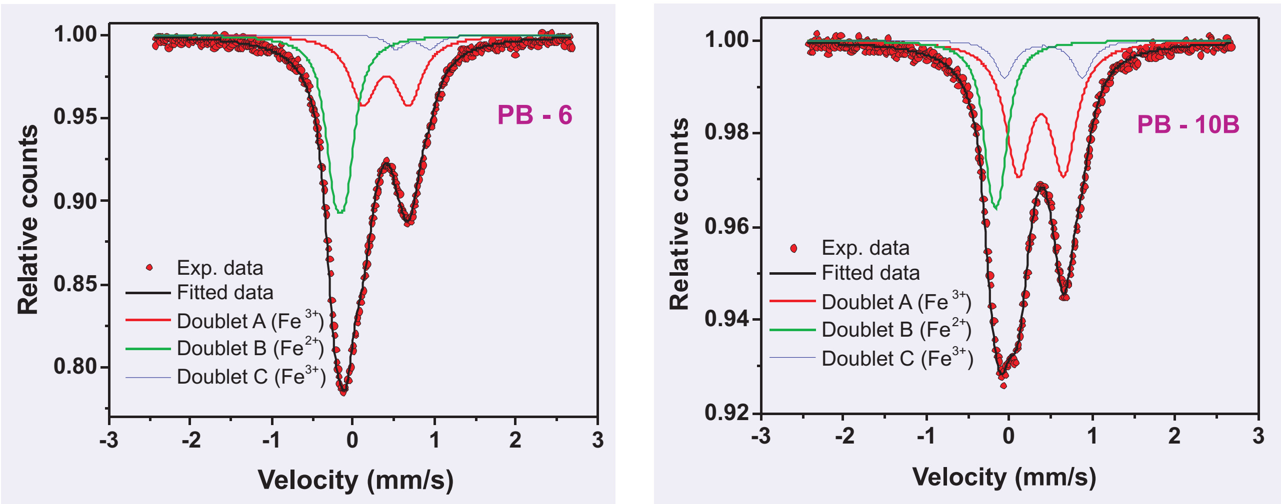

Fig.3: Mössbauer spectra of synthesized PB.

(RA_B = 44.7%) values corresponds to low spin (LS) Fe(II) ions. The remaining two doublets (A and C) with higher IS values (IS_A = 0.401 and IS_C = 0.732 mm/s, QS_A = 0.569 and QS_C = 0.416 mm/s, RA_A = 50.4 and 4.9%) are corresponding to Fe(III) ions in high spin (HS) state. Similarly, the PB-10 sample was also analyzed. It can be noted that the IS values are relative Fe-metal foil. Amount of Fe^{III} and Fe^{II} presented in these two samples were determined from the relative area of doublets. The calculated values of Fe^{3+}/Fe^{2+} ratio arrived at 1.45 and 1.51 for PB-6 and PB -10B, respectively, as against the theoretical value of 1.33 from molecular formula.

Identification of the trace impurities in the samples was done by EDX (energy dispersive X-ray) study. The absence of heavy elements and potassium ion peaks is confirmed from the EDX spectrum of the PB-6 sample. In contrast, a substantial amount of potassium contamination is noted in the PB-10B sample, as the product is made from $K_4Fe(CN)_6$.

Table 1 shows the results of Cs sorption performance of PB-6 powder at different pH. It can be seen that PB-6 samples have very high Cs uptake affinity, and it is same for the entire pH range investigated. Results of the study can be correlated with its Cs decorporation performance from the human body. As PB capsule is administered orally and is insoluble in nature, it will pass through the digestive system like non-digestible foods and finally excretes through faeces. While passing through the digestive system sample, it will mix with different types of food juices and body fluids of varying pH levels, such as 1.0 to 2.5 in the stomach, 4.9-6.4 in the duodenum, and 4.4 to 6.4 in the jejunum and ~7.5 in Colon. The high Cs sorption capability of PB indicates that it can effectively pick up Cs from all parts of our digestive system. The binding mechanism is ion exchange and physical adsorption (electrostatic or mechanical trapping) in the PB crystals, the former being predominant. The Cs pick up by PB can be depicted as follows:

$$\{Fe_4(FeCN_6)_3.\,H_3O^+_{[S]} + Cs^+_{[L]} = Fe_4(FeCN_6)_3.\,Cs^+_{[S]} + H_3O^+_{[L]}\}$$

The release of a higher concentration of K^+ during Cs decorporation will have a significant detrimental effect and lead to potassium imbalance in the body. With this consideration, it can be stated that the PB 6 is more suitable for decorporation of Cs from the human body.

As a final step, formulation for active decorporating agent has been constituted, and around 0.5 g product has been filled in each zero-size empty gelatine capsule. Afterwards, the tablets were packed in a glass bottle and sealed. A photograph of the capsules prepared in laboratory is presented in Fig.4. Efforts are being made to obtain regulatory clearance as applicable for medical administration.

Fig.4: Photographs of PB capsules.

Conclusions

A simple process has been developed for the synthesis of insoluble Prussian blue. The process is efficient for the synthesis of high purity materials. It is confirmed that the synthesized products have high cesium uptake ability from a wide variety of solutions similar to that produced at different regions of our digestive system. Development of the indigenous capability is the first step towards self-reliance for treatment of personnel having internal cesium contamination and ensuring the supply of the product at the need of the hour.

