

**INDIAN ASSOCIATION OF NUCLEAR CHEMISTS
AND ALLIED SCIENTISTS**

Nuclear Waste Management

Practices and Trends

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Editorial

Industrial growth of a country is largely dependent on the availability of power and hence the per capita consumption of electricity is an index of the progress of any nation. Rapid industrialisation of our country in the last twenty years and the uncontrolled growth of population have resulted in high demand on the power sector. Hence, there is a need to tap all available natural resources for power production and supplement them with unconventional energy sources. Amongst the unconventional energy sources, nuclear fission is one of the most economically viable alternatives for large scale production of electricity.

The running of nuclear reactors, for research or power production, leads to the generation of nuclear waste. While a majority of the isotopes produced are short lived, a considerable amount of long lived fission products and actinides are also produced during the operation of reactors. These nuclear waste need careful handling to avoid radiation exposure to humans and contamination to ground water resources. Hence, management of long lived nuclear wastes assumes great significance.

The present issue of the Bulletin is dedicated to nuclear waste management. The authors elaborate on processes which go into nuclear waste management such that these wastes pose no problem to the present and future generations. This issue on nuclear waste management was initiated by Dr. P.K. Pujari during his tenure as Editor and hence I would like to thank him for choosing a subject of great relevance.

Dr. S.K. Samanta, the Guest Editor of this issue has taken great pain in selecting the topics and authors; and editing the articles to bring them to a uniform format. I would like to thank him and all the authors who contributed articles in this issue for their efforts.

I look forward to the members for suggestions for improvement of our Bulletin and contributions in the form of articles for future issues.

M.R.A.Pillai

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New Thrusts and Challenges in Nuclear Waste Management



Shri K. Balu is presently Director, Fuel Reprocessing and Nuclear Waste Management Group, Bhabha Atomic Research Centre. He joined the 4th Batch of BARC Training School in 1960 after obtaining his Bachelor's degree in Chemical Engineering from Annamalai University. He also undertook an Advanced Course in Nuclear Engineering in Argonne National Laboratory, USA. During his long association with the field of nuclear waste management, he has been responsible for the development of a range of processes for the effective treatment, conditioning and disposal of various categories of radioactive wastes from the nuclear fuel cycle. Several waste management plants set up on the basis of these developments have been in successful operation for over two decades now. He has been a consultant to the IAEA on a number of occasions and was associated with many of their activities including preparation of safety and other technical documents in the field of nuclear waste management. During 1986-95, he headed the Directorate of Purchase and Stores as Director and was responsible for materials management for the various units of the Department of Atomic Energy.

Present experience and knowledge in handling of radioactive wastes has led to identification of major thrust areas and challenges in the development and optimization of treatment processes and waste forms, technology for quality control of waste packages, development of passively safe land-based repositories and their performance assessment.

Waste Minimization

This is an essential step to reduce the overall burden of waste management. Among others, proper selection of materials and adoption of processes to facilitate recycling and reuse of waste are the major considerations to achieve this objective. Other approach is volume reduction by adopting techniques involving incineration, melt densification and super compaction. The growing need for disposal of wastes in engineered structures, with highly durable waste forms suggests adoption of processes like vitrification of low and intermediate level wastes leading to substantial volume reduction for disposal. Because of their high volumes and the fact that these wastes may contain significant quantities of non-radioactive constituents, a concentration step before vitrification is called for. Use of highly selective sorbents and ion exchangers is an attractive proposition for achieving this volume reduction. In this approach for low and intermediate

level waste management, cost of vitrification gets offset by substantially reduced product volume and post disposal surveillance. Vitrification will also establish uniform waste form unlike diversified approach followed currently for these wastes.

Improved matrices

Vitrification using silicate glasses has been proven and industrially established technology for the immobilization of high level liquid wastes. Present process of vitrification implies "melting technology" involving higher temperatures in the range of 1000-1200°C. This results in higher evaporation and volatility losses and also involves highly corrosive molten glass-metal interactions. This severely affects the service life of the melter. Besides, liquid states present at elevated temperature allow segregation as well as macroscopic inhomogeneities in the vitreous mass. Cooling down from higher temperatures leads to temperature gradients generating internal stress in the solidified glass. Alternatively, efforts are directed to develop other glass based matrices like sintered glass where emphasis is on immobilization by powder technology involving reduced temperatures (500-550°C, 25-30 MPa) and not by melting and casting. Also present international interest is focussed on multi-barrier waste forms like

VITROMET which is made by encapsulating glass marbles in vacuum-cast lead alloy matrix. Multi-barriers not only result in higher chemical durability but also improved thermal conductivity, decrease in canister centre line temperature, increased waste loading and improved mechanical strength. Besides glass based matrices, thermodynamically stable ceramic waste forms like SYNROC are also under development. SYNROC is a multi-assembly of polycrystalline and polyphase ceramics containing mainly four titanate minerals, viz., zirconolite, hollandite, perovskite and titanium oxide. Nearly all elements in high level waste can be incorporated into crystal structures as solid solutions via hot isostatic pressing. SYNROC is more stable at elevated temperatures in hydrothermal environment than borosilicate glass. The solubility of the main matrix component, TiO_2 is three to four orders of magnitude lower than that of SiO_2 . However, unlike vitrification, "hot" operation required to demonstrate and evaluate industrial application of SYNROC process is yet to be established.

Actinide Partitioning

The actinides are the most important long-lived nuclides to be partitioned from high level wastes. This strategy is essential from the point of view of reducing the need for long term isolation of these wastes. Partitioning of actinides employing extraction processes are under development and could be employed as an extension of PUREX

process. The major problems to be solved are in the separation of minor actinides, mainly americium and curium without producing large quantities of secondary waste and development of extractants which are amenable to treatment and conditioning. Partitioning may not eliminate the need for geological disposal unless highly mobile and long-lived fission products like ^{99}Tc and ^{129}I , representing the main residual hazard, are isolated from high level wastes.

Isolation from Environment

Components of waste package (waste form, waste container, over packs) are designed to provide complete confinement of radionuclides for a period of a few hundred to thousand years. More attention has to be paid to the long term behaviour and this will require generating information about their physical and chemical properties as well as the geological processes that may progressively change their properties.

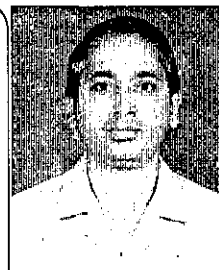
Detailed studies are to be undertaken for the chemical containment of radionuclides in the near field and improve barrier function of the engineered components of the repository. Studies to investigate long term impacts of various interactions between the waste packages and immediate environment of the repository would be necessary, since its selection will be governed by geological formation and geochemical environment of the multi-barrier disposal system.

Nuclear Waste Classification, Management Philosophy and Regulatory Criteria



Shri P. Vijayan obtained his M.Sc(Chemistry) degree from the University of Bombay. He underwent one year training in Health Physics at Bhabha Atomic Research Centre before joining the Operating Plants Safety Division, Atomic Energy Regulatory Board. Since 1991 he is associated with the licensing of disposal/transfer of radioactive wastes in various nuclear installations and also with the review of periodical returns of radioactive wastes handled by all the major units of DAE. His field of interest also includes environmental studies of radionuclides/trace metal ions in sediment/water and their uptake by plants in the coastal environment.

Shri K.K Chandraker graduated in Chemical Engineering from Ravishankar University, Raipur. He joined Waste Management Division of Bhabha Atomic Research Centre in 1972. He was associated with design and site installation of radioactive effluent treatment plants at Tarapur, Narora and Variable Energy Cyclotron, Calcutta. In 1985 he joined Atomic Energy Regulatory Board (AERB) and was entrusted with the responsibility of reviewing operations of Waste Management Facilities in DAE. He was instrumental in effectively introducing G.S.R 125 - Atomic Energy (Safe Disposal of Radioactive Wastes) Rules 1987 in all DAE units. He has participated in meetings held by International Atomic Energy Agency at Beijing and Vienna and was associated with drafting of safety guide, "Licensing of Radioactive Waste Management Facilities". Shri Chandraker is also associated with various other DAE units as AERB safety committee member.



Introduction

Radioactive waste differs from other industrial wastes due to its radiation exposure and its radiological toxicity to human beings and their environment. Indian nuclear industry consists of mining and milling of uranium ore, thorium extraction, fuel fabrication, reactor operation, fuel reprocessing, and the production and application of radioactive isotopes for various industrial, medical and research purposes. The low level radioactive wastes (solid, liquid and gaseous) arising from these nuclear installations either in normal or anticipated operational occurrences are to be controlled in order to protect the public and their environment from any unacceptable risks under all reasonable circumstances. Development of safe, efficient and economically viable strategies of waste disposal systems are essential for safe and effective management of radioactive waste. National strategies of waste management system may vary from country to country depending on the national objectives and needs. However, the overall objective

of any waste management system is the protection of human beings and their environment from the short and long term effects of radiotoxicity.

Waste Management Philosophy

The objective of nuclear waste management is the effective isolation of radionuclides from the environment to ensure adequate safety and welfare of the public. The philosophy of radioactive waste management embodies three basic principles:

- delay and decay (for short lived radionuclides)
- dilute and disperse (for very low active effluents)
- concentrate and contain (intermediate and high active wastes)

The main advantage of this philosophy is simplicity and consistency with general practice. For the implementation of such philosophy in the waste management system, the safety requirements of the infrastructure have to be satisfied within the regulatory frame work to ensure that radiation

exposure to the occupational workers and the public is reasonably minimum without imposing undue burdens.

Waste Classification

Radioactive wastes may arise in a wide variety of physical and chemical forms. Hence the classification parameter is typically related to the physico-chemical characteristics and the radionuclide content of a particular waste which is identified for the disposal purpose. In this system, the radioactive wastes are categorised into low, intermediate and high level wastes. This classification system expanded by IAEA is more compatible with general practice. Under this new classification system exempt waste is identified and disposed of into the biosphere without any regulatory control. The disposal requirements are mainly based on the length of isolation of a particular radionuclide from the environment to decay to a level of insignificant radiological risk. The classification system may also depend upon the local disposal conditions and the possibilities for handling and storage. During the recent years the authorised limits for radioactive discharge into the biosphere have reduced considerably. These changes are coupled with the requirements for accurate classification and categorisation of radioactive wastes at different stages of waste management operation. Various steps involved in the management of all kind of waste are:

- identification and segregation
- reduction and recovery
- transportation and treatment
- disposal and surveillance

The solid, liquid and gaseous wastes embodied in various matrix forms contain asymmetric activity levels. Different types of wastes require a variety of treatment and conditioning methods prior to the disposal. Due to this physico-chemical and radioactive asymmetry, Atomic Energy Regulatory Board has categorised these wastes conforming with internationally acceptable norms and standards (Table 1).

TABLE 1. Categorisation of Radioactive Wastes

Category	Solid	Liquid	Gaseous
	Surface Dose (mGy/hr)	Activity level ₁ (Bq/M ³)	Activity level ₂ (Bq/M ³)
I	< 2	< 3.7 x 10 ⁴	< 3.7
II	2 - 20	3.7 x 10 ⁴ to 3.7 x 10 ⁷	3.7 to 3.7 x 10 ⁴
III	> 20	3.7 x 10 ⁷ to 3.7 x 10 ⁹	> 3.7 x 10 ⁴
IV	Alpha Bearing	3.7 x 10 ⁹ to 3.7 x 10 ¹⁴	-
V	-	> 3.7 x 10 ¹⁴	-

Solid Waste

Low level radioactive solid wastes are generated by nuclear power reactors, nuclear fuel cycle facilities, radio-isotope manufacturers and users of radioactive materials. These wastes can be classified in various ways according to their chemical and physical stability, chemical content, density, flammability, radionuclide content and potential risk of radiation hazards.

Physico-chemical properties of the wastes influence the structural integrity of the waste repository. The waste material should be chemically inert and physically stable and should not be pyrophoric, explosive or toxic. An appropriately conditioned waste can be disposed of in underground repositories. The generic options for the disposal of solid wastes are:

- emplacement of solid waste at shallow depth with or without engineered barrier above or below ground surface, where the final protective covering is of the order of a few metres thickness.
- emplacement of solid wastes in mined repositories especially designed and excavated for waste disposal at suitable depth in continental geological formations, such as salt, crystalline rocks or argillaceous formations.

- emplacement of solid wastes in man-made or natural rock cavities at various depth.

In India shallow land disposal facilities are generally employed for low and intermediate level wastes and geological repositories are intended for high active wastes. The shallow land facilities generally consist of earth trenches, reinforced concrete vaults and tile holes. The natural and engineered barriers along with the waste form and the backfill material retard the migration of radionuclides into the biosphere by isolating them within the facility.

Liquid Wastes

Liquid wastes are classified based on the radioactivity content, ionic impurity levels, dissolved or suspended solid content, organic impurities, detergent and chemicals. Irrespective of the origin, radioactive liquid wastes can be broadly classified into five categories based on the activity levels (Table 1). The main source of liquid wastes from nuclear industries are the active floordrains from different areas, decontamination centre, chemical laboratory, upgrading plant rejects, detergent waste from active laundry and drains from change room and showers, etc. These waste streams require treatment to reduce their activity concentration to a level at which they are allowed to be discharged according to the national regulations.

The liquid effluent management system may contain either underground or above ground pipelines which should satisfy various safety measures stipulated by Atomic Energy Regulatory Board. Some of the important regulations are :

- All the effluent lines laid above ground should be inspected at least once in a year to check whether the protective measures are intact.
- All the effluent lines laid underground should have indicating markers above ground at suitable intervals. If there is a cluster of pipelines above ground in any location, clear indelible identification marks should be made on them at suitable intervals.
- The effluent lines used in pumping mode should be pressure tested once in six months at the shut-off pressure of the pump or 110 % of the operating pressure whichever is higher.

- The branch lines connecting various sources of waste generation to the main header leading to the effluent collection tank, should be physically inspected at least once in a year by qualified personnel.
- Facilities should try to install up-to-date instrumentation for the measurement of parameters like (i) liquid level in the sump/hold-up tanks (ii) flow rate during pumping (iii) pumping pressure (iv) pressure at the discharge and receiving ends and (v) pressure profile inside the pipeline.

Gaseous Wastes

Gaseous wastes from any nuclear installation can be classified into primary system gas, secondary system gas and the building ventilation. The primary system gases include fission products, hydrogen and nitrogen generated due to radiolysis. The secondary system gases arise from the leakage of various component systems and the activity levels are low compared to primary gas system. The third category of gaseous waste is the large volume of ventilation air, most of which arises from auxiliary buildings where radioactivity exists. This air is often discharged to the atmosphere at sufficient height through various filters to reduce the radionuclide concentrations. According to Atomic Energy (Safe Disposal of Radioactive Wastes) Rule 1987, gaseous wastes are classified into three categories based on the activity concentration (Table 1).

Regulatory Criteria

The effective management of any radioactive waste system depends on the management policies from waste generation, treatment, conditioning, handling, transportation, storage and final disposal to the environment. In India, Atomic Energy (Safe Disposal of Radioactive Wastes) Rule 1987 governs the disposal or transfer of radioactive wastes for the installation engaged in radioactive waste management operations. Atomic Energy Regulatory Board (AERB) is conferred with the authority for the enforcement of this rule and Chairman, AERB is the competent authority for the implementation and review of these regulations and to issue/suspend/amend the authorisation for the safe disposal or their transfer to any waste management agency.

The Atomic Energy (Safe Disposal of Radioactive Wastes) Rule 1987, has divided the nuclear installations into two categories. The first category includes installations like UCIL, NFC, power reactors, spent fuel reprocessing plants and waste management units which generate or handle bulk quantities of radioactive wastes having significant amount of activity and contain radionuclides which possess sufficiently long effective half lives.

