

Editorial

Management of high level waste and spent fuel is a key issue which will shape the global environment surrounding nuclear power in the world. The large quantities of highly radioactive wastes must be isolated from the environment for hundreds of thousands of years. The high level waste generated during the reprocessing of the spent nuclear fuel is being vitrified in suitable glass matrix, which after an interim subsurface storage of a few decades, will ultimately be buried in a deep geological repository. Some of the countries have zeroed in on the sites for the repository. Any decision about the site of a deep geological repository must be backed by a sound scientific basis, which will provide an assessment of the probability of the long lived radionuclides finding their way into the biosphere in a distant future. It is therefore imperative that a sound data base is generated to assess the performance of the deep geological repository in retaining the long lived radionuclides over a time span of hundreds of thousands of years.

The present bulletin is aimed at highlighting the R&D efforts towards the management of the high level waste and the selection of a site for the deep geological repository. I am thankful to Shri R.K.Bajpai to have readily consented to be the guest editor of this bulletin. I am also grateful to Shri S.D.Mishra, Director Nuclear Recycle Group to give the focus of this thematic bulletin. Lastly I thank all the authors for their timely submission of articles. I hope the bulletin will generate interest among our readers from DAE as well as Non-DAE institutes so that they can contribute in this important activity of the department of atomic energy.

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From the Secretary's Desk

Greetings from Mumbai,

Biodiversity - the immense variety of Life on Earth - is what makes our planet not only habitable but beautiful. We depend on the natural richness of our planet for the food, energy, wood, raw materials, clean air and clean water that make life possible and which drive our economy. But we also look to our natural environment for less tangible things such as aesthetic pleasure, artistic inspiration and recreation. Such a healthy treasure is threatened in the wake of running for the development resulting in more and more CO₂ emissions.

Just a days after the Nobel prize was awarded for global warming work, an alarming new study finds that warming signals are stronger, and happening sooner than expected, due to increased human emissions of carbon dioxide and an Earth less able to absorb them.

The ocean's plankton can suck up far more airborne carbon dioxide (CO₂) than previously realised, although the marine ecosystem may suffer damage if this happens, a new study into global warming says. The sea has soaked up nearly half of the CO₂ that has been emitted by fossil fuels since the start of the Industrial Revolution.

The gas dissolves into surface waters and is then transported around the oceans. But a key role is played by plant micro-organisms called phytoplankton, which take in the dissolved gas at the ocean's sunlit surface as part of the process of photosynthesis. This plankton dies and eventually sinks to the ocean floor, thus storing the carbon for potentially millions of years.

One of the big questions is how much more of CO₂ the sea can absorb. If, like a saturated sponge, the oceans cannot take up any more, atmospheric concentrations of CO₂, the principal greenhouse gas, would sharply rise and stoke global warming. Another concern is that rising levels of dissolved CO₂ also causes acidification of seawater. Wildlife such as coral, which secretes a skeletal structure, are known to be affected by acidification but the impact on other marine species is largely unknown.

Supporters of so-called geo-engineering — unconventional projects aimed at easing global warming — have been closely looking at plankton, seeing in it fantastic potential as a carbon sponge.

The deep geological repository option results in the eventual permanent emplacement of the used nuclear fuel which reduces or may eliminate the necessity for long-term institutional and operations continuity and financial surety. As a consequence, after emplacement and closure, provision of long-term resources and funding are not required, although further actions are not precluded. Deep emplacement reduces security concerns, both before and after closure.

IANCAS compliments the authors of this bulletin on 'Georepositories', an important contribution in the management of spent nuclear materials.

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Georepositories

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FOCUS

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The concept of geological disposal of long lived wastes has matured considerably in last two decades especially in areas concerning the understanding, characterization and quantitative modeling of the geological and engineered barriers. As most of nuclear power producing nations are in advance stage so far as completing the nuclear fuel cycle is concerned, the programmes on deep geological repository have gained noticeable impetus in last ten years. As a result, the debate among waste managers have shifted from “whether or not, the geological disposal is a preferred mean for ultimate disposal of such kind of waste?”, to “when and where disposal should take place?”. There is consensus among nuclear power producing nations that geological disposal is a feasible route for assuring permanent isolation of long term wastes from human environment. This is evident by commencement of construction of many new Underground Research Laboratories (URL's) in nations like France, Japan, Finland etc. a part from already existing URL's in USA, Sweden, Belgium, Switzerland and Canada.

Alternative means of radioactive disposal have often appeared time to time. There are opinions strongly advocating extended surface storage or partitioning and transmutation. Feasibility of these is being assessed worldwide.

If we take stock of the developments in this field in last ten years, we find that the technology and methodology required for such an exercise has advanced significantly. While the site selection activities have entered into advanced stages in countries like Sweden, Finland, Canada, Japan, Hungary etc, substantial progress have been registered in quite a few countries towards development of methodology and technology for construction of deep geological repositories world wide due to two decades of experimentations in URL's. Most notable work has been carried out in granite based underground research laboratory in Sweden, USA, Canada, and Switzerland. A number of experiments related to site characterization, radionuclide transport through rocks, emplacement of engineered barriers, tunnel sealing, fracture tomography etc have been attempted in these URL's under international collaborations.

The need of a deep geological repository thus, is now widely recognized internationally. However in India, waste inventories for ultimate disposal in geological repository are limited, nevertheless, in view of our ambitious nuclear power generation programme, R&D studies are in progress.

I hope this special issue on deep geological repositories will be highly useful and informative to its reader as it will provide an overview of the overall development in this vital field in recent time.

Guest Editorial

Shri R.K. Bajpai



The research in various aspects of geological disposal has advanced considerably in last two decades especially due to some epoch making efforts in Sweden, France, Canada, Belgium and USA. In the initial years geological options like seabed, inland basin, seaward dipping strata, subduction zone, active volcanoes etc were also assessed. These options were found more imaginary in nature than real. Gradually consensus among nations evolved about the possibility of disposing such wastes in suitable rocks at depth.

The initial years from 1955 to 1980 were mainly devoted for identification of suitable rock types and regions world wide without much success. The focus of these investigations always centered around finding a site devoid of groundwater and seismicity and also trying to build up models demonstrating the evolution of these sites over next few thousands of years . The most important development in recent year is the commencement of disposal of TRU wastes in WIPP, a deep geological repository (2700ft) in bedded salt at new Mexico. However realization of a deep geological repository for heat emitting high level long-lived wastes both the spent fuels as well as reprocessing wastes is yet to happen. The Yucca Mountain Site in USA stands closest to become first repository of this type as license application to NRC is expected to be submitted by mid 2008 and it is expected to receive waste by 2011. It has been evaluated extensively since early eighties and has been subjected to extensive characterization for demonstration of safety. The impact of waste emplacement in this site has been calculated by conducting a large number of insitu experiments wherein the movement of heat front across the rock, migration of radioactivity through groundwater, performance assessment of various glasses, metals, concrete, etc , and long term evolution of site in next twenty thousands of years has been established both by experiments as well as predictive numerical modeling.

On the other hand, in early eighties most of the nations like France, Japan, Hungary, etc with substantial nuclear power generation programmes started assessing various processes and parameters of importance in underground mines while a few other like Sweden, Belgium, Canada, Switzerland etc went ahead with the construction of dedicated Underground Research Laboratories (URL) in suitable rocks in the depth range of 400-500m. Geological research on nuclear waste disposal in these mines and URLS mainly included development of waste transport and emplacement technology, excavation technology, sealing technology etc and assessment of rock response to heat generation, accelerated ground water movements, insitu stresses, excavation, geochemical changes, radionuclide migration through fractures and also processes like seismicity, volcanism, uplift, fault movements etc. For such purpose highly sophisticated instrumentation and methodology to measure and monitor these variations in situ over extended period of time have been developed. A variety of rocks like basalt, granites, shale, clay, volcanic tuff and salt beds have been extensively characterized . Currently a number of nations like Japan, Finland, France etc are working towards setting up Underground Research Laboratories. The message from this research is clear. The existing rock mass characterization methodology, construction technology, instrumentation and techniques require large-scale refinement to meet the requirement of a geological repository.

The extensive research in these laboratories has brought to light the magnitude of technical uncertainties in predicting natural processes over longer time duration successfully and hence demonstration of the capabilities of geological repository to protect the environment for radiological hazards.

Taking into consideration the enhanced production of waste in view of the projected growth of nuclear power generation in next decade, increased vitrification capacity, limited interim storage capacity for vitrified overpacks and accelerated pace of work on geological repository worldwide, there will be a pressing need to commence disposal by 2035-40. The available time ie 30-40 years though appear enough , is just sufficient to complete pre-disposal activities specially the site investigations and experimentations that run into decades

before declaring a site suitable for geological repository. Indian programme on geological repository commenced in early eighties with underground experiments in an abandoned section of a gold mine at a depth of about 1000m in Kolar Gold Fields (KGF). The investigations were mainly directed towards development of methodology for in-situ assessment of thermo mechanical behaviour of the host rock (amphibolite) and to develop and validate the mathematical models. It also addressed the development of associated instrumentation for the measurements and monitoring. Regional screening of a few geological domains, mainly granitic, with the objective of locating suitable sites for a geological repository has also been initiated over an area of about 0.1 million square kilometers.

Identification of a possible site for geological repository remains the key challenge worldwide. Already identified sites in nations like USA, Sweden, France etc as well as future sites, if any, will continue to face Not In My Back Yard Syndrome (NIMBY). Nevertheless, situation is likely to improve in future mainly due to large scale public demonstration programmes in Underground Research Laboratories.

This issues covers the entire spectrum of radioactive waste disposal from vitrification to deep geological repositories and I hope will be well received by its readers.

Processes & Practices for Management of Radioactive Wastes – Indian Scenario



Shri Kanwar Raj joined BARC in 1973 after obtaining B.E. (Chemical) with honours from IIT Roorkee. As Head, Waste Management Division, BARC, he is responsible for operation of Waste Management Facilities at Trombay, Tarapur and Kalpakkam. He is advisor to NPCIL and AERB in the matters related to Waste Management. He has played a key role in the design and commissioning of Polymerisation and vitrification of intermediate level and high-level radioactive liquid waste. His other interests are safety of waste management systems, public awareness and long term evaluation of vitrified waste products and stimulated repository conditions. He has served as Technical expert at IAEA and is a member of its waste safety standards committee (WASSC). He has more than 30 publications.

Shri C. P. Kaushik, a Post Graduate in Chemistry is responsible for development of matrices for treatment/ conditioning of different types of radioactive waste and its implementation in the plant scale. He is also actively involved in characterization of waste and waste forms. He is recipient of INS gold medal award of year 2004 in view of his outstanding contribution in the field of nuclear waste management. He is having around 50 papers in National/International symposia, conferences and journals.



Introduction

Rapid industrialization 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 unconventional energy resources. Amongst the unconventional energy sources, nuclear fission is one of the most economically viable and environmentally clean alternatives for large scale production of electricity. The running of nuclear reactors, for research or power production, leads to generation of nuclear waste. While a majority of isotopes generated during the fission process are short lived, a small amount of long lived fission products and actinides are also produced during the operation of reactors. These nuclear wastes require careful handling to avoid radiation exposure to humans and contamination to ground water resources. Hence management of nuclear waste assume importance for providing nuclear

Power as a safe, sustainable and broadly acceptable alternative option to meet the ever-increasing demands of electricity. The main stages of the nuclear fuel cycle which generate radioactive waste include mining and milling of uranium ore, fuel fabrication, reactor operation and spent fuel reprocessing. The underlying objective governing the management of radioactive waste is protection of human being and the environment, now as well as in the future. As a waste management philosophy, utmost emphasis is given to waste volume minimization at all stages of design, operation and maintenance [1]. The development of innovative treatment processes for low and intermediate level wastes (LLW & ILW) in recent times has focused on volume reduction as one of the main objectives [2].

The present paper summarize Indian programme on management of radioactive waste and also identifies major areas for further development to meet the future challenges in view of expansion of nuclear energy programme.

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Current Waste Management Process/Practices

In view of a large variety of radioactive wastes being generated, processes used for their treatment are also diverse. Work on development of these processes and relevant technologies was started in early sixties in the laboratories and pilot plants in Bhabha Atomic Research Centre at Trombay. This pioneering work has resulted in the development of various processes and matrices for treatment and conditioning of radioactive waste. A brief summary of the processes and technologies adopted in India for management of different types of radioactive waste is described as follows.

Management of Gaseous Waste

In order to control and minimize discharge of activity through air route in conformity with the principle of ALARA, all nuclear installations in the country are equipped with an elaborate off-gas cleaning system. These systems are designed depending on specific activity, type of radioactivity, particulate density and its size distribution, specific volatile radioisotopes and their concentration, etc. Different types of scrubbers like ventury, dust, packed bed; cyclone separators, high-efficiency low-pressure drop demisters, chillers and high-efficiency particulate air (HEPA) filters are used to practically retain most of the particulate radionuclides.

Management of Liquid Waste

Low level radioactive waste (LLW) is generated from reactor operations, off-gas scrubbers of nuclear facilities, active floor drains, decontamination centre, laboratories, drain from change room and showers as well as during management of high and intermediate level waste. These waste streams require treatment to reduce their activity concentration to a level at which they are allowed to be discharged according to national regulations. The processes that are employed for treatment of this type of waste are chemical treatment, ion-exchange, steam and solar evaporation and membrane processes [3].

Chemical Treatment Process

Liquid wastes with low levels ($37-3.7 \times 10^6$ Bq/l) of activity containing ^{90}Sr and ^{137}Cs as the

major radionuclides are treated by co-precipitation using chemicals like barium chloride, sodium sulphate, potassium ferrocyanide, copper sulphate, etc. Subsequent to precipitation, the resultant sludge from clarifloculator is further concentrated by decantation, filtration and centrifugation. The resulting solids containing bulk of the radioactivity originally present in the liquid waste are immobilized in cement matrix before disposal.

Ion Exchange Process

A variety of sorbents and ion exchangers are in use in India for the treatment of diverse types of radioactive aqueous waste streams. Conventional synthetic organic ion exchange resins are used for clean-up of spent fuel storage pool and for polishing of effluents from chemical treatment of low level waste. Amongst inorganic materials, synthetic zeolites and clay mineral vermiculite have found industrial application. While vermiculite is used for decontamination of low level effluents, a synthetic zeolite is used for reduction of ^{137}Cs activity in spent fuel storage pool water [4].

A treatment process based on radionuclide separation by selective ion exchange is used for the effective management of alkaline intermediate level waste (ILW). An ion exchange plant is in regular operation at Tarapur. A unique transportable shielded ion exchange facility has been used at Trombay for processing of ILW in large volumes at processing rate of $10 \text{ m}^3/\text{day}$ using 100 litre column [5]. In this process, an indigenously developed Resorcinol Formaldehyde Polycondensate Resin (RFPR) is used in repeated loading-elution-regeneration cycles for efficient removal of ^{137}Cs which is the major radionuclide present. In this system, a chelating iminodiacetic acid resin is used for the removal of ^{90}Sr traces.

Membrane Processes

Membrane based processes like reverse osmosis and ultrafiltration are used essentially for treatment of low level liquid waste. These are generally employed in combination with other treatment methods like chemical treatment or ion-exchange process to further improve the decontamination. A reverse osmosis plant of capacity $100 \text{ m}^3/\text{day}$ using polyamide membrane in

spiral wound configuration is in operation for treatment of low level ($37-3.7 \times 10^6$ Bq/l) waste at Trombay. The volume of waste is normally reduced by a factor of ten and decontamination factor of 8-10 is achieved in this process.

Thermal / Solar Evaporation

Thermal evaporation using low pressure steam in thermosyphon evaporators is deployed for concentration and denitration of high level radioactive waste (HLW). These equipments have the advantage of low maintenance due to the absence of rotating components and inbuilt features for remote maintenance. Solar evaporation has been successfully used for concentration of large volume of low level waste at Rajasthan site, where as climatic conditions like low humidity, high temperature and low rain fall favour adoption of this technique.

Waste Immobilization Processes

Cementation and polymerization methods are in use for immobilization of LLW, ILW and spent ion exchange resins. Vitrification is being used for conditioning of HLW

Cementation

Cement and cement composites are extensively used for immobilization of low level radioactive concentrates, chemical sludges etc. Special cement formulations have been developed indigenously by blending cement with suitable additives to improve product characteristics [6]. Cementation facilities having in-drum mixing system using re-usable agitator for conditioning of radioactive waste are installed at various sites. Cementation process has also been used for in-situ immobilization of intermediate level waste in specific cases, which results in large waste processing rate with extremely low exposure to the radiation workers. At WIP, Trombay cone mixers located in hot cells with easy remotised operational amenability is in use for conditioning of intermediate level waste in cement matrix.

Polymerization

Polyester styrene is in use for immobilization of ILW concentrates and spent ion exchange resin

from nuclear power stations and other facilities. This matrix has also been used for in-situ solidification of low-heat generating liquid waste from reprocessing plant [7].

In resin fixation plant, radioactive spent resins are hydro pneumatically transferred to resin storage tank. A batch of 90 kg resin is transferred to a specially designed product drum kept on a load cell. Excess water is removed by vacuum de-watering system. Requisite amount of polyester styrene polymer is premixed with optimized concentration of accelerator (dimethyl aniline) and catalyst (benzoyl peroxide). This polymer is then gradually poured into a product drum with constant stirring. These resin fixation facilities exist at nuclear power plant sites in Narora, Kakrapar and Tarapur. Salient features of cement and polymer waste products are presented in Table 1.

Vitrification

HLW generated during reprocessing of spent nuclear fuels is concentrated by evaporation and stored in stainless steel tanks. A three-step strategy for management of HLW has been adopted in India. This involves: (i) immobilization of waste oxides in stable and inert solid matrices, (ii) interim retrievable storage of the conditioned waste under continuous cooling and (iii) disposal in deep geological formations.

In order to meet the challenging task of vitrification of HLW, research and development work was started in the late sixties encompassing various areas of HLW conditioning including formulation of matrices and their characterization. The solidified waste form must have certain qualities so that its interim storage, ultimate disposal and long term durability is technologically feasible and safe. Homogeneity, chemical durability and pour temperature of the glass waste product are the three most important criterion and for the matrix composition selection. The first two are considered as product durability factors, whereas the third one is processing parameter related to the plant application. The other desirable properties of the vitrified waste product (VWP) include thermal conductivity, waste loading, viscosity, impact strength, thermal and radiation stability. Borosilicate matrix has been developed and adopted in present

TABLE 1. Salient properties of cement and polymer waste products

Properties	Cement Waste Product	Polymer Waste Product
Waste loading (%)	60 – 70	55 – 60
Compatibility	With alkaline waste	With alkaline waste
Density (gmL)	1.8 – 2.0	1.2
Compressive strength (kg/cm ²)	100-150	270
Porosity (mL/g), (Total pore volume)	0.18-0.27	Non-continuous pores
Setting time (minutes)	100-300	NA
Leach rate (g/cm ² /day)	10 ⁻⁴ – 10 ⁻⁵	10 ⁻⁵
Radiation stability	Up to 10 ⁸ rads	Up to 10 ⁸ rads
Homogeneity	Good	Very Good
Thermal Stability	Very good up to 100°C	Good up to 100°C

TABLE 2. Compositional details of various glass formulations

Composition	Tarapur		Trombay	
	Basic Sodium Borosilicate IR110	Modified Sodium Borosilicate IR111	Lead based borosilicate WTR-62	Barium based borosilicate SB-44
Glass formers (SiO ₂ + B ₂ O ₃)	46	46	50	50.5
Glass network intermediate (TiO ₂)	7	7	—	—
Glass modifiers (Na ₂ O+ MnO+ PbO + BaO)	26	16	30	28.5
Waste Oxide	21	31	20	21

vitrication facilities at Tarapur and Trombay. Compositional details of various glass formulations in use are presented in Table 2. As we know that glass is an amorphous material, checking the homogeneity of VWP in this context include (a) checking the amorphous nature of VWP by X-ray diffraction (XRD) and (b) checking the homogeneous distribution of glass forming and waste constituent by Electron Probe Micro Analyzer-Wavelength Dispersive X-ray Spectroscopy. A typical X-ray diffraction pattern of

VWP made from chemically simulated waste and barium borosilicate glass matrix adopted for vitrification of sulphate bearing HLW is shown in Fig. 1. Optical and BSE (Back Scattered Electron) images of glass samples based on barium borosilicate formulation are presented in Fig. 2.