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Nuclear Technology Spinoffs

Indigenously Developed Glass Fiber Media and Development of Various Types of Masks

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EVT Face Mask

NGR Face Mask

ABSTRACT

The COVID-19 pandemic has created an unprecedented demand of respiratory face masks, for personal as well as medical applications, due to the highly contagious nature of the virus. Masks with high filtration efficiency are essential to serve this purpose. WMD, BARC has been working on an indigenous development of filter media for High Efficiency Particulate Air (HEPA) filters for efficient filtration of radioactive aerosols and particulates activities. This technology has now been adopted for the design of a High-Quality Respiratory Face Mask (HQRFM), for common use during the pandemic to serve the society in the time of a health crisis, on an immediate basis. This glass fiber media has minimum retention efficiency of 99.97% for 0.3-micron size particles. Additionally, advanced respirators i.e. Engineered Valveless Transparent Face Mask (EVTFM) (P-100 type), first of its kind in the country, has also been developed using same filtration media. Its key features such as replaceable cartridge, more breathing area and mask transparency etc. make it superior to other masks, and it has potential for use in medical & industrial areas, including nuclear applications. Imported glass fiber media is being used for respirators, such as half face and full-face mask for personal protective equipment, for over four decades in nuclear industry. Utilizing the indigenously developed glass fiber media, nuclear grade half face mask has been designed, for use in nuclear and other industries, at very reasonable cost, thus following Atmanirbhar Bharat ('Self-reliant India'). The paper discusses the work on indigenous development of glass fiber media, development of various types of masks and its technology transfer for ensuring their availability in public domain at an affordable cost in this challenging time.

KEYWORDS: *Face mask, Filter media, Respirator. National Institute for Occupational Safety and Health (NIOSH), High Efficiency Particulate Air (HEPA) filter. Glass fiber medium, Engineered Valveless Transparent Face Mask (EVTFM). High-Quality Respiratory Face Mask (HQRFM). Nuclear Grade Respiratory Face Mask (NGRFM).*

Introduction

Many categories of masks are available in the market depending upon their intended application. These available masks are generally made of synthetic fibres and are being used as medical face masks/respirators. Respirator face mask is categorized by National Institute for Occupational Safety and Health (NIOSH), US. Respirator face masks that collect at least 95% of the challenge aerosol are given a 95 rating. Those that collect at least 99% receive a "99" rating. And those that collect at least 99.97% (essentially 100%) receive a "100" rating. Respirator filters are rated as N, R, or P for their level of protection against oil aerosols. Respirators are rated "N" if they are not resistant to oil, "R" if somewhat resistant to oil and "P" if strongly resistant (oil proof). Thus, there are nine types of particulate respirator filters:

i. N95, N-99, and N-100
ii. R-95, R-99, and R-100
iii. P-95, P-99, and P-100

Filtration mechanism in synthetic media based masks highly depends on electrostatic charge and is vulnerable to charge neutralization during disinfection[1]. Also, filtration mechanism of these masks gets largely affected by various environmental factors. Development of high quality mask was initiated with an aim to utilize indigenously available glass fiber media known for high particulate efficiency for submicron size particles. Glass media mask sterilization can be easily carried out by oven heating (at $60-70^{\circ}C$). Performance of these masks were checked in approved labs at different stages and have reported particulate filtration efficiency, breathing resistance, splash resistance etc. effective enough to fight the present pandemic situation as well as any contagious environment.

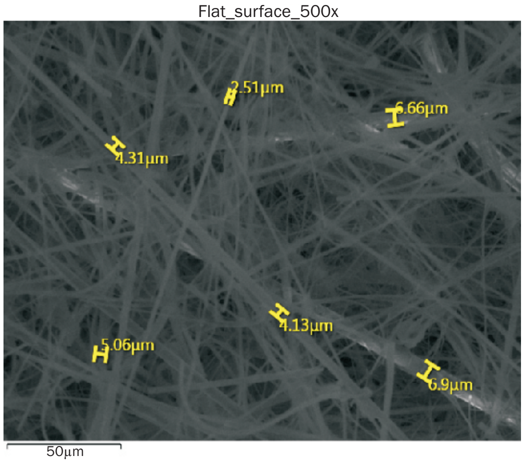

Fig.1: SEM micrographs of developed filter Media.

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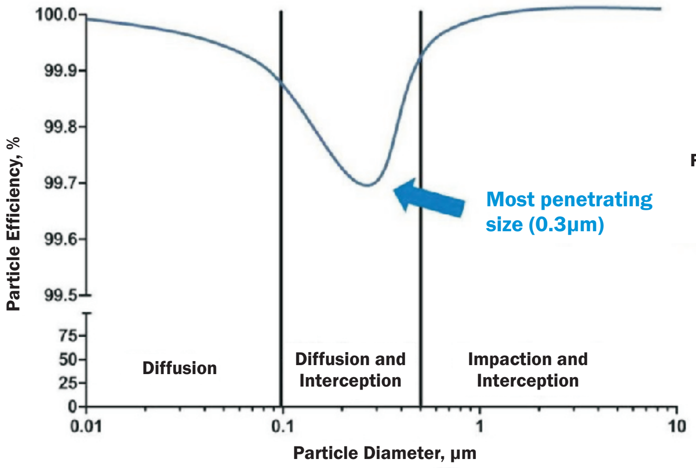

Fig.2: HEPA Filtration Mechanism.