The second category consists of installations such as hospitals, research laboratories and industries which produce small amount of radioactive wastes having trace levels of activities and contain radionuclides having short effective half lives. Prior to authorisation, the operating installation has to submit an application to the competent authority seeking permission for radioactive waste disposal or transfer to the waste management agency. The application for granting the authorisation may call for the following information:

- physical form or packaging of solid wastes, chemical characteristics of liquid and gaseous wastes
- methods of conditioning
- annual volume (M^3)
- radionuclides present
- total annual activity (MBq)
- location of disposal site
- safety features provided for the solid, liquid and gaseous waste management operation
- site drawings upto a radius of 200 metres from the installations and the nature of occupancies and land/water utilisation in this area
- Complement of trained personnel and radiological safety officers

For the compliance of regulatory requirement and the enforcement of this rule, the operating organisation should maintain monthly performance records and submit periodical returns to the competent authority within the stipulated period and these should be available as and when the regulatory body representative requires it for inspection.

For the development and the assessment of waste inventory systems, accurate information on waste generations and waste disposal facilities are

essential. A computerised data base has been developed for this purpose and this gives the qualitative and quantitative information on the waste management system. The database system has three modules (site wise, unit wise and installation type wise) for the solid, liquid and gaseous wastes management. Each module of the data base system separately facilitates the storage and rapid retrieval of specific information regarding the disposal or transfer of radioactive waste under Atomic Energy (Safe Disposal of Radioactive Wastes) Rule 1987.

The installations belonging to second category have special provision laid in G.S.R. 125 (Atomic Energy Safe Disposal Radioactive Wastes) Rule 1987. Rule 15 of the above statutory rule permits three appropriate modes of local disposal of radioactive waste containing short-lived radioisotopes:

- (i) Release into sanitary sewerage system or soak pit in case a sewerage system is not provided.
- (ii) Burial into pits in an exclusive area of the institution.
- (iii) Incineration in an appropriate incinerator designed to avoid dispersal of contamination.

The licensing or authorisation for the safe disposal or transfer of radioactive wastes involves several stages of safety assessment, such as

- identification and understanding of proposed waste generations
- evaluation of data on quantity and activity of waste
- assessment of radiation safety measures provided for waste management operations
- justification for the chosen sites
- assessment of the radiological and non-radiological impact on the public and ecological system during operational and post-closure phase
- analysis of emergency preparedness plans.

The safety features of the radioactive waste disposal system must be convincingly shown to the regulatory body prior to the operational phase of the waste management system. In case of any non-compliance with the legal requirements the regulatory body is empowered to take necessary actions against the installation depending on the severity of safety implications.

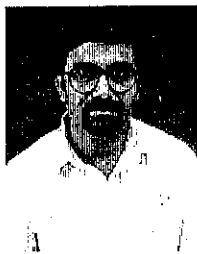
Conclusions

Nuclear installations are designed, constructed and operated according to stringent regulations of safety measures. Since nuclear energy has a significant role to play, the nuclear industries are required to develop a comprehensive system of policies for the management of radioactive wastes in a safe, efficient and economical way.

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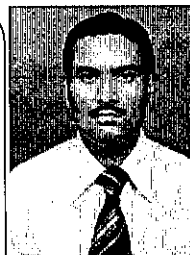
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Chemical Treatment of Radioactive Liquid Waste



Dr. P.K.Sinha joined the 19th batch of BARC Training School in 1975 after obtaining his M.Sc degree from the University of Bihar and is presently looking after the Process Development and Control Laboratory, Centralised Waste Management Facility, IGCAR, Kalpakkam. He obtained his Ph.D degree from Anna University, Madras. He is engaged in process development studies related to treatment of radioactive liquid effluents by chemical precipitation and ion exchange methods. He has carried out detailed investigations on the use of locally available synthetic zeolites for removal of radionuclides from waste effluents followed by their fixation by thermal treatment. Dr. Sinha has thirty publications to his credit.

Shri Jaleel Ahmed is presently Head, Centralised Waste Management Facility, IGCAR, Kalpakkam. He joined the 13th batch of BARC Training School in 1969 after obtaining his Bachelor's degree in Mechanical Engineering from the University of Madras. He has a Postgraduate Diploma in Business Administration from Annamalai University. He has been responsible for the Operation and Maintenance of various Waste Management Facilities treating different types of wastes from nuclear installations at Kalpakkam. He was also responsible for the design of many of these facilities. Presently he is also looking after the R&D activities in this area. He has served the IAEA as Technical Expert in the field of Collection and Treatment of Low and Intermediate Level Waste from Nuclear Facilities. Shri Ahmed has twenty five technical presentations and publications to his credit.



Introduction

Since the advent of nuclear power, the search for suitable technology for the treatment of different types of radioactive wastes generated in the nuclear fuel cycle, has been continued. Unlike the wastes encountered in other industries, radioactive wastes assume special importance and a different dimension, owing to the associated radiation hazard. Many alternatives for their treatment have been investigated and some of them applied successfully in the waste treatment plants. However, no method or material is universally applicable and the adoption of any treatment technique for a given type of waste will depend upon the efficacy of the method, characteristics of the waste, availability of the materials, and of course, economical considerations, which must be in keeping with the ALARA (As Low As Reasonably Achievable) principle.

Sources and Characteristics of Radioactive Waste

The nuclear fuel cycle consists of various steps, viz., mining and milling of uranium ores, extraction of uranium, its conversion to oxide, fabrication of

U-oxide fuel assemblies for loading into a nuclear reactor, and finally, reprocessing of the partially irradiated fuel for extracting useful materials, such as unreacted uranium and plutonium (produced by the absorption of neutrons by uranium) for reuse in future reactors.

In almost all the steps mentioned above, waste matter is generated which needs proper management. However, the radioactive content of the wastes obtained in the first three stages i.e., from mining to fuel fabrication, is only due to natural U and its daughter products and does not pose any serious problem. The liquid waste contains lot of suspended matter and is treated by retention and settling in tailing ponds. Lime addition is also used as and when required.

The main sources of radioactive liquid waste are the reactor and the reprocessing plant. These wastes contain, in varying concentrations, a wide spectrum of fission products, activated corrosion products, both of which are beta-gamma active, and actinides possessing alpha activity. Most of the

radioactivity is in the form of cations (Cs^+ , Sr^{2+} , Co^{2+} , Ce^{3+} , Am^{3+} etc.) and only a few anionic radiopollutants are encountered (iodides, iodates, ruthenates, technetates, anionic complexes of U, Pu etc.). The waste from reactor has high volume but low radioactivity, while that from reprocessing plant contains almost 99% of the total inventory of radioactivity in the whole fuel cycle and is contained in a relatively smaller volume. Besides the usual system of classification (dealt with elsewhere in this issue), radioactive wastes are also conventionally classified as Potentially active (PAW, Category I), Low level (LLW, Category II), Intermediate level (ILW, Category III), and High level (HLW, Category IV and V) wastes. Effluents containing significant quantities of alpha active isotopes (actinides) in addition to beta-gamma activity, are termed as 'Alpha waste'. Reprocessing plants generate all types of waste, whereas effluents received from a reactor, are generally of low and intermediate levels, with insignificant amounts of alpha active actinides. In these wastes, the concentration of two fission product isotopes viz., ^{137}Cs and ^{90}Sr , is generally high and due to their long half-lives (30 and 28 years, respectively), these elements are important in the treatment of wastes. Actinides have still longer half-lives, of the order of 10^4 to 10^6 years, and demand special attention. Other elements of importance are Ru, Ce, Zr-Nb, Co etc.

Treatment Processes

The treatment of high level waste is dealt with in a separate article in this issue. For the treatment of low and intermediate level radioactive liquid wastes, three processes are generally adopted viz., Chemical Precipitation, Ion-exchange and Evaporation [1]. Other processes like Reverse Osmosis, Electrodialysis and Ultrafiltration, are under investigation as supplementary treatment techniques. All these methods aim at reducing the volume of the waste, which is achieved by redistributing the activity in two phases, one dilute (liquid) and the other concentrated (liquid or solid). The dilute phase, depleted in radioactivity, may be disposed of to the environment, after providing necessary dilution, in order to meet the regulatory limits set for its discharge. The concentrated phase has small volume but contains almost all the radioactivity and is conditioned i.e., fixed in cement,

bitumen or polymer matrices [2], before storage/disposal in specially made near surface underground (3 to 5 M deep) facilities, like Earthen Trenches, RCC (reinforced cement concrete) Trenches and Tile Holes.

The efficacy of a treatment scheme is judged by the values of Decontamination Factor (DF), which is defined as the 'ratio of radioactivity in the liquid phase, before and after treatment'. In addition to obtaining high DF values, the process should also yield high Volume Reduction Factor (VRF), defined as the 'ratio of the initial volume of the waste to the volume of the concentrated phase generated after treatment'.

Among the processes mentioned above, Evaporation is an efficient process, providing very high DF (10^3 to 10^4) in the condensate, which is suitable for disposal. The concentrate exists as a thick liquid of small volume and contains most of the activity. But the process is costly and energy-intensive and is used only for the treatment of low volumes of waste, containing moderate levels of radioactivity and low concentration of salts (e.g., ILW). Chemical treatment is a well-proven technique, less expensive and tolerant to variations in effluent volume, characteristics etc. This is used as a batch or a semi-batch process for large volumes of effluents, containing low activity. It provides lower DF values (10 to 100) but if the material can be preformed in a granular form and used in a column as a continuous process, it would show high efficiency of removal. Ion-exchange treatment offers a good compromise between efficiency (DF 10^2 to 10^3) and cost, and can be applied to a number of effluent streams, varying in volume and radioactive content. This can be used as an on-line, continuous process and is a very promising treatment method. Its limitation is the presence of other non-active interfering ions in the effluent.

In the present review, however, only the Chemical Treatment of radioactive liquid waste has been discussed at length.

Chemical Treatment of Radioactive Liquid Waste

The chemical treatment method is generally applied to low and sometimes, intermediate level liquid effluents wherein the radionuclides are

precipitated, coprecipitated, carrier precipitated or adsorbed by insoluble compounds. The mechanism of removal may be precipitation, adsorption, ion-exchange, sweep flocculation (involving physical entrapment) or a combination of some or all of them. The precipitation is carried out in situ in big tanks holding the effluent. Solutions of the precipitants are mixed in a Flash Mixer under rapid stirring and the mixture flows into a Clariflocculator for flocculation and clarification to occur. If needed, suitable coagulant and flocculants e.g., ferric ions, polyelectrolytes etc., may be added to the system for improving the efficiency. After the sludge settles, the supernatant is allowed to overflow for further treatment by ion-exchange or for disposal to a large water body, after providing the required dilution, with a view to ensure that the specific activity levels are below the prescribed regulatory limits. The sludge is filtered through a rotary drum vacuum filter or better through an ultrafilter and the dry cake is fixed in cement matrix.

The overall efficiency of the system will depend on two phenomena : i) uptake of the radionuclide by the precipitate and ii) separation of the solid and liquid phases. For the first, the precipitate should have substantial selectivity and specificity for the radioactive ions and for the second, the flocs obtained should have favourable coagulation, flocculation and separation characteristics. This calls for the choice of an appropriate precipitation system and a precise optimization of the process parameters to ensure as complete a phase separation as possible.

A large number of materials that can be used in precipitation systems in batch process have been, and continue to be, investigated for the separation/recovery of radioactivity. Some of them may be useful for the gross removal of a group of radionuclides while the others may be specific to a particular one. Amongst the non-specific precipitation systems, one may mention the oxides and hydroxides that are used for the removal of metallic ions that form insoluble hydroxides e.g., Fe^{3+} , Al^{3+} , some of the transition metals, lanthanides and actinides. An example is the use of ferric hydroxide precipitation for Sr and Pu removal from simulated and actual alkaline waste [3]. Other such precipitants include various salts like phosphates,

sulphates, oxalates, titanates, etc. Sulphate of Ba has been used in batch process for the removal of Ra and also Sr. Oxalate can be used for the precipitation of Sr in alkaline medium and of lanthanides/actinides in acidic medium.

Specific Precipitation Systems

Removal of Cs

Cs ions are by nature hydrophobic, due to their large ionic radius (small hydrated ionic radius), and hence their removal is rather easy. Insoluble heteropolyacids, hexacyanoferrates and sodium-tetraphenylborate are materials found to be specific for the uptake of Cs ions from aqueous medium. Of these, the heteropolyacids (e.g., ammonium molybdophosphate, AMP) sodium tetraphenyl borate are generally suitable in acidic medium and alkaline media respectively, while hexacyanoferrates are applicable in a wide range of pH and hence among the most favoured materials. Extensive studies have been carried out on the removal of Cs from simulated and actual wastes using hexacyanoferrates and related compounds. Freshly precipitated copper hexacyanoferrate (Cu-HCF) has been used for the carrier precipitation of Cs in chemical treatment plants in many countries, viz., India, Germany. The results of investigations on use of Cu-HCF and Co-HCF for the removal of Cs from simulated waste solutions have been reported [4]. The flocculation aspects of Cu-HCF using ferric chloride and polyelectrolytes, have also been studied [5]. A good review on the separation of Cs by different hexacyanoferrates has recently been published [6]. The use of sodium tetraphenylborate precipitation for Cs removal from simulated and actual alkaline wastes has been reported [3,7].

Removal of Sr

No specific material has been identified that can remove only Sr from aqueous waste. However, systems normally employed for the removal of Sr are phosphates of Ca, Ti and Zr.

Removal of Actinides

Specific removal of individual actinides is difficult and in fact, they are generally separated in

combination with the lanthanides (beta-gamma active). Further partitioning is done only subsequently, using a combination of methods like solvent extraction, ion-exchange and precipitation. Studies on separation of lanthanides and actinides by precipitation with Ce-oxalate, known as the OXAL process, have been reported [7,8]. Removal of thorium by carrier precipitation with Ce-oxalate in acidic medium (pH 1 or below) was also studied [9,10]. The alkaline earth and transition metals do not precipitate in this highly acidic medium. Freshly precipitated magnetic ferrite has been found to be effective for the removal of radioactive materials including actinides [11]. The removal of actinides by ferric floc precipitation [12] is well known but there are reports that ferrate (FeO_4^{2-}) ions are superior to ferric ions in removing actinides [13].

Removal of Ru

Ruthenium is one of the most elusive elements escaping removal, because it exists in a number of chemical forms in aqueous solution. These forms include neutral, cationic, anionic complexes, elemental Ru and particulates. The cationic forms may be removed by hydroxide precipitation while the complexes are more difficult to remove. In reducing medium, however, precipitation of FeS and CoS have been found to provide significant removal of Ru. Cu-HCF has also provided removal of Ru-complexes by precipitating the ruthenocyanide [14].

Radioactive Liquid Effluent Treatment Plant at the Centralised Waste Management Facility (CWMF), Kalpakkam

The Centralised Waste Management Facility (CWMF), at Kalpakkam, comprises the following units:

- A Liquid Effluent Treatment Plant (LETP) for segregation, collection, treatment and safe disposal of all low and intermediate level radioactive effluents.
- A Decontamination Centre (DC) for reclamation of contaminated equipment and a laundry for decontamination of clothing and protective wear from active areas.

- A Solid Waste Management Facility (SWMF) with provision for segregation, packing, incineration and baling.
- A radioactive solid storage-cum-burial area for handling and disposal of all radioactive solid wastes.

Collection of Liquid Waste

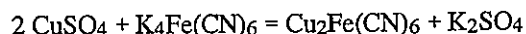
As the regulatory limit on gross beta-gamma discharge to sea is 10^{-6} mCi/L at Kalpakkam site, the Category I effluent is directly discharged to sea through the Central Discharge Facility (CDF) at MAPS. The Category II effluent is collected through underground HDPE pipes (encased in secondary containment of cast iron pipes) that connect various site storage tanks to CWMF. These effluents are collected in Pre-treatment tanks, (three in number, each with capacity 250 M^3 and an additional sump tank of capacity 125 M^3). The Category III effluents are collected in tanker/carbuoys from various facilities and stored in stainless steel tanks. Small quantities of Category IV wastes and organic wastes are also collected in carbuoys with secondary containment in HDPE or MS drum.