Evaluation of the chemical durability of nuclear waste incorporated glass, the so called vitrified waste product (VWP) is of paramount importance for ascertaining safe containment of

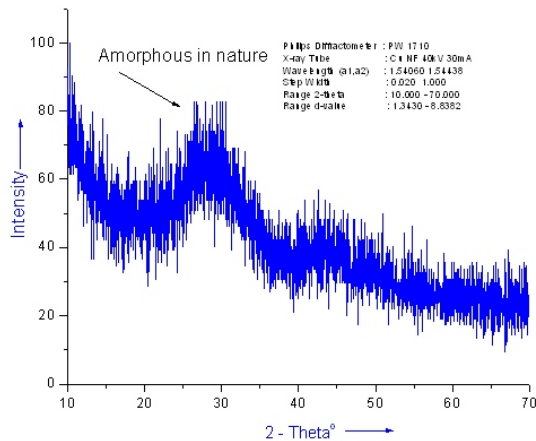


Fig. 1 XRD pattern of barium borosilicate waste glass (SB-44)

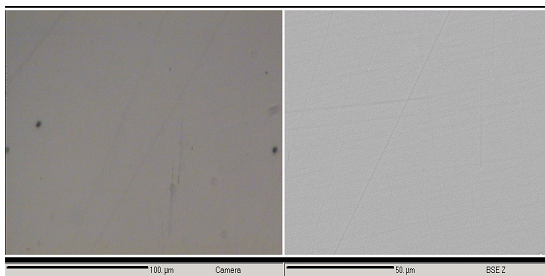


Fig. 2 Optical and BSE images of SB-44 glass showing absence of phase separation

radionuclide immobilized in the matrix. Leaching is one of the most important properties of VWP because it is the principal mechanism through which radionuclide can migrate to human environment. The release of radionuclides from the glass is closely related to the dissolution of matrix constituents. The degree of matrix dissolution is a reasonable measure for the release of radioactive species and hence for the chemical durability of the waste form. Leaching of VWP depends on large number of factors like temperature, compositions of waste, glass and leachant etc. Presence of radiation also affects leach rate by causing radiolysis of the leachant. Leaching or broadly speaking corrosion of a glass involves a number of sequential processes like hydration, ion exchange, network dissolution and precipitation of phases as surface layers. These processes may be evidenced by compositional changes in the aqueous



Fig. 3 Conventional boiling water leaching unit

liquid, elemental zonation of surface layers, formation of altered or hydrated zones etc.

Leaching experiments were generally performed under severe conditions. Accelerated leaching tests were performed by exposing higher surface area of the vitrified waste product sample, at high temperature to enhance the rate of dissolution and using demineralised water as leachant thereby producing large concentration gradient. The objective of putting these stringent conditions is to generate leach rate data within realistic time frame and use them as input in suitable mathematical models to have prediction of release of radionuclides as a function of time. Leaching studies were carried out by semi static leach tests using a conventional boiling water unit as shown in Fig.3. In order to avoid loss of leachant during the test, the experiments were performed under total reflux conditions. The water was replaced at regular interval of time as per standard procedure and analysed for the amount of sodium leached out during each interval using a flame photometer. Normalised leach rate for Na^+ ions is given by the equation

$$(\text{LR})_{\text{Na}} = \frac{A_{\text{Na}}}{A_0} \frac{W_0}{S T}$$

Where, $(\text{LR})_{\text{Na}}$ = Leach rate in $\text{g} \cdot \text{cm}^{-2} \cdot \text{day}^{-1}$ normalised with respect to the behaviour of component Na

A_{Na} = Amount of Na leached during a particular time interval

A_0 = Initial amount of Na in the waste form specimen

TABLE 3. Salient Features of Vitrified Waste Product

Properties	Sodium Borosilicate Glass (IR-111)	Lead Borosilicate Glass (WTR-62)	Barium Borosilicate Glass (SB-44)
Mechanical Properties : Density (gm.cm ⁻³) Impact strength (RIAJ)#	2.99 1.06	3.5 1.12	3.0 0.85
Thermal Properties: Thermal conductivity, 100°C (Wm-1K-1) Co-eff. of thermal expansion (°C ⁻¹) Viscosity, 900°C (Poise) Pouring temperature (°C) Softening temperature (°C)	1.045 102 x 10 ⁻⁷ 40 1000 540	1.15 83 x 10 ⁻⁷ 135 950 490	0.95 101 x 10 ⁻⁷ 70 925 536
Chemical Properties: Average stabilized leach rate @ (gm cm ⁻² .day ⁻¹) Waste Oxides (Wt.%)	9.2 x 10 ⁻⁶ 31	1.8 x 10 ⁻⁵ 20	4.2 x 10 ⁻⁶ 21
Homogeneity: Microscopic examination	Homogeneous very few crystals observed.	Homogeneous by and large, little phase separation is observed.	Homogeneous, no phase separation observed.

RIAJ - Relative increase in area per joule of impacted energy.

@ The leach rate determined at 100°C in conventional boiling water leaching unit on weight loss basis.

W_o = Original weight of the waste form specimen (g)
S = Surface area of the waste form specimen (cm²)
T = Time interval of leaching (days)

Since the normalized leach rates will be different for each component even under similar leaching conditions, the leach rates in the present study are expressed with respect to the behavior of component Na. Leaching of vitrified waste products made using simulated waste and barium borosilicate glass (SB-44) has been studied for a period of 710 days. Leach rate of the product made from chemically simulated waste and barium borosilicate glass formulation is presented in the Fig. 4. Salient features of the vitrified waste product are given in Table 3.

In parallel, research and development of process, equipment and assemblies for use in vitrification facilities was continued. These inputs were used in the design and construction of the first Indian vitrification facility at WIP, Tarapur and interim storage facility at Solid Storage and Surveillance Facility (SSSF), Tarapur. The second

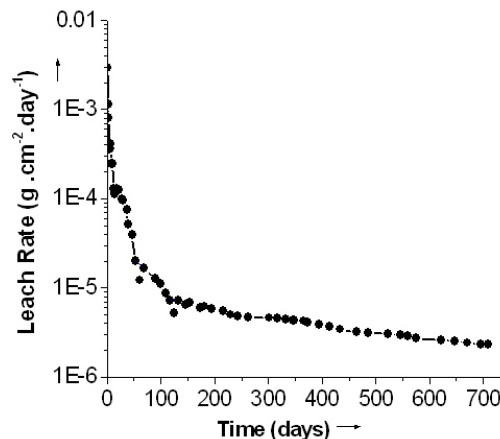


Fig. 4 Leaching pattern of Vitrified Waste Product

vitrification facility is operating at BARC, Trombay to manage HLW generated during reprocessing of spent nuclear fuel from research reactors. Process schematic employed for vitrification of HLW is shown in Fig. 5. This consists of metering of

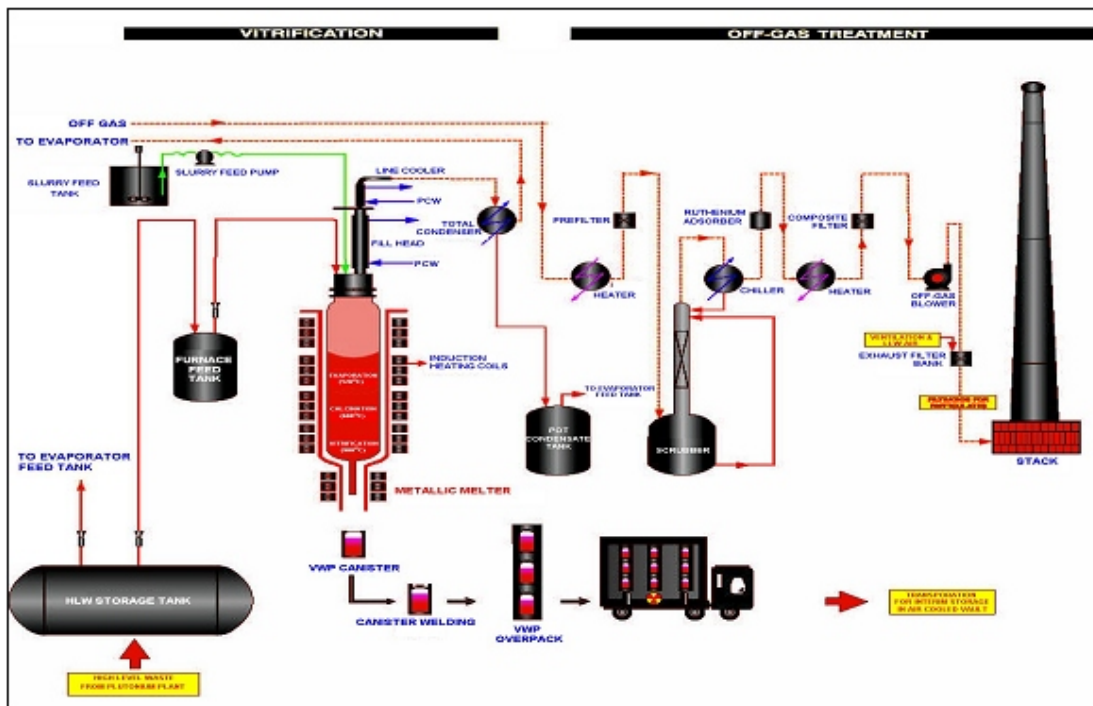


Fig. 5 Process for Vitrification of High Level Radioactive Liquid Waste

pre-concentrated waste and glass forming additives in the form of slurry into the process vessel located in a multi-zone furnace. The process vessel is made of high Ni-Cr alloy so as to withstand high temperature, oxidizing and corrosive conditions. The calcined mass is fused into glass at about 950°C and is soaked at 950-1000°C for eight hours to achieve homogenization. The molten mass is then drained into stainless steel AISI 304L canisters by operating the freeze valve. This is then welded remotely by the Pulse Tungsten Inert Gas method.

Based on the experience at WIP, Tarapur; multi-cell multi-compartment concept has been adopted at Waste Immobilisation Plant, Trombay, so as to facilitate segregation of equipment and ease of maintenance. The process cells are equipped with state-of-the-art remote handling systems. Some of the main remotisation gadgets are servo-manipulators, close circuit television cameras and remote welding machine. An elaborate off-gas cleaning system consisting of condenser, scrubber, chiller, demister and absolute HEPA filter is used to treat the gas before discharge through a 100 m tall

stack to the atmosphere. The plant has a central data acquisition and control system to monitor and control the critical process parameters during vitrification operation. Vitrified waste canisters are further enclosed in secondary stainless steel containers called overpacks. A Waste Immobilisation Plant is being set up at Kalpakkam. It has been designed for the treatment and conditioning of high level liquid waste generated during reprocessing of irradiated fuel from Pressurized Heavy Water Reactors and Fast Breeder Reactors.

In comparison to metallic melters used in WIPs at Tarapur and Trombay, use of ceramic melter has distinct advantage of higher throughput on account of continuous operation and better product durability due to higher achievable processing temperature. In view of this, development and testing of small scale ceramic melter has been successfully completed, and an industrial scale ceramic melter based vitrification facility is operational at Tarapur (Fig. 6). A similar facility is planned to be set up at WIP, Trombay.



Fig. 6 Compact ceramic melter installed at AVS, Tarapur

Treatment /Management of Organic Liquid Waste

Organic liquid waste is generated from reprocessing plants in the form of spent PUREX solvent (30% tri-butyl-phosphate in diluent) which has undergone chemical and radiolytic degradation with repeated use. A plant based on indigenous technology is used to treat the spent solvent by the 'alkaline hydrolysis' process at ETP, Trombay. The treatment leads to the recovery of diluent virtually free of activity. The aqueous bottom arising from alkaline hydrolysis process is immobilized in cement. An incineration facility is also in operation at ETP, Trombay for thermal destruction of non-recyclable diluents.

Management of Solid Waste

Radioactive solid wastes cover a wider range of materials, sizes, shapes and degrees of contamination. These wastes are categorized depending on the radiation field, concentration and type of radioactivity. They are segregated as compressible or non-compressible and combustible or non-combustible. As a typical example, various research reactors and nuclear laboratories at BARC,

Trombay generate approximately 600 m³ of radioactive solid waste annually. The major portion of this waste is received in standard 200 litre carbon steel drums. The waste is categorized with the help of an assaying system, based on radioactivity content and radionuclides present. A real time digital imaging system is used to segregate compactable and non-compactable low-level waste.

Incineration/pyrolysis

Major portion of the total solid waste has low activity and is either combustible or compressible. Specially designed incinerators are employed for burning the combustible wastes achieving a volume reduction of about 50. A unit for volume reduction of low active solid waste using plasma paralysis process is being set up at RSMS, Trombay

Compaction

Hydraulically operated baling press is used to compress low active non-combustible waste to obtain volume reduction of 5 at Kalpakkam. At Trombay, the compactable waste packed in drums is pelletised using 200 ton hydraulic press. The pelletisation system comprises facilities for conveying, indexing and compacting. All operations are controlled by programmable logic controller based control system. Apart from drum pelletisation, the system is also equipped for the compaction of used HEPA filters.

Storage and Disposal of Radioactive Waste

Various concepts are used for storage and disposal of radioactive waste e.g. near surface disposal for low and intermediate level short lived waste and interim storage of high level vitrified waste.

(i) Near Surface Disposal Facilities

As a national policy, each nuclear facility in India has its own Near Surface Disposal Facility (NSDF) co-located. There are seven NSDFs currently operational within the country. These NSDFs have to address widely varied geological and climatological conditions. The various disposal modules currently adopted in NSDFs are (i) Stone Lined Earth Trenches (SLT), (ii) Reinforced Concrete Trenches (RCT) and (iii) Tile Holes (TH).

TABLE 4: Solid waste categories and disposal options

Category	Surface dose/activ-ity	Disposal options	Nature of waste
I	< 2 mGy/h	Stone Lined Earth Trenches	Paper trash, concrete chips, cotton mops, rubber items etc.
II	2-20 mGy/h	RC Trenches	Contaminated equipment, hardware and filters.
III	20-500 mGy/h	RC Trenches	Conditioned/processed concentrates, sludges, spent resins.
	>500 mGy/h	Tile Holes	Hardware from reactors, highly contaminated equipment, conditioned spent resins etc.
IV	Waste bearing alpha activity (< 4000 Bq/g) (> 4000 Bq/g)	RC Trench and Tile Holes	Solidified alpha waste with
		Tile Holes	

The different types and categories of wastes disposed of in these modules are listed in Table 4.

(ii) *Interim storage of vitrified waste*

High level vitrified wastes are characterized by decay heat and need to be cooled to a level where transportation and disposal in geological repository become viable and economical. This period of cooling is also used to generate data on the product behaviour under constant surveillance and monitoring. These data are essential for prediction of long term behavior of the vitrified products. These requirements necessitate interim storage of over packs spanning over 30 years and more. A storage and surveillance facility co-located with the vitrification facilities is operational at Tarapur. This facility has a capacity for storing nearly 1700 overpacks with an inventory of nearly 80,000,000 TBq of radioactivity. The facility consists of an underground outer vault and houses two inner thermal vaults. Removal of decay heat (design value of 3.8 kW/overpack) from the overpack is achieved by natural convective ventilation induced by a 100 m high stack. Air cooling system has been designed on the basis of storage unit geometry, array design, filling pattern and stack dimension. This is an



Fig. 7 View of air cooled Solid Storage & Surveillance Facility, Tarapur

inherently self-regulating system and takes care of the changes in decay heat. The cooling system ensures that the temperature within the vitrified waste product, under no circumstances, exceeds softening point of the vitrified mass. A view of the air-cooled Solid, Storage and Surveillance Facility, Tarapur is shown in Fig. 7.

(iii) Geological disposal

Disposal of high level waste in deep geological repository envisages emplacement of vitrified wastes at depths of about 500-600 m in appropriate host rocks, e.g., granite, granite gneisses, charnockite, basalt and other geological set ups.

The Indian programme on geological repository commenced in the early eighties with underground experiments in an abandoned section of a gold mine at a depth of 1000 m. The investigations were mainly directed towards development of methodology for in-situ assessment of thermo mechanical behaviour of the host rock (amphibolite) and to develop and validate the mathematical models. It also addressed the development of associated instrumentation for the measurements and monitoring. Selection of a few suitable sites for development of site-specific Underground Research Laboratory (URL) possibly leading to setting up of a pilot repository is being pursued.

Management of Spent Radiation Sources

Radiation sources of various types and strengths, containing ^{60}Co , ^{90}Sr , ^{99}Tc , ^{99}Mo , ^{125}I , ^{131}I , ^{137}Cs , ^{192}Ir and ^{226}Ra , are used in hospitals, industries and research institutes all over the country. The strength of spent sources varies from millicuries to thousands of curies depending upon the area of application. After their utility period is over, the spent sources are immobilized in cement grout to make them suitable for disposal in engineered near surface disposal facilities. Waste management facilities located at Trombay and Kalpakkam are the nodal centres for storage/disposal of spent radiation sources.

Future Scenario in Radioactive Waste Management

As indicated earlier, radioactive waste in larger volumes and of different characteristics are likely to be generated in future. Hence, radioactive waste management needs sustained development with new R&D inputs. It is also necessary to induct new technologies to enhance performance of existing designs and minimize waste. This is essential to ensure very low impact on the environment and for enhancement of safety. Some of the areas in

radioactive waste management for continued and future R&D are as follows :

Minimization of Radioactive Waste

Various process and techniques need to be developed for further reduction of volume of waste meant for disposal. Development of specific sorbents and magnetic assisted separations will be useful for future waste management plants. The volume of hulls from PHWR reprocessing are estimated to be more than the conditioned HLW volume. Besides, there is merit in recycling of zirconium. Therefore, recovery of zirconium from the hulls, though a challenge, would be highly desirable. Other challenging area is management of waste from pyro-chemical reprocessing in the future. Materials compatible with high corrosive and high temperature environments encountered during vitrification and resultant secondary waste generation determine the life of vitrification melter. There is a need to further improve the composition and manufacturing procedure of these high Ni-Cr alloy components to increase their corrosion resistance and creep properties.

Extensive R&D efforts are desirable to evaluate the possibility of bio-sorption and phyto-sorption of actinides and long-lived fission products onto microorganisms and sorbents of plant origin. Ultra-filtration and reverse osmosis technologies for low level waste (LLW) and intermediate level waste (ILW) treatment need to be developed on pilot and plant scale. Presently, a pilot-plant of 10 m³/day capacity is in operation for biodegradation of nitrates present in LLW which reduces 1500 ppm of nitrates to less than 10 ppm. Development of fluidized bed de-nitration and its adoption in waste management programme is essential to keep the discharges of nitrates present in ILW through aqueous route within prescribed limits.

Enhancement of Decontamination Factor

Considering low levels of effluents being discharged at present of the range of 10³ to 10⁻⁴ micro Curie per milliliter (µCi/ml) from nuclear power operations, there is requirement of increasing the decontamination factors of the treatment system. Adoption of technologies like bio-separations and mano/ultra-filtration need to be developed to address

these challenges. This requires indigenous development of membranes, development of overall process engineering and retrofitting of these processes and technologies in the existing and new plants.

Higher Waste loading in Vitrification

In view of expected larger output of spent nuclear fuel and enhancement in reprocessing capacities, annual generation of high level waste will increase by a factor of 5 or more in next 10-15 years. As our nuclear power programme expands, these volumes will keep increasing. To handle these increased waste volumes, adoption of robust vitrification melters with higher throughputs are necessary with improved off-gas treatment enhancing the decontamination of volatiles like ruthenium and cesium.

Induction heated pot melter presently being used for the vitrification has limited throughput and short melter life. The major operating constraint for the ceramic melter is that its electrodes are not to be exposed to temperatures higher than 1100-1150°C in order to ensure its design life of 3-5 years. Globally emerging vitrification technology based on the cold crucible induction melting (CCIM) offers several advantages such as long life, high temperature availability, high waste loading, high specific capacity, compatibility to new matrices etc. Cold crucible melting technology has recently been demonstrated at Trombay [8]. This is a water-cooled induction heated melter in which vitrification is accomplished by direct high frequency induction. The cooling of the crucible produces a solidified glass layer, which acts as a protection against corrosion along the melter inner wall. The cold wall (a protective, corrosion-resistant layer) is formed during the start-up of the melter and is stable at 1 to 5 mm depending on the melt temperature and on the physical characteristics of the glass. Since the heat is transferred directly to the melt, high-operating temperatures can be reached with no impact on the melter itself. The advantages of CCIM are at the cost of higher power consumption than for a conventional melter since a carefully insulated melter has been replaced by a water-cooled crucible. Detailed works pertaining to remote maintenance, waste/matrix feeding, off-gas treatment etc. are planned to be pursued.

Separation of Long Lived Isotopes

To reduce the long term environment impact of disposal of HLW, partitioning of the minor actinides and long lived fission products from HLW is the long term strategy. This calls for development of multi-step processing involving the use of suitable solvents.

This strategy aims at (a) removal of uranium and plutonium for recycling, (b) recovery of fission products like ^{137}Cs and ^{90}Sr for use in radiation processing and as heat source, (c) separation of short half life fission products and their storage under institutional control, and (d) separation of long half life fission products and minor actinides for disposal in deep geological repositories after conditioning.

Development of process for Organic Waste

In order to treat organic radioactive waste streams, there are several promising R&D areas like advanced oxidation processes including wet air oxidation, photochemical oxidation, supercritical water oxidation etc. Organic wastes are problematic in the sense that they are not, generally, amenable to treatment by conventional radwaste management practices. Moreover, flammability, and chemical instability of the organic matter in the wastes poses additional problems. One promising approach is the destruction of the organic portion in the radioactive waste to make it amenable to treatment by conventional methods. This approach has been evolved for spent resin treatment and for some other organic-bearing streams.