Indigenous Development of HEPA Filter Media

The filter medium used in a HEPA filter is a continuous sheet of paper of around 30 m length and 572 mm width. The thickness of the paper is around 0.4mm. The most commonly used filter medium all over the world is composed of borosilicate type micro glass fibers. Very small quantities of certain binders and additives are also present to impart strength and water repellency. The sub-micron fibers of the filter paper are in random distribution and orientation as shown in Fig.1. The particles in an air stream follow a tortuous path while passing through the paper and get trapped by interception, inertial and diffusion mechanisms. Theoretical as well as practical observations indicate 0.3 micron size particles as the most penetrating through such a fibrous filter medium (Fig.2) and hence the filter media are generally evaluated for removal efficiency against this particle size . In addition to providing the desired filtration properties, the filter medium requires to possess some special physical properties regarding tensile and folding strength, water repellency etc. The annual requirement for HEPA filter media is around 20-30 tonnes for nuclear industry that is presently met by imports.

BARC's effort for indigenous development of micro glass fiber media with the participation of private Indian manufacturers has resulted in development of technology for mill-scale processing of filter medium within the country. The efforts with the firm for establishment of process parameters, composition of additives etc. for nuclear grade is nearly in qualification stage.

The requirement of high efficiency reusable face masks due to the onset of the Covid-19 pandemic, compelled the department to utilize the glass fiber media for production of masks, since the technology for production of glass fiber media is already in a matured stage in India. In this regard, for customization of filtration media for qualification for mask grade, certain parameters were modified to qualify for both

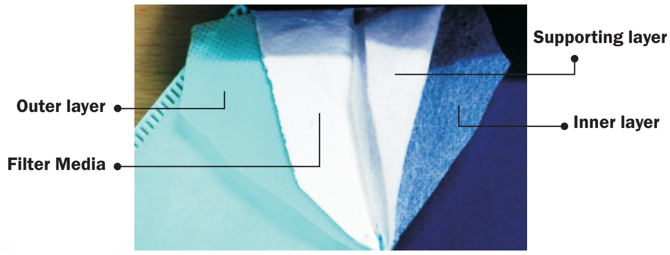

Fig.4: High Quality Respiratory Face Mask.

Fig.5: Technology transfer of HQRFM.

national and international standards. This resulted in development of filter media of superior quality in terms of reusability, cost and suitability in all environmental conditions. Mill scale of filter media manufacturing is shown in Fig.3. One limitation with respect to the fragile nature of the media has also been suitably addressed with the development of gauging layer on glass fiber medium, resulting in excellent improvement in its manufacturing quality and for reusability.

Development of Different Types of Respiratory Face Mask

1. High Quality Respiratory Face Mask (HQRFM): While the entire world was under lock down due to Covid 19, Scientists at BARC rose to the occasion and offered solutions to mitigate risk and save precious lives of human kind, by developing very high quality face masks. There has been a huge demand of face masks with efficient filtering of sub-micron sized particles at low cost for both personal as well as medical applications. This specially designed mask has very high particulate filtration efficiency. The main features like comfortable breathing, high filtration efficiency and affordable price make it more attractive. It is an oil resistant and environment friendly mask and is reusable through oven heating. The mask material is a combination of porous synthetic media, glass media and polypropylene (40 GSM), prepared using automated ultrasonic sealing method as illustrated in mask configuration in Fig.4. These reusable masks minimize the waste generation too[2]. Performance of HQRFM has been tested in different BIS/NIOSH approved test set ups for breathing resistance, splash resistance and particulate

Fig.3: Mill scale of filter media manufacturing

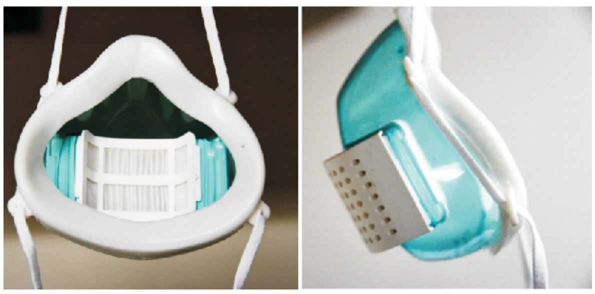

Fig.6: Engineered Valve-less Transparent Face

Fig.7: Technology transfer of EVTFM.

Fig.9: Technology transfer of NGRFM.

Fig.8: Nuclear Grade Respiratory Face Mask.

filtration efficiency etc. and qualifies as better than N95. Advanced version of mask with gauging layer has resulted in enhanced reusable life. So far, more than two lakhs of HQRFM have been produced and have been sent to different departments, hospitals, ministries and also in public domain. This technology is a step towards an Atma-Nirbhar Bharat. Presently, technology for manufacturing of mask has been transferred to three Indian manufacturers under BARC technology transfer scheme.