Liquid Effluent Treatment Plant (LETP)

The Category II effluents are subjected to a two stage Chemical Treatment followed by Ion-exchange using natural vermiculite, which is specific for the removal of Cs and serves as a final polishing step. The Category III effluents are evaporated.

Chemical Treatment

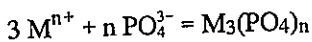
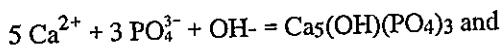
This plant has been designed to process $230 \text{ M}^3/\text{day}$ (8 hours operation) of effluents. In the first stage, the effluent from one of the pre-treatment tanks is pumped to Flash Mixer (FM - 1), wherein $\text{K}_4\text{Fe}(\text{CN})_6$ and CuSO_4 solutions are added along with $\text{Fe}(\text{NO}_3)_3$ solution. The pH of the effluent is adjusted to 8.5 by the addition of NaOH solution and the total content is mixed thoroughly using a turbine type stirrer, operating at 60 rpm. The chemical dosing is as follows: 20 ppm of Cu^{2+} as CuSO_4 , 30 ppm of $\text{Fe}(\text{CN})_6^{4-}$ as $\text{K}_4\text{Fe}(\text{CN})_6$ and 25 ppm of Fe^{3+} as $\text{Fe}(\text{NO}_3)_3$ solutions.



The added $\text{Fe}(\text{NO}_3)_3$ leads to the formation of ferric hydroxide that helps in the coagulation of the precipitate and ferric ferrocyanide which is also a good carrier of Cs.

The precipitated $\text{Cu}_2\text{Fe}(\text{CN})_6$ scavenges ^{137}Cs from the effluents. After a retention time of about 5 min. in the flash mixer, the overflow is let into the flocculating compartment of Clariflocculator (CF - 1), through a trough. The flocculator paddles, operating at 1.62 rpm, promote particle contact, resulting in the growth of the particle size and enabling quick settling. A retention time of about 4.5 h is provided in the CF for efficient growth of the particles and removal of Cs. The overflow is collected in an underground sump and the same is pumped to FM-2.

In the second stage, 75 ppm of Ca^{2+} as CaCl_2 , 130 ppm of PO_4^{3-} as Na_3PO_4 and 25 ppm of Fe^{3+} as $\text{Fe}(\text{NO}_3)_3$ are added in the form of solutions, to the effluent in FM-2, followed by the addition of NaOH solution to maintain the pH at 10.5. This results in the precipitation of calcium hydroxy phosphate, $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$ and other phosphates.



M represents Fe^{3+} and some transition metals, lanthanides and actinides. The bulk precipitate of Ca-phosphate or Fe-phosphate carries traces of Sr and as the precipitation is carried out at high pH (10.5), the flocculation of the phosphate is aided by the precipitation of hydroxides of metals present in the system.

The suspension is taken to CF-2, where again a settling time of 4.5 h is provided. The overflow from this clariflocculator is taken to an underground sump provided in the ion-exchange room for further treatment. The settled mass of suspended solids in the clariflocculators is removed with the help of diaphragm pumps and stored separately in sludge storage tanks installed in filter room. The sludge is filtered using precoat vacuum rotary drum filter, to ensure utmost clarity of filtrate and the solid cake is collected in standard 205 litre drums and sent for concreting prior to disposal. The filtrate is pumped either to Post-treatment Tank or Pre-treatment Tank

for further treatment depending upon its specific activity.

The cumulative decontamination factor (DF) is calculated by multiplying the DF values obtained in the two stages and may range from 10 to 100. Figure 1 shows the flow-sheet of the Chemical Treatment Plant of CWMF, Kalpakkam.

Discharge of Liquid Waste

At Kalpakkam site, the regulatory upper limit for the discharge of gross beta-gamma specific activity to sea is 10^{-6} mCi/L. The corresponding limit for alpha activity is 10^{-7} mCi/L. The limits on discharge of tritiated aqueous waste are : Tritium specific activity 6.5×10^{-3} mCi/L, and total Tritium activity 15 Ci/day and/or 400 Ci/month. Till date, the discharges have always been maintained within the specified limits.

The treated effluent (by chemical treatment/ion exchange or evaporation) is stored in the Post Treatment Tanks (three in number each with capacity 250 M^3 and an additional sump tank of capacity 125 M^3) at CWMF. From these tanks, the effluent is discharged into sea, through the Central Discharge Facility (CDF) at MAPS. Necessary dilution is provided using the condenser cooling water of the reactor, that is pumped through the Emergency Process Sea Water pumps, at a flow rate of 400 litres per second. Potentially active waste and tritiated waste with low activity, are discharged directly to sea through the CDF after dilution.

Collection and Discharge Data (annual)

Typical year : 1995

Given below are the quantities and activities of various types of liquid effluents received and disposed to sea, after dilution/treatment.

The total volumes of liquid waste, received from MAPS and IGCAR/CWMF, were $11,922 \text{ M}^3$ and $7,807 \text{ M}^3$, respectively. The gross beta-gamma activity was 1018 mCi and 142 mCi while the tritium activity was 2529 mCi and 259 mCi, respectively. The volumes discharged were $12,251 \text{ M}^3$ and $7,903 \text{ M}^3$, respectively, from MAPS and IGCAR/CWMF. The difference between the volumes collected and discharged may be due to some effluent

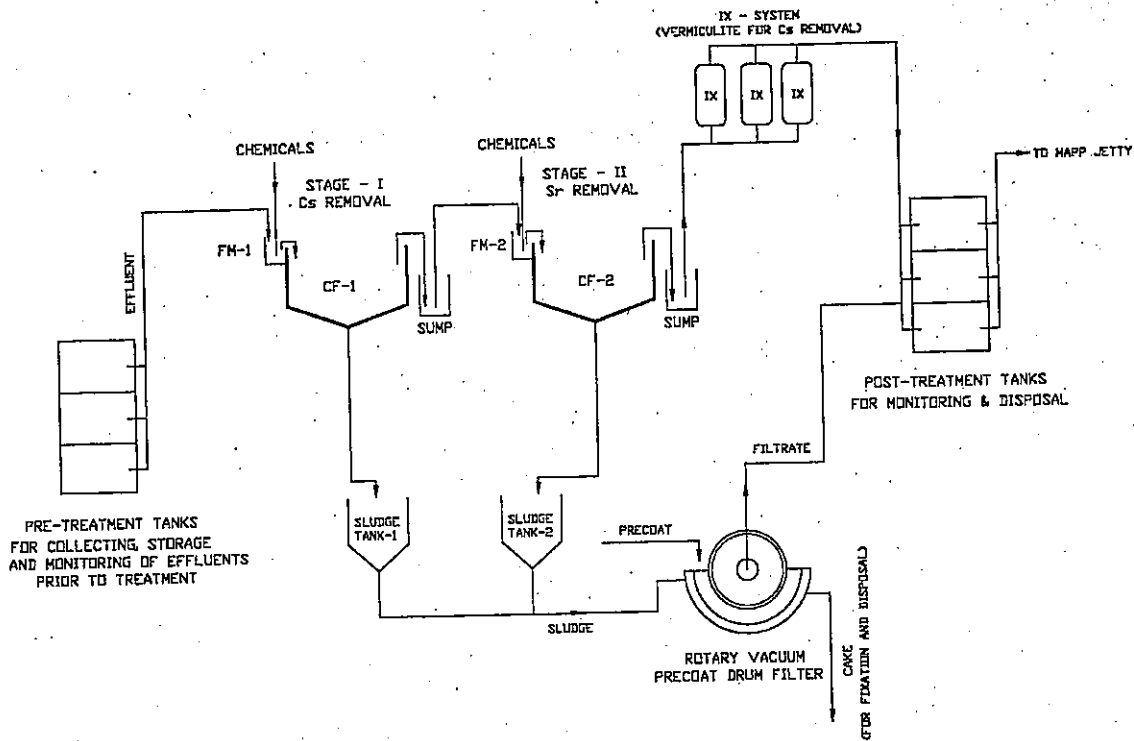


Fig. 1 Chemical Treatment Plant at CWMF, Kalpakkam.

already present in the tanks. The discharges were very much within the stipulated limits. The alpha activity in the effluent received from IGCAR was only 4.46 mCi that was discharged to sea after adequate dilution.

Of the large volumes of effluent received, only 350 M³ was treated by chemical precipitation (DF 79) followed by ion-exchange (DF 12). This was because a major portion of the effluents contained gross beta-gamma specific activity less than 10⁻⁴ mCi/L, and subjecting such low level waste to chemical treatment will not result in any appreciable DF. Hence, the desired limit of less than 10⁻⁶ mCi/L was achieved by providing necessary dilution to the effluent, before disposing it to the environment.

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Use of Selective Sorbents and Ion Exchangers for the Removal of Radionuclides from Aqueous Wastes



Dr. S.K. Samanta joined the 19th batch of BARC Training School in 1975 after graduating from the University of Calcutta and is presently in the Process Engineering and Systems Development Division, BARC. He obtained his Ph.D degree from the University of Bombay. He has made substantial contribution in the development of a number of processes mainly based on selective sorbents/ion exchangers for the efficient removal of radionuclides from various waste streams generated at nuclear installations. Some of these processes have been successfully translated into plant applications. He has participated in Coordinated Research Programme of International Atomic Energy Agency (IAEA) and also served as Technical Expert of IAEA in the area of Treatment of Low and Intermediate Level Radioactive Liquid Waste. Dr Samanta has to his credit over thirty publications in International journals and various symposia/conferences.

Introduction

Aqueous wastes of various categories (viz., low, intermediate and high level, depending on the content of radionuclides) are generated at different stages of the nuclear fuel cycle. Various technologies exist and are used routinely at nuclear installations world-wide for the safe management of these effluents as well as other wastes that are generated. The overriding consideration in radioactive waste management is to comply with radiation protection principles for safeguarding the health of present and future generations and to preserve the quality of our natural environment. The principles of radiation protection that are applied throughout the world are based on the recommendations of the International Commission of Radiation Protection (ICRP). Limits for the quantities and activities of liquid effluents that may be discharged or immobilized matrices that may be sent for storage or disposal are arrived at after evaluating the various pathways by which radioactivity released into the environment can reach man. Besides setting limits on the quantity of radiation that the public can receive, the ICRP goes further by stating that the radiation exposure of people should be kept "As Low As Reasonably Achievable" (ALARA).

Based on the above considerations, it will be obvious that the most effective idea in radioactive liquid waste management is to partition radioactive effluents into two separate components, viz., a small

volume of concentrated waste containing most of the radioactivity that can be immobilized before storage/disposal and a relatively large volume of decontaminated effluent suitable for direct discharge. The above strategy of liquid waste management is commonly referred to as the "Concentrate and Contain" strategy and it is in this context that treatment processes based on sorption and ion exchange phenomena play an important role. Obviously, for the process to be effective, the twin objectives of volume reduction and decontamination are to be met. Fig.1 gives a clear picture of these general principles and also includes definitions of volume reduction and decontamination factors that are widely used in assessing the performance of any waste treatment process.

Sorption and Ion Exchange

Sorption is a general term commonly used to describe the uptake of radionuclides (ionic or non-ionic) by certain materials (sorbents) which have this property. Ion exchange specifically refers to the process of reversible exchange of ions having charges of the same sign between an electrolyte solution and the ion exchanger. Thus, an essential prerequisite for ion exchange is that the radionuclide of interest should be present as ions. The process of ion exchange can be illustrated for the removal of two fission product radionuclides, ^{137}Cs and ^{131}I , that are commonly found in waste effluents:

Conventional Organic Ion Exchangers

The ion exchangers most commonly used for a variety of purposes in the nuclear fuel cycle are the strong acid and strong base ones based on styrene-divinylbenzene (DVB) copolymers. The functional groups present in these ion exchangers are sulphonate ($-\text{SO}_3^-$) and quaternary ammonium ($-\text{N}(\text{CH}_3)_3^+$) ion, respectively. These conventional organic ion exchange resins are not very selective, removing both radioactive and nonradioactive materials. In many waste streams originating from nuclear installations, the concentrations of non-radioactive constituents are many times ($>10^6$) higher than that of the radioactive contaminants. When the conventional resins are applied to the decontamination of such streams, most of their exchange capacity is spent removing materials that could be released to the environment and only a very small fraction is utilised in removing the radioactive species. Hence such resins are normally suitable for the decontamination of relatively clean solutions with a low salt content. The total dissolved solid (TDS) concentration should preferably be less than 1000 ppm.

In contrast to the ordinary ion exchange resins which are of the gel type with nominal cross-linking of 8% divinylbenzene, the new range of "macroreticular" or macroporous resins with higher cross-linking are characterized by higher chemical, thermal and radiation stability. A very useful feature of high cross-linked strong acid resins is their pronounced selectivity for strontium. An example is Amberlite IR-200, which was found to be highly effective for removing radiostrontium from fuel storage pond water as compared to the gel type resins and various other ion exchangers [2].

The chief areas where conventional resins find extensive application in the nuclear industry are the cleaning of water from the primary circuit of reactors and from fuel storage ponds, the purification of evaporator distillates, and the polishing of effluents from conventional chemical treatment plants for low level wastes.

Inorganic Sorbents / Ion Exchangers

Inorganic sorbents/ion exchangers possess many properties which make them suitable

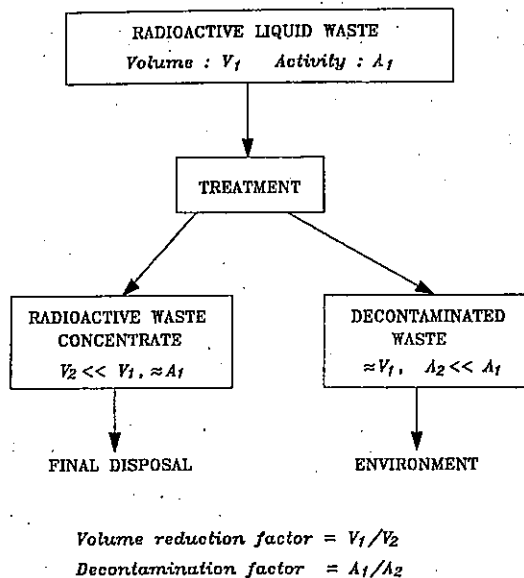
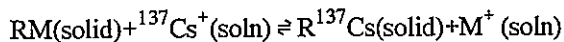
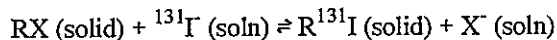


Fig. 1 General strategy for radioactive liquid waste management

Cation exchange



Anion exchange



where R represents the insoluble ion exchanger matrix and M^+ , X^- are the exchanging ions.

A variety of sorbents and ion exchangers find application in the treatment of diverse types of radioactive aqueous waste streams [1]. Improvement of existing materials and development of new ones for the removal of specific radionuclides are also being actively pursued. A brief survey of the various types of sorbents/ion exchangers that are being used or developed as promising candidates for potential application in radioactive aqueous waste treatment is given below.

candidates for the treatment of various types of wastes. For example, they have high thermal, radiation and chemical stability, they can exhibit very high selectivity for certain ions and they are compatible with various immobilization matrices. The materials of interest include natural inorganic exchangers (clay minerals and zeolites), synthetic zeolites, oxides and hydrous oxides, insoluble hexacyanoferrates, acid salts of multivalent metals, heteropolyacid salts and others.

Naturally occurring materials

The naturally occurring sorbents/ion exchangers are mainly aluminosilicate minerals. Of these, the clays have a structure consisting of alternate parallel layers formed from silicate tetrahedra and aluminate octahedra. Illite, montmorillonite and vermiculite are typical examples. Of these, vermiculite is particularly well-known for its selective uptake of cesium followed by irreversible trapping due to lattice contraction. This material is often used for removing traces of ^{137}Cs in effluents from chemical treatment plants [3].

Zeolites

The zeolites are crystalline aluminosilicates having three-dimensional framework structures and can be represented by the general formula $M_x/n[(\text{AlO}_2)_x(\text{SiO}_2)_y]\cdot z\text{H}_2\text{O}$ where M is the exchangeable metal ion of valency n. Some familiar examples of naturally occurring zeolites that are of interest in radioactive liquid waste treatment are clinoptilolite, chabazite, mordenite and philipsite. Of these, clinoptilolite finds large-scale use in UK for treatment of spent fuel storage pond waters [4]. Both cesium and strontium radionuclides are effectively removed by this zeolite.