Spent ion-exchange resins are presently, managed by direct immobilization in poly ester-styrene matrix. In order to achieve volume reduction and chemically more stable waste product, an alternative process based on advanced oxidation involving photo-Fenton method has been developed and demonstrated up to pilot scale on simulated resins [9]. In this process, resin is initially liquefied (water-solubilised) by chemical reaction with small amount of H_2O_2 . The liquefied resin is subjected to photo-Fenton oxidation (H_2O_2 oxidation in the presence of iron salt catalyst and uv/visible light) to convert the organic resin into CO_2 , water, etc. under ambient conditions. Organic decontamination formulation-bearing aqueous radioactive wastes and

aqueous surfactants represent another example where the photo-Fenton oxidation reaction has been found effective. The organics in these wastes were found to be completely destroyed in pilot scale studies in a variety of photo-reactor geometries. The organic-free aqueous waste can then be readily treated by conventional methods.

Off-gas Treatment

In the field of radioactive off-gas treatment, there is a need to further improve the decontamination factor in vitrification facility with respect to volatile components namely ^{106}Ru and ^{137}Cs . Use of washable pre-filters and adsorbers are being studied to meet this objective which will also help in reduction of secondary solid waste generation. In future, efforts are also required for development of technologies for retention of long lived gaseous radionuclides like ^3H , ^{14}C , ^{85}Kr , ^{129}I , etc. Improvements in design of filter banks to meet the seismic qualification is another important area of further work.

Advancement in Robotics and Controls

Presently, master slave and servo manipulators are in use in the vitrification facilities. Adoption of advanced robotics in operation and maintenance of waste management facility is desirable to meet the objectives of higher plant throughput, reduction in radiation exposure and deployment of less human resources. Similarly, use of the state-of-art instruments and control systems will result in safer operations, less dependence on operators skill and higher productivity.

Improvement in Fabrication and Quality Assurance

Considering prevailing corrosive environment and challenges in maintenance of components, it is essential to further improve the fabrication procedure and technique used in equipment and piping of waste management plants to minimize their failures. In few equipment like evaporators, fractionators and melter components; use of better material of construction needs to be investigated and pursued. Since, plant equipment are not accessible after commencement of radioactive operations, special in-service inspection techniques need to be

developed to assess the condition and residual life of components.

Development/Demonstration Of Geological Disposal

Although the present generation of HLW is of modest volumes, on a long term basis, demonstration of feasibility and safety of deep geological disposal is essential. The national level multidisciplinary programme needs to be continued further for setting up an underground research laboratory to develop and demonstrate methodologies and technologies for a deep geological repository.

Human Resource Development

Presently, O&M personnel are being trained for a period of 1 to 2 years in various operation and safety aspects before their induction. Enlargement of waste management operations will require higher manpower deployment. Besides, due to induction of newer technologies, systematic re-training of existing staff will also be essential. Use of simulators for training along with other advanced methodologies will go in a long way in enhancement of safety in waste management operations

Summary

Waste management facilities at various nuclear installation sites are operating safely and successfully for more than four decades. Indian experience in management of nuclear waste from power plants, fuel reprocessing and allied installations is rich and comparable with international practices. By suitable treatment and conditioning of waste it has been demonstrated that prime objective of safety of environment is fully achieved. Elaborate surveillance ensures safe performances of the systems.

Among the many possible forms, borosilicate glass has been adopted for immobilization of HLW. India has developed sufficient expertise in this advanced technology with respect to matrix development, process design, construction, commissioning, operation and remotised maintenance. As far as the technology for waste conditioning is concerned, metallic melter technology has been established and demonstrated.

The continuous ceramic melter based process technology has been recently adopted at Advances Vitrification System, Tarapur. In parallel, cold crucible technology is being perfected to achieve still higher processing temperature to solve problem of materials suitable under such challenging process environment.

A valuable base of human resources has been built up which consists of scientific and technical personnel well versed in design, construction, operation and maintenance aspects of the vitrification facilities and related R&D systems. Expertise has been provided to national and international institutions.

Extensive experience is available in the handling, storage and disposal of low and intermediate level solid waste in near surface disposal facilities (NSDFs). Besides, expertise exists in site selection, characterization and safety analysis for NSDFs. Technology has been developed for the design, construction and operation of interim storage facility for vitrified waste products under surveillance. A large-scale site selection programme has been initiated to identify a few suitable geological domains for locating a repository for high and long lived radioactive wastes. Presently granites have been studied extensively as a natural barrier. Long term evaluation of vitrified high level waste under geological conditions is being pursued to help demonstrate safe containment of waste in deep geological repositories, with no impact on the environment.

The radioactive waste management needs sustained developments with new R & D inputs to cater to new challenges arising out of decommissioning of older facilities and enlargement of nuclear power programme. Waste management facilities, in future, will be part of an integrated nuclear fuel cycle complex along with other facilities like fuel fabrication and spent fuel processing to take advantage of common utilities and services as well as minimization of liquid waste storage and inter-facility transfer requirements.

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High Level Liquid Radioactive Waste, their Characterization & Quality Assurance



Shri R.G. Yeotikar (M. Sc. in Chemistry and M. Tech. in Chemical Technology from Nagpur University) has joined Waste Management Division, BARC Trombay, in 1977, after graduation from 20th Batch of BARC, Training School. Presently he is Officer-in-Charge, Training, NRG and working in HCD&ES. He is responsible for manpower of complete NRG, training of new recruits of Cat-I and II of NRG and NFG, training of supervisors and technicians of NRG & implementation of Qualification Incentive Scheme to the staff of reprocessing and waste management plants. He has contributed for the developments of treatment methods such as chemical treatment of low-level waste, treatment of intermediate level waste by RF resin, conditioning of ILW in cement matrix and vitrification of high level radioactive liquid wastes. He has also established various laboratories at WMF Tarapur. He was involved in commissioning of India's first storage vault facility for interim storage of high level waste packages. He has made HAZOP analysis study for Advance Vitrification System, Tarapur, which is done for the first time for waste management plant. He was a member of many Coordinated Research Programmes of International Atomic Energy Agency (IAEA) and participated in India and abroad. He has also contributed significantly for updating and finalisation of IAEA's Source Book on Nuclear Waste Management". He is having about 60 publications to his credit.

Introduction

The demand of energy for the human being is getting increased day by day. However the sources of conventional energy like coal, gas and oil are limited and their life is also limited. Secondly, the non-conventional energy sources, like solar, wind, tidal energy etc. have their own limitations. Hence these non-conventional sources are supplementary to the primary sources. The only energy source available to the mankind to fulfill this continuous and ever increasing demand is the nuclear energy. The public acceptance and popularity of nuclear energy depends to a large extent on management of nuclear radioactive waste. The nuclear waste management demands ecofriendly process / system, so that the well being of the present and future generations are very well taken care. Nuclear waste is generated at every step of the nuclear fuel cycle. The complete nuclear fuel cycle consist of following:

Mining and Milling

Processing of U concentrate

Fuel Fabrication

Reactor Operation

Fuel Reprocessing

Waste Management

Types and Categories of waste

Various types of waste are generated in the entire fuel cycle. They can be segregated / classified as follows depending on their physical state.

Gaseous waste

Liquid waste

Solid waste

Special waste

Amongst these wastes, liquid wastes need more attention due their volumes and mobility.

Liquid Wastes

Large quantum of liquid waste is generated in the entire nuclear fuel cycle and is basically aqueous

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TABLE 1.

Category	Solid	Liquid	Gaseous
	Surface Dose (mGy/hr)	Activity Level (Bq/m ³)*	Activity Level (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	

* 3.7 x 10¹⁰ Bq = 1 Ci.

in nature. This type of waste also has various concentrations of activity and requires special attentions due to its liquid nature. Depending on the activity content, this waste is further classified into three categories.

- (i) Low Level Waste (< 1 mCi/l)
- (ii) Intermediate Level Waste (1 mCi/l-1Ci/l)
- (iii) High Level Waste (>1 Ci/l)

The general classification of radioactive waste as per AERB guidelines given in Table 1 [1].

Objectives of Waste Management

In general, the objective of waste management is to manage the radioactive waste materials in a manner, which prevents any unacceptable detriment to man and environment either now or in future. This includes following.

Radiological Protection and Safety Objectives

To keep the effluent discharges within the effective limitations approved by the regulatory body so that the dose equivalent to individuals shall not exceed the applicable dose limits.

The waste management systems design and construction shall comply with authorization for plant discharges to the environment as set by the regulatory authority.

Radiation exposure to the public and plant personnel shall be kept as low as reasonably achievable (ALARA principle) taking social and economically factors into account.

The overall management strategy shall include demonstrative 'ON-SITE' & 'OFF - SITE' Monitoring Programme.

Operational Management Objectives

To treat and manage the waste.

To apply ALARA principle to all waste management operational decision.

To assess the long term implications of waste disposal, during operation and decommissioning and post operation stages.

To exercise effective control on generation and accumulation of waste.

To minimize frequency of abnormal occurrences and maintain spare capacity for abnormal exigent condition.

Design Objectives

To ensure compliance with the limiting safety and operational objectives.

To ensure compliance with limiting operating condition.

To provide the measures for high reliability.

To eliminate adverse effects on plant capacity.

To minimize secondary waste generation.

To provide the possibility of reuse of treated materials, if possible, in the plant.

To provide sufficient system flexibility.

To limit the effect of significant risk identified in the safety analysis (man made or natural).

It is also emphasized that all the activities capable of generating radioactive waste should

reduce the waste generation as far as reasonably possible by implementing administrative control, identification, classification, segregation and incorporating possible changes in the plant operating procedures, etc.

Management of Radioactive Waste

Following steps are involved in the management of radioactive waste:

- Collection
- Segregation
- Treatment/ conditioning
- Interim storage
- Disposal

Depending on the nature of the waste there could be multiple steps in a single step or two / three steps could be in a combined form.

Management of Liquid waste

The basic principles followed in liquid waste management are:

- Dilute and disperse
- Delay and decay
- Concentrate and Content

The “delay and decay” philosophy is adopted only on the waste having short-lived isotopes. The “dilute and disperse” method is adopted for very low-level waste. Mostly concentrate and content is the method followed in case of liquid waste treatment.

Sources of High level liquid radioactive waste (HLW)

Spent Fuel Reprocessing

Spent fuel contains almost entire quantity of radioactivity encountered in the nuclear fuel cycle. In a reprocessing plant, the spent fuel is chopped into pieces and the heavy metal (spent fuel) oxide is leached into nitric acid. From this solution U and Pu are removed by solvent extraction process. During this reprocessing of spent fuel, major stream in the form of aqueous high level liquid waste (HLW) is generated from the first cycle of the extraction scheme. The volume of HLW is small but its specific activity is very high.

Management of HLW

Almost all activity of spent nuclear fuel cycle is there in HLW. Presently this waste is stored in high integrity stainless steel tanks. Though experience in SS tank storage worldwide is very good, this is an interim storage only and requires stand by tankage for handling accidental situation. The activity of HLW is of the order of few hundreds of curies per liter and is acidic (3-4 M nitric acid) in nature. The composition of high level liquid waste (HLW), generated during reprocessing of spent nuclear fuel, depends on various factors such as, type of fuel, cladding material, burn up and reprocessing schematics. The major components of HLW are :

- (a) Fission products, e.g. Cs, Ba, Sr, Zr, Y, Mo, Ru, Rh, Pd, La, Ce, Pr, Nd, Pm, Sm, Eu, etc.
- (b) Corrosion products, e.g. Fe, Cr, Ni, Mn, etc.
- (c) Actinides, e.g. U, Pu, Np, Am, Cm, etc.
- (d) Chemical introduced during reprocessing, e.g. NaNO_2 , impurities of nitric acid, tributyl phosphate and its degraded products, etc.
- (e) Alloying elements, e.g. Fe, Al, Si, Mo, etc in the fuel particularly when U metal is used as fuel.
- (f) Soluble poisons such as Ga, Cd and boron, if used in reprocessing of enriched fuel.

Management of HLW in India

To ensure that long lived radioactive nuclides of HLW do not pose hazard, this waste need to be kept isolated in the bio-sphere for extended period of time. The management of such high level radioactive waste processing is carried out as per the following steps.

- (i) Conditioning of high level liquid waste resulting in the immobilization of the waste oxides in stable and inert solid matrix.
- (ii) Interim retrievable storage of the conditioned waste under cooling and constant surveillance to ensure substantial dissipation of decay heat and also the integrity of the waste product.
- (iii) Ultimate disposal of the waste in suitable geological repository ensuring isolation of the waste product in the biosphere for extended periods of time.

Immobilization of HLW

To kill the mobility of HLW it is necessary to convert in to a stable inert solid matrix. Hence first step in management of HLW is to immobilize into an inert and stable solid matrix.

The ultimate stable and inert solid form of this waste should have following characteristics.

- Inensitive to loss of services,
- Potentially better from safety and environment point of view,
- Possible to transport,
- Its interim and ultimate disposal should be technologically feasible,
- Readily available raw material and simple to manufacture,
- It should have good thermal, chemical, mechanical and radiation stability for extended length of time,

Desirable Characteristics of a Solidified Waste form of HLW

The solidified waste form should have certain properties so that its interim and ultimate disposal is technologically feasible, safe, economical and environmentally compatible. The solidified waste form i.e. the conditioning matrix should have following properties:

- (a) Good chemical durability, i.e. low leachability so that the activity released into the environment is negligible.
- (b) Good thermal conductivity so that the heat generated due to decay of active isotope is well dissipated.
- (c) Resistance to all types of radiations such as alpha, beta, gamma and neutrons.
- (d) Compatibility with the container / canister.
- (e) Minimum volatility of the constituents during manufacture and storage.
- (f) The matrix should have high concentration of waste so that volume reduction factor is high.
- (g) Good mechanical strength and shock resistance so that transportation to storage or disposal is safe.

- (h) Good thermal and radiation stability over extended period of time.
- (i) The manufacturing process should be simple and easily adoptable for remote operation. The temperatures of operation should be acceptable. The raw material should be cheap and readily available.

The plutonium plant (PP) at Trombay, power reactor fuel reprocessing plant (PREFRE) at Tarapur and KARP at Kalpakkam, are reprocessing the spent fuel. The high level radioactive aqueous waste generated during reprocessing is temporarily stored in high integrity stainless tanks located in stainless steel lined under ground concrete vaults nearby these facilities.

Matrices or Waste Forms for Immobilization of HLW

The candidate matrixes for immobilization of the waste are :

Calcine : Calcines are produced by dehydration and denitration of waste with no appreciable addition of chemicals. They are produced either as interim product or as intermediate product during its final solidification. They are amorphous and are not considered suitable for long term disposal.

Glasses : This is the most extensively studied and used product form. Two types of glasses are being adopted in various countries depending on their waste characteristics and process facilities. They are phosphate and borosilicate glass systems [2].

Phosphate glass matrix was found attractive for the waste containing molybdenum and sulphate. The formation temperatures are relatively low and the main raw material is phosphoric acid which is liquid, thereby feeding is simple. However the process is very corrosive due to phosphoric acid. Also the products are inferior from long-term durability point of view etc and there is tendency for devitrification. In Russia phosphate glass was studied for vitrification of high sodium aluminium waste[3].

Borosilicate glass matrix is now universally accepted as the matrix for immobilization of waste on account of good product durability[4]. The formation temperature is moderate in the range 950-1100°C. The glass forming additives are to be

fed either in the form of aqueous slurry of mixed nitrate/oxide or glass frit. The borosilicate glass composition can be tailored depending on the HLW composition and the process requirement. The borosilicate glasses also have good set of properties.

Ceramic Waste forms : Other matrices includes various ceramic waste forms. They are super calcines, Synthetic rocks (synroc), sodium zirconium phosphate (NZP), etc. Out of these matrices, synroc matrix is getting prepared on lab scale and evaluated world wide for immobilization of HLW.

Development of Glass Matrix

Basic Need for Glass Matrix Development

The normal commercial glasses are basically soda lime glasses, e.g. window glasses or borosilicate glasses, e.g. glass utensils, etc. These glass compositions are having high formation and pouring temperatures. For immobilization of HLW, these compositions, as such, cannot be used. They need to be modified for the following reasons.

- (i) The formation temperature should be moderate so that it is possible to operate either the metallic or ceramic melter remotely.
- (ii) By limiting the formation temperature to a moderate level, the volatility of the most of the fission products get reduced drastically.
- (iii) The glass composition should have maximum accommodation of waste oxide so that the volume reduction factor is maximum.
- (iv) The operating parameters like electrical resistivity / conductivity is in desirable range for operation of joule melter.
- (v) The glass composition should have a set of desirable properties. The important property being is the chemical durability.

The desirable properties and factors to be assessed in the choice of suitable solidified waste products, thus, includes:

Chemical durability,
Thermal conductivity,
Resistance to alpha, beta, gamma and neutron radiations,

Compatibility with the container / canister,
Minimum volatility of constituents during processing and storage,
High density,
Ability to contain high proportion of waste so that the product is having high volume reduction factor,
Stability for extended period of time,
Suitable for transport to storage / disposal site –
Good mechanical strength and shock resistant .

Structure of Glass

The glass is a three dimensional continuous but random network of oxygen polyhedron of glass forming oxides like SiO_2 , B_2O_3 , etc. The silicon tetrahedrons are connected with each other through the oxygen atom forming the Si-O-Si bridge. This 'O' is called the bridging 'O'. The monovalent components of HLW like ions of Na, Cs, Rb, etc., are accommodated in the glass network in the interstices creating a non-bridging oxygen atom. Other multivalent components like divalent, trivalent and tetravalent ions of the waste participate in the glass network formation depending on their valency and ionic size. These multivalent elements do keep oxygen bridging atom intact but the nature of the bond between this atom and 'O' is different than that of the bond of 'O' with Si.

Glass Development for WIP & AVS Tarapur

For WIP Tarapur, sodium borosilicate glass matrix has been developed for immobilization of HLW. The five component glass matrix constituents silica, titanium di-oxide, boric oxide, sodium oxide and manganese oxide apart from the waste. Out of these silica and boric oxide are the glass forming chemicals whereas the others including the waste oxide are glass modifiers. Large numbers of glass compositions were made in this system. These compositions were evaluated for formation & pouring temperatures and chemical durability [5]. From these compositions, IR110 glass composition, which is five component glass system as indicated above, was accepted for immobilization of reference TPI waste. Thereafter for adoption for immobilization of HLW stored at PREFRE, Tarapur, this composition was modified to IR 111 so as to get more volume reduction factor, moderate formation & pouring temperatures and better

chemical durability [6]. In this composition the sodium oxide component of the waste and glass forming chemical slurry was adjusted and the volume reduction factor of the order of 60 was achieved. This composition was then adopted on plant scale for operation of WIP, Tarapur.

The glass forming additives in the form of oxide/nitrate are fed in the form of slurry into the inconel metal process pot which is heated by multiphase induction furnace, The waste is added to the process pot and this process is continued till the desired level of glass is formed. Later on , the addition of the slurry and waste is stopped and the glass product is allowed to soak for about 5-6 hrs. After soaking, the glass is poured into the SS canister and remotely welded after the cooling of the glass . Two such canisters are packed in SS over pack and remotely welded. This over pack is the ultimate storage unit.

Phase separation during vitrification: It is observed that Cr and Mo in higher quantities do not take part completely in vitrification. They separate out as yellow phase from the liquid glass. Normally the separated phase constitutes chromates and molybdates of sodium and other alkali metals and is soluble. Since the color of this phase is yellow, it is also called as 'yellow phase separation'. Normally the yellow phase separation is controlled by addition of reducing agent during vitrification. The present VWP composition was also characterized for yellow phase separation. Since the Cr and Mo are very small quantities in the present HLW, yellow phase separation during it vitrification was negligible [7].

At AVS, Tarapur, the joule heated ceramic melter has been installed and commissioned. This melter has molten glass pool of about 300 kg. The melter has pair of inconel electrodes on the opposite sides. Electric current is passed through the pair of inconel electrodes through the glass. The resistance of the molten glass, between the electrodes, itself is used for joule heating. For this melter, iron borosilicate glass matrix has been used. The glass forming chemicals are added in the form of preformed glass beads, called as frit. The frit has diameter of about 2-3 mm and are made from base glass after crushing and agglomerating in the form of beads. The frit and HLW are fed to the joule melter and when a 100 kg mass has been added above the

glass pool mass, the glass product is drained from the bottom.

Composition of high level reference waste and that of the glass developed IR-110 for the same are given below.

Composition of Reference TPI HLW waste

Components oxides of	Concentration of Reference TPI waste, (gm/l)
Corrosion product	7.80
Added Chemical, (Mainly Na ₂ O)	6.20
Actinides, (basically UO ₂)	4.60
Fission Products	30.80
Total	49.40

Composition of IR-110 VWP

Sr. No.	Components	Weight %	Mole%
1	Waste Oxide	29.3	16.0
2	SiO ₂	34.4	43.5
3	B ₂ O ₃	06.4	7.0
4	Na ₂ O	14.3	17.5
5	TiO ₂	06.3	6.0
6	MnO	09.3	10.0

Glass Development for WIP Trombay

For WIP, Trombay, barium borosilicate glass composition was developed, since the HLW stored at PP contains appreciable concentration of sulphate. After development, the matrix was characterized for various properties and adopted on plant scale at WIP, Trombay successfully for regular operation [8&9]. Composition of HLW stored at Trombay and developed composition of barium borosilicate glass are given below.