Engineered valve-less Transparent Face mask (EVTFM): In general, face masks are designed to seal off nose and mouth using a cloth, plastic, or silicone mask, and allow air to only pass through via designated vents or zones. These vents or zones are covered with a special fabric filter that allows clean air to pass through, blocking anywhere from 70% to 99% of particulate matter from entering. In the case of cloth masks, the entire mask acts as a fabric filter, and with something that's non-porous, like plastic or silicone, air valves and smaller filters that can be detached, cleaned, or replaced are provided. That's the basic schematic of a mask and this design encounter roadblocks. Cloth masks are often too flimsy, and while they are easier to breathe through, they don't create a proper seal around face, allowing air to leak through the sides. Plastic and silicone masks, on the other hand, have the reverse problem. They come with an air-tight seal, but those small air-valves make it difficult to breathe through after prolonged usage and are provided with exhalation valves which are not desirable. Opaque nature of these face masks is also a major issue in face recognition during security measures. In order to overcome these limitations, an Engineered Valve-less Transparent Face Mask (EVTFM), a first of its own kind in the country, has been developed using fully indigenous glass fiber (HEPA) filter medium,. It comes with modular construction, ensuring a perfect fit around the face, but instead of opting for tiny air valves and small filters, use of a special curved filter which has an area greater than a typical mask, making it much easier to breathe 99.97% filtered clean air through. Furthermore, due to its increased area it allows both inhalation and exhalation to be filtered, thus avoiding valves for exhalation. Indigenously developed HEPA media is used in a pleated and curved form that covers entire mouth. It constantly filters air while easily trapping all sorts of micro particles into its pleats/folds. The filter qualifies as P100 standard, trapping even the finest particulate matter including viruses, allergens, pollen, and bacteria to deliver 99.97% clean air to nose and mouth. The mask comes with a multi-part design featuring an external plastic cover made from recycled Acrylonitrile Butadiene Styrene (ABS), and an oronasal mask made from Thermoplastic Poly Urethane (TPU) that provides the perfect seal around the face in a way that feels comfortable.

This design is engineered to control the airflow so that the inside of mask never gets hot or humid. The geometry of the filter allows sound waves to propagate and transmit through the mask more readily, further improving usability. The mask's design is entirely modular and can be disassembled to either replace the filter cartridge or to sanitize the rest of the components as shown in Fig.6. These unique key features make it superior to applications in highly contagious environment e.g. medical, industrial & nuclear field[2]. EVTFM developed by BARC has been tested & approved as per international standards set by NIOSH and qualifies as a P100. The technology also has been transferred to an Indian manufacturer and is also being readied to be launched on a commercial platform in the name of "Jivnaank".

2. Nuclear Grade Respiratory Face Mask (NGRFM): Half face and full-face masks with glass fibre media in cartridges form are being used in nuclear applications over the last four decades. These cartridges are presently imported and assembled to form half face masks. Indigenously developed glass fibre filtration (HEPA) technology has been utilized to develop and manufacture full and half face masks as an import substitute in a better configuration making country self-reliant. Since it is indigenous, it is very cost effective. Performance of filter cartridge of NGRFM also has been tested in BIS approved Test set up and the manufacturing technology also has been transferred successfully to an Indian manufacturer as shown in Fig.9.

In-house Development of Media and Mask Test Rig Facility

Indigenous development of media and manufacturing of various types of respiratory face masks demanded in-house test set up for validation of product designed, prior to final certification at Bureau of Indian Standard (BIS) approved lab[3,4]. Procurement of readily available test set up was not feasible due to urgent requirement, pandemic constraints and higher cost. This compelled us to design & manufacture a test set up in-house equivalent to NIOSH standard at a very low cost in a minimum time frame. BARC-developed test rig facility incorporates parameters equivalent to NIOSH approved test set up. It has features for testing of various types of masks as well as filtration media. During the testing of masks, "most

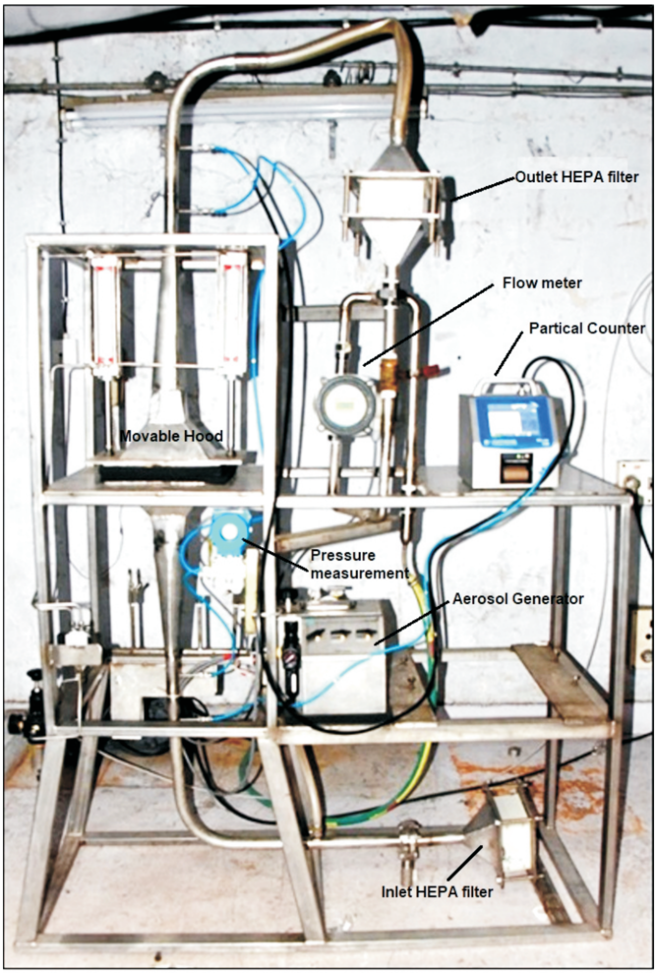

Fig.10: In-house developed Test rig facility.

rigorous" or "worst case" conditions are taken such as test aerosols should include particles at or near the most penetrating particle size range. Air flow should be near the highest level encountered during heavy work, because higher air flow leads to more particles through the filter. The detection method is to measure particles in the most penetrating particle size range with high sensitivity and precision. In the test set up, an Aerosol generator generates aerosols and the concentration of aerosols is controlled using air flow and nebulizer feed pressure etc. Test chamber is operated under vacuum, which is continuously monitored using manometer.