Of the synthetic zeolites, the three most familiar ones in radioactive waste treatment are Zeolon 900 (mordenite type), Linde AW-500 (presently called Linde Ionsiv IE-96, chabazite type) and Linde A (presently called Linde Ionsiv A-51, A type). The first two have high selectivity for cesium whereas the last one is strontium selective. Though zeolites are recommended to be used in mildly acidic or alkaline solutions, some like mordenite have higher acid

resistance. Linde Ionsiv IE-96 was chosen for removing cesium from alkaline waste solutions stored at the West Valley, New York, fuel reprocessing site [5]. Zeolite ion exchangers were used extensively in the cleanup of large volumes of contaminated water at Three Mile Island after the reactor accident. A mixture of 60% Linde Ionsiv IE-96 and 40% Linde A-51 were used in columns to remove ^{137}Cs and ^{90}Sr with very high efficiency [6]. Nearly 600,000 gallons of contaminated water in the Reactor Containment Building sump was decontaminated and the spent zeolite columns, loaded with about 260 Ci/L of radioactive cesium and strontium, were sent for disposal.

From the radioactive waste management point of view, an important advantage of the use of zeolites is the possibility of fixation of sorbed cesium or strontium by thermal/hydrothermal treatment of the loaded zeolite prior to disposal.

Oxides and hydrous oxides

Various oxides and hydrous oxides have been studied for their application in radioactive waste treatment. Notable examples include sodium titanate [7] and hydrous titanium oxide [8] which show significant uptake of strontium ions. The former is a member of the family of layered compounds which consist of metal oxide layers with exchangeable cations located between the layers. Sorption on hydrous metal oxides takes place by simple ion exchange reaction in which surface -OH groups are involved. Apart from strontium, hydrous titania is also known to sorb plutonium from alkaline waste solutions [9]. Similar compounds of manganese, zirconium and antimony also have the property of sorbing a variety of radionuclides.

Insoluble Hexacyanoferrates

The insoluble hexacyanoferrates(II) which are used as highly selective precipitants for cesium can be represented by the idealized formula $M_2[M^{\text{II}}\text{Fe}(\text{CN})_6]\cdot n\text{H}_2\text{O}$, where the transition metal ion M^{II} (e.g., Co^{2+} , Cu^{2+} , etc.) forms part of the structural framework and M^{I} (e.g., K^+) is the exchangeable alkali metal ion. These materials can be prepared in granular form [10] or incorporated

inside macroporous anion exchange resin beads and used as ion exchangers in columns [11]. Pilot scale column experiments using copper hexacyanoferrate loaded resins have shown that cesium can be effectively removed from low level effluents and spent fuel storage pond water [12,13].

Potassium cobalt(II) hexacyanoferrate(II) is presently emerging as a very promising cesium selective inorganic sorbent which can be prepared in granular column-usable form without using any resin support or organic binder. Recent examples of large-scale use of this sorbent include the decontamination of reactor waste evaporator concentrates in Finland [14] and of ion exchange regenerant waste at Tarapur Atomic Power Station [15]. In the latter case, a 5 L column of the sorbent was used to reduce ^{137}Cs activity in 12000 L of waste from $1.0 \mu\text{Ci/mL}$ to $10^{-4} \mu\text{Ci/mL}$. The sorbent has also been found promising for the removal of ^{137}Cs from alkaline reprocessing wastes [16].

Acid Salts of Polyvalent Metals and Heteropolyacid Salts

Amongst the acid salts of multivalent metals, the best known are the various forms of zirconium phosphate and titanium phosphate [17]. A highly cesium selective exchanger is ammonium molybdophosphate (AMP) which is a heteropolyacid salt and can be represented by the formula $(\text{NH}_4)_3[\text{PMO}_{12}\text{O}_{40}]$, where it is possible to exchange ammonium ions for other ions giving insoluble salts. This ion exchanger, which removes cesium from acidic wastes very efficiently, is microcrystalline in nature and difficult to handle in columns. A "suspended bed technique" developed recently [18] overcomes this problem.

Phenolic Resins

The conventional synthetic ion exchange resins used in radioactive liquid waste treatment are all based on a styrene-DVB copolymer. Before the advent of these polymers, the synthetic ion exchange resins were all based on a phenolic matrix into which the desired functional groups were introduced. However, interest in the use of phenolic resins, because of the presence of phenolic -OH groups alone, started with the work of Miller and Kline [19]

of the Kellex Corporation, USA, in 1951. These authors compared the cesium uptake properties of two commercial synthetic ion exchange resins, Amberlite IR-120 and Amberlite IR-100. The first is a nuclear sulphonic acid resin based on a styrene-DVB copolymer and the second one a phenol-sulphonic acid resin based on a phenol-formaldehyde polycondensate. In alkaline solutions, the latter showed very high uptake of cesium as compared to the former. This was attributed to the presence of phenolic -OH groups in Amberlite IR-100. Such groups, being weakly acidic, ionize only at higher pH and start functioning as ion exchange sites, specific for cesium. Since this first report, the cesium specificity of phenolic -OH groups has been established in numerous studies and applications. Amongst the known commercially available cesium selective phenolic resins are Duolite CS-100 (phenolic-carboxylic), Duolite ARC-9359 (phenolic-methylene sulphonic), Duolite S-761 (phenolic), etc.

Recently, a Resorcinol-Formaldehyde Polycondensate Resin (RFPR) was developed, characterized and tested extensively for efficient removal/recovery of radiocesium from alkaline reprocessing wastes containing large concentration of competing sodium ions [20-22]. Incorporation of iminodiacetic acid $(-\text{CH}_2-\text{N}(\text{CH}_2\text{COOH})_2)$ functional groups into the phenolic polymer matrix gives it the additional feature of strontium uptake by chelation and such a resin is presently being used in a full-scale plant at Tarapur [23]. Several lakh litres of alkaline intermediate level wastes from the Power Reactor Fuel Reprocessing Plant (PREFRE), Tarapur have already been treated using this process. Development of a similar process for removal/recovery of radiocesium from neutralised high level wastes has also been reported from USA [24].

Chelating Resins

Chelating resins with suitable functional groups incorporated in a styrene-DVB copolymer matrix are also available commercially. The most notable example is Dowex A-1 which is a gel type resin having iminodiacetic acid groups. Similar resins of the macroporous type are also available, e.g., Amberlite IRC-718. This resin has shown promising results in selectively removing

radiostrontium from alkaline radioactive wastes containing large concentrations of inactive sodium salts [25]. Commercially available chelating resins containing aminophosphonic acid ($-\text{CH}_2\text{-NH-CH}_2\text{-PO(OH)}_2$) groups are also being tried for possible application in this area.

Miscellaneous Sorbents and Ion Exchange Materials

Of late some new types of selective ion exchangers have become commercially available under the trade name "Durasil" from Duratek Corporation, USA. The majority of these proprietary materials are glass-based, although some are based on carbon or inorganic oxides. These materials containing ion exchange sites with tailored selectivity for a variety of ions, e.g., Cs^+ , Co^{2+} , Sr^{2+} , etc have been found satisfactory when tested in the laboratory as well as in several nuclear power plant waste treatment operations [26]. A crystalline silicotitanate (CST) synthesized recently at Sandia National Laboratories, USA has shown high selectivity for both cesium and strontium ions in alkaline solutions containing high concentration of sodium salts and is being considered for potential application in the treatment of neutralised high level wastes [27]. The plant scale use of bone char, a commercially available form of calcium hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, for removal of traces of plutonium from aqueous effluents has been reported from USA [28]. Interest is also noted in the preparation and application of the so-called composite sorbents which include inorganic sorbents, either singly or in combination, prepared in granular form using a variety of organic binders [29].

One of the most troublesome and intractable radionuclides present in PUREX wastes is ^{106}Ru which is difficult to remove completely. It is generally present in the form of a variety of complexes of nitrosyl ruthenium. Recently, some success was obtained in trapping this radionuclide from reprocessing waste solutions using a combination of zinc and activated charcoal in a fixed-bed process [30]. The usefulness of this method was also demonstrated in plant scale trials. The potential application of biosorption in concentrating radioactivity from waste effluents is also being examined [31]. Promising candidates in this area include several tailored biopolymers and immobilized microorganisms.

Mode of Application

The most common mode of application is fixed-bed ion exchange. In this mode, the exchanger material, usually in the form of beads of 0.3 - 0.8 mm size, is supported within a cylindrical vessel on a perforated plate. The feed is normally passed downward. When the bed is exhausted, it is either hydraulically flushed out as radioactive waste or it is regenerated and used again. Regeneration can also be done downward but it is more efficient to regenerate the resin using countercurrent flow, i.e., the regenerant is passed in a direction that is opposite to that of the feed.

In the case of mixed-bed ion exchange, where cation and anion exchange beds are intimately mixed in the column, regeneration can be done only after separating the beds. This is done by making use of the different densities of the anion and cation exchange resins. On fluidizing the mixed-bed with water, it separates into two layers with the lighter anion resin on top. The layers are then regenerated separately and mixed again by means of air agitation. Besides the fixed-bed mode, modern ion exchange technology also includes moving packed beds, fluidized beds and stirred tanks.

The operation of a fixed-bed ion exchange process either in the loading-elution-regeneration mode or in the once-through mode has important implications in radioactive waste management. In the first case, rinsing, elution and regeneration of the loaded bed result in significant volumes of secondary aqueous wastes which need further treatment and conditioning. Operation in the once-through mode is not associated with these problems and only a solid radioactive waste is the product which can be conditioned and packaged for storage/disposal. Obviously, for such a process to be attractive, the sorbent must have high capacity, i.e., it should be possible to treat very large volumes of waste using a single volume of the sorbent column. Some of the inorganic sorbents developed recently appear promising for application in the once-through mode.

Substantial interest has been shown in recent years in another mode of application of inorganic sorbents. In this method, very small quantities of radionuclide-specific sorbents are either precipitated in the waste solution or added as pre-formed

material. Cross-flow membrane filtration techniques are then used for removal of the loaded sorbent particles [32]. High decontamination and volume reduction factors can thus be achieved. This technique offers a way for utilisation of even those inorganic sorbents which, though highly specific for radionuclides, cannot easily be prepared in column-usable granular form.

Concluding Remarks

It will be evident from this brief survey that selective sorbents and ion exchangers are already playing a useful role in fulfilling the important goal of nuclear waste management, viz., confinement of radioactivity. It will also be noted that, of the hundreds of sorbents/ion exchangers that have been reported to possess radionuclide uptake properties, only a few have so far found large-scale practical application. This situation suggests that radionuclide uptake by itself is not a sufficient criterion for selection of a sorbent/ion exchanger for plant use. For application in a fixed-bed process, it is essential that technology for bulk preparation of the material in granular, column-usable form is also available. Moreover, the implications of the use of such a process must be judged from the total waste management point of view. This includes the management of secondary aqueous wastes and disposal of spent sorbent columns after use. The ultimate objective is concentration of radioactivity in as small a volume as possible followed by conditioning of the concentrated activity in a form suitable for disposal. Proper emphasis on these considerations will be essential in ensuring further wide-spread use of selective sorbents/ion exchangers in nuclear waste management in future.

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Use of Membrane Methods in Nuclear Waste Management



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Introduction

Though the phenomena of semipermeability of biological membranes and osmotic pressure relationships using inorganic precipitate membranes were established in the eighteenth and nineteenth centuries, the first recognised research work in the field of reverse osmosis (RO) for water desalination appeared only in early sixties. Since then R & D work on RO has been receiving major attention and newer membranes and better module designs have been under development primarily for economic saline water desalination. Apart from desalination, RO has been successfully applied for a variety of industrial applications including water treatment for process industries, treatment of waste waters, treatment of effluents containing valuable products, treatment of paper and pulp effluents, concentration of food products and others. A number of membrane processes are developed in recent times and their application to waste water treatment is considered more attractive compared to conventional separation operations such as evaporation, solvent extraction, adsorption, ion exchange and chemical precipitation.

An important deficiency of conventional treatment systems is their inability to make one step separation for all the dissolved constituents on a molecular or ionic level. Membrane processes operate at ambient temperature and offer one step separation for all the dissolved constituents on molecular or ionic level without any need for further chemical addition. Among the disadvantages of membrane processes, the fouling of membrane surface and the operational instability of polymeric membrane systems under adverse chemical and thermal conditions are often cited. However, these

problems may be partly overcome by proper pretreatment of the effluents, optimising the process variables and selecting suitable membrane materials.

Membranes are synthetic barriers across which selective permeation of the desired species can be effected by employing an appropriate driving force like electrical potential, hydrostatic pressure or concentration gradient (Table 1). Membrane processes are classified depending on the nature of the membrane and the driving force employed to bring about the required transport of molecular species. A number of different polymeric/inorganic membranes have been developed in recent times in basically four types of modular assemblies, namely, plate and frame, spiral, tubular and hollow fine fibre. The general features of a membrane process are shown in Fig. 1.

For radioactive effluent treatment, the relevant membrane processes are microfiltration, ultrafiltration, reverse osmosis, electrodialysis, diffusion dialysis and liquid membrane processes and they can be used either alone or in conjunction with any of the conventional processes. The actual processes employed would depend on the physical, physicochemical and radiochemical nature of the effluents. The basic factors which help in the design of an appropriate system are the permeate quality, decontamination and volume reduction factors, disposal methods available for secondary wastes and the permeate. It is an optimal trade off between the economics, efficiency and operational aspects. For example, in the case of fission product effluents wherein radiocontaminants having longer half lives are present, the emphasis should be on very high volume reduction with permissible/acceptable

Table 1. Characteristics of principal membrane separation processes

Process	Driving force	Objective
Gas, vapour and organic liquid permeation	Concentration gradient (pressure, temperature assisted)	Product enriched in a desired component
Dialysis	Concentration gradient	Solution of macrosolutes free of microsolute
Electrodialysis	Electrical potential	i. Solvent free of ionic solutes ii. Concentration of ionic solutes iii. Ion replacement iv. Fractionation of electrolytes
Microfiltration	Pressure	Sterile, particle free solution
Ultrafiltration	Pressure	Solution of macrosolutes free of microsolute
Nanofiltration	Effective pressure	i. Removal of organics, dyes from effluents ii. Fractionation of electrolytes
Reverse Osmosis	Effective pressure	i. Solvent free of all solutes ii. Concentration of solution

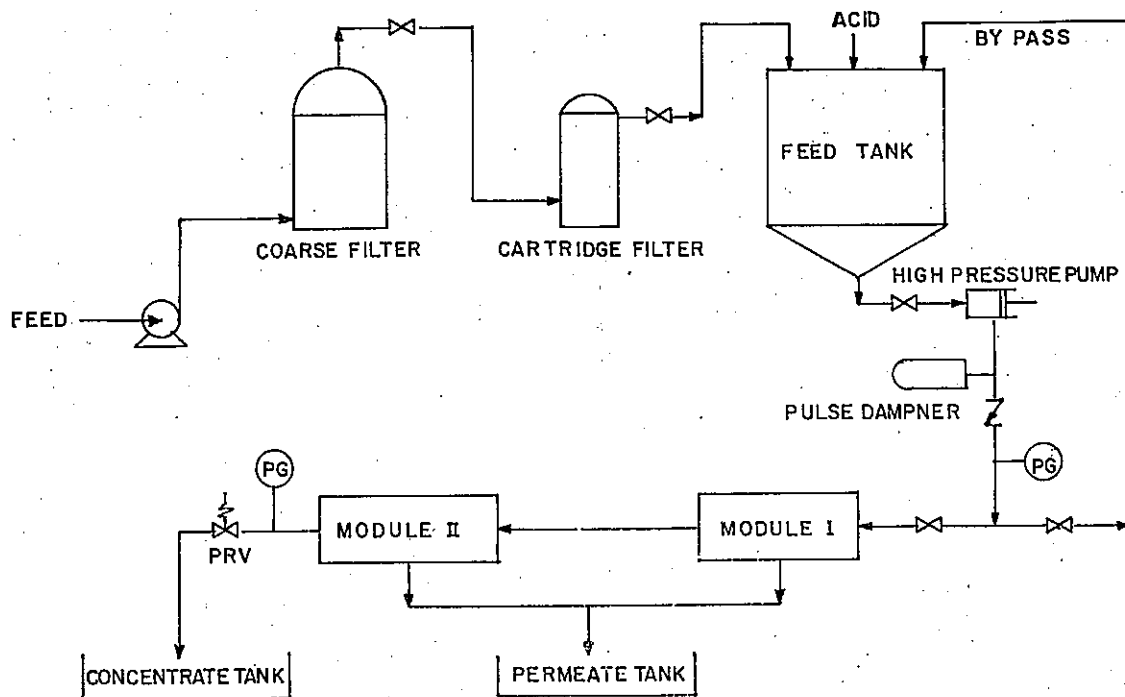


Fig. 1 Flow sheet of reverse osmosis plant.

decontamination factors so that the permeate could be directly discharged. In the case of effluents contaminated with radionuclides of shorter half lives, a good decontamination with reasonable volume reduction may be acceptable because the concentrate could be stored till the activities decay before discharge. The radioactive effluents requiring treatment may vary with respect to the type of radionuclide, its chemical nature, concentration, pH, concentration of inactive solutes and presence of suspended matter.