Composition of HLW waste stored at Trombay	
Component	Value
Molarity, free acid, HNO ₃ ,	1.34 M
Density,	1.22 g/ml
TS (U, Na, Fe, Al, Ca, Cr, Ni, Mn, etc. in the form of nitrate),	317 g/l
Specific Activity	
Gross beta-gamma,	8.77 Ci/l
Gross alpha,	4.22 mCi/l
Sulphate	9.95 g/l

Composition of Selected Barium Borosilicate Glass	
Oxide Component	Weight %
Glass Formers (SiO ₂ + B ₂ O ₃)	50.5
Glass Modifiers (Na ₂ O + BaO)	28.5
Waste Oxide	21

This barium borosilicate glass composition has been successfully adopted for regular vitrification operation of HLW at WIP, Trombay. The phase separation due to sulphate has been totally avoided due to use of Barium in the glass matrix.

Development of Ceramic and Other Crystalline Waste Forms

The ceramic and other crystalline waste form includes supercalcine, synroc, sodium zirconium phosphate / tungstate, etc. Out of these waste forms, more developmental efforts are put in the synroc matrix. In nature, the rocks are very stable for millions of years and their leaching and formation of alteration layers are also very small. Based on this concept it was thought that if a synthetic rock is made for immobilization of HLW, the same will have properties comparable with the rock. This synthetic rock is called as Synroc and will have mineral phases similar to the rock. In general the synroc composition is comprised of phases like perovskite (CaTiO₃), zirconilite (CaZrTi₂O₇), hollandite

(BaAl₂Ti₆O₁₆), Ba-felspar (BaAl₂Si₂O₈), kalsilite (KAlSiO₄), leucite (KAlSi₂O₆), etc., depending on the precursors used. Normally the precursor such as TiO₂, CaO, ZrO₂, BaO, Al₂O₃, SiO₂, etc are used. In general, the hollandite phase accommodates the elements like Mo⁴⁺, Ru⁴⁺, Rh³⁺, Fe³⁺ & Fe²⁺, Cr³⁺, Ni²⁺, K⁺, Cs⁺, Rb⁺, Na⁺, etc, the zirconolite phase accommodates the elements like U⁴⁺, Th⁴⁺, Pu⁴⁺, Cm⁴⁺, Am³⁺, Y³⁺, REE³⁺, Na⁺, etc. and the perovskite phase accommodates elements like U⁴⁺, Th⁴⁺, Pu⁴⁺, Cm⁴⁺, Am³⁺, Y³⁺, REE³⁺, Sr²⁺, etc.[10]. For preparation of syroc, precursors and calcine of HLW are taken in a thick metal crucible and hot pressed either uniaxially or isostatically at a temperature of 1200 – 1300°C. Under these conditions, rapid and complete subsolidus equilibrium and recrystallisation of HLW calcine components occurs and a well crystallized synroc is formed. The process is being modified for operation at pilot and plant scale by adopting the collapsible metal bellows for holding the mixture before hot pressing. The other crystalline forms such as sodium zirconium phosphate and sodium zirconium tungstate are also being developed as an alternative waste forms.

Development of Other Waste Forms

Coated Particles

Coated particles are produced as a multi barrier development concept. This gives enhance inertness and improvement in thermal stability, mechanical strength and leachability[11]. The HLW is converted into spherical agglomerates of supercalcine powder in the form of 1-5 mm size range. Thereafter they are coated with an impervious layer of alumina and / or pyrolytic carbon to given added leach resistance.

Metal Matrix Products

This was also developed as a multi barrier system. The high heat load HLW is immobilized in the glass matrix. The glass matrix is converted into the beads of 2-4 mm size. The beads are then distributed in the molten lead. This metal matrix is having very good thermal conductivity due to the metal matrix and heat dissipation is very good.

Glass Ceramics

The glass ceramics are generally prepared from the borosilicate glasses by a special heat treatment. First the glass is manufactured and then annealed at a temperature of maximum nucleation rate. Once the nuclei have formed, a second annealing step is carried out at a temperature high enough to have maximum crystal growth. The product consists of continuous glassy phase with crystals homogeneously dispersed in it. For getting the fine grained product, nucleus forming oxides such as TiO_2 / ZrO_2 are normally added. With the proper composition of base glass and schedule of nucleation, it is possible to generate the desired crystals where the fission products and actinides can be accommodated. However accommodation of a particular element into a desired crystalline phase uniformly throughout the glassy phase is difficult. The glassy phase and crystalline phase should be very good with respect to chemical durability. The glass ceramics are generally more mechanically stable than the base glass.

Characterization of Waste forms

The solidified waste forms must have certain characteristics which make their interim and long term storage and ultimate disposal technically feasible, safe and economically attractive. The principle properties of the waste product / forms should have are (i) thermal, (ii) chemical, (iii) mechanical and (iv) radiation stabilities for a time period of the order of 10^5 years. This can be divided into five periods.

- (a) During solidification of HLW and transfer of solid waste product to interim storage – Effect of temperature will be at the greatest.
- (b) During first 10 years of interim storage –Over 90 % of fission products heat will decay and maximum temperature will drop. Stability at higher temperature will be essential.
- (c) During the period of 10 to 100 years, the radiation dose to the product will get build up and the product will cool to virtually the ambient temperature. Stability to the radiation and in the storage environment will be important.

- (d) During the period from 100 to 1000 years, the remaining fission products will have decayed including Cs and Sr, but the chemical durability is essential. After 1000 years, all the heat and beta-gamma radiation effect will be insignificant.
- (e) During the period from 10^3 years to 10^5 years, the presence of the transuranics elements in the glass will become very important and the product should have stability for alpha decay and chemical durability.

The solidified waste product should be characterized fully before it is adopted in the plant for regular operation. In general three-step procedure has been adopted for quality control of solidified waste products.

- (i) Development of solid waste product with simulated inactive waste and full characterization of the same. During this step, the composition and the process parameters are also finalized.
- (ii) Production of solidified waste product with above composition and finalized process parameters.
- (iii) Evaluation of simulated active /actual active solidified waste product for few important properties.

The details of characterization for the inactive simulated waste products constitutes following.

Formation characteristics for the vitrified waste products (VWP)

There is acceptable upper limit of formation temperature of the product. This is imposed by the choice of construction material of the process pot / melter and that of the canister. Secondly by restricting the upper limit of operating temperature, the volatility of many fission products also gets reduced. Hence generally the maximum operating temperature is in the range of $950 - 1150^\circ\text{C}$.

For the formation properties, the fusion and pouring temperatures of the vitrified waste products are evaluated. In a SS tray, the glass forming chemicals and inactive simulated waste are added. The mixture is heated on a hot plate slowly till the dry powder is obtained. This dry powder is removed and

then taken in a dry fire clay crucible and heated in a furnace slowly. The heating is generally started from 600°C. If required, second lot of powder is added and heating is continued. The crucible is removed periodically and the surface of the mixture is observed for fusion. If fusion is not seen, then the temperature of the furnace is increased by a step of 50°C and the crucible is kept at that temperature for about one and half hour and again examined as above. Once the glass product is fused, then the temperature of the furnace is increased further by 50°C. Thereafter the crucible is removed and pouring of the glass is tried immediately. If not pourable, then the above process is repeated by increasing the temperature by 50°C till the glass gets poured. Thus the temperatures of fusion and pouring are evaluated. These are very important parameter for VWP for formation and draining of waste product from the melter.

Chemical Durability Study of waste products

This is the most important characterization of the waste form. This property directly indicate the possibility of release of activity from the waste from into the environment. The chemical durability study is also termed as leaching study. In general the leaching tests falls into two broad groups.

- (a) Accelerated tests, mainly used for short term sorting of samples and studying the effect of variables,
- (b) Long term tests to simulate the actual environmental condition in storage / disposal.

Within these two methods, many other factors are to be considered. They are:

- (i) Concentration of species in the leachate solution : many times, they are very close to the detection limit of any analytical instrument,
- (ii) Sample preparation – either in the form of grains or a pellet. In case of pellet, thermal history and annealing etc are also to be considered,
- (iii) Choice of leaching media used for leaching study- it can be reference distilled / DM water or any other media such as ground water, backfill saturated water, buffers, etc.,

- (iv) Ratio of volume of leachant to sample mass / surface area of the VWP sample,
- (v) Method adopted for leaching study such as static, Soxhlet or dynamic, etc.,
- (vi) Frequency and periodicity of leachate removal / termination of leaching period,
- (vii) Topographic study of leached glass samples and correlation with the leachate analysis,
- (viii) Reporting of leach rate / incremental leach rate / normalized leach rate or corrosion rate etc with time.

In general measurement of leach rate has many objectives. Some of them are[12]:

- (a) For rapid screening and comparing the durability of many developed compositions and selection of the most durable amongst them,
- (b) For study the effect of compositional parameter during development,
- (c) For evaluation of impact on other physical parameters such as heat treatment, devitrification (in case of glass), irradiation, etc on chemical durability.
- (d) For evaluation of different storage / disposal environment,
- (e) For generation of basic data and prediction of long term behavior of waste product,
- (f) For study of mechanism of leaching
- (g) For study the effect of various parameters like temperature, pressure, leaching media, element being released, etc on leaching,

Thus the factors affecting the leaching includes composition, structure, surface area of the sample, leaching method, leaching media, temperature of leaching, leachant flow rate (in case of dynamic leaching), etc.

During eighties and nineties many workers were engaged in standardization of the method for determination of chemical durability of waste form. In India, three methods, e.g (i) Accelerated conventional leaching method, (ii) Modified Soxhlet leaching methods and (iii) Dynamic leaching methods were developed [13]. The accelerated conventional leaching method was adopted for

evaluation of the waste form / waste matrix for short listing during development of waste form for particular type of waste. The second method was developed for adoption of Soxhlet type of system at various temperatures. In soxhlet system, the VWP sample is always submerged in distilled water. The flow through the Soxhlet can also be controlled in this method. The third method was adopted as dynamic leaching method where temperature, leaching media, leachant flow etc. can be controlled. During eighties, in USA, a Nuclear Waste Material Characterization Centre has been established at Battelle Pacific North-west Laboratories, Richland Washington. This centre has put efforts for standardization of the leaching methods. They are named as MCC-1 to MCC-5 tests. They are (i) MCC-1 static test, (ii) MCC-2 static high temperature test, (iii) MCC-3 solubility test, (iv) MCC-4 low flow rate test and (v) MCC-5 Soxhlet test [14].

Recently ASTM has finalized leaching method for the evaluation of chemical durability [15] and has been labeled as “Standard test method for determining chemical durability of nuclear, hazardous and mixed waste glasses and multiphase glass ceramics : The product consistency test (PCT)”. This method has now been widely accepted and used for evaluation of VWP for chemical durability. The sample either in the form of grains or pellet are kept in a Teflon lined SS bottle. Adequate leachant is added and the bottle is closed. Then this bottle is kept in a constant temperature oven for the predetermined time. The temperature can be 90°C or can be selected for that objective. At the end of that period, the leaching is terminated, the bottle is opened and the leachate is analyzed for various constituents and elements by usual analytical method. The leach sample is evaluated for topographic study.

This method or other suitable method when extended for 5 to 10 years with modifications offers evaluation of VWP under long term behavior. In these methods, the repository components is introduced for simulation of repository environment. This is done either by addition of repository components like corrosion product of steel, backfill, rock powder / grains, etc in the static method[16] or by using a column packed with

repository components and use of water passing (saturated with components) through this column as leachant.

Data presentation can be in the form of plotting of leach rate / normalized leach rate / incremental leach rate and cumulative fraction leached v/s total cumulative time period of leaching.

Thermal Stability of waste products

The glass samples (in form of small pieces) are taken and given heat treatment in a silica / alumina / platinum boat in a tubular furnace maintained at constant temperature. Thereafter the samples are removed and analyzed for crystallization. The sample size can be pieces of glass (0.1-1 g) and range of heat treatment can be 500 –900°C (increase step by 50°C). The time for heat treatment could be of 1 hr to 8 hr (increase step by 1 hr), 16hrs, 1day to 10 days (increase step by 1 day), etc. The identification of the crystallization of the glass can be by usual means such as optical microscope, SEM, XRD, etc. The data presentation is done in the form of : Time – Temperature – Transformation Curve for 5% crystallization[16].

Radiation Stability of glass

To study the alpha damage

This is either done by irradiation of glass sample in a reactor to have B-10(n, alpha)Li-7 reaction or by immobilization of simulated waste containing alpha emitting radionuclide such as Pu-238, Cm-242 or Cm-244 in the glass.

In the first case the study of radiation stability of glass is done by exposing the glass samples in the research reactor having neutron flux as 1×10^{12} – 10^{14} neutrons per sq.cm per second. The glass samples either in the form of glass grains of desired mesh size e.g. ASTM 16 and 25 mesh sieves or thin pellets can be used for irradiation. The small pencils also can be used for irradiation. The exposure period in the reactor can be of 30 –90 days depending on the flux and the requirement of alpha dose. Thereafter the irradiated samples are removed and allowed to cool for a period of 30 – 45 days so that all the short cooled isotopes are decayed out. The boron (B-10 of natural isotopic abundance) of the glass formation system will absorb neutrons and the of B-10(n,

alpha) Li-7 nuclear reaction occurs in the VWP. During this reaction, alpha particles are emitted from the VWP. The method can also be used for other waste forms where similar nuclear reaction can be there.

Testing of effect of alpha dose can be done by evaluating the chemical durability of the irradiated glass grains for leaching study. The leaching can be done at a predetermined temperature with un-irradiated glass as a reference either in a reference leachant or in distilled / DM water. The leaching experiments can be done in a constant temperature oven in a Teflon leaching cell either as per ASTM method or by any standard method. The leachate can be analyzed for various elements and activity by usual analytical techniques.

Other characterization done on the irradiated waste form is the change in mechanical properties such as hardness, density, stored energy, etc. Second aspect of this study is to evaluate the impact of Helium (He) gas generation and accumulation in the solidified waste form. Helium is having certain solubility in the glass and excess of He in the glass will get accumulated or released from the sample.

In the second case, the simulated HLW containing waste containing short lived alpha emitting radionuclides are added during fabrication of solidified waste form. The energetic alpha particles with energies of a few MeV and recoil (few hundreds of KeV) will have effect on the properties of waste form.

To study the beta-gamma damage

For gamma irradiation, the glass samples is irradiated in a gamma irradiator and the irradiated samples is evaluated for leaching study, mechanical strength and other properties. For beta-gamma (self) irradiation, the waste form can be preserved for long time (effect due to self irradiation) and evaluated for chemical durability study and other properties.

Chemical durability study of glass in presence of radiolysis products of water

When the radioactive waste product comes in contact with water of surrounding, there are chances of radiolysis of water due to interaction of gamma radiation with water. This leads to the formation of

HNO₃ and H₂O₂. To study the effect of these components on chemical durability method similar to study of chemical durability of waste form can be adopted in presence of radiolysis products (e.g. HNO₃, H₂O₂ etc.).

Viscosity

Viscosity is very important property which is useful during pouring of VWP (glass melt) in a canister. This also is an important aspect for design of freeze valve of the melter. In general, the spindle made of platinum is kept rotated in a glass melt kept at constant temperature and the torque is measured. ASTM has standardized the methods where either the spindle or the crucible can be rotated and the torque can be measured. The viscometer needs to be standardized with normal viscosity standards[17].

In low temperature region above 400°C and below the viscosity data is required for calculation of the hoop stress in the steel canister, which is having higher expansion coefficient than glass. The viscosity of glass at lower temperature is measured by beam bending technique.

Electrical Conductivity

The knowledge of electrical conductivity of VWP is very much essential for operation of joule melter. Electrical conductivity is very much dependant on temperature[18,19]. At ambient temperature, the glass is insulator and in the molten state is electrically conducting. Electrical conductivity of glass at particular temperature is also dependant on its composition.

Density

Normally the density of glass is determined by water displacement method. However density of porous calcines and minerals is determined by mercury and carbon tetrachloride displacement method. Most of the normal borosilicate glasses (except those of lead borosilicate glasses), the density is in the range 2.6-3.4 g/ml.

Thermal conductivity

Thermal conductivity of glass below its softening temperature is measured either by cut-bar method or by hot wire technique. The cut bar technique is much popular and has been widely used

for inactive samples. In this technique, the glass sample size (mostly cylindrical e.g. 25 mm dia and 25 mm height) is made similar to the quartz or glass references. Between two references, the glass sample is sandwiched. The circular side surface of complete assembly is covered with thermal insulation. Above one reference, the heat source is there and below the second reference, heat sink is there. After attaining the thermal steady state, temperatures of both end phases of references and glass sample are measured and by comparison method, thermal conductivity of glass is evaluated. In hot wire technique, the glass sample of small size is kept at the junction of thermocouple and the variation of emf is measured. Both the methods have been adopted in India for measurement of thermal conductivity of inactive glass samples.

Thermal Expansion Coefficient

Thermal expansion coefficient is required to calculate the stress imposed on the canister / container when the product cools. This is measured by usual dilatometer.

Mechanical Strength

During handling and transport of canister containing VWP for interim storage and for disposal, if the overpack / canister gets dropped, then there will be increase of surface area of VWP due to impact. Hence mechanical strength or effect due to impact is very important. In India, the impact strength determination is carried out by using the shattering technique. In this method, standard weight (1.5 Kg) is dropped from 1 m height on the glass pellet of standard dimensions. The Relative Increase in the Surface Area per unit Joule of imparted energy (i.e.RIAJ) is determined.

Homogeneity

This is the most important property for any type of waste form. For glass waste product, there could be following inhomogeneities [16],

- (i) Liquid- liquid phase separation,
- (ii) Crystal phase separation,
- (iii) Soluble phase separation,
- (iv) Precipitation of metal tellurides and

- (v) Precipitation of noble metals,
- (vi) Other type of inhomogeneities such as porosity, trapped gases, insoluble particles, etc.

The probability of that inhomogeneities will occur in the final product depends on how it is produced and hence it is different for various solidification procedures. Precipitation of noble metals and metal tellurides are very important in case of joule melter since its presence will directly shorten the electrodes. This accumulation of noble metal is avoided by adopting the conical bottom of joule melter and regular draining of the glass.

Important properties of IR-110 composition, which was adopted for WIP, Tarapur is given in Table 2.

Quality Assurance for Vitrified Waste Product

Quality assurance for vitrified waste products (VWP) i.e, glass matrix constitutes following :

- (a) Development of glass matrix for a particular HLW and finalisation of composition. The finalized composition is evaluated for various properties as given in subsequent sections.
- (b) Operation of vitrification facility with optimized and finalized parameters. They include composition, operating temperatures, hold time for various steps such as evaporation, calcinations, fusion, homogenization during vitrification to get the desired quality of product.
- (c) Quality assurance during surveillance period during storage. This is carried out for homogeneity and leaching on few selected representative vitrified waste product canisters.

Interim Storage at Solid Waste

The second step for management of HLW is its interim storage. In India, the first storage facility, called as Solid Storage Surveillance Facility, existing is at Tarapur. The high level radioactive aqueous waste is conditioned by incorporating waste oxides in a vitreous matrix at waste immobilization plants (WIPs), at Trombay and Tarapur. The vitrified waste product (VWP) is contained in a high

TABLE 2.

Sr. No.	Properties		
1	Fusion temperature	°C	850
2	Pouring temperature	°C	950
3	Thermal conductivity at 100°C	(W/m/oK)	1.0
4	Co-efficient of thermal expansion	(°C ⁻¹)	102 x 10 ⁻⁷
5	Softening temperature	°C	560
6	Impact strength		1.09
7	Average leach rate on sodium loss basuis at 100 °C (gms/cm ² /day)		1.5 x 10 ⁻⁴
8	Density, (gms/cm ³)		2.992

integrity stainless steel canister. The canister at Tarapur is designed to store 45 liters of VWP having a total activity of 0.6 million curies. Solid Storage Surveillance Facility (SSSF) storage block at Tarapur has been set up and is operative for interim storage of vitrified waste product (VWP).

The canister, containing solidified high level radioactive waste, need to be stored under constant surveillance for interim period. This will serve following purposes:

- (a) To assure the integrity of vitrified waste product and the canister before commitment is made to irretrievably dispose off the canister in a repository located in a suitable geological environment.
- (b) To assure that the heat due to decay of radio nuclides in the immobilized waste products is dissipated to prevent of melt down of product, until the heat output is reduced to a safe value.
- (c) To facilitate the retrieval and inspection of each storage unit and re-canning in the unlikely event of loss of its integrity.

To meet the requirement of storage of solidified high level waste product (VWP), the storage block of SSSF has been set up. This facility is designed to store about 2000 storage units. The design value pertaining to a single storage unit with respect to activity inventory is about 1.2 million

curie, which in turn generates 4 KW of heat. The removal of dissipated heat from the storage unit is achieved by natural convection air cooling with induced draft. The decay heat and stack provides the driving force for the movement of air through the storage vault. Details of this facility are being covered in a separate paper in this volume.

For surveillance during the interim storage of solidified waste product, a facility has been built for characterization and evaluation of VWP at SSSF, Tarapur. It consists of shielded boxes and laboratories. Sampling of VWP from the canister will be in shielded boxes housed in product characterization laboratories (PCL). The solidified waste storage unit will be brought from the interim storage facility in a shielded cask for taking core samples. In product characterization laboratories, core samples will be cut, sliced, cleaned, polished and mounted as per the experimental requirements. For homogeneity characterization various instruments like SEM, XRD, etc. will be utilized and for leachate analysis, ICP-AES system is being utilized.