As per international standard, 85 lpm of flow rate is being maintained for Di-Octyl-Pthalate (DOP) based aerosols and to simulate this flow rate as breathing conditions, air is continuously drawn using an air suction pump. Differential pressure is being measured to simulate breathability of masks.

Conclusions

The present requirement of HEPA Filter medium of DAE, about 20-30 tonnes per year, is met by 100% import. Efforts by BARC for indigenization of nuclear grade glass fiber media for HEPA filters are at qualification stage. The development of this filter media is an import substitute, a major step towards Atmanirbhar Bharat. Presently available masks made of synthetic materials (spun bound and melt blown polypropylene fibers) are generally recommended for single use due to main filtration by electrostatic charge. Masks developed using indigenous developed HEPA filter based technology are reusable in nature and this will further minimize the waste generation. Complete indigenous development of filtration technology for mask grade material not only contributes to humanity in times of a global health crisis but also makes our country 'Self Reliant' in letter and spirit. Till date, more than 2 lakh units of High Quality Respiratory Face Masks, 1000 nos. of EVTFM have been produced and deployed in public domain and are being widely appreciated. The technology of HQRFM, EVTFM and NGRFM has also been successfully transferred to an Indian manufacturer for launching on commercial platform.

Acknowledgements

Authors are very thankful to all seniors of Nuclear Recycle Group, BARC for giving valuable support and motivation throughout the entire work. Development of this system would not have been possible without his vision and guidance. The authors are also thankful to the staff of Waste Immobilization Plant, BARC Trombay, for helping throughout the development process.

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NEWS DIGEST

INTER-DISCIPLINARY SYNERGY FOR INNOVATIVE TECHNOLOGIES

Pediatric Ruthenium Brachytherapy Plaques for Eye Cancer Treatment

Ramakant

Ruthenium Brachytherapy (RuBy) plaques of two different configurations (Round and Notched) developed earlier are being used for the treatment of eye cancers in seven Indian hospitals. In addition, development of paediatric plaque has been completed and it will be dedicated to the nation shortly for the treatment of retinoblastoma, which is prevalent in eye cancer of children below 4 years of age. Development of paediatric plaque was taken up based on the demand from RP Centre of AIIMS, Delhi.

The Paediatric RuBy plaque is a sealed source (silver material with 99.9% purity, Grade 999 of IS2112), bearing ^{106}Ru radioisotope as a radiation source. ^{106}Ru is electroplated on a flat circular disc (with 9.55 mm diameter and 0.2 mm thickness), which is then sandwiched in between two circular silver discs (with 0.9 mm and 0.1 mm thicknesses) and sealed by a brazing process. Fig.1 shows the construction features along with a photograph of the finished plaque.

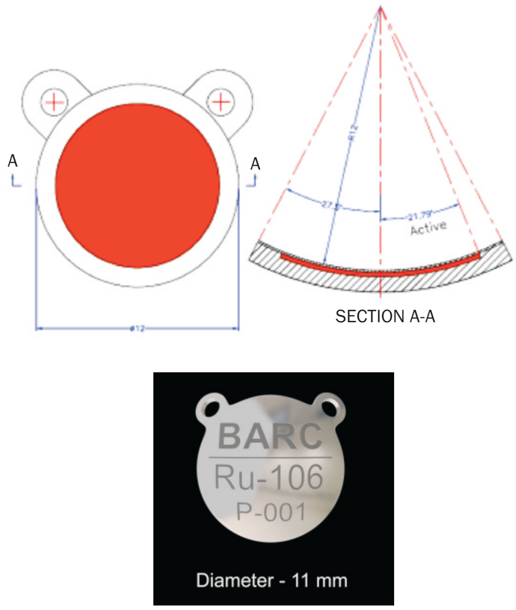

Fig.1: Construction features (Top) and photograph (Below) of the paediatric RuBy plaque.

Major challenges faced during the development include shaping the smaller sized product in conformity with children's eye configuration, and fabrication meeting the stringent specifications stipulated by AERB Safety Standard NO. AERB/SS/3 (Rev. 1). The overall plaque is very thin (1 mm), lightweight, easy to handle by the doctors, and comfortable for the paediatric patient. Each year, about 1000 retinoblastoma cases are reported in India. These children can directly benefit from this development.

Radiation Resistant Nuclear Battery using Ru-106 source

C. P. Kaushik

A radiation-resistant nuclear battery was demonstrated, jointly by Physics Group and Nuclear Recycle Group, utilizing the principles of beta-photovoltaic, wherein high beta energy of an electro deposited ^{106}Ru (recovered from high-level liquid waste) source is allowed to fall on a scintillator (indigenously grown Ce-doped $Gd_3Ga_3Al_2O_{12}$ by TPD), and the generated photons are converted to electricity using a photovoltaic device. Performance of the radiation resistant battery (beta-photovoltaic) was compared with that of a beta voltaic battery (see Fig.1). Long term radiation stability test carried out revealed no significant reduction in the output of the beta-photovoltaic device (Fig.2).