Microfiltration

Microfiltration membranes have pore sizes ranging from 0.1 μm to 1 μm and this technique is used for the removal of suspended particles of submicron size. The prime removal mechanism is mechanical retention. This process is generally used for removal of turbidity and microorganisms from drinking water sources. The pressure applied is around 30 psi. This technique has been used for separation of cruds from waste water generated in light water reactor power plants. In the primary cooling water of LWR type power plants, corrosion products are produced which mainly consist of metal oxides containing radioactive nuclides (usually called "crud"). While precoat or cartridge type filters are prevalently used for removing such crud, these filters produce secondary radioactive wastes such as filter sludge and spent cartridges. Further these filters do not satisfactorily remove submicron size cruds. In Japan, microfiltration membrane elements made of polycarbonate were used [1] in place of cartridge filters. Membrane elements could be used for longer periods of time as compared to cartridge type filters. Membrane filters are already in commercial use in some radwaste plants in Japan.

This process could also be used in conjunction with chemical precipitation methods. Under optimum conditions, an integrated method of chemical precipitation and microfiltration could give a better decontamination and lower quantity of sludge for disposal. Polymeric as well as ceramic microfilters can be used depending on the environment. Polymeric microfiltration membranes are generally based on regenerated cellulose, cellulose acetate, polysulfone, polycarbonate, polypropylene, polytetrafluoro-ethylene, polyvinylidene difluoride, aromatic polyamide or

polyvinyl chloride. These membranes have limited radiation resistance and chemical tolerance. Ceramic microfiltration membranes such as the recently developed Ceraflo, Membralox, etc. have high radiation stability and are capable of withstanding severe chemical cleaning to restore membrane surface.

Ultrafiltration

Ultrafiltration process utilises membranes having pore sizes in the range of 0.01 to 0.1 μm and can retain large molecules, suspended and colloidal particles but allows dissolved salts to pass through with the bulk of the water. The operating pressure is in the range of 50 to 100 psi. Cellulose esters, polyamide class of polymers, polyacrylonitrile, polyvinylidene difluoride and polysulfones are largely used as membrane materials. The mechanism of separation is essentially based on the size based retention of the components. It has application in the concentration of radioactivity by selective removal of a particular radionuclide which can be converted to a finely suspended state or incorporated in a large complex molecule. It operates at lower pressures than does reverse osmosis and offers higher membrane permeate fluxes. Inorganic ultrafiltration systems such as Carbosep[®] have higher radiation and chemical stability.

Like microfiltration, ultrafiltration process can also be used in conjunction with chemical precipitation technique to improve decontamination factors (DFs). Mound Laboratories, USA has evaluated ultrafiltration for alpha wastes emanating from laundry and wash water streams of plutonium processing plant. A 8.2 M^3/h pilot plant was successfully operated to collect design data for a full scale treatment facility. Removal of ^{137}Cs by copper ferrocyanide precipitation followed by ultrafiltration using polysulphone membrane having molecular weight cut-off of 1000 has been successfully evaluated [2]. This method gives higher DFs (100-1000) under optimum conditions as compared to a DF of about 10 that is obtained in conventional methods of solid-liquid separation like settling or clariflocculation. It also requires lower dosage of chemicals thus making it cost effective. Strontium activity was reportedly separated by adsorption on colloidal titanium hydroxide solution and subsequent ultrafiltration.

Complexation-ultrafiltration has been projected as a promising process with high decontamination factors for specific ions. Water soluble polymeric complexing agents like polyethyleneimine, polyacrylic acid, polyvinyl pyrrolidones or their various chemical derivatives are successfully used for selective removal of target radionuclides from effluent streams. Radioactive cerium was separated in our laboratory with polyethyleneimine complexation using indigenously developed ultrafiltration membranes [3]. Published information [4,5] indicates that decontamination factors in the region of 1000 for alpha and 100 for beta-gamma species can be achieved with overall volume reduction of the order of 10^4 .

Reverse Osmosis

Reverse osmosis involves the passage of solvent through a semipermeable membrane, when a solution is pressurised in excess of its own osmotic pressure. A variety of reverse osmosis membrane systems based on cellulose acetate, aromatic polyamides and other polymers have been tested for their potential applications. The possibility of radioactive effluent treatment by RO was recognised in the early seventies and several studies have been reported on the laboratory scale as well as on the pilot plant scale. In USA, RO has been evaluated for treating contaminated laundry waste water and other liquid radioactive wastes. Several RO systems ranging in capacity from 0.45 to 11 M^3/h are operating. The Idaho Chemical Processing Plant, USA has used 6.8 M^3/h RO unit for the fuel storage pool water treatment. At Harwell, UK, a small pilot plant using RO process has been installed to study the performance with effluents from reprocessing plants. In Chalk River Nuclear Laboratories, Canada, RO is used as a primary process on a bench scale for volume reduction of aqueous wastes containing 0.5% dissolved solids. The Australian Atomic Energy Commission has reported pilot plant study using commercial RO module. Disposable RO kits for use at source plants are also reportedly developed. Treatment of boric acid wastes arising from the dissolution of control rods of PWRs for the recovery of boric acid from the radiocontaminated solutions also has been carried out using reverse osmosis process.

Reverse osmosis process cannot serve as an ultimate treatment method. It is a preconcentration technique and the concentrates, depending on the inactive load can be sent to evaporation or chemical precipitation step. The permeate, depending on the feed activity level may be either discharged directly or after dilution or after passing through polishing columns. Normally the decontamination factor achievable varies from a few tens to hundreds, depending on the nature of the input stream and the membrane. The volume reduction factors depend on the inactive salt load, operating pressure and the selectivity of the membrane used.

The ammonium diuranate filtrate (ADUF) effluent generated in Uranium Metal plants contains around 30,000 ppm of ammonium nitrate and small amounts of dissolved and suspended uranium and its daughter products. The beta activity levels due to ^{234}Th and ^{234}Pa are significant and require processing before disposal to sea. The treatment of ADUF by RO was found [6] to be useful in concentrating the activity in a small volume while making a larger volume of decontaminated effluent suitable for direct disposal. Porous cellulose acetate membranes prepared in-house were used in plate module configurations. The concentration of ammonium nitrate in the permeate stream is not very much different from that of the contaminated effluent. With addition of flocculant aids, the decontamination factors in the range of 1000 with volume reduction factors in the range of 100 were achieved.

Nanofiltration membranes have average pore size of 10-30 Å, an intermediate range between reverse osmosis (< 10 Å) and ultrafiltration (> 30 Å). Nanofiltration has the advantage of very low solute rejection for monovalent species, probably due to their very small hydrated radii and higher rejection for multivalent species which are large enough. The decontamination of ADUF was also investigated in a pilot plant study using nanofiltration membranes in plate module configuration [7]. Because of the poor separation of ammonium nitrate, NF membranes have the potential to achieve high volume reduction factors with high decontamination factors for radionuclides which are multivalent. The studies carried out indicate that nanofiltration is better suited for the decontamination of ammonium diuranate

filtrate effluents due to near constant fluxes, high decontamination factors and low ammonium nitrate solute rejection.

In BARC, a reverse osmosis pilot plant in plate module configuration was successfully operated for decontaminating low level radioactive effluents having total dissolved solids in the range of few hundred ppm contaminated with radioactive cesium and strontium. The reverse osmosis demonstration plant consists of two reverse osmosis modules in plate configuration connected in series using indigenously developed cellulose acetate membranes. The pretreatment section on the upstream side of the modules consists of upflow particulate filter and cartridge filter, connected in series. The demonstration unit had a capacity of 8 M³/d and gave a decontamination factor of nearly 20 with a volume reduction factor of 15 for an initial feed activity of 10⁻³ µCi/mL. Such a preconcentration by membrane process is considered desirable from the point of view of low volume of the final waste sent for safe disposal and the possibility of in-house treatment at the point of generation whereby a much smaller volume of concentrate could be transported to a centralised treatment plant.

Electrodialysis and Diffusion Dialysis

The basic principle of electrodialysis for desalination is to drive cations or anions from saline water feeds under the influence of an electric potential gradient through cation selective or anion selective membranes. Radioactive liquid waste treatment by electrodialysis provides a non-contaminated dischargeable fraction and a more concentrated smaller volume for further treatment and solidification. The extent to which salt can be removed from the feed stream is limited by the increasing electrical resistance of the dilute stream. Also the ion exchange membrane gets fouled by the solids present in feed. A variety of radionuclides, e.g., ¹³⁷Cs, ¹³¹I, ⁹⁰Sr and ⁸⁹Sr are efficiently (97 to 99%) removed from radioactive effluent streams [8]. The removal of zirconium and niobium is poor, being colloidal materials. This process is successfully tested on pilot scale for decontamination of radioactive effluent streams in several countries. A specific application of this process is in the treatment

of regenerant solutions from boric acid loaded ion exchange resins in heavy water reactors.

Highly acidic radioactive streams could be deacidified by diffusion dialysis process where specially developed ion exchange membranes are employed in a conventional electro-dialytic stack design forming alternate diffusate and dialysate compartments. Free acid selectively diffuses through these anion exchange membranes. The deacidified radioactive streams could be again treated by electro-dialysis technique. An integrated membrane process consisting of diffusion dialysis followed by electro-dialysis was evaluated [9] to deacidify and subsequently decontaminate high level radioactive stream depleted of alpha activity. It was found that diffusion dialysis process could be used to bring down the nitric acid concentration in the radioactive effluents from 3 M to less than 0.3 M and decontamination factor obtained with respect to cesium and strontium are in the range of 80 to 100.

Liquid Membranes

Liquid membranes are made when a carrier mixed in a suitable solvent is converted into immiscible layer between two aqueous solutions. One of the components in aqueous solution has preferential permeation into the immiscible membrane layer. The species in the feed can be neutral, cationic or anionic species. Subsequently these are removed by the permeate side solution due to the decoupling of the carrier complex. The success of the liquid membrane is primarily due to the fact that the diffusivity of ionic/nonionic species in liquids is an order of magnitude higher than in polymeric film. Further the carrier molecules used in the liquid membrane systems are very specific to different species and hence result in selective separation. This, therefore, allows separation against activity gradient. Two common forms of liquid membranes are emulsion and supported liquid membrane. Supported liquid membrane systems are extensively investigated where the carrier is held in a porous polymeric membrane. At Argonne National Laboratory, development of liquid membrane process for removal of plutonium, uranium and americium from dilute acidic streams is actively pursued. The removal of uranium and plutonium using supported liquid membranes with different carrier agents has been studied in BARC [10]. The

recovery of uranium from phosphoric acid by this process has been considered to be an economical and efficient process as compared to solvent extraction.

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Immobilization of Low and Intermediate Level Radioactive Wastes with Cement and Polymers



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Introduction

Nuclear industrial operations, while meeting the primary objective of generating power, inevitably give rise to some radioactive wastes. These exhibit wide variation in their activity levels and radiochemical composition, depending upon their origin in the nuclear fuel cycle. These may be highly active heat generating wastes or non-heat generating low and intermediate level wastes. It is imperative that precautions be taken to minimise potential of release of radionuclides during their handling, storage and disposal. One may easily appreciate that the best recourse for this is to convert them into stable monolithic forms by solidification, i.e., immobilization.

The choice of the solidification matrix is primarily governed by its compatibility with the specific waste. In case of availability of alternatives, it is natural that material with well understood chemistry, processing technology and lower cost gets an automatic preference, without overlooking the all important aspect of product behaviour during its extended storage/disposal.

Cement has long been used for incorporation of non-heat generating low and intermediate level wastes. However, there are cases of specific waste compositions which are problem prone due to their tendency to interfere with the setting and curing of cementitious matrices. This raises questions about its

versatility as a binder for any type of waste and has led to a search and evaluation of alternative solidifying agents like organic polymeric binders, natural or synthetic in origin. It is proposed to present here a brief state-of-the-art review of technology for fixation of radioactive waste in cement and polymers. The topics covered in the review include basis of their selection, the mechanism responsible for their binding action, modification of their properties and/or that of the waste to render them mutually compatible and finally the status of global technology with special reference to Indian scenario.

Sources and Characteristics of Low and Intermediate Level Wastes

The source of any waste governs its characteristics. In the nuclear fuel cycle, stages like mining and milling, fuel fabrication, power generation, spent fuel reprocessing are the principal waste generating stages. Other sources include the application areas such as isotope production and utility as well as research centres. All these nuclear installations have systems or subsystems which are radiochemical plants employing unit operations like water purification systems (filtration, ion exchange, precipitation), volume reduction (evaporation, drying, crystallisation), air cleaning (filtration, adsorption) and radioactive species separation (extraction, floatation). The operations, maintenance, decontamination and finally

decommissioning of these systems give rise to wastes which fall into one of the types such as a) liquids b) wet solids and c) dry solids. The liquids cover the regenerants of ion exchangers or their concentrates, the decontamination solutions, washes and rinses, spent solvents, etc. The major wet solids are the spent resins (beads/powdered), chemical sludges and liquid filter media. The dry solid wastes arise mainly from ventilation air-cleaning systems and comprise filter cartridges, adsorption media (charcoal, silica gel, molecular sieves and contaminated articles like wood, plastic, etc).

The low and intermediate level wastes arising from all these facilities are characterised by large volumes, lower radioactivity and negligible heat generation. Their physico-chemical nature is governed by the chemicals and radioactivity either produced or handled in them. Wastes from fuel reprocessing, mining/milling, fuel fabrication may be alpha bearing; while those from nuclear reactors have only beta-gamma contamination. Wastes from Pressurized Heavy Water Reactor (PHWR) are characterised by their tritium and ^{14}C contamination. From purely chemical composition point of view, there are borated concentrates from Light Water Reactors (LWR), while sulphate waste results from regenerants from Boiling Water Reactor (BWR) and LWR purification systems. It will be of interest to see how these waste sources and hence characteristics will have an impact on the choice of their solidifying agents and the resulting solidified products.

Characteristics and Chemistry of Matrices for Immobilization

Among the first binders chosen for solidification of non-heat generating low and intermediate level wastes were cements followed by bitumen. The reasons obviously were their easy availability, low cost and long industrial experience.

Solidification with bitumen involves higher processing temperatures, which can lead to potentially hazardous situations when specific waste streams containing reactive components like nitrates/nitrites are involved. The material in general is difficult to handle due to the operating problems like tarring and choking. The final product has a tendency to soften in hot climate rendering it susceptible to easy degradation during

storage/disposal. Owing to these factors, bitumen is gradually falling out of favour in tropical countries like India, although some European countries from cold climatic belt are still persisting with it. The attention therefore has shifted to synthetic polymeric materials which offer a temperature resistant, hard and durable product, with processing achieved at ambient temperatures like in the case of cementitious matrices. It is thus the inorganic cement and synthetic organic polymers that are the major binding materials being exploited today on industrial scale.