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Interim Storage



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Shri Mittal Shah is graduate Chemical Engineer from Laxminarayan Institute of Technology, Nagpur. He joined BARC in 46th batch of BARC Training School. He is involved in design of Waste Management Plants. He is also involved in design of Vitrified Solid Storage Facility at Kalpakkam. His area of interest includes heat transfer analysis, equipment design and material and activity balance.

Introduction

Indian Nuclear Power Programme envisages closed fuel cycle in which spent fuel is processed for recovery of fissile / fertile materials. The resultant High Level Waste (HLW) contains more than 99% of the radioactivity associated with the entire fuel cycle in relatively very small volume. The success of entire nuclear power programme depends on safe management of HLW as radio toxicity of HLW demands isolation from biosphere for extended period. A three stage programme has been adopted for management of this waste:

- (i) Immobilisation of HLW in inert solid matrix.
- (ii) Interim Storage in suitably engineered facilities.

- (iii) Disposal in deep geological repository.

High level aqueous waste is first evaporated, calcined and mixed with inactive glass additives to form glass in vitrification melters. Vitrified HLW from melters is then poured into stainless steel canisters and lids are welded by remote welding machine. These canisters are characterized by extremely large radioactivity inventory resulting in high decay heat generation and their transport immediately after solidification to the ultimate disposal site would involve high unit cost and result in poor utilization of repository space. Sufficient knowledge and experience regarding the behavior of the product is not yet available. The mode of final disposal of the product to the environment, leading to relinquishment of control over the solid wastes,

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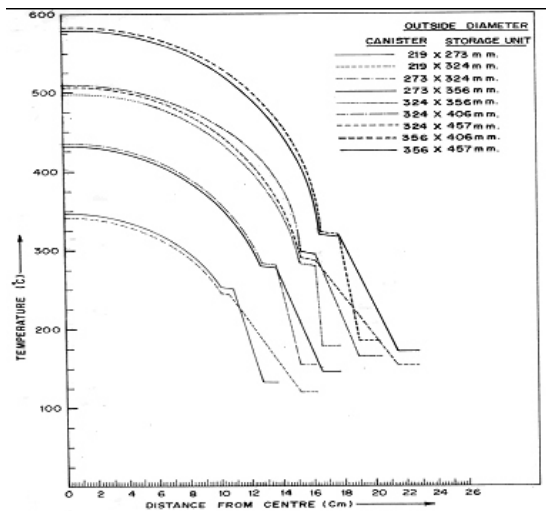


Fig. 1 Canister Sizing for glass with 40 KW/Lit heat generation rate

has also yet to be established. In view of these constraints, it is necessary to store the solidified radioactive wastes at the solidification site for an interim period of time. The products need to be stored in suitably engineered facilities under continuously cooled conditions to dissipate decay heat and constant surveillance of the integrity of the waste product and its container until the major portion of the decay heat is stabilized. One such facility Solid Storage Surveillance Facility (SSSF) is operational at Tarapur and second one Vitrified Waste Storage Facility (VWSF) is under construction at Kalpakkam.

This article presents issues associated with Interim Storage and Indian practices to tackle them.

Optimisation of Canister Dimensions

Optimisation and Standardisation of canister dimensions is very important as it has bearing on remote handling in all the facilities namely Immobilisation plants, storage facilities and ultimate repository. The specific radioactivity of the HLW glass from Indian PHWR's, in the canister ranges from 4000-12500 Ci/Lit. depending on off reactor cooling period which results in 12-40 W/Lit decay heat generation rate. These canisters need

continuous cooling to maintain maximum glass temperature below permissible limit of about 500°C.

To meet design safety objectives, secondary stainless steel containment is provided between canister and cooling air. This is called over pack in SSSF and Thimble in VWSF. Canister and over pack /thimble diameters have direct impact on temperature gradients within the glass. Universally safe dimensions are selected such that the glass temperatures remain within permissible limits under any condition i.e., within the cell under natural connective cooling, during transportation inside shielded cask and inside the storage facility. Temperature profiles for different canister / over pack dimensions under natural connective air cooling for 40W/Lit glass are shown in Fig. 1.

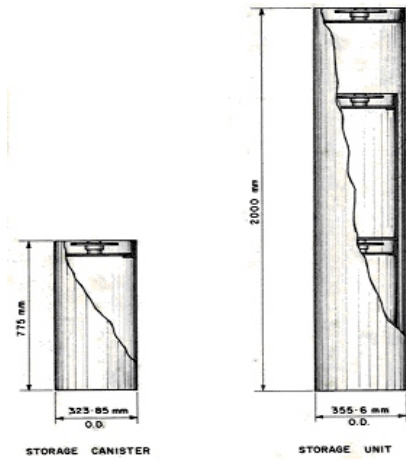
Canister diameter of 324 OD and over pack diameter of 356 OD satisfy the temperature limit. Canister height of about 775mm and over pack of about 2000mm is selected. Each canister contains about 45 liters of HLW glass with radioactivity inventory of about 0.6 million curies generating about 2 KW of decay heat. Height of the canister / over pack is selected on the basis of vitrification cell / melter dimensions, cask design and amenability for remote handling.

Fig.3 & Fig.4 shows Radioactivity and decay heat for single canister as function of time. In about 30 years radioactivity and decay heat stabilize and as such this period is taken for interim storage period in India.

In the storage unit there are three barriers for outward movement of activity; first, the glass matrix in which the waste oxides are incorporated, the second, the high integrity all welded stainless steel canister and the third the stainless steel over pack / thimble.

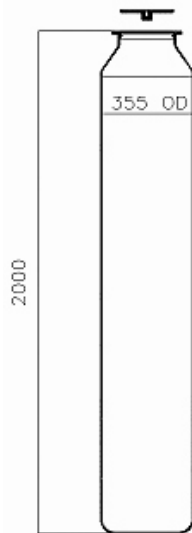
Storage Vault

Several alternative designs have been considered for interim storage. Use of water ponds for providing interim storage for the solidified wastes is only an extension of the existing mode of storing spent fuel. The water needs to be continuously chemically adjusted and demineralised. On the basis of safety and detailed techno-economic considerations, both air cooling



Total Heat generation: 1.8 KW/Canister

Fig. 2a shows canister/ over pack for 40 KW/Lit glass, Tarapur Facility (SSSF)



Total Heat generation: 1.8 KW/Canister

Fig. 2b shows canister for 12 KW/Lit glass, VWSF Facility Kalpakkam

and water cooling are found to be acceptable, though water ponds have certain additional advantages. Water, in view of its high heat capacity and thermal conductivity as compared with air, acts as a better coolant, it also ensures total containment of activity

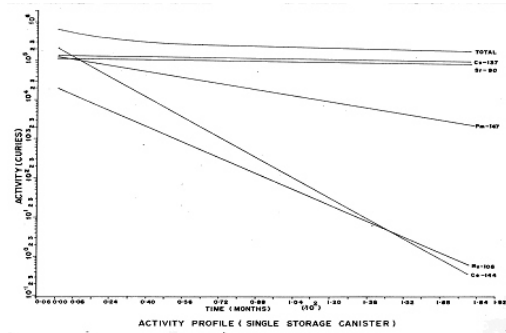


Fig. 3 Activity Profile for Canister at SSSF, Tarapur

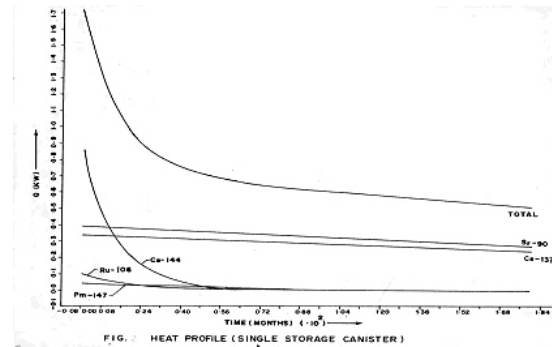


Fig. 4 Heat generation rate profile for canister at SSSF, Tarapur

in case of canister failure. However, considerations of corrosion and high make-up water requirement are some of the disadvantages. Based on the detailed techno-economic analysis air cooled storage is adopted in India.

Air cooled storage of solidified high level waste in India is based on passive design of natural convection air cooling assisted by induced draught due to stack, not dependent on man or machine. It utilizes the decay heat and a suitably designed stack to provide the driving force for the movement of air through the storage vault. In effect, the waste heat will increase the air temperature, causing an upward movement of air due to buoyant forces. The driving force due to buoyancy is balanced by the friction effect of air passage through the system to establish equilibrium for the loading condition of each compartment of the vault. Cross flow of air across

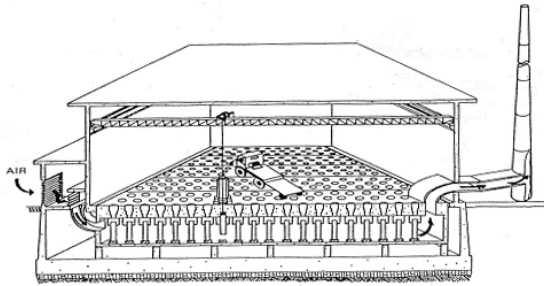


Fig. 5 Schematic view of air-cooled storage facility at Tarapur

canisters is adopted for SSSF where as channelized axial flow is adopted for VWSF facility.

SSSF, Tarapur

The facility is designed to receive one canister per day. It has total storage capacity for about 300 tones of glass which will be generated in 30 years of vitrification operation. To ensure optimal heat transfer efficiency, coolant air distribution, storage unit array and filling pattern are optimized. To facilitate this, the storage vault is divided into two blocks and each of the block is further divided into three compartments. This would also help in isolation of any particular compartment in an emergency.

The structural design of the facility has to take into account certain basic requirement which in some cases are contradictory and are to be reconciled. The project site has a higher ground water table which in the latter days of monsoon season is likely to rise up to nearly surface level. Ensuring stability of the structure against uplift at all times and further ensuring water tightness calls for higher wall thickness for the vault. However, for use of ordinary concrete for the structure calls for minimisation of thermal effects. This can only be achieved by minimizing the temperature gradients across the concrete wall, which in turn can be achieved by minimizing the vault wall thickness. To reconcile the above requirements, it is necessary to isolate the thermal effects from the load bearing structure and also isolate any water ingress. This is achieved by recourse to a double vault design. The inner storage vault is designed on thermal considerations and the design of the external vault is

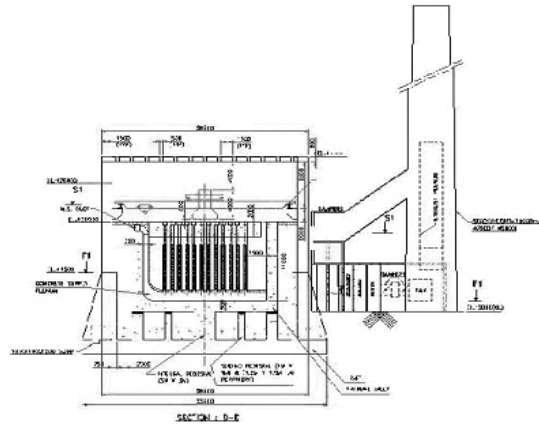


Fig. 6 Schematic view of Storage Facility at Kalpakkam (VWSF)

based on structural and biological shielding considerations. The external vault would also isolate any seepage of ground water from the immediate environs of the storage units. Seepage water will be monitored for activity and further processed. The thermal vault is supported on specially designed bearings from the outer vault. This makes possible, the free sliding of the thermal vault thereby relieving temperature stresses on the thermal vault. The schematic is shown in Fig.5

VWSF, Kalpakkam

VWSF is designed to receive one canister every week, containing about 0.5 tones of active glass. It can store about 1000 tones of glass in four independent above ground storage vaults. Cumulative radioactivity and decay heat as function of time are shown in Figs. 7&8. An additional safety feature in the form of induced draft air cooling with HEPA filtration is provided which is brought in line as and when air born activity is detected in the cooling air. Each storage location has provisions for monitoring temperatures and air sampling. The schematic is shown in Fig.6

Radioactivity inventory of the vault in fully filled condition around billion curies generating few mega watts of decay heat. The stack design takes into account the above requirement and will provide enough draught to counter pressure drop across the

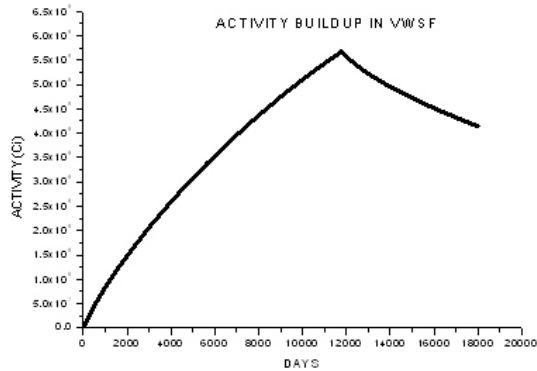


Fig. 7 Cumulative Activity Profile in Storage Facility at Kalpakkam (VWSF)

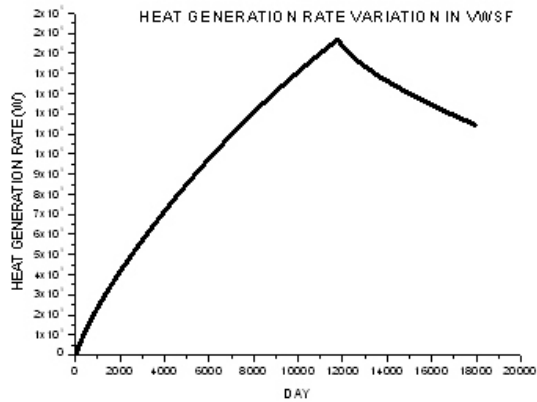


Fig. 8 Cumulative Heat Generation Profile in Storage Facility at Kalpakkam (VWSF)

vault, inlet port and exhaust plenums and kinetic energy losses at the exit of the stack.

The system is self regulating and can compensate for changes in heat load or seasonal / weather conditions. As decay heat reduces, both the air flow and air temperatures decreases as shown in Fig 9.

Maximum Credible Accident

The maximum credible accident which could severely affect the cooling is one in which the stack

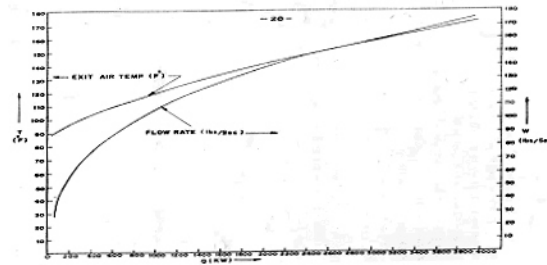


Fig. 9 Air Flow and Exit Air Temperature as Function of Cumulative Heat input in

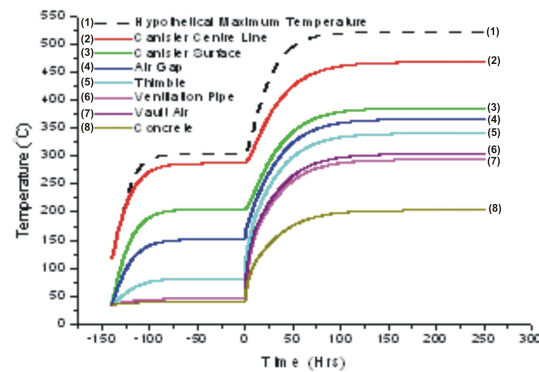
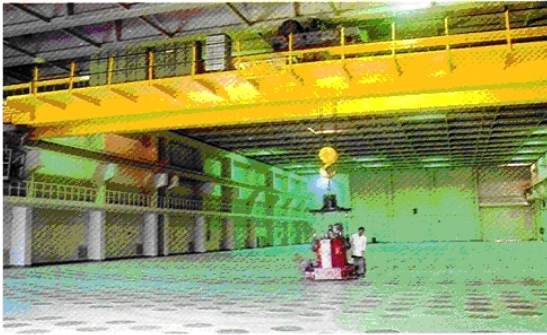
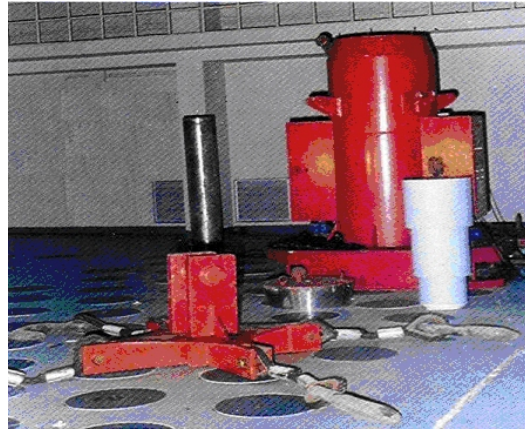


Fig. 10 Temperature Profile during Stack Collapse at VWSF, Kalpakkam

collapses and blocks the exhaust plenum, thus blocking the air passage. Such condition could presumably continue till the plenum is unblocked. A theoretical analysis of the consequences of the maximum credible accident has been carried out. Fig 10 presents the transient temperature profiles under such accidental condition. It should be noted that this analysis is based on a highly pessimistic approach. It has been assumed that both exit and entrance plenums of the vault are blocked. Further the contribution of vault walls to the dissipation of heat has not been considered. The actual temperatures are expected to be much lower than indicated in the figure.



Over Pack Handling at SSSF Tarapur



Over Pack Handling at SSSF Tarapur

Deep Geological Repositories for Vitrified High Level Long Lived Wastes



Shri P.K. Narayan graduated from Patna Science College and joined Bhabha Atomic Research Center through 15th training school batch. He has over thirty years of experience in the field of safety assessment of shallow waste disposal facilities and site selection and characterization for deep geological repositories. His main areas of expertise include groundwater and contaminant transport modeling through geological media, methodology for site characterizations and underground experiments. He has published over forty research papers in national and international journals and has also coauthored a number of safety guides for AERB and IAEA. Currently he heads repository programme section of Nuclear Recycle Group and holds the responsibility of setting up Underground Research Laboratory in granite rocks.

Shri R.K. Bajpai obtained his Master of Technology degree from Center of Advanced Studies in Geology, University of Sagar (MP) in 1987. Sri Bajpai a recipient of prestigious VS Prabhakar Rao Gold Medal of Sagar University, served its Applied Geology department as Assistant Professor before joining Regional Center for Exploration & Research, AMD, Shillong in 1990. He carried out extensive uranium exploration in Meghalaya, Assam and Arunachal Pradesh. He later joined Repository Projects Section of Nuclear Recycle Group Bhabha Atomic Research Center, Mumbai. His expertise lies in the field of geological disposal of radioactive wastes, stability assessment and remote sensing and geographic information systems. Currently Sri Bajpai, holds the responsibility of site selection and characterization for radioactive waste disposal facilities ie near surface as well as deep geological repositories, reactor sites and geotechnical evaluation of other nuclear establishments besides setting up Underground Research Facilities.



Introduction

A deep geological repository can be defined as a purpose built underground facility specifically designed to isolate the radioactive wastes from the biosphere for extremely long periods of time and to ensure that residual radioactive substance reaching the biosphere will be at concentrations that are insignificant compared, for example, with the natural background level of radioactivity. Besides, it should also provide reasonable assurance that any risk from inadvertent human intrusion would be very small.

The concept of geological disposal

One of the most accepted radioactive waste management strategy rely on concentrating and

containing radioactive waste, and isolating it from the biosphere [1,2]. In the case of reprocessed wastes, the containment is achieved by immobilizing the aqueous high level waste in suitable matrix like sodium borosilicate glasses or synrock. The depth of geological repository (400-500m) and suitable geological environment generally ensure isolation of the waste from the biosphere. Thus, a deep geological repository offers high degree of containment for such waste and the necessary degree of isolation from the accessible environment. As such it is widely considered to be an appropriate method for its disposal and as the final step in the management of such waste within this strategy.

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Aims of Geological Disposal

Geological disposal cannot provide a guarantee of complete containment and isolation of the waste over all time. Rather, the aims of geological disposal are:

1. to contain the waste until most of the radioactivity, and especially that associated with shorter lived radionuclides, has decayed;
2. to isolate the waste from the biosphere and to substantially reduce the likelihood of inadvertent human intrusion into the waste;
3. to delay any significant migration of radionuclides to the biosphere until times in the far future when much of the activity has decayed; and
4. to ensure that any levels of radionuclides eventually reaching the biosphere are such that possible radiological impacts in the future are acceptably low.