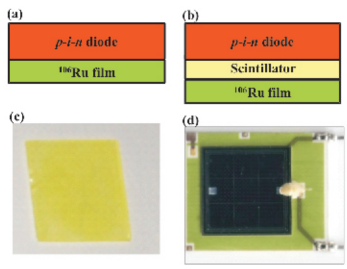

Fig.1: Battery configurations: (a) betavoltaic (b) beta-photovoltaic (c) Ce-GGAG scintillator (d) p-i-n diode.

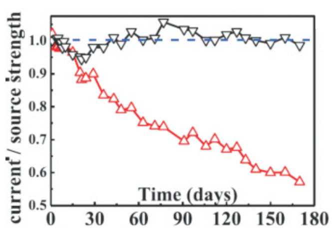

Fig.2: Current-voltage characteristics of betavoltaic (red) and beta-photovoltaic batteries (black).

Radioisotope based Thermoelectric Generator

C. P. Kaushik

BARC has indigenously built a Radioisotope Thermoelectric Generator (RTG) using minor actinide based sealed sources and bismuth telluride based thermoelectric legs(Fig.1). The device converts decay heat produced by the radioisotope into electricity through *Seebeck* effect. By virtue of having no moving parts, RTG offers high reliability with long service life, and hence it is an ideal power source for remote applications. Proof of concept for applications of RTG in remote sensing and remote surveillance was demonstrated successfully. This demonstration suggests its utility as a power source in the future deep space mission of the Department of Space.

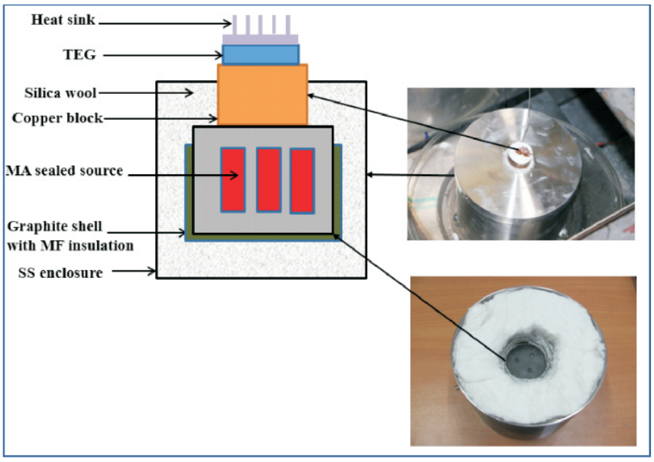

Fig.1: RTG based on MA sealed sources used for demonstration.

Technology Transfer for Bulk Production of T2EHDGA

C. P. Kaushik

Technology Transfer for Bulk Production of T2EHDGA.

The solvent, N, N, N', N'- Tetra-2-ethylhexyl-diglycolamide (T2EHDGA) is a speciality extractant used for the co-extraction of trivalent lanthanides and actinides via a solvent extraction process from High-Level Liquid Waste (HLLW). This separation of minor actinides, commonly known as actinide partitioning, helps in reduction of long-term radioactive hazards of the waste. This in turn, results in a substantial reduction in the repository footprint in terms of volume and thermal load, thereby decreasing the surveillance time and cost of managing the waste significantly. The solvent T2EHDGA has been successfully deployed in two Waste Management Plants and is envisioned to be the mainstay of India's nuclear waste management programme in the years to come. Towards this, efforts have been made to develop manufacturers capable of producing the speciality extractant on a commercial scale at a reasonable cost. The in-house developed technology for the manufacturing of the solvent is therefore transferred to an Indian manufacturers under BARC technology transfer scheme on February 14th 2022. The event is marked as a first step towards self-relience and Atmanirbhar Bharat.

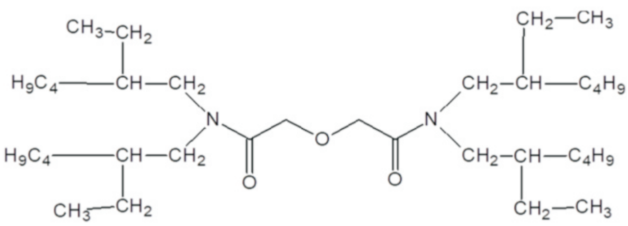

Fig.1: Chemical structure of T2EHDGA.

SNAPSHOTS OF DOCTORAL THESES

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 y) and ^{90}Sr ($t_{1/2}$ = 28.9 y) are major heat emitting nuclides contributing largely on heat and radiation load of HLLW. ^{99}Tc, a beta emitting radionuclide ($t_{1/2}$ = 2.11x10^5 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-dioctyloxycalix[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-butyldicyclohexano]-18-crown-6 (DtBuCH18C6) for selective separation of Sr^{2+} from HLLW and 4,4(5)-[di-tert-butyldibenzo]-18-crown-6 (DtBuDB18C6) for selective separation of $Na^+TcO_4^-$ 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 $Na^+TcO_4^-$ from LLW using 0.2 M DtBuDB18C6 +50% IDA/*n*-dodecane and stripping of $Na^+TcO_4^-$ from loaded solvent with DM water. Radiolytic and hydrolytic degradation studies indicated high stability of solvents.