Cementitious Matrices

The basic components of any cement are its building blocks, lime (CaO), silica (SiO_2) and alumina (Al_2O_3). The most commonly used portland cements have small quantities of magnesia (MgO), ferric oxide (Fe_2O_3), sulphur trioxide (SO_3) and other oxide impurities introduced along with the raw materials. Calcareous materials (lime stone/sea-shells) and argillaceous materials (clay/shell/silica/sand/iron ore) are used as starting materials which, after processing, provide mixtures of combinations of these oxides, i.e. cement. The four basic compounds in portland cement are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite ($\text{C}_4\text{A,F}$). Each of these constituents has a specific behavioural impact on cement; thus by varying their compositions, five types have been evolved - Types I (normal), II (modified), III (high early strength), IV (low heat) and V (sulphate resistant). The type titles themselves give an insight into their properties.

In case of cement, water plays the role of the curing agent. When mixed with water, the cement constituents undergo a series of hydration reactions leading to hardening. The complex reactions are not thoroughly understood. The hydration reactions give rise to $\text{Ca}(\text{OH})_2$, a calcium silicate hydrogel (CSH), the tobermorite gel, hydrated calcium aluminoferrite and aluminate hydrates. The hydrated compounds form a colloidal disperse called a sol, which starts coagulating marking start of setting (gelation). The end of setting is associated with complete precipitation of hydrated compounds. After this begins the process of hardening, during which the gel starts to dry and crystallize in the form of micro slabs and needles. A compound called ettringite is formed

during the hydration stage, from calcium aluminate and available sulphur ions. The ettringite phase makes the cement expansive and helps reduce problem of shrinkage during setting that can lead to cracks.

The hardened cement product therefore is actually a mixture of crystalline and amorphous phases, with CSH gel remaining in equilibrium with $\text{Ca}(\text{OH})_2$ in solution giving it a high alkaline pH. Washing away or deterioration due to chemical attack of $\text{Ca}(\text{OH})_2$ can shift the equilibrium with calcium from CSH gel entering into the liquid phase, initiating matrix deterioration. Cemented product is thus a solid mass containing within itself an aqueous phase. It is important that the properties are modified to reduce its porosity and permeability. Additives like vermiculite, fly-ash, different types of slags, sodium silicate, polymers etc. are incorporated at the manufacturing or application stage as property modifiers in improved blended cement formulations.

A typical development on these lines, done in India is in respect of special cements for specific wastes like intermediate level wastes (ILW) from reprocessing plants. While adequacy of OPC for immobilization of low level wastes is well established, there was a need to develop improved formulations to accept highly alkaline and high salt loaded ILW. Hence, a slag based cement was developed indigenously, jointly with a cement manufacturing company. The slags which are usually rich in iron oxide are cementitious and pozzolanic. The special cement developed, while offering a process to handle a mix of high workability, adequate setting time, low heat of hydration gives product of high compressive strength and chemical durability (low leach rates) due to a fine control of the matrix microstructure and vermiculite, a naturally occurring cesium specific exchanger blended with it. The special cements will be used for the ILW wastes at WIP, Trombay and Kalpakkam.

Polymeric Matrices

Organic binders like polymeric materials achieve their job of fixation by physically coating the wastes, which may be aqueous or solid. For this, it becomes necessary to disperse the waste materials into the matrix formulation uniformly and then let

the curing take place. Therefore the aqueous wastes are emulsified as a water-in-oil emulsion, and the solids like ion-exchange bead resins are thoroughly mixed in the polymer formulations for uniform distribution. It is important that the waste particles/droplets have sufficient matrix material to cover them and bind with the adjoining ones leading to the formation of a monolith.

Generally, the products of polymerisation are inert materials. The process of polymerisation and cross-linking, which is taking place in situ, involves chemical reactions governed by ingredients like accelerators and catalysts. These can be sensitive to constituents that act as accelerators or retarders of these reactions. It is especially so when the free radical mechanism forms the basis for propagation of such reactions, since the scavenging of free radicals can end the gelation/curing reactions abruptly affecting product quality.

Different polymer formulations that have been studied and widely used are polyesters and epoxys with urea formaldehyde (UF), polystyrene, PVC, PMMA also having received some attention. Some of these are patented, e.g., DOW (USA) vinyl ester-styrene formulation. Compatibility with water is one of the important considerations and Water Extendible Polymers (WEPS) are developed for this purpose. Alternative approach has been the use of high shear to form water-in-polymer emulsion so as to solidify the micro-water droplets within the binder envelope in case of aqueous waste and minimisation of free water in case of wet solid wastes. Polymer formulations with additives like silica-fume, inhibitors, biocides, radioactivity migration retarders, exotherm depressants, etc. are also being developed. Each of these additives has a specific role to play during processing or in the characteristics of resulting product.

The mechanism of polymerisation in respect of polyester resins proceeds on following lines. The basic ingredients in the formulations are an unsaturated linear polyester resin and cross linking monomer like styrene. The linear polyester is typically formed from an unsaturated dibasic acid or its anhydride (e.g., maleic anhydride) and a glycol (e.g., propylene glycol). A saturated dibasic acid like isophthalic acid is used to modify the degree of unsaturation and hence the reactivity of the resulting

resin. The basic resin formulations which are generally proprietary in nature may also include ingredients to enhance specific properties like shelf-life, dispersion ability, bio-degradability, etc. The synthesized resins undergo polymerisation to form hard solids through the three dimensional cross linking achieved by styrene. A free radical mechanism governs the process of polymerisation. The peroxide catalyst gives rise to the necessary free radicals which are highly reactive due to the presence of an unpaired electron. These are formed either due to thermal decomposition or due to the chemical decomposition of the peroxide catalysts at ambient temperatures. The free radicals attack the styrene monomer breaking it at the double bonds; the reactive monomer, a free radical, in turn takes part in cross linking polymerisation and chain reaction continues till the availability of the monomer or the free radical comes to an end. Typical accelerator-catalyst combinations are cobalt octoate/MEKP (methyl ethyl ketone peroxide) or DMA/BOP (dimethyl aniline/benzoyl peroxide.)

Product Characteristics, Quality Control and Acceptance Criteria

The waste form properties related to their chemical, mechanical, thermal, radiation and bio-degradation stability are studied in detail at various stages starting from laboratory studies to the full scale product. The acceptance criteria related to these properties are developed taking into consideration the safety analysis of Near Surface Disposal systems and operating experience of the processing plant and disposal system as an aid in validation of such an analysis. The properties are controlled through design, procurement, process control and acceptance decided based on inspection and testing of the product.

The cement and polymer products are also developed on these lines. As far as chemical, mechanical, thermal and radiation durability are concerned, both have excellent properties with use of specially formulated cements in case of cementitious wastes. With respect to biodegradation, the inorganic cement matrix offers excellent resistance and the polymer product, the thermoset variety, exhibits adequate resistance, which can be further enhanced by addition of biocides.

The polymer products have exhibited compressive strength in excess of 100 Kg/cm², leachability of less than 10⁻⁵ cm/day and radiation stability in excess of 10⁷ Rad. Cement products offer comparatively lower values due to the inherent presence of free moisture and porosity when formed in the normal way with normal cements. But all these properties are enhanceable by employing techniques such as pressure pelletization, in situ polymerisation of voids, product coating, selection of special cements, etc. This has led to renewed interest in cement as a versatile matrix.

Cementation/Polymerisation Technologies

The process of solidification of waste streams in either case involves mechanical mixing of two components together with additional ingredients wherever applicable. Rest of the process stages deal with receipt, metering of liquid or solid wastes and the binders, their transfer to the mixer and collection of the fluid state mix into a disposable container. Pretreatment of waste before immobilization is sometimes necessary for ensuring compatibility with the matrix material. This may involve chemical pre-treatment and/or dewatering (applicable in case of polymers) and alongside can also help in volume reduction of final product. Typical examples are the pretreatment of borated waste using alkali treatment and chemical saturation, pH adjustment of spent resins and/or their dewatering/drying to lower down their reactivity.

Cementation and polymer fixation with thermosetting resins using the more popular polyester/epoxy polymer process are carried out at ambient temperatures. The thermoplastic organic binders like bitumen, PVC, etc. require heating/melting during or prior to the stage of mixing. In some cases, especially where the waste volumes to be dealt with are small, in-container (disposable) batch mixing is employed; the mechanical agitator may be reusable or disposable. Some plants, encountering large waste volumes (needing direct fixation) employ an on-line compact continuous mixer or a large capacity batch mixer which delivers the mix to smaller low cost disposable containers, usually standard mild steel drums. Variations like drum mixers, tumbling mixers, screw conveyer cum mixers, cone mixers are also in use. Requirements like high shear mixing and/or

throughput govern the selection of type of mixing system.

One possible variation in respect of immobilization with polymers is in fixation of solid wastes like ion-exchangers, where the dewatered resin may be solidified by maintaining pressurised flow of polymer formulation through it, totally avoiding any mechanical mixing and merits further study.

Cementation Practices in India

In India, the process is a common feature of most waste management facilities located at various nuclear plant sites at Trombay, Tarapur, Narora, Rajasthan and Kalpakkam. There are in all three types of variations in the basic design. These are evolved over a period of time to meet specific demands of a particular site or of a campaign meant for dealing with stored waste needing immediate attention. Technological long term advancements are incorporated in the newer plants. Thus, in the earlier plants, provision of an in-drum mixing system with waste pre-filling and reusable agitator blades was a standard practice. Variations such as drum tumblers or closed drums with disposable agitators were also developed. Due to their totally enclosed feature, the closed drums hold promise for fixing of alpha bearing waste. In recent plants like WIP, Trombay, cone mixers located in hot cells, with easy remotised operational amenability have been installed. In-drum mixers have been using the sequence of waste addition followed by addition of dry cement. A variation of cement pre-filled drums and closed pneumatic conveying system are being studied to avoid problems due to airborne cement dust in active areas.

A campaign code named CLEAR was successfully completed at Tarapur and involved in-trench fixation of a large volume of alkaline intermediate level waste. The process employed low-cost once-through trench mounted mild steel turbine agitators. Another operational ingenuity was use of industrial concrete mixer located at disposal site for cementation of lean sludges stored in trenches.

Polymerization Practices in India

Large quantity (about 250 M³) of Low Heat Generating Waste (LHGW) stored at PREFRE Plant, Tarapur needed to be conditioned and disposed of. The task was successfully accomplished over a period of one year. A specially developed barrier-impregnated (vermiculite) polymer matrix was developed for in-situ solidification in 4000 L mild steel vessels emplaced in the concrete trenches. This massive campaign has provided immense valuable experience in the handling/storage of polymer chemicals, waste pre-treatment and the polymer solidification process proper.

The polymer process for in-plant industrial application was also developed and demonstrated and is now a part of the Waste Management Plants at power stations like NAPS and KAPS. In these plants, the spent resins (an ILW) will be conditioned in polyester matrix. The present generation plants envisage direct fixation of the ion exchange resins after dewatering. Possible future developments include controlled drying of resins as a pretreatment for volume reduction and as a compatibility enhancing step.

Ion Exchange Resin Fixation Facility at Narora

Spent ion-exchange resins from reactor purification systems are received in Waste Management Plant as approximately 100 litre bed columns. These resins are hydraulically fluidised, on a closed loop water recirculation basis, into a receiver located in a hot cell. The resin slurry from the receiver, which also acts as a batching tank, is drained into a specially designed drum and then subjected to vacuum dewatering. The necessary chemicals, the polymer, accelerator, catalyst, are added in a predetermined sequence, quantities and rate. The contents are well mixed and allowed to gel and cure, before the drum is taken out for disposal. All operations in the cell are remotised. The facility, after successful conclusion of inactive trials followed by hot commissioning trials is now scheduled for regular operation (Fig.1).

Future Scenario

Continuing studies and operational feedback form the basis of further development in the area of cementitious and polymeric matrices. Thus a simple,

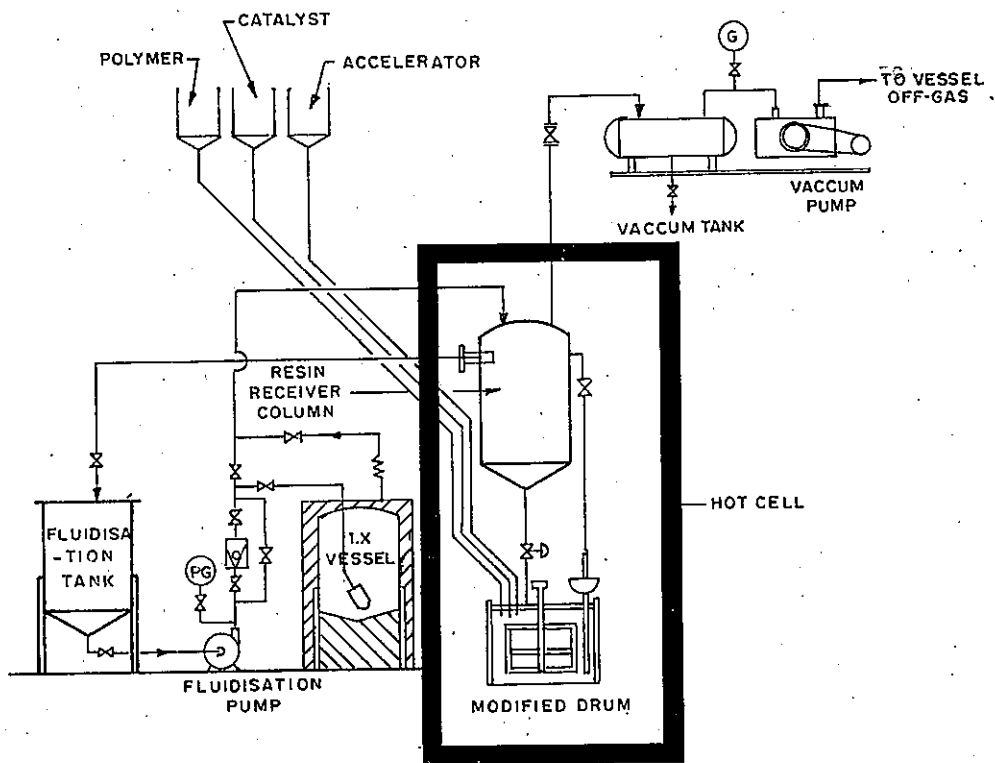


Fig. 1 Resin fixation system (Polymerisation).

safe, less expensive cementation process offering a product with better characteristics in relation to the raw waste, is put into practice as a starting step. With the discovery of synthetic polymeric materials offering better compatibility and products, these are being preferred for special category wastes. Further development is showing emergence of pre-treatment methods for wastes and/or specially formulated cements which hold promise for enhancement in their versatility. Here the attempt will be to develop cementitious matrices which can accommodate a minimum waste loading comparable to polymers (i.e. 50 wt%) without any compromise on the characteristics of the final product. A composite matrix like cement/polymer is also being developed so as to realise benefits of both the matrices. Alternative polymer formulations with improvement in techno-economic and safety aspects are under investigation. The development of some of these polymeric formulations, blended cements and

process equipment call for considerably long joint efforts with industry. It is therefore to be expected that some of these could be made proprietary or patented. The higher costs, if any, due to their proprietary nature may be offset by the benefits of standardisation and ease of procurement and quality control of raw materials.

All these will however need more study before their industrial application can be taken up. Till such time cement for general wastes, polymers for special wastes appears to be the judicious choice. Such is generally the scenario world over; and is also true in the Indian context.

Acknowledgement

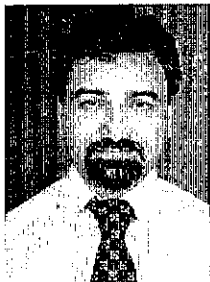
A review of status of such a vast subject in a paper of limited length is difficult, but challenging. The task could be achieved with the help of

numerous references, major ones of which are listed under bibliography and thankfully acknowledged.