Multibarrier Concept

Repositories for disposal of radioactive waste generally rely on a multi-barrier system to isolate the waste from the biosphere. This multi-barrier system typically comprises the natural geological barrier provided by the repository host rock and its surrounding and an engineered barrier system (EBS). The “Engineered Barrier System” represents the man-made, engineered materials placed within a repository, including the waste form, waste canisters, buffer materials, backfill, and seals (Fig. 1). Repositories are designed to ensure both operational and post closure safety. Operational safety is provided by means of engineered features and operational controls. Post closure safety is provided by means of engineered and geological barriers; not relying on monitoring or institutional controls after the facility is closed. That is, it is designed to be passively safe. The geological repository mainly comprises regions known as near field and far field respectively. The “near-field” includes the EBS as well as the host rock within which the repository is situated, to whatever distance the properties of the host rock have been affected by the presence of the repository. The “far-field” represents the geosphere (and biosphere) beyond the influence of the repository. This multi-barrier principle creates an overall robustness of the system

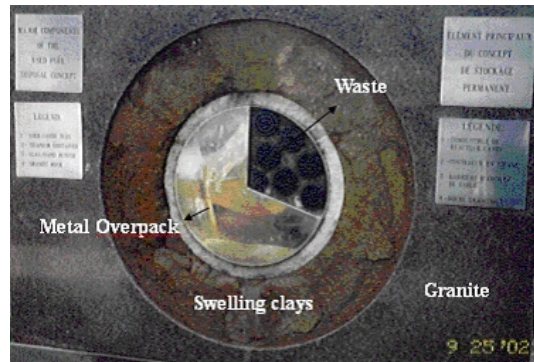


Fig. 1 A model of multibarrier concept displayed at Pinawa Underground Research Laboratory, Winnipeg, Canada

that enhances confidence that the waste will be successfully contained.

Radiological Protection

Geological disposal facilities shall be sited, designed, constructed, operated and closed so that protection in the post closure period is optimized, social and economic factors being taken into account, and a reasonable assurance is provided that doses or risks to members of the public in the long term will not exceed the dose or risk level that was used as a design constraint. The criteria for radiological protection sets the dose limit for members of the public from all practices as an effective dose of 1 mSv in a year [4], and this or its risk equivalent is considered as a criterion not to be exceeded in the future. To comply with this limit, a geological disposal facility needs to be designed so that the estimated average dose or risk to members of the public, who may be exposed as a result of the disposal facility in the future, shall not exceed a dose constraint of not more than 0.3 mSv in a year or a risk constraint of the order of 10^{-5} per year [4,5]. It is recognized that radiation doses to individuals in the future can only be estimated and the uncertainty associated with these estimates will increase with longer times into the future.

Natural Barrier

Natural Barrier in deep geological repository includes the host rock and the surrounding geological media. This environment forms an

extremely effective barrier for almost any radionuclide which escapes from the engineered barriers that immediately surround the wastes. The ability of the host rock to limit the amount of water entering the repository and the ability to restrict the migration of radionuclides away from the repository form the two most important requirements of any host rock.

The geological medium to a large extent controls the chemical conditions of the repository and determines the movement and availability of water. Water may contain chemical species which are capable of corroding the canister materials. If the canister is breached and water is present, leaching of the waste from will occur. Water is the only medium by means of which leaching of the wastes will occur and generally is the only mean by which radionuclides can be transported to the biosphere.

Host Rocks under Consideration Worldwide

A number of host rocks are under consideration worldwide for deep geological disposal of radioactive wastes. The choice of host rock is driven by a number of considerations. Properties of the homogeneity of the rock unit, physico-chemical properties, hydraulic properties, the mineralogy and petrology of the rock unit, thermal and mechanical properties, and the anticipated response to waste emplacement are few technical aspects influencing the choice of host rocks. A reasonably suitable host rock is expected to possess the following properties.

1. High strength
2. High thermal conductivity
3. Low thermal expansion
4. High sorptive capacity
5. Self-sealing capacity through plastic flow
6. Minimum amount of flowing water or brine
7. Minimum unfavorable chemical reactions between rock, fluids and the waste package.

As none of the natural rock can be expected to possess all these properties, the assessment of their suitability is generally made in terms of their relative merits and limitations. Rock types currently under investigation as potential repository host rocks are salt (either in salt domes or bedded formations), granite, argillaceous rocks, tuff and basalt. The potential host rocks differ in many properties that

can have significant effects on the design and performance of waste-isolation systems. Every host rock offers a combination of potentially advantageous and disadvantageous characteristics. However, in the design of a repository it should be possible to compensate for potential problems by appropriate design of the engineered barrier system. The most significant properties of the host rocks now being considered for potential repository development are described in the following sections.

Various types of geological formations can act as host-rocks for a spent nuclear fuel or vitrified processed waste repository. The earliest considerations were given to the salt deposits. Salt is soluble in water. However, the fact that formations still exist after many millions of years proves that it is possible to find salt domes or beds to which no water has had access for these very long times. The US National Academy of Science (NAS) proposed salt as a host rock. This resulted ultimately in an operating deep repository in bedded salt at the WIPP facility in New Mexico, USA, and in comprehensive exploration of the salt dome at Gorleben in Germany. Currently the German government has imposed a moratorium on further work at Gorleben and investigations on alternative host rocks and potential sites have begun there. The most investigated host rocks to date are crystalline rocks, primarily granite and gneiss. The main countries working in granites are Sweden, Canada, India, Finland, Japan, Spain etc. The Finnish government and local population have recently approved a preferred site for spent nuclear fuel disposal in granite at Olkiluoto on the Baltic Coast. Sweden has narrowed into two granitic areas in its siting programme. Canada has extensively studied granitic formations at a depth of 450m in its underground research laboratory (URL). These studies of granitic rocks of the ancient Canadian Shield is one of the most comprehensive appraisals, although specific siting was not an objective. The Canadian approach was to investigate crystalline rock types that were sufficiently abundant in terms of locations to provide a variety of sites, but to leave the actual siting until the generic concept had been approved as safe.

Another future potential host rock type that has been very extensively studied is clay. Clay is a variable material that can be harder or softer,

depending on the temperatures and pressures to which it has been exposed in its geological history. The common features that are of great value when looking for a suitable repository host rock is that clays normally have very low permeability, they tend to have little or no fissures, or have fissures which self-heal under pressure, and they have chemical properties that are very helpful in retarding the transport of radionuclides dissolved in groundwater. Clays have been studied for a long time in Belgium, which has an underground test facility in soft clay at the Mol site, in Switzerland, which has just chosen a region with a harder clay (opalinus clay) as its preferred siting region, and in France, where an underground laboratory has been constructed in clay at the Bure site.

In USA, after extensive characterization of granites, salts and basalts, a final host, volcanic rock, tuff occurring in Yucca Mountain, has been selected and is being characterized by means of large scale insitu mock up experiments. This is a singular choice of host rock and site since the tuff is in a horizontally accessible formation that lies some hundreds of meters below the summit of the mountain but still hundreds of meters above the groundwater table in an oxidizing environment.

After decades of characterization studies on variety of host rocks and site worldwide, there emerges a clear indication that there is no single "best host rock type". All have their individual advantages and disadvantages. Further, there will likely be spent nuclear fuel /vitrified reprocessed waste repositories constructed in all of the rock types mentioned, salt, granite, clay and tuff and also that the host rock itself may be less important than the overall "geological setting" of the repository [6].

Indian Deep Geological Repository Programme

Site Selection and Characterization

Detail site characterization is an indispensable part of a deep geological repository programme to obtain data on its homogeneity past evolution and likely future natural evolution over the period of interest for safety, and a specific understanding of the impact on safety of features, events and processes associated with the site and the geological disposal facility. A reasonably good understanding

of the site and its associated geology is necessary in order to present a convincing scientific description of the geological disposal system. The focus must be on features like water conducting fractures, lithological variations etc, events like earthquakes, floods, meteorite impact, glaciations etc and processes of the site like coupled hydraulic, thermal and mechanical processes, that can have an impact on safety. In particular, it is necessary to demonstrate sufficient geological stability, the presence of features and processes that contribute to safety, and to demonstrate that other features, events and processes do not undermine the safety case.

Characterization of the geological aspects includes activities such as investigation of: long-term stability, faulting and the extent of host rock fracturing, seismicity, volcanism; confirmation of the volume of rock suitable for construction of disposal zones; geotechnical parameters relevant to design; groundwater flow regime; geochemical conditions and mineralogy. Site characterization in an iterative manner provides input to the safety case. Additionally investigation of, for example, the natural background radiation, radionuclide content in soil, groundwater and other media may contribute to a better understanding of the disposal site and assist in the evaluation of radiological impacts on the environment by providing a point of reference for future comparisons.

Indian Geological Repository Programme considers granite as suitable host rock for geological disposal of high-level nuclear wastes and envisages identification of multiple sites in granites in different geographical domain for their relative assessment so as to select a better site in advance stages of the programme. The siting methodology is based on the principle of narrowing down the target regions of large extent to narrower ones through systematic investigations. Nation wide screening of Indian granites covering parts of Rajasthan, Madhya Pradesh, Uttar Pradesh and Maharashtra covering an area of about one million square kilometers was initiated early 90's with a view to select a few potential regions for further characterization to locate a potential candidate site for hosting a geological repository for high level waste. The investigation mainly based on remote sensing and Geographic Information System based studies

coupled with application of other published geological and hydro geological information . This led to identification of a few regions in these states as suitable for further studies. Later on some of the regions thus identified specially those lying in NW and Central India were further investigated with a view to identify a few zones measuring about 100 sq km each. Under this exercise, a total of 22 zones were short listed for follow up investigations. One of such zones was further narrowed down to about 5 sq km using geophysical and subsurface investigations. Similarly another was narrowed down to about 25 square kilometers [7,8,9,10,11].

Why granites ?

Granites is a general name given to igneous crystalline rocks of acidic nature made up chiefly of feldspar, quartz and mica with minor amount of zircon, corundum, sphene etc. A number of chemical varieties of granites have been identified and the corresponding nomenclature has been well established. India has a wide geological spectrum with availability of almost all rocks currently under consideration world wide as repository host rock viz clays, basalts, shales, gneisses, granites etc. India has about 0.6 million square kilometer area covered by granites amounting to about 20% of the total area of the country. These are known to occur in different seismic zones throughout the country. The most important and vast granites with large depth persistent occur in parts of Rajasthan, Madhya Pradesh , Jharkhand and Bihar. There are also good quality granites in Andhra Pradesh and Karnataka . In India, about 0.6 million square kilometer area occupied by granites have been investigated so far due to availability of large volume of these rocks in low seismic zones, with very good structural homogeneity and very favorable hydro geological properties.. However, in this paper, the most extensively studied granites of NW India will be discussed in detail.

Depth of geological repository

The depth of Indian Geological repository will be decided by site geology and hydrogeology to a large extent. Nevertheless, the following considerations have been taken into account for initially deciding a depth range of about 400-500m

In situ stresses

The depth of proposed geological repository in Indian case is 400-500m. Siting criteria requires location of such facility away from active subduction zone/faults. Indian regions under considerations lies more than 200km away from such zones. In these areas, the magnitude of horizontal stresses at 500m depth is mainly on account of the overburden and are of the order of 10-11 MPa. Stresses of such orders even when supplemented by thermal stresses generated by waste, do not pose serious problems in terms of the stability of disposal pit, buffers and canisters. However, when, horizontal stresses reaches to a value of about 20MPa, the problem of rock spalling, micro fracturing in buffers, and formation of excavation damage zone crop up.

Hydraulic Conductivity

The hydraulic conductivity of granites is one of the most important parameter as it will control the transport of released radionuclide from the geological repository. The hydraulic conductivity in granites are known to decrease with depth. While it is of the order of about 10^{-4} to 10^{-5} in first 50m due to intense weathering, it reduces to about 10^{-12} to 10^{-14} m/s in the depth range of 400-500m. Further deep there is no appreciable change in this value. Hence, in a normal undeformed granite, a depth of about 500m has been considered adequate. Besides, the depth is also controlled by cost involved.

Impact of Earthquakes

At a depth of about 500m, in-situ stresses have been calculated to be the order of 10 MPa. The regulatory requirement of such a facility requires assessment of the impact of depth on the possible damage to the underground structure when struck by earthquakes of varying intensity and magnitude. Sharma and Judd (1991) have compiled about 192 cases of earthquake impact on tunnels. The cases where tunnels were damaged in igneous rock at an overburden depth ≥ 300 m are very unusual (Fig. 2). This is very important observation from geological repository point of view. As the geological repository in India is planned at a depth of 500-700m, the probability of seismic induced damage is no longer a safety issue.

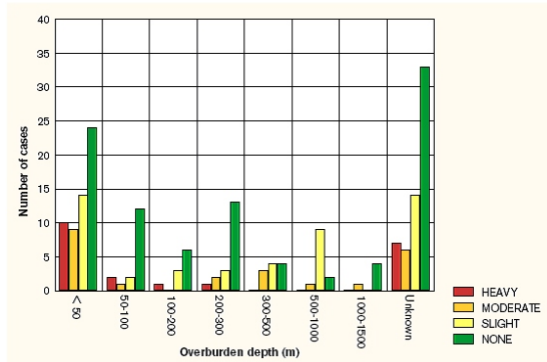


Fig. 2 Showing damage to underground tunnels as a function of depth



Fig. 3a Rock samples retrieved from 400m depth

Description of Studied Region

Though a number of potential regions have been identified in India, but focus here will be on one of the best studied zone of about 100 square kilometers lying in NW India.

Homogeneity

The zone has been assessed for its structural homogeneity up to a depth of about one kilometer with the help of geophysical surveys like Resistivity, Magnetic and Induced potential. The surveys were conducted on ground on a regular grid pattern. The data acquired through instruments were processed with the application of software like Magmod, Rockware etc to generate three dimensional geophysical and geological model. The models were later validated by direct deep drilling of boreholes. A total of about 5000m drilling was carried out and complete columns of the granite rocks were recovered from these boreholes (Fig 3 (a-d)).

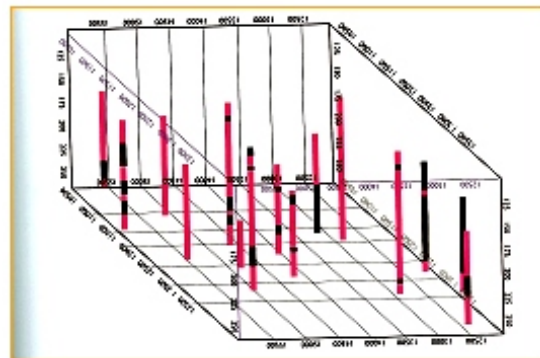


Fig. 3b Showing location and depth of boreholes

Fracture Analysis

A total of about 26000 fractures from this zone have been studied in detail. The important parameters of these fractures controlling hydraulic conductivity of rock mass are aperture, density, spacing, orientation, number of sets, filling material etc. Thus a total of about 0.3 million observations have been recorded on these fractures. These fractures have been processed with the application of ROCKSOLID software to produce three dimensional rock mass quality model of this zone Fig 4a &b).

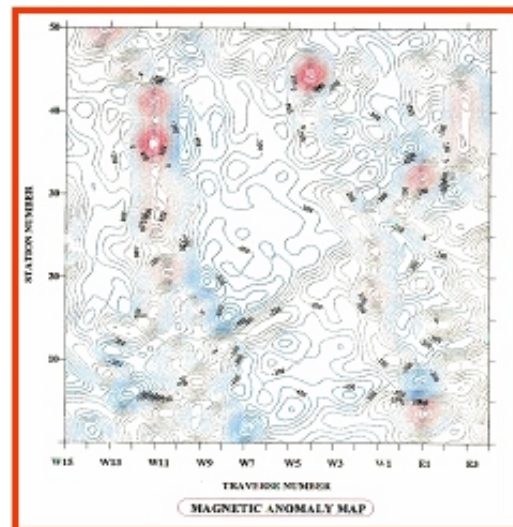


Fig. 3c Magnetic Intensity map of the zone

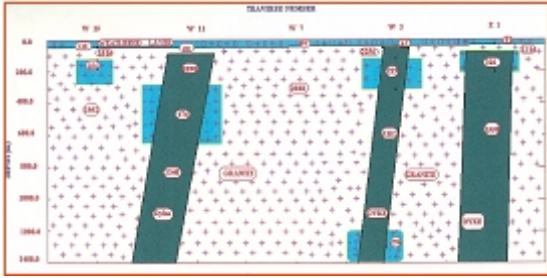


Fig. 3d Cross section upto a depth of one km using magnetic data



Fig. 4a Natural fractures in granites

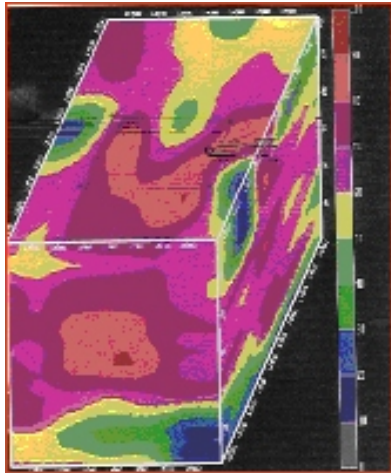


Fig. 4b Isofracture density model

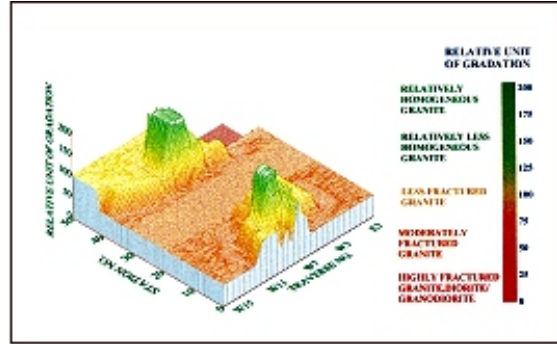


Fig. 5a 3D model of the zone (25 sq kms) obtained through data integration

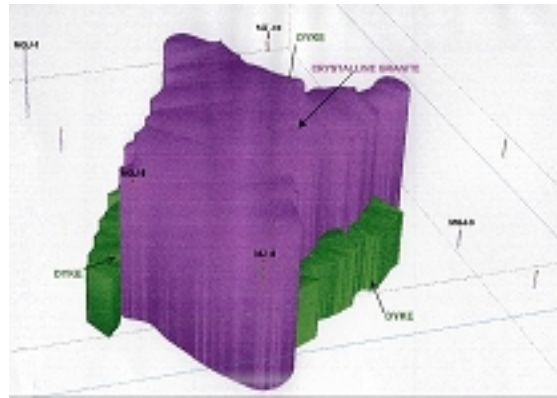


Fig. 5b 3D model of a zone)

Site data Integrations

During the site investigation and characterization, large volume of data on geology, structure, hydrogeology, seismicity, surface hydrology, population distribution, land use information etc have been generated with the application of satellite images, surface based geological and geophysical surveys, deep drilling and seismic monitoring. These data are integrated in suitable softwares like ROCKWARE, ILWIS(GIS),EARDAS etc to identify the zones having maximum ratings in terms of their suitability for hosting a deep geological repository (Figs. 5 a &b).

Seismic Response

During the national screening of Indian granites for locating a suitable zone for hosting such

a facility, only regions located in seismic zone I & II were considered. The satellite based digital image processing coupled with application of available regional geological and structural maps helped in discarding the areas with major lineament and fault zone. The zone was monitored for micro seismic events continuously for five years to identify seismic events and their correlation with geological features. The database on seismic events generated through this exercise reveals the complete absence of any seismic event in the area. Detail structural analysis of core samples retrieved by deep drilling for features like slickenside, mylonites etc were conducted to identify any reactivation along weak planes.

Damage to a deep geological repository due to shaking in an underground facility may occur if the peak ground acceleration exceeds 2 m/s². The zones under consideration in India for locating such facility lies in seismic zones I & II and hence such accelerations are not expected in these zones in the next coming 50-year period, in which the repository is planned to be constructed and operated. Further studies carried out in underground mines specially in Japan and Sweden have revealed that damage due to shaking is very rare in underground facilities. Where such damage has occurred, the rock is either very poor or subject to very high stresses. The strength of granites rocks in India ranges from 150MPa to 220 MPa and the magnitude of insitu stresses does not exceed 12MPa at about 500m depth . The one of the most important siting criteria requires location of these facilities at least 200 km away from active subduction zone. The horizontal stresses therefore in this depth ranges are mainly due to overburden of granite rocks where the plate induced stresses do not contribute any significant components. Thus conditions inducing rock damage to waste disposal facility will not prevail in the Indian repository. Most damage recorded in underground mines have been correlated to the presence of faults and shear zones also. The systematic screening of site reduce the change of the occurrence of fault and shear zone in the repository.

Laboratory based studies

Petrography

A total of about 6 kilometer long core samples have been retrieved. Of this about 256 thin sections

of granite from various depth have been studied for their petrology and petrogenesis. The rock in general is a coarse grained rock exhibiting hypidiomorphic granitic texture. The major minerals include quartz and feldspar (Orthoclase & Plagioclase) with minor minerals like biotite and accessory minerals like apatite and zircon

Quartz and Feldspar are equigranular, anhedral to subhedral exhibiting wavy extinction. Plagioclase percentage appears to be very less compared to orthoclase. Plagioclase is sericitised and occur as pseudomorphs. Orthoclase is turbid and show different stages of alteration to kaolinite. Twinned crystals and oscillatory zoning are common features noticed in altered plagioclase. Grain size of biotite is finer than the quartz-feldspar and is brownish in colour. The flakes of biotite show minor alteration to chlorite. Accessory constituents in euhedral to subhedral form are primary apatite and zircon.