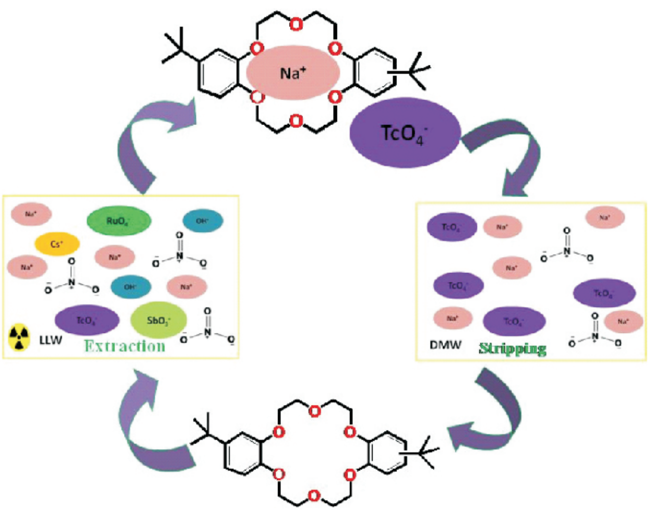

Fig.1: Extraction and stripping of $Na^+TcO_4^-$ from low level waste DtBuDB18C6 and demineralised water.

Highlights of the work carried out by **Joti Nath Sharma** under the supervision of **Dr. Tessy 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-cesium 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: CBC > CNC > CMC >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.

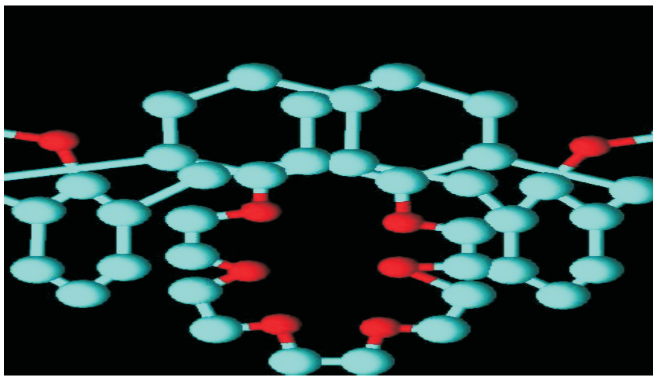

Fig.1: Structural formula CC, CBC, CNC & CMC.

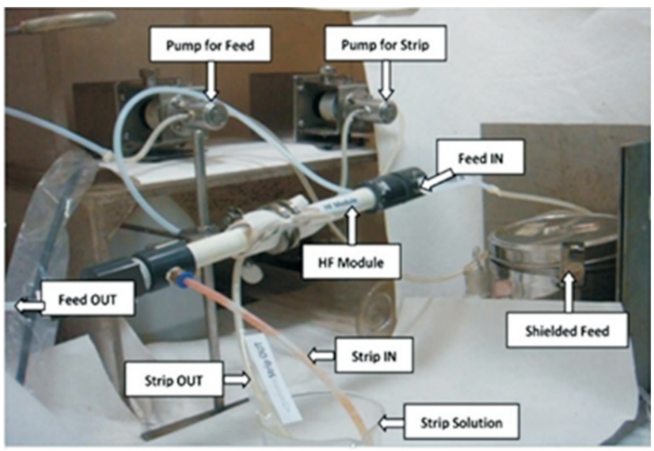

Fig.2: Photograph of the hollow fiber contractor set up used in the present study.

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

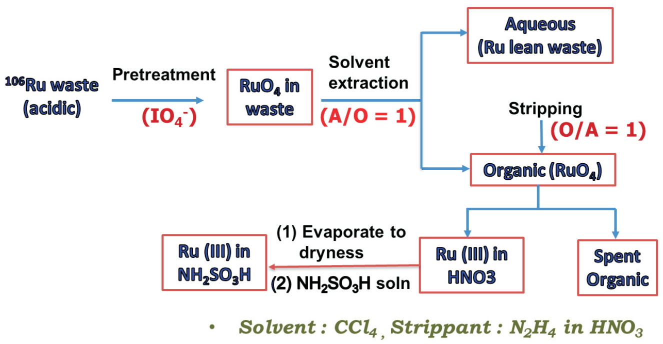

Fig.1: Process for Ruthenium separation.

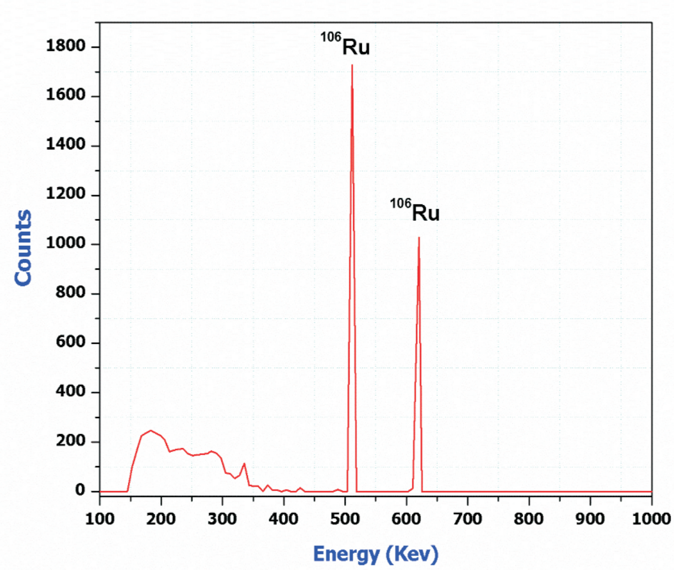

Fig.2: MCA spectrum of Ru product.