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Vitrification of High Level Radioactive Liquid Waste



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Introduction

The existence and popularity of nuclear energy depends to a large extent on the safe management of radioactive waste. Nuclear waste management demands ecofriendly process/system, so that well-being of present and future generations is taken care of. The majority of the radioactivity in the entire nuclear fuel cycle is concentrated in high level radioactive liquid waste (HLW), which is generated during reprocessing of irradiated nuclear fuels. The HLW is generally concentrated by evaporation and stored in high integrity stainless steel tanks as aqueous nitric acid solution. These storage tanks require essential services like cooling to remove the decay heat, off-gas treatment, purging for homogenisation, etc. Though liquid storage has been proved to be largely safe and acceptable for a few decades, this cannot be considered as the ultimate system for storage and disposal of HLW. Hence alternative system for management of HLW is advocated. This system should be insensitive to loss of services, should not require same degree of surveillance, should be potentially better from the safety and environmental point of view and should make it possible for HLW to be stored, transported and disposed of. It turns out that such a system is based only on solidification and immobilization of the active components of HLW.

Conversion of HLW into a suitable solid matrix has been studied extensively in many countries. The selection of matrix and process depends on the waste stream. Composition of waste stream is based on type

of fuel, its history in the reactor including burn-up, the process used for reprocessing of the irradiated fuel and the off-reactor cooling period. The solid matrices being investigated are calcines, vitreous products, ceramics, glass ceramics, synroc, composites like glass metal vitromet, etc. Amongst these, the vitreous matrices are the most extensively studied and used worldwide for immobilization of HLW.

Since the radioactivity of the waste has to be isolated in the biosphere for extended periods of time, a three-stage strategy has been adopted for its management in most countries. This involves (i) immobilization of waste oxide in stable and inert solid matrices (ii) interim retrievable storage of conditioned waste packages under cooling and surveillance and (iii) deep underground disposal in suitable geological formations.

In this article, the properties of vitreous matrices, methods/facilities available worldwide for vitrification of HLW and their future development with emphasis on the Waste Immobilization Plant, Tarapur and the work done at the laboratories of BARC at Trombay and Tarapur are reviewed.

High Level Radioactive Liquid Waste

As mentioned earlier, this category of waste is generated during reprocessing of spent nuclear fuels in reprocessing plants. The most common flow sheet employed in the reprocessing plant is the PUREX process. This process involves steps like dissolution of the fuel in nitric acid, separation of unburned

uranium and plutonium from the fuel solution, partitioning of Pu & U and concentration of waste. The aqueous waste generated during separation of U & Pu is first cycle raffinate. It consists of about 99% of all the radioactivity generated during the entire fuel cycle and it is categorized as high level radioactive waste (HLW). The activity of HLW is of the order of few hundred curies per litre and is acidic (4M nitric acid) in nature. The major components of HLW are:

- (i) Fission products, e.g., Rb, Sr, Y, Zr, Mo, Ru, Rh, Pd, Cs, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, etc.
- (ii) Corrosion products, e.g., Fe, Ni, Cr, Mn, etc.
- (iii) Actinides, e.g., U, Pu, Np, Am and Cm.
- (iv) Chemicals introduced during reprocessing, e.g., NaNO_3 , impurities in HNO_3 , tributyl phosphate and its degradation products, etc.
- (v) Alloying elements, e.g., Fe, Al, Si, Mo, etc. in the fuel particularly when uranium metal is used as fuel.

Desirable Characteristics of a Solidified Waste Product

The solidified waste form must have certain qualities so that its interim and long term storage and ultimately its disposal is technologically feasible, safe, economical and environmentally compatible. The desirable properties include:

- (i) Good chemical durability, i.e., low leachability so that activity released into the environment, which is mainly due to leaching, is minimum.
- (ii) Good thermal conductivity so that heat dissipated due to activity is not accumulated.
- (iii) Resistance to alpha, beta, gamma and neutron radiation.
- (iv) Compatibility with the container.
- (v) Minimum volatility of the constituents under storage conditions.
- (vi) Ability to contain high proportion of waste and to have high volume reduction.
- (vii) High mechanical strength and shock resistance, thereby ensuring safe transport to the storage/disposal site.
- (viii) Stability over extended periods of time.

It should also be possible to prepare the solidified waste form using a simple technique with readily available chemicals and additives and acceptable maximum processing temperature.

Vitreous Matrices

This matrix has been extensively studied by most of the laboratories for immobilization of HLW. The two main types studied are phosphate glass and borosilicate glass.

Phosphate Glass

The phosphate glass matrix received a lot of attention in early studies as possible matrix for immobilization of HLW. This was mainly due to use of phosphoric acid as liquid feed, low formation temperature (approximately 900°C) resulting in lower volatilization losses for Cs and Ru and incorporation of sulphate and molybdenum in the waste in reasonable quantities. However material of construction is a major limitation in phosphate glass manufacture due to severe corrosive conditions. Also, there is tendency of phosphate glass to undergo massive devitrification at relatively low temperature of around 400°C , resulting in a significant loss of chemical durability. In Russia phosphate glasses are studied for vitrifying high sodium- aluminium waste [1].

Borosilicate Glass

Borosilicate glass is now the most widely accepted matrix for immobilisation of HLW [2]. The techniques of manufacture have been tested and demonstrated on an industrial scale. The formation temperature is moderate in the range of $1000 - 1100^\circ\text{C}$. The waste loading in the glass can be variable depending on the total salt content of the waste. However the glass forming additives are to be fed either in the form of aqueous slurry of mixed glass forming chemicals or glass frit. Extensive development work was carried out at BARC, Trombay for finalisation of borosilicate glass composition for immobilization of TPI HLW [3]. The development efforts at BARC, Tarapur, were concentrated towards modification of the above selected matrix for immobilization of existing HLW, where presence of sodium in the waste was taken into

consideration [4]. The modified final composition has been adopted at Waste Immobilization Plant (WIP), Tarapur for immobilization of HLW. A remarkable volume reduction factor of about 60 is obtained in this process.

Waste Glass Structure

In pure silica glass, the SiO_4 tetrahedra are linked via bridging oxygen atoms at the vertices so that continuous three dimensional network is established. The glass forming components other than silica (SiO_2) are boric oxide (B_2O_3) and phosphorous pentoxide (P_2O_5). In P_2O_5 system, there is tetrahedral unit as in case of SiO_2 , whereas in case of B_2O_3 glass system the basic unit is triangular [5]. Thus in the borosilicate glass system silicon and boron are network formers and become located in the centre of the oxygen polyhedra in the configuration of tetrahedra and triangles respectively. These polyhedra are then tied together by sharing corners, generally in accordance with Zachariasen's rules. Modifiers like most of the elements in HLW occupy positions in this three dimensional network structure depending on their electronegativity, ionic size and field strength.

Vitrification of HLW

The basic aim of this conditioning process is to convert the HLW into an inert matrix such as glass with the help of certain additives. Hence the steps involved in the process are evaporation, denitration, calcination, addition of glass former and modifier and finally preparation of glass. Vitrification, adopting borosilicate matrix with minor variation with respect to glass modifier composition on account of different waste characteristics, is now an acceptable technology being pursued by many countries. Both batch and continuous processes are used for vitrification.

Batch Processes

Batch or semi-batch pot vitrification processes using metallic melter heated either by resistance heating (e.g. FINGAL process in U.K.) or by induction (e.g. PIVER in France and WIP in India) are the earlier developments for vitrification of HLW [6,7]. In FINGAL process, the HLW and the glass forming chemicals were introduced into a metallic

pot heated by electric resistance furnace. The pot was disposable and used afterwards as canister. A scaled up facility based on FINGAL pot vitrification, called HARVEST, has been experimented on inactive scale. In the PIVER process which used induction heating the pot was reusable for 30 operations. The glass was poured batch wise into canister. In China, vitrification process similar to PIVER was adopted. They operated a plant for 438 hours and 134.5 Kg of inactive waste glass was produced. Due to limited throughput capacity of the batch process, it was given up at the end of 1985. The ESTER process was developed at the Commission of the European Communities (CEC) Joint Research Centre at Ispra, adopted in Italy at Saluggia and tested in inactive condition. The process was also based on pot vitrification process and red phosphorous was added to the glass forming chemicals to minimise ruthenium volatilization.

Continuous Processes

Due to the accumulation and fresh generation of HLW in large volumes, in most of the developed countries, attention is now focused on the development of continuous processes for vitrification of HLW [8]. These can be grouped in two major categories:

Two stage process : HLW is calcined in a rotary calciner along with minor additives for improving the rheology of the calcine. This calcine and the glass forming additives in the form of primary glass (frit) are fed to the metallic melter. The metallic pot melter is heated by induction furnace. The glass pouring is triggered by heating the freeze valve zone by induction heating. Pouring continues until the decreasing glass level inside the pot reaches the upper level of freeze valve and pouring stops by itself, since the heating is switched off. The canister is provided with lid and welded. Afterwards the canister is decontaminated externally and sent to interim storage. In France the vitrification plant AVM at Marcoule, based on this process is operating since 1978 and three scaled up similar facilities, namely R7 and T7 at La Hague, France and WVP at Sellafield, UK, are being set up and are operating.

Single stage process : The operation schematics of the single stage processes are based on liquid fed

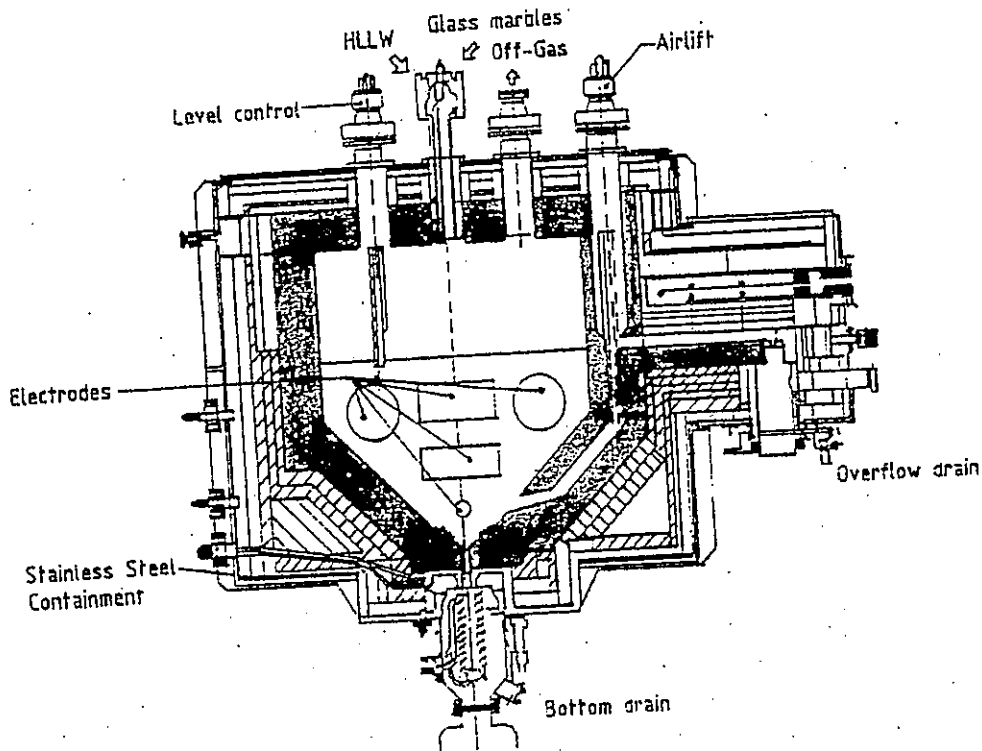


Fig. 1 WAW test melter with inclined bottom developed by KfK/INE, Germany

ceramic melter. The HLW is directly fed to ceramic melter containing pre-formed glass matrix. The ceramic melter uses joule heating employing inconel electrodes, since glass is a good electrical conductor at high temperature. The melters are constructed from high temperature refractory materials such as chrome alumina (e.g., Monofrax K-3). Secondary electrodes of molybdenum disilicide are used for start up of the melter. Draining of the glass from ceramic melter can be done either using an overflow system or from the bottom drain. Ceramic melters of different designs have been used in Germany and Russia as PAMELA (at the Belgium Eurochemic Reprocessing Plant) and as EP-500 processes respectively. The PAMELA melter faced partial damage after two years of operation due to settling of noble metals and forming conducting sludge at the bottom. The modified design with a sloped bottom has been developed at Wackersdorf, Germany to tackle this problem. The details of the design of the above modified ceramic melter is given in Fig.1 [9].

The EP-500 melter operated in Russia, has two separate compartments. One is being used for vitrification and the other is for storage and draining. Two plants based on ceramic melter are being set up at Savannah River and West Valley in USA and one in Japan at Tokai. A mock up facility is being set up in China with provision for both ceramic melter and two stage processes.

Waste Immobilization Plant, Tarapur

The Waste Immobilisation Plant (WIP), Tarapur is based on pot glass process [10]. The process flow diagram is given in Fig.2. The waste is concentrated in a thermosyphon evaporator and is then fed to the metallic melter. Glass forming chemicals are also fed to the melter in the form of slurry. The melter pot is accommodated in an inconel susceptor which is heated in a multizone induction furnace. The process pot is made of inconel and incorporates a freeze valve section which is operable by the independent induction coil. The susceptor

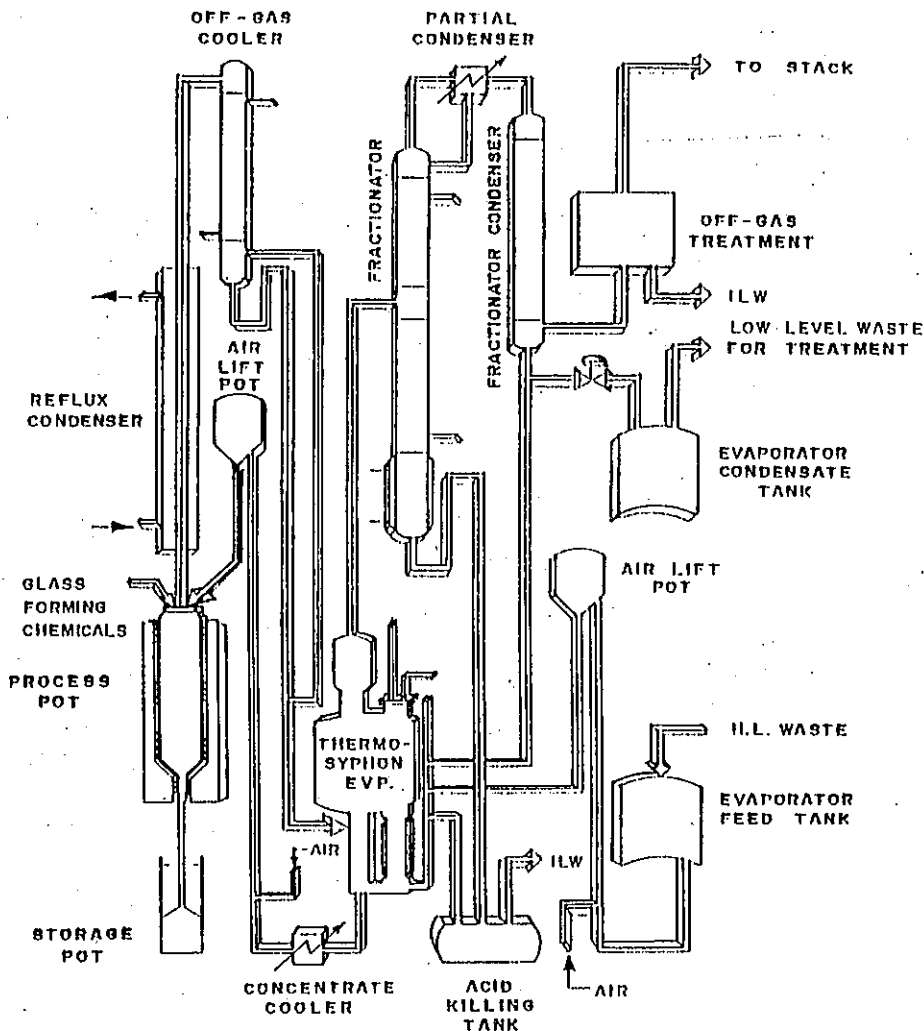


Fig. 2 Simplified flow diagram of vitrification plant at WIP Tarapur.

temperature is initially maintained at 600°C. There are simultaneous processes of evaporation and calcination of the HLW, so that solid-liquid interface moves vertically upward. The levels of the glass, calcine and liquid are sensed by the thermocouples located at different heights in the process pot. Temperature of the bottom zone is increased to 950°C so that the calcined mass is fused into glass. Thus three distinct zones e.g. glass, calcine and waste are established in the process pot. When the pot is filled about 60 % of the capacity with glass, the feed is stopped and the glass is allowed to be soaked at

950-1000°C for 6-8 hours to achieve homogenisation. The molten mass is drained into an insulated canister by operating freeze valve. In WIP, there are two such induction furnace systems which can be operated in parallel in a staggered operating cycle.