Geochemistry

Detail geochemical studied have been carried out on granites to assess their suitability as a host rock for deep geological repository. Such studies also help in analyzing the possible modifications in the groundwater chemistry around disposed waste overpacks but also give insight on the possible degradation of waste glass and clay barriers in long term . Trace element and major oxides geochemistry clearly divide the samples into two distinct assemblages. The first group is defined by a cluster of low), MgO and V and high K₂O,Zr,Y,Co,Sr and very high Rb and are typical A type granites. The other group with silica ranging from 68 to 72%, high CaO, Al₂O₃,MgO, Na₂O, Sr, V and lower K₂O,Zr and Rb represent I type magmatism. These results when studied in conjunction with Rock Quality designation (RQD) obtained from granite core samples obtained by deep drilling, it becomes abundantly clear that I type variety of granites are characterized by better rock mass quality as compared to their S type counterpart. As these two variety do not differ much in their visual appearance and also petrographic signatures, geochemical studies have helped in discrimination of various varieties of granites on the basis of their geochemical composition, thus leads to selection of better granites for hosting a deep geological repository.

Rock Mechanical Studies

Rock at depth in the vicinity of disposed waste overpack will be subjected to an elevated temperature due to decay heat in the thermal phase of a repository (first 300 years). As a result, such studies are exceedingly important part of rock characterization related to deep behaviors as function of increasing temperature. Very detail studies have been carried out on granite samples to understand variation in rock mechanical parameters. The formation of micro cracks due to heating has also been evaluated (Figs. 6 a-d). The table below shows some typical variations in rock mechanical parameters of these granites with increasing temperatures.

Properties	Temperature (°C)				
	27	65	100	125	160
Uniaxial Compressive Strength (MPa)	118.2	112.8	122.4	133.7	133.3
Tensile strength (MPa)	29.1	9.6	10.5	8.9	8.9
Young modulus (GPa)	29.1	31.5	29.0	26.7	23.2

Conceptual Design of Indian Geological Repository

The design of the conceptual Geological Repository is based on the site geological and structural characteristics and includes One Main shaft (6m) for accessibility and another ventilation shaft of 4m diameters. The facility at 500m depths comprises two orthogonal transportation tunnels of 800m length each. A total of 63 disposal tunnels (110 m) with capacity of holding about 40 waste overpacks each are aligned at right angle to each transportation tunnels and parallel to the direction of principle insitu stresses. The tunnel spacing has been optimized as 12m and pitch of disposal pits have been worked out to be 2.5m. Due to prevalence of closely spaced vertical fractures in the site, pit mode disposal is selected to avoid overpack-joint intersection (Fig 7 a-c).

It is found that maximum 8.3 m diameter tunnel can remain stable without support. The disposal tunnel is of 4 m diameter and 4 m height. As the fracture density in the depth range of 500m is very low (fracture spacing of shallow joints is of the order of 1m to 1.5m), a vertical pit mode disposal is selected as best suited for this zone. The over-packs are placed in disposal pits and surrounded by appropriate buffer material. The disposal tunnels are then completely backfilled to provide for complete isolation. The reliability of closure is dependent upon favorable deformation behavior and integrity of the support system. Disposal tunnels are planned at a separation of 12m i.e. three times the diameter with over-packs placed at 2.5m intervals. In one disposal tunnel, a total of 20 over packs are planned to be disposed in a total tunnel length of 55m. This spacing is based on an optimum occupied area per waste over-pack from thermal loading point of view .

Underground Research Laboratories (URL)

Underground Research Laboratories (URLs) have been in use for almost 40 years The earliest work dates back to the mid-1960s, when the Asse salt mine in Germany was used for the trial demonstration of LLW/ILW disposal. Major experimental R&D programmes commenced in several countries in the late 1970s, notably in salt at Asse and in granite in Sweden (Stripa) and the USA (Climax). Since that time, more than a dozen URLs have been in use world-wide. The URL's can be classified as under:

Generic

These are developed at locations that will not be used for a repository. These can, therefore be developed as extensions to existing mines or tunnels (Stripa, Grimsel) or can be built exclusively as test facility eg Whiteshell, Äspö, Pinawa, Bure.

Site specific

These are developed at sites intended for development as repositories eg ESF in Yucca Mountain, Mol. Eventually, all programmes are likely to need a site specific URL

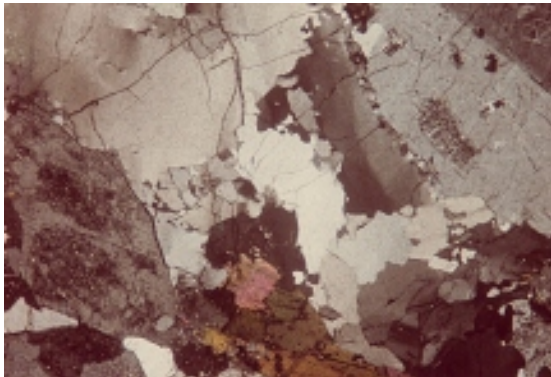


Fig. 6a Unheated sample of granite

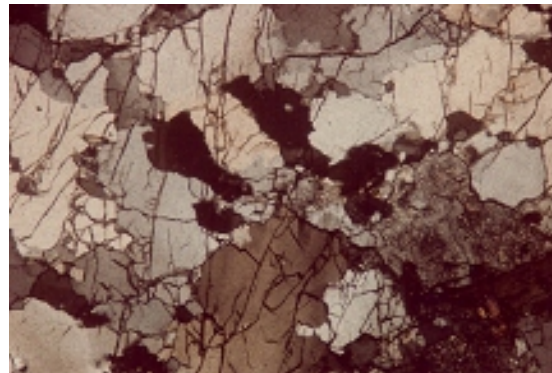


Fig. 6b Fracture development at 100°C

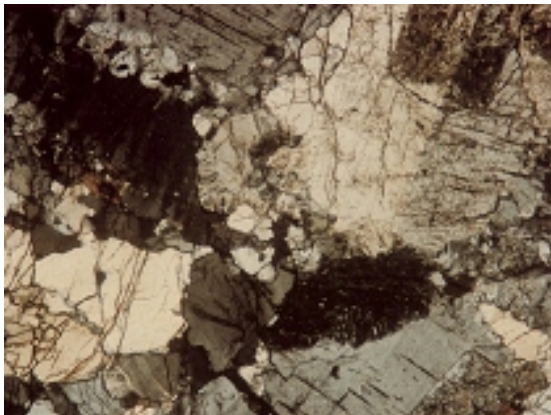


Fig. 6c Fracture development at 200°C

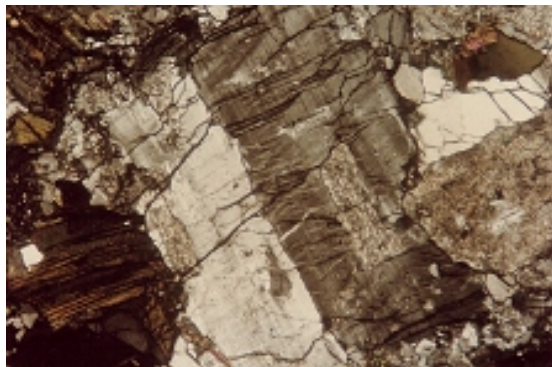


Fig. 6d Fracture development at 300°C

Purpose of URL

An URL irrespective of whether generic or site specific, serves the following purposes:

Experimentation

These are mainly used to investigate, and to develop and test models for processes that affect repository evolution (e.g. water, heat and gas transport) in a particular geological environment and rock type. In the past, most of this type of work has been carried out in generic URLs and is generally experimental R&D.

Rock characterization

Such facilities are also used to develop, test and deploy rock and groundwater characterization techniques and strategies for different rock types and

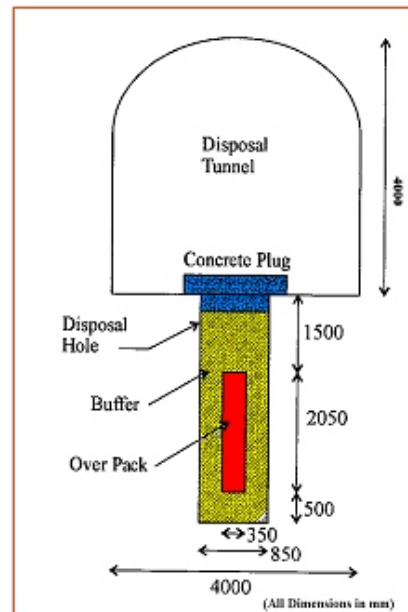


Fig. 7a Layout of disposal pit in Indian context

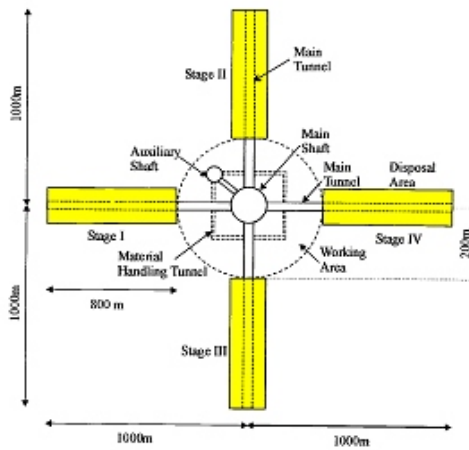


Fig. 7b Plan view of four panel Indian Geological Repository

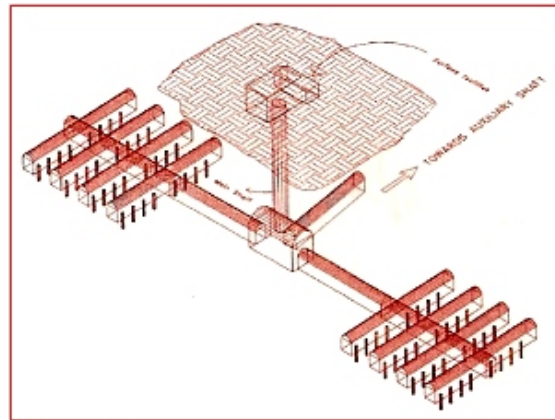


Fig. 7c 3-D layout of Indian Geological Repository

environments. It can be carried out in generic URLs (technique and strategy development) or site specific URLs, where it can be used to investigate the particular characteristics of a specific rock formation and geological environment at a site being investigated for, or developed as a repository. Site-specific URLs, are sometimes called rock characterization facilities (RCFs). Both generic and site-specific rock characterization involve using underground site investigations to extend and supplement those carried out from the surface, in order to gather data for the design and safety assessment of either a conceptual or an actual repository.

Test and Demonstration (T&D)

Another important application of these laboratories is to develop, test and demonstrate the engineering aspects of repository operation, including excavation, EBS and waste emplacement (and retrieval), closure and sealing, and monitoring. This type of work can be carried out in either generic or site-specific URLs: in the latter case, some programmes refer to the URL as a Pilot, or Demonstration and Validation facility.

Indian Generic URL at Kolar Gold Mine

In India, experiments in generic URL commenced in early eighties and continued till 1990.

To begin with an attempt was made to understand the mechanism of heat dissipation from disposed waste overpack into the surrounding host rock. The experiments were performed over a period of 5 years in two stages (i) Single Heater Experiment (Feb. 1988 to August 1991) and (ii) Multi Heater experiment (July, 1992 to March, 1993). Electrical heaters of dimension 0.355m diameter and 2.0 m length were used to simulate the actual high level waste over-packs. The experiments were conducted at a depth of about 1000m in KGF, simulating dissipation of the decay heat from the vitrified waste products. Structural and mineralogical changes in the rock induced by these heaters as a consequence of thermal stresses were also studied. The studied measured heat profile across heaters were compared with predicted ones. Reasonably good agreement between the two, was observed (Fig. 8 a-c).

Heater experiment

Apart from main rock-mass. Thermocouples were installed at various distances and depths around the main heaters. Vibrating wire stress meters and extensometers were heater simulating the waste over pack, as given above, auxiliary heaters at a radial distance of 1m were also provided to accelerate the heating of the placed at heater mid-plane at different distances for measurement of heat induced stresses and extensions in the rock mass [14] This experiment was supplemented with In Multi-Heater Experiment in which, 5 identical heaters each of 2.0

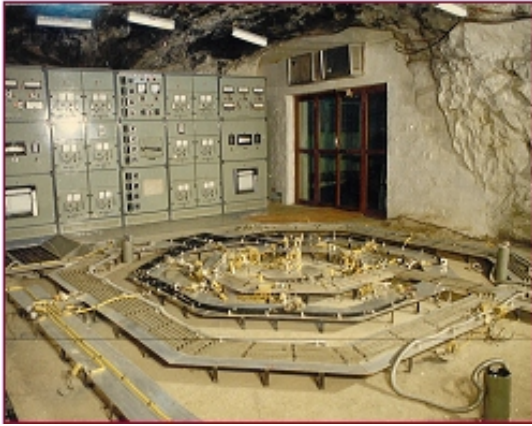


Fig. 8a View of Indian Underground Heater Experiment

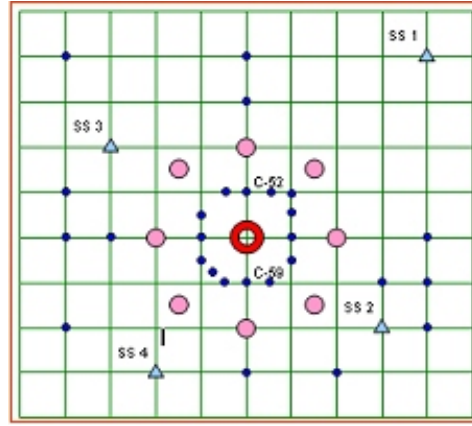


Fig. 8b Distribution of heater and sensors

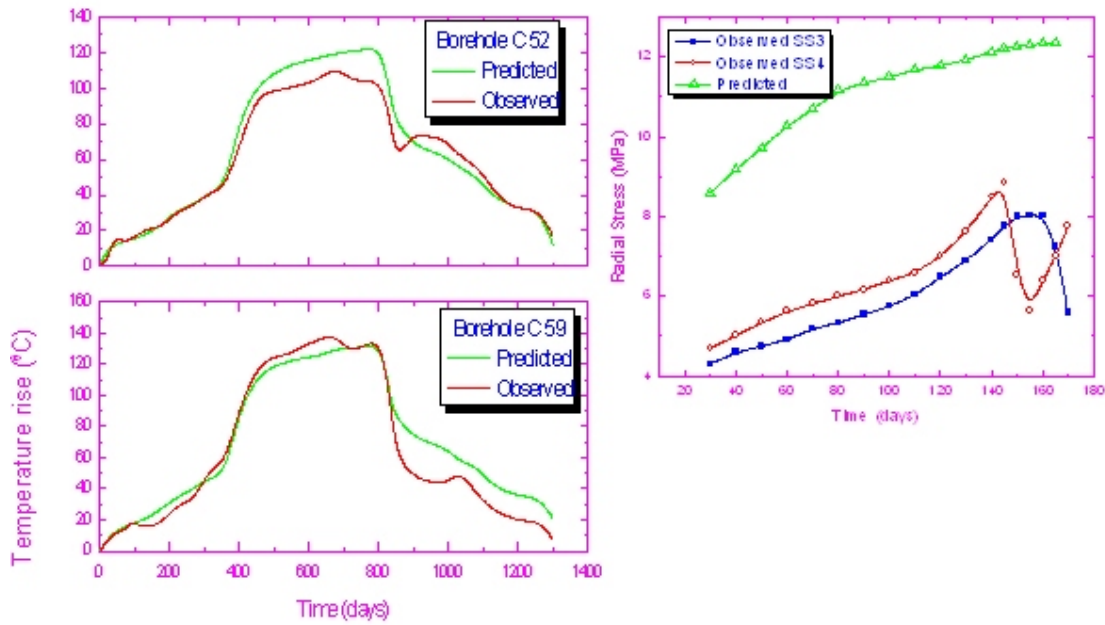


Fig. 8c Comparison of predicted and observed thermal profiles

m length and 355 mm in diameter were used. For the measurement of thermal stresses in the rock mass, Vibrating Wire Stress Meter and USBM gage were used. Good agreement between the predicted and measured thermal profiles was observed [15] However the observed thermal stress values were varying from one fourth to half of the predicted thermal stresses. A few typical comparisons between

predicted and experimentally observed temperature and thermal stress profiles are given in Figs.

The underground experiments were abandoned following the closure of the mine. There are studies going on currently on feasibility of setting up a generic URL at upcoming uranium mines.

Numerical Modeling

Capability to numerically simulate coupled mechanical-hydraulic-chemical-thermal near field as well as far field processes, that will operate subsequent to disposal of radioactive waste, forms another very important aspect of the deep geological repositories. This is mainly due to very long time scales over which safety offered by such facilities against radiological impact on environment needs demonstration. The short term underground experiments in URL can certainly offer vital parameters concerning to these processes but their extrapolation to larger time scale can only be achieved through numerical simulations. In India, such analysis have been attempted using commercially available codes to study combined thermal and mechanical stress field and temperature field around disposed waste overpack in a pit. The site specific values of important rock mechanical and thermal parameters have been used in these analysis. Thermal field around disposed overpack after 30 years is shown in Fig. 9 as typical case. The detail analysis has revealed that at no point of time, temperature in deep geological repository will exceed 100 deg C. Also redistribution of stresses after excavation is also very low (max 29 Mpa), showing good stability of rockmass.

Cost of Deep Geological Disposal

A geological repository is an expensive facility. Typical total costs for site selection and characterization, repository construction, and some decades of operation are a few tens of billions of US dollars (USD). The total cost depends upon the engineered features such as the size, depth and detailed design of the repository, but also upon scientific investigations during site selection phases as well as insitu underground experimentation phases. For instance, just encapsulation and disposal costs for 100,000 tonnes of spent nuclear fuel at the Yucca Mountain Facility in the USA have been estimated at 10,000M USD. Similarly, the small Finnish disposal programme, envisages 760M USD to dispose of 1,840 tonnes of fuel from the two currently operating power plants.

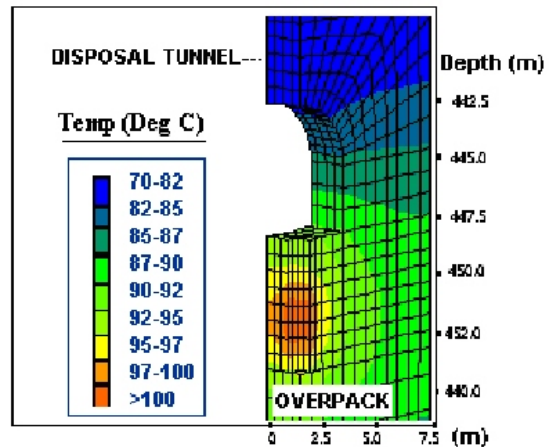


Fig. 9 Temperature field around disposed waste overpack after 30 years as modeled using codes

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Bentonite Clay Backfills and Buffers in Granite Based Geological Repository



Shri R.K. Bajpai obtained his Master of Technology degree from Center of Advanced Studies in Geology, University of Sagar (MP) in 1987. Sri Bajpai a recipient of prestigious VS Prabhakar Rao Gold Medal of Sagar University, served its Applied Geology department as Assistant Professor before joining Regional Center for Exploration & Research, AMD, Shillong in 1990. He carried out extensive uranium exploration in Meghalaya, Assam and Arunachal Pradesh. He later joined Repository Projects Section of Nuclear Recycle Group Bhabha Atomic Research Center, Mumbai. His expertise lies in the field of geological disposal of radioactive wastes, stability assessment and remote sensing and geographic information systems. Currently Sri Bajpai, holds the responsibility of site selection and characterization for radioactive waste disposal facilities ie near surface as well as deep geological repositories, reactor sites and geotechnical evaluation of other nuclear establishments besides setting up Underground Research Facilities.

Shri M.R. Joshi joined the XX Batch of Training School after graduating in Science from Karnatak University, Dharwad and passed the same. His discipline is Chemistry. As Officer-In-Charge he conducted in-situ thermomechanical studies in the Underground Research Laboratory at Kolar Gold Fields, Karnataka. Afterwards he has been engaged in Trombay in the geochemical studies pertaining to radioactive waste disposal. His current fields of interest are evaluation of naturally available bentonites for their use as buffer and backfill in the geological repository. He is a member of many scientific societies and published several papers in scientific journals.



Introduction

International consensus suggests that disposal, in a deep repository in stable bedrock, is the only viable alternative and presently available option for disposal of high level long lived nuclear wastes [1]. The geological disposal system in Indian context typically comprises the natural geological barrier provided by the repository host rock and its surrounding and an engineered barrier system (EBS). The “Engineered Barrier System” represents the man-made, engineered materials placed within a repository, including the waste form, waste canisters, buffer materials, backfill, plugs and seals. This multi-barrier principle creates an overall robustness of the system that enhances confidence that the waste will be successfully contained. As the natural barrier has been discussed in detail in another chapter in this issue, focus here will mainly be on backfill and buffer components of EBS.

Concepts of Backfills and Buffers

Clay is the collective name for various earthen materials having particle diameters less than 0.002 mm in civil engineering application irrespective of the material properties. However, when used in the field of nuclear waste disposal, it is essentially a mineralogical and textural term with a definite geochemistry. Bentonite clays normally used for such purposes are essentially sedimentary rocks with ages ranging from few million years to hundreds of million years. Most of the beneficial properties of clays in waste disposal are derived from their mineralogical compositions coupled with very low permeability due to their very small particle size. The clays, therefore, will be referred as bentonite clays to signify their mineralogical importance in this paper. In most of the deep geological repository concepts worldwide, the bentonite clays are proposed to be

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used as either buffer or as backfills. These two terms are defined as below:

Buffers

These are either in situ compacted or pre compacted bentonite clay bricks proposed to be used between host rock and disposed waste overpack to protect it against rock movement and also decouple it from the flow and transport processes taking place in host rock (Fig. 1).