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

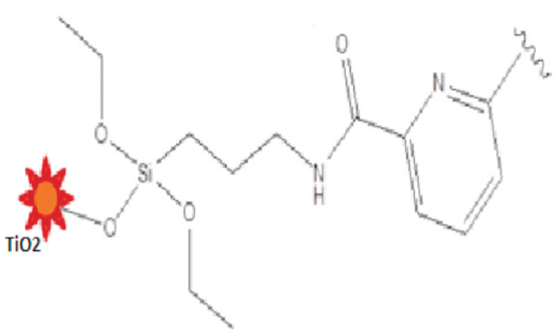

Fig.1: Dipicolinic acid functionalized.

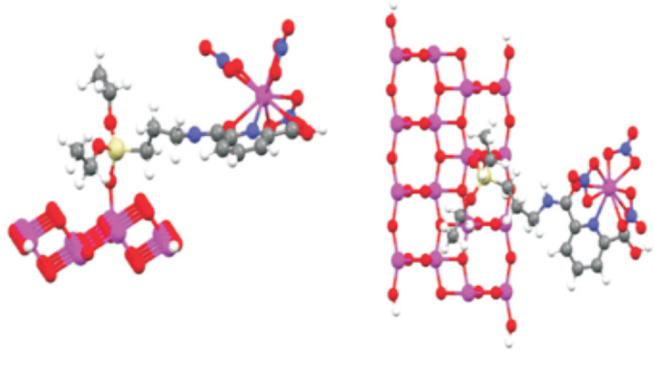

Fig.2: DFT complexation of the sorbent with Am^{3+} and Eu^{3+} .

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 absorptionof $Eu^{3+}$by DPA functionalized TiO_2 .

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

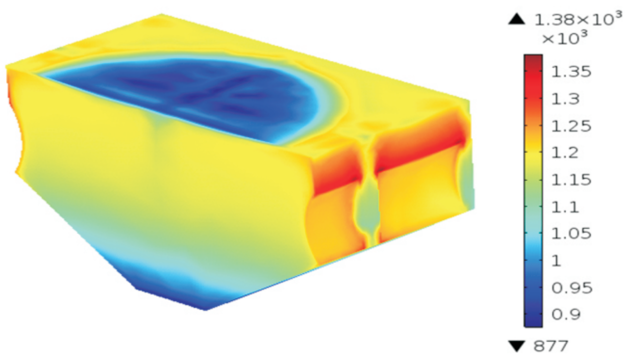

Fig.1: Temperature field inside the symmetric melter cavity (Temperature in Kelvin).

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 Al_2O_3, MoO_3 and CrO_3 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.

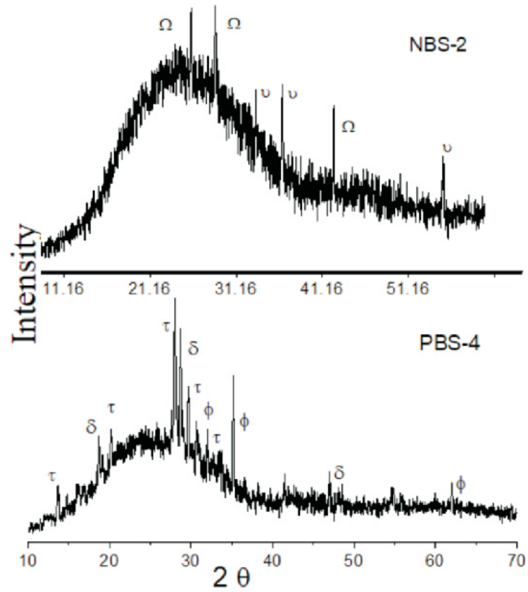

Fig.1: XRD patterns of product glass samples (Ω- $BaCrO_4$, υ-Cr_2O_3, τ- Pyroxene, δ-Powellite, Φ-spinel).

An important finding arising from this thesis is that the incorporation of ~5 mol% P_2O_5 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 P_2O_5, exhibits reflections corresponding to $BaCrO_4$ and Cr_2O_3 crystalline phases on addition of 27% wt. waste oxide. The presence of 5 mol% P_2O_5 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 thoria 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 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) $Na_2Al_2Si_3O_{10}(H_2O)_2$ zeolite phase, formed both in laboratory autoclave leaching studies and with hot springs leaching. These phases have been stable for millions of years.

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

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 $(U_{1-y}Pu_y)O_2$; (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 ±0.13% and ±0.31%, respectively. In addition, clean rejected oxide powders were also analyzed for Pu content using the WDXRF methodology.

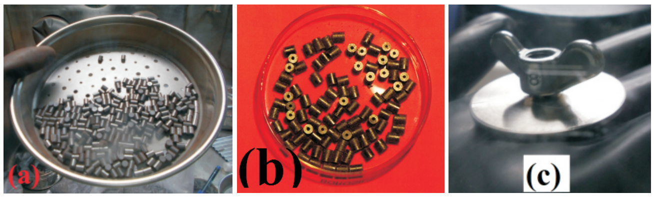

Fig.1: Portion of a batch of sintered (a) $DDUO_2$, (b) $(U, Pu)O_2$ Pellets and (c) Stainless Steel Collet.

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.

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