The storage canister is 324 mm in diameter, 775 mm long and is made from SS 304 L. The filled canister after 40 hours of cooling is sealed with a lid by pulsed gas tungsten arc welding. The integrity of the welding is ensured by helium leak detection technique. Two such storage canisters are employed

in a carbon steel overpack of 356 mm in diameter and 2 M long. The overpack is sealed with a lid as above, decontaminated and then transported to Solid Storage Surveillance Facility (SSSF), located adjoining to WIP, for interim storage.

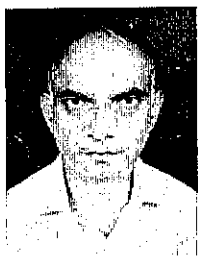
Summary

Among various matrices used for immobilization of HLW, borosilicate glass has been more commonly adopted by various facilities in the world. For waste conditioning metallic melter technology has been established and demonstrated to be proven technology. However, continuous liquid fed ceramic melter based process technology is being pursued by many countries.

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Partitioning of Minor Actinides from Highly Radioactive Waste Solutions



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Introduction

The fuel used in most of the nuclear reactors is entirely uranium. Each tonne of spent fuel contains about 10 Kg of transuranium (TRU) actinides, of which ~ 0.8 Kg are Minor Actinides (MA). It also contains 30 Kg of fission products, including 4 Kg that are long lived nuclei (having half lives greater than 30 years) [1]. The plutonium produced in the reactors is the hope for the future since it accumulates fissile inventory equivalent to millions of tonnes of oil and coal in terms of its energy content.

The choice for the final disposal of the spent fuel depends entirely on the fuel cycle policy of the nation. There are three options for the management of spent fuel, viz., a) recycle, b) throw-away, and c) wait and watch. Almost one half of the spent fuel from the world's nuclear power plants is being reprocessed where the valuables like plutonium and uranium are recovered and the waste vitrified and kept for disposal. The other half is undergoing the "once-through cycle", kept under long-term storage in engineered facilities and finally to be disposed of in suitable geological formations. Countries like France, United Kingdom, Japan, Germany, Belgium, Switzerland, Russia, India keep the reprocessing option. Out of these countries France and United Kingdom have large facilities for fuel reprocessing in operation, whereas Japan and Russia are catching up in a big way. In India, the reprocessing plants at Trombay and Tarapur are operational. One at

Kalpakkam is being commissioned for active runs and another plant at Kota is in the planning stage.

The solutions left after recovering U and Pu, normally known as high level waste (HLW) solutions, contain small amounts of unextracted U, and Pu, and minor actinides (Np, Am, Cm) and a host of fission products (FP). The FPs in fact include large amounts of valuable metals like Pd, Rh and Ru which are strategically and economically important materials. The fission products also contain the long-lived and heat-generating nuclides ^{137}Cs and ^{90}Sr . The HLW solutions, in fact, contain the maximum radioactivity handled in the entire fuel cycle activities.

There is a great environmental concern about the safe disposal of nuclear wastes especially those containing long-lived alpha-emitters. The presence of long-lived alpha active actinides in the waste necessitates its surveillance for several tens of thousands of years even after vitrification and storing in deep geological repositories. This is a global problem facing the nuclear industry at present. The half-lives of minor actinides are given in Table 1.

Partitioning and Transmutation

There is renewed interest all over the world in Partitioning (Separation and Recovery) of minor actinides from HLW solutions, followed by their Transmutation into short-lived nuclides (P & T option). This is mainly due to the problems in finding suitable geological repositories which are acceptable

Table 1. Minor actinides in high level waste

Nuclide	$t_{1/2}$, years
^{237}Np	2.14×10^6
^{238}Pu	8.77×10^1
^{239}Pu	2.44×10^4
^{240}Pu	6.55×10^3
^{241}Am	4.32×10^2
^{243}Am	7.37×10^3
^{246}Cm	4.73×10^3

to the general public. The P&T option considerably reduces the radioactivity and reduces/eliminates the need for long-term surveillance of vitrified waste. The present article deals with the first part, i.e., partitioning of Minor Actinides from HLW solutions.

Partitioning of Minor Actinides

Two possible approaches are considered for partitioning of MA depending on whether the HLW is freshly generated in a reprocessing plant or it is stored in tanks awaiting disposal. In the first case, the high radioactive aqueous raffinate waste (HAW) coming directly from the Purex process (without any concentration step or pretreatment) can be subjected to further partitioning of MA. This will involve a waste treatment facility attached to the existing reprocessing units. In the second case, for the treatment of already stored HLW solutions, a separate waste treatment facility for partitioning of MA can be planned.

Many countries such as USA, France, Japan, China, Russia and India are making concerted efforts on the partitioning of long lived minor actinides from HLW solutions utilizing various suitable extracting agents, such as:

- i. Dihexyl-N,N'-diethylcarbamoylmethyl phosphonate (DHDECMP)

- ii. N,N'-dimethyl N,N'-dibutyltetradecyl malonamide (DMDBTMDA)
- iii. Trialkyl phosphine oxide (TRPO)
- iv. Diisodecyl phosphoric acid (DIDPA)
- v. Octyl(phenyl)-N,N'-diisobutylcarbamoylmethyl phosphine oxide (CMPO)

A large amount of data are being generated on the partitioning of MA using the above as well as some other extractants and, it will soon be possible to compare and evaluate these various systems. Table 2 gives data for comparison of a few important extractants in aliphatic hydrocarbon diluents for the partitioning of MA based on laboratory experiments.

A brief description of the work on partitioning of MA from HLW solutions utilizing the above reagents along with a status report on the work carried out in BARC under a collaboration between Radiochemistry Division, Bio-Organic Division, Fuel Reprocessing Division and Process Engineering and Systems Development Division is given below.

Dihexyl-N,N'-diethylcarbamoylmethyl phosphonate (DHDECMP)

Although DHDECMP (or CMP) has widely been used for the extraction of tri-, tetra- and hexa-valent actinides from nitric acid solutions in many aromatic diluents, only recently a mixture of CMP and TBP in an aliphatic diluent, such as NPH or ISOPAR has been reported [2] for the extraction of U(VI), Pu(IV) and Am(III) and other metal ions like Fe(III), Zr(IV), Bi(III) etc. Very high concentration (0.75 M) of CMP had to be used to get a reasonable D value for Am(III). Even in presence of 1.05 M TBP, the extractant mixture when contacted with 7.5 M HNO_3 produced a third phase. In presence of complexing agents like F^- and $\text{C}_2\text{O}_4^{2-}$, although the D values of Am(III) and U(VI) at 2-3 M HNO_3 remained more or less the same as that in the absence of these ions, the D values drastically decreased in the case of Pu(IV). Pu was conveniently stripped only after reducing it to the trivalent state along with the fraction containing Am(III). In their future work programme, the authors propose to design a flowsheet in which the transuranic elements are separated from the majority of U and Bi excepting the trivalent lanthanides. However, no

Table 2. Important extractants for separation of tri, tetra- and hexa-valent actinides from nitric acid, simulated HLW or actual HLW solutions.

Extractant, concentration (mole/L)	HNO ₃ conc. ^a for Am extraction (mole/L)	HNO ₃ conc. ^b for Am stripping (mole/L)	Diluent	Country
DHDECMP 0.75	> 2	< 0.15	NPH or ISOPAR + 1.05 M TBP	USA
CMPO 0.2	2 - 3	< 0.04	NPH or DODECANE + 1.2 M TBP	USA, Japan, India
DMDBTDMA 0.72	> 2	< 0.5	TPH	France
TRPO 30 vol %	< 0.5	> 4	DODECANE	China
DIDPA 0.5	0.5	4	DODECANE	Japan

^afor D [Am(III)] > 3;

^bfor D [Am(III)] < 0.1.

NPH, ISOPAR and TPH are aliphatic hydrocarbon diluents.

attempts have been made to recover ²³⁷Np from the waste solutions using the above extractant mixture.

N,N'-dimethyl N,N'-dibutyl tetradecyl malonamide (DMDBTDMA)

Extensive studies have been carried out on the extraction of MA from HNO₃ solutions and from HLW solutions using various derivatives of diamides [3-5]. Many of the diamide derivatives have limited solubility in aliphatic diluents. Formation of third phase was another limitation while using nitric acid solutions higher than about 3M. The recently prepared derivative DMDBTDMA is highly miscible with dodecane type diluents and 0.72 M of the reagent in TPH has been successfully used by Musikas and his group in France for the separation of MA from >2M nitric acid solutions. The main features of this reagent are that: (i) it is easier to synthesize, (ii) cheaper as compared to some of the other reagents being used for this purpose, (iii) they are completely incinerable and (iv) the degradation products formed can easily be removed. The process thus developed, called DIAMEX, has been successfully tested on medium activity liquid

waste whereas the tests on high activity liquid waste are in progress [6].

Trialkyl Phosphine Oxide (TRPO)

TRPO, a mixture of trialkyl phosphine oxides (alkyl is C₆-C₈) has been synthesised from petrorefining byproducts and utilized for the extraction of Np, Pu and Am from highly active waste (HAW) solutions. TRPO (30 Vol %) in kerosene is used as the extractant. For Np, the valency is adjusted to IV by electrolytic reduction and then extracted into the organic phase. In a preliminary run with actual HAW, U, Pu, Am and Cm were extracted with 30% TRPO after adjusting the acidity of the feed solution to nearly 1M. The loaded organic phase is stripped thrice with 5 M HNO₃, twice with 0.5 M oxalic acid and once with 5% Na₂CO₃ solution to get back all the actinides. It is reported that if the acidity of the HAW solution is higher than 2.5M, the process is not effective for the recovery of Am. Among the nonactinide constituents in HAW solutions, it is found that Cs, Sr, Ba, Cd and Rh are not extracted, Fe, Ni, Ru, Ag and Tc are partly extracted whereas Pd, Zr, Mo and the rare earths are nearly completely extracted. It has been emphasized

that Tc is one of the most complicated fission products encountered during TRPO extraction process [7-9].

Diisodecyl Phosphoric Acid (DIDPA)

Extraction with DIDPA has been studied for the separation of transuranium elements from HLW solutions. A 0.5 M solution of DIDPA containing 0.1M TBP in dodecane can efficiently remove trivalent Am and Cm from 0.5 HNO₃ solution. Np is reduced to the tetravalent state with hydrogen peroxide and extracted into the organic phase along with other actinides. Experiments on counter-current continuous extraction of MA from simulated HLW have given very encouraging results. During stripping process it is proposed to separate trivalent actinides from the lanthanides. The only negative point in this process seems to be that the acidity has to be brought down to about 0.5 M, for which denitration is the most suitable method [10,11].

Octyl(phenyl)-N,N'-diisobutylcarbamoylmethylphosphine oxide (CMPO)

CMPO has been judged as the best reagent for the recovery of MA from HLW solutions. Horwitz and coworkers at the Argonne National Labs., USA have developed the TRUEX (Transuranium Extraction) process for the recovery of all the actinide elements from highly acidic nuclear waste solutions. The extractant mixture used by them is 0.2 M CMPO + 1.2M TBP in paraffinic hydrocarbon (dodecane). The process claims to be highly efficient for the removal of all the actinide elements and also to be cost effective in the management and disposal of transuranic wastes [12-14].

Ozawa and coworkers in Japan have also used the mixture of CMPO and TBP in dodecane to carry out a series of counter-current tests. The results have shown good extraction of MA yielding a raffinate with sufficiently low alpha contamination [15].

Work at BARC

A comprehensive programme on the partitioning of MA from HLW solutions using CMPO has been initiated in BARC since 1990. An initial extraction with 30% TBP in dodecane is carried out to deplete the HLW of uranium from ~ 10-20 g/L to ~ 20 mg/L. Separation of Pu and Np

is also carried out in the uranium depletion step using 30% TBP/dodecane by oxidising Np to Np(VI) and Pu to Pu(VI) using 0.01M K₂Cr₂O₇. Four types of HLW solutions are treated, (a) simulated sulphate bearing (SB), simulated HLWs originating from the reprocessing of fuels from (b) pressurised heavy water reactors (PHWR) and (c) fast breeder reactors (FBR), and (d) the actual HLW solutions generated from the reprocessing of research reactor fuels [16]. The effluent thus obtained after the initial TBP extraction is treated with 0.2M CMPO + 1.2 M TBP to extract any remaining U, Np, and Pu, and the trivalent Am, Cm and the rare earths. Both solvent extraction [17,18] and extraction chromatographic [19] techniques have given excellent separation and recovery of the above metal ions. Studies have also been carried out for the counter-current extraction of MA from simulated SBHLW [20] and PHWR HLW [21] employing a mixture of CMPO and TBP as the extractant. The findings of these runs were highly encouraging. Studies on the radiation degradation, clean-up and reusability of the CMPO mixture after exposure to radiation doses up to 50 MRad as well as mixer-settler runs with actual HLW solutions are under progress.

Actinide (III) Lanthanide (III) group separation

Once actinides and lanthanides have been recovered from the HLW solutions, it is necessary to separate the lanthanides before recycling the actinides back to the reactors. In the DIDPA extraction process [11], the Japanese group have recently introduced the stripping of Am and Cm from the loaded organic phase by a mixture of DTPA and lactic acid and finally the rare earths are stripped by 4M HNO₃. They report a separation factor of about 10 between the trivalent actinides and the lanthanides in batch experiments and plan to evaluate the DF under continuous counter-current stripping experiments.

Musikas [5] used a mixture of tripyridyltriazine (TPTZ) and dinonyl-naphthalene sulphonic acid (DNNS) in carbon tetrachloride in batch extraction experiments with trivalent Am, Ce and Eu in dilute nitric acid and found a high separation factor for Am as compared to the lanthanides. The use of α -bromocapric acid in place of HDNNS and an aliphatic diluent was proposed for large scale separations.

In BARC, while CMPO is being utilized for bench scale and mixer-settler runs for the separation of MA from HLW solutions, different complexing agents are being tried while stripping MA from the loaded organic phase to get a clean separation of trivalent actinides from the lanthanides. It has been shown that a clean separation of ^{147}Pm can be achieved from actual high active waste solutions by first extracting with CMPO mixture, stripping trivalent actinides and lanthanides together with 0.04 M HNO_3 and then loading this solution on an extraction chromatographic column containing 2-ethylhexyl-2-ethylhexyl phosphonic acid (KSM-17) adsorbed on Chromosorb-102 and eluting with different concentrations of dilute HNO_3 [22].

Conclusion

The present efforts using suitable extracting agents world wide have given very encouraging results for the partitioning of minor actinides from the HLW solutions. Special attention is now being directed towards making the process cost-effective and also minimising the volumes of secondary waste streams. This programme has two distinct advantages, viz., recovery of significant quantities of valuables from HLW solutions and reducing the alpha activity levels of the resulting raffinate, which in turn will help nuclear industry in the safe and environment-friendly disposal of highly radioactive waste solutions.

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