Backfills

These are clay based materials obtained through suitable admixture of clay and sand or clay and crushed rock for backfilling disposal tunnels and access route to repository so as to avoid them becoming major conductors of groundwater and transport pathways to contaminant. Besides they also provide mechanical stability to underground excavations and help in keeping the buffer in place around the overpack in the disposal pit. It is estimated that about 0.14 million tones of clays will be needed in a granite hosted repository.

Key Requirements of Backfills/Buffers

As the repository is planned to be located in hard bedrock below the groundwater level, the bentonite buffer must limit the water flux and restrict the release of radionuclides into the host rock in the event of canister failure. The required properties of the buffer can therefore be summarized as below:

1. **Low gas permeability:** This refers to the ability to prevent gases formed by chemical and nuclear reactions from escaping to the bedrock and ultimately dispersing in the environment,
2. **Low hydraulic conductivity:** This refers to the ability to limit the flow rates of groundwater, potentially containing corrosive substances, to the canister surface and of pore water, perhaps contaminated with radionuclides from a leaking canister, to the bedrock.
3. **High radionuclide retardation capacity:** This refers to the ability to remove dissolved radioactive material from pore water by sorption on the surface of the bentonite particles.

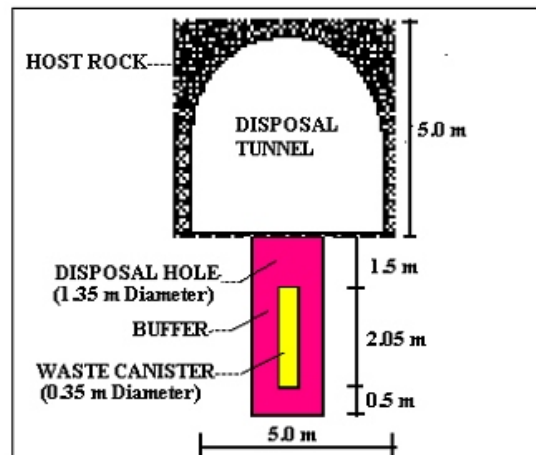


Fig. 1 Cross section of a disposal pit of deep geological repository showing components of EBS

4. **High swelling potential:** This refers to the ability to adsorb large quantities of water such that the bentonite expands and seals any cracks in the buffer to hinder material transport to and from the canister. In a disposal pit, the bentonite clays are proposed to be used as highly compacted bricks as shown in the Fig. 2. When a compacted block of moist bentonites is saturated with water, layers of water molecules will grow around each and every crystal, causing them to swell and pushing the particles away from each other. If the bentonite adsorbs water in a confined enclosure, in the present context, in a disposal bore hole, then swelling is limited to the space available around the buffer and the internal pressure in the block will rise. The bentonite will then reach its' maximal capacity as a barrier against the transport of gases and dissolved compounds.

Other important requirements include sufficient strength, high thermal conductivity, radiation stability and ductility.

Characteristics of Indian Clays

The term bentonite is used actually for a mixture of several different kinds of natural clays. India has good reserves of the swelling clays located in various parts of the country. A large number of



Fig. 2 Use of highly compacted clay bricks around waste overpack

bentonite deposits have been located by Geological Survey of India and State Department of Geology and Mining. Among these, deposits of Rajasthan, Gujrat, Jammu Kashmir and Uttar Pradesh are important in terms of tonnage and quality. To identify, most suited bentonite, that can be used as backfill and buffer in granite hosted geological repository, comprehensive geochemical, thermal and hydraulic characterization studies of these deposits are carried out. Currently, Na rich bentonites of Barmer, Rajasthan are being characterized in details. Rich deposits of about 20 million tonnes have been identified in northwestern zone of the country.

Origin of Barmer Bentonites

It is postulated that Bentonite, which essentially composed of montmorillonite is derived from volcanic and plutonic rocks of Malani Igneous Suite. The presence of metamorphic minerals like garnet and kyanite implies that the metamorphic Aravalli terrain in the east also played a minor role. The present arid climate prevailing in Barmer area does not favor the formation of bentonite. Recent finding of a rich lamellibranch horizon in the northern and northwestern limit of the basin associated with bentonite formation indicates a shallow normal marine environment for the Barmer basin. Under the humid tropical condition, hydrolysis of volcanic glass with flocculation of SiO_2 by a multivalent cation in a slightly alkaline environment might have greatly facilitated the weathering of volcanic rock in to montmorillonite

rich clays that have subsequently been transported into the Barmer basin.

Mineralogical Characterization

This is one of the most important requirements deciding the suitability of a clay to be a useful backfill/buffer, as this in turn decide the geochemical environment around the disposed steel overpack as well as their key properties like sorption. The other important properties like geotechnical, hydraulic and thermal etc are also controlled by mineralogy of such clays. Barmer clays contains mainly Na-montmorillonite (50-60%) and quartz along with small amount of kaolinite, calcite, pyrite and organic matter (Table 1).

TABLE 1. Representative chemical compositions of Barmer clays and

Weight%	Barmer clays	Mineral
SiO_2	48-56	Smectite/Kaoline Quartz
Al_2O_3	15-20	Smectite/Kaoline
Fe_2O_3	3-6	Biotite
MgO	3-4	
Na_2O	1-2	Salt, smectite
CaO	0.14-0.42	Calcite, Gypsum
Organic matter	4-6	

Structure of montmorillonite

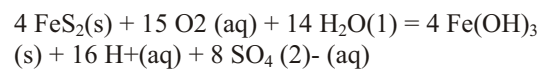
Montmorillonite is an aluminosilicate clay mineral with a layered structure. The central layer has an octahedral geometry, and consists of aluminium (Al), oxygen (O) and hydroxyl (OH) groups. Two tetrahedral sheets sandwich this layer, and are composed of silicon (Si) and oxygen, some of the latter being shared with the central layer in which some of the Al is replaced by trivalent iron, Fe(III), or divalent magnesium, Mg(II). Radioactive waste species, generally cations, are adsorbed onto clays to balance the negative charge on the aluminosilicate structure caused by substitution of silicon or aluminium by lower valent cations in the

tetrahedral or octahedral sheets, respectively (e.g., trivalent aluminium for tetravalent silicon in the tetrahedral sheet). In montmorillonite, some of the trivalent aluminium atoms get substituted by divalent magnesium producing a net negative layer charge predominantly in the octahedral sheet. This is generally balanced by incorporation of monovalent sodium ions (Na⁺) in, or on cavities in the basal plane of oxygen in the tetrahedral layers. Significant amounts of water can occur between the sheets.

Impact of clay mineralogy on near field geochemical environment

Swelling and sorption characteristics of buffers are essentially controlled by Na montmorillonite content of clays. In Barmer bentonite, hydrated sodium ions are sorbed on the surface to neutralize the surface charge. The large ionic radii of these ions help to maintain the spacing between the structural layers, allowing water molecules to penetrate. This accounts for the large swelling- and water adsorbing-capacity of sodium bentonite. Groundwater in potential Indian repository sites at a depth of 450-500m are expected to be rich in aluminum and potassium mainly due to the presence of mineral like orthoclase and biotites. In such case, trivalent aluminium will, to some extent, replace tetravalent silicon in the tetrahedral layers leading to a more pronounced negative surface charge. With the ingress of potassium rich groundwater, surface charge neutralization will be made by potassium ions. These ions can relatively easily shed their waters of hydration. The resultant, dehydrated, potassium ions are effectively incorporated in the spacing between the tetrahedral layers of adjacent mineral particles leading to formation of mineral illite. Thus illitisation, in combination with a supply of potassium ions from infiltrating groundwater, would cause shrinkage of the buffer material. Such transformation can be best studied in natural analogues of montmorillonite-illite conversion to quantify such changes [2,3]. It is desirable to look for sites with low potash granite and groundwater to limit this conversion. Considerable uncertainties remain regarding the kinetics of the process and the concentrations of potassium in the backfill. So further investigations of the illitisation process are required.

Barmer bentonite contains a minor component, calcite, a basic mineral, which will have an important role in determining the nature of the chemical environment within the buffer. This is capable of neutralizing strong acids and thus of maintaining alkaline conditions (pH>7) in the buffer zone. High pH values of water in contact with the steel canister/sodium borosilicate glass surface are comparatively favorable in terms of preventing corrosion. In the deep repository, it is generally assumed that oxygen will be flushed out by water or consumed in chemical reactions following, sealing of the shafts and tunnels. For example, presence of pyrite in Barmer bentonite as impurity will consume significant free oxygen and lead to acidic groundwater conditions as per reaction below:



The acidity is neutralized by immediate reaction with calcite present in these bentonites thus avoiding any substantial lowering of the pore water pH. All oxygen is effectively removed from these clays in this way, leading to anoxic conditions in the deep repository. Under such conditions, the canisters are expected to have a substantial lifetime[4].

The presence of organic material in clays has a decisive role in its selection for use in the backfill and buffers. Barmer Clays contain high amounts of organic matter (4 %) . The organic matter in clay minerals consists of approximately 50 % by mass of carbon. So-called humic substances constitute 70–80 % by mass of this material. As clay surfaces are, themselves, negatively charged, humic substances are bound through multiply charged cations, such as calcium (Ca), that form a bridge between the organic anions and the mineral substrate. The remaining organic matter is not soluble in water, but binds hydrophobically to the surface complexed humic sub-stances. Irradiated bentonite samples exhibit a greater tendency to release organic matter to the aqueous phase, as a result of partial decomposition to water-soluble products. Most, though not all, radionuclide are present as positively charged ions in solution and are therefore sorbed on negatively charged mineral surfaces, retarding their migration through the bentonite .Being negatively charged, dissolved

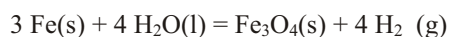
organic acids can also form soluble complexes with many radionuclide. These so-called organically complexed radionuclide will not interact as efficiently with mineral surfaces, thus their rates of transport towards the bedrock as neutral species may be enhanced. It appears that the concentrations of dissolved organic matter in bentonite pore water are lower than those typically present in groundwater. Consequently, there will be an influx of dissolved organic matter from the groundwater into the bentonite over time. This means that measured diffusivity values, based on experiments made using organic-free water, possibly represent lower limits. It can be concluded that insufficient data are currently available to assess the importance of radionuclide transport as organic complexes through bentonite. On the other hand, there is ample evidence that humic substances form very strong complexes with numerous actinides (thorium, uranium, americium, curium) and fission products formed during the decay of the spent nuclear fuel.

Sulphide ions due to the presence of mineral pyrite (FeS_2) in bentonite and host granites and residual dissolved oxygen are probably the only two substances capable of corroding steel overpacks. It is anticipated that the concentrations of both will be low in the immediate vicinity of the canister. Nevertheless, the possibility that sufficient sulphide ions could be generated, by sulphate-reducing bacteria; to induce canister corrosion at an accelerated rate need to be considered. Sulphate-reducing bacteria have been encountered in deep geological formations. Water saturated bentonite also offers considerable resistance to diffusional gas transport from granites to the canister or vice versa. Sulphide sources outside the buffer are therefore unlikely to pose a major problem. Another possibility is microbial sulphide production inside the bentonite. Again, the highly compacted bentonite contains water strongly bound to particle surfaces and is thus unavailable for active life forms. Bentonite thus creates exceedingly hostile environment for microbes due to limited moisture, nutrient and energy sources. Accumulation of hydrogen sulphide, owing to the poor diffusional gas transport characteristics of saturated bentonites, also contributes to making the buffer uninhabitable, as this gas is toxic to microbes. It should be recognized that the gaseous

impermeability and the water binding properties of montmorillonite, constituting the buffer material, are instrumental in inhibiting microbial corrosion processes. On the contrary, illite derived from smectite is known for sustaining the sulphate reducing microbial strains found in deep geological formations. Hence clays with high illite content should be avoided.

Gas generation in Buffers and its impact

Water corrosion of iron (Fe) in the steel canister causes water reduction [5] leading to the formation of magnetite (Fe_3O_4) and hydrogen (H_2) gas.



Additional gaseous products will be generated by radioactive decay, such as radon gas and by radiolysis of water, producing H_2 (g) and O_2 (g). In a worst-case scenario, accumulation of a high gas pressure could compromise the stability of the bentonite by inducing crack formation and propagation through the buffer [4]. This would, in turn, provide a convenient escape route for dissolved radionuclide present in solution. At lower gas pressures, migration is only possible via diffusion of gas molecules in the buffer pore water. Diffusion is a slow process, and as more gas is evolved, the solubility limits of gases in the pore water will ultimately be exceeded, allowing a build up of pressure at the canister. In order for gas to penetrate the buffer, the gas pressure must exceed the total pressure exerted by the swollen, water saturated bentonite and the groundwater [5,4]. The swelling pressure of bentonite increases with the density of the dry, pre-compacted material. In Indian case, the densities are being maintained greater than 1.6 g/cm^3 , hence the swelling pressure will exceed 7 MPa. The groundwater pressure at a repository depth of 500 m will be about 5 MPa. Thus the gas pressure generated by anoxic corrosion, radioactive decay processes and radiolysis of water needs to be greater than 12 MPa to cause micro fracturing of the buffer. In the absence of such cracks, water saturated bentonite is completely impervious to gas. Such damage is not permanent, as clay is self-sealing when the gas-filled voids are gradually flushed with inflowing ground water. However, as long as gas-filled pockets persist in the bentonite, the

TABLE 2. Geotechnical Properties on Indian Bentonite

Sr. No.	Properties	Range
1	Moisture content (% w/w)	10 – 12
2	pH	7.01 – 8.68
3	True density (g/ml)	2.04 – 2.58
4	Bulk density (g/ml)	1.19 – 1.29
1	Liquid limit (%)	420 – 430
2	Plastic limit (%)	53 – 55
3	Plasticity index (%)	369 – 375
4	Shrinkage limit (%)	11 – 15
5	Porosity (%v/v)	43 – 50
6	Free swelling volume (ml/g)	20 – 30
7	Swelling pressure (kPa)	2100-2200
8	Saturated hydraulic conductivity (cm/sec)	1- 5 10 ⁻¹¹
9	Density (Kg/m ³)	1600
10	Poisson's Ratio	0.2
11	Young's Modulus (GPa)	2.0
12	Uniaxial Compressive Strength (UCS) (MPa)	0.5
13	Tensile Strength (MPa)	0.0
14	Cohesion (MPa)	0.25
15	Angle of Internal Friction	300
16	Thermal Conductivity (W/m/ K)	0.78

threshold pressure for gas breakthrough will be significantly lower than the initial value[4]. At present, it is still impossible to accurately predict the risks for gas breakthrough. To avoid such fracturing of buffers, it is essential to confine the H₂ 9g) generated at the point of production. This will help the anoxic reaction to reach equilibrium before sufficient gas pressures to break through the buffer are realized. At equilibrium, no further corrosion can

take place unless the gas is removed. The other way to overcome this problem is to provide gas vent in buffers.

Impact of pore water chemistry

This is one of the very important geochemical consideration in backfill/buffer studies. Such studies are yet to commence on Barmer bentonite. Nevertheless their importance is discussed here. In any Na-Montmorillite clays saturated with water, the ions initially present are predominantly sodium (Na⁺, calcium (Ca²⁺) and chloride (Cl⁻), with minor contributions of potassium (K⁺), magnesium (Mg²⁺), sulfate (SO₄²⁻) and hydrogen carbonate (HCO₃⁻). When bentonite is exposed to groundwater having a different chemical composition to that of the pore water, ions will be transported into and out of the material. The function of bentonite as a barrier in the deep repository equalize the concentrations and eliminate ionic strength gradients. Therefore, an understanding of the pore water chemistry and ion transfer in bentonite is vital in the assessment of repository behaviour. Over time, the pore water chemistry will evolve, reflecting interactions between the species present at the time of closure, and ions entering with the groundwater during saturation .

Geotechnical Characterization

Barmer clays contain more than 84 % clay size particle . Free swelling volume ranges from 20 – 30 mL/g and is directly proportional to montmorillonite (smectite) content of these clays (50 – 65 %) . Temperature field around disposed waste overpack in Indian case for periods of 1, 2, 5, 15, 20,50,100 and 500 years will not exceed 100°C[6]. Temperature in buffers will also not exceed 100°C. The free swelling volume of Barmer clays remains unaffected up to a temperature of 150 C, hence indicating good suitability of these clays as buffers. This in turn also rule out temperature induced alteration of montmorillonite to nonswelling clay variety. The hydraulic conductivity of these highly compacted clays is another important consideration so far as their use in deep geological repository is concerned. The larger swell potential of Barmer bentonite based on index property evaluation and prediction based on compaction characteristics

apparently makes it an ideal clay material for use as buffer in geological repository (Table 2).

Sorption Characterization

The final role of bentonite is its ability to retard the transport of radioactive material escaping from a canister completely penetrated through the steel overpack and cansisters.. Fortunately, radionuclide transport through bentonite has been quite thoroughly investigated worldwide. Thus there is a wealth of data available on the transport mechanisms, as well as the effects of dry clay density, type of cation associated with the bentonite and pore water chemistry. In India, a limited effort have been made in this direction and studies reveal good sorption capabilities of Barmer clays (Table 3& 4) [7]

TABLE 3. Sorption parameters of Barmer clay

	Sorption Properties	Values
1	Cation Exchange Capacity (meq/100g)	50 – 65
2	Kd (90Sr)	245 – 350
	Kd (137Cs)	400 – 580
	Kd (241Am)	280 – 400

TABLE 4. Sorption parameters as function of temperature

Temperature (C)	CEC(Meq/100g of clay)	Montmorillonite (%)
27 (ambient)	54.00	50 – 65
60	59.52	60
90	58.24	44
120	54.72	44
150	55.36	40

Impact of mineralogy

The radionuclide incorporated in the bentonite for neutralization of surface charge controls the rate of radionuclide transport. One of the important mineralogical characteristics of these clays is lack of calcium rich bentonite in Barmer clays. The pores in

Na-bentonite are much smaller than in calcium bentonite and results in long tortuous pathways known for very slow diffusional transport of radionuclide. In compacted sodium bentonite, surface diffusion of cations is the most important mechanism of radionuclide migration [8,9]. Viscosity of water also control the radionuclide transport in clays. The viscosity of bulk water is known to decrease monotonically with increasing temperature, and thus the rate of diffusion will be enhanced [10]. Temperature effects are also coupled with changes in hydraulic conductivity and sorption efficiency.

Impact of steel corrosion products

Recently, the effects of steel canister corrosion products on processes occurring in the deep repository have been studied in detail. The presence of magnetite produced during anoxic corrosion of steel enhances the formation of colloids, which could have two possible effects on radionuclide transport. The first is that larger colloids, incorporating radioactive isotopes, will be deposited in pores in the bentonite. This should effectively reduce transport of all species by limiting the number of pathways available for radionuclide flow. The second is that small, uncharged colloids will be able to migrate, relatively unhindered by electrostatic effects, freely through the buffer, enhancing the rate of radionuclide migration. The first mode is dominant in clays.

Hydraulic conductivity

In highly compacted clay with low porosity, water sorbed at pore surfaces is immobile . Bulk water, on the other hand, which does not experience the electrostatic attraction and is thus mobile. Radioactive decay of nuclear waste in the canister will generate a temperature, and thus pressure-gradient in the buffer. At the elevated temperatures close to the outer canister walls, the hydraulic conductivity in water saturated bentonite will increase. This will result in an enhanced rate of transport of water and dissolved species from the canister, towards the bedrock, through the buffer[11,12,13].

Some of the water may be released from the bentonite particle surfaces, at higher temperatures.

This would increase the permeability owing to an increase in the effective flow channel volume. Both the viscosity and the density of water decrease as the temperature is raised, which also contribute to an increase in the hydraulic conductivity. . As in Indian case the temperature in buffer will be maintained below 100°C, the hydraulic conductivity would be low enough to prevent significant radio-nuclide transport by advection from the nuclear waste to the bedrock. In the case of temperature more than 100°C at canister outer surface , steam could be generated. Investigations have shown that steam markedly decreases the swelling capacity and increases the permeability of loosely compacted bentonite. These effects could adversely affect the buffers' transport properties. However, the influence of steam on the highly compacted bentonite to be used in a deep repository appears to be of minor impact . Higher temperatures would also cause the buffer near the canister to dry, shrink and crack due to heat-induced moisture migration along the temperature gradient away from HLW container. Crack formation can also be initiated by hydraulic fracturing or gas accumulation .

Long term behavior of buffers

Salinity

The long-time effectiveness of the clay barrier may be influenced by some short-term processes like accumulation of solutes transported through the bentonite during the hydration ,the eventual formation of cemented zones (precipitation) and the influence of pore water composition on the hydromechanical properties of bentonite . Furthermore, these processes are probably influenced by the thermal gradient from the canister and outwards in the repository, which can give rise to a concentration gradient. Barmer bentonite contains very high salt mainly due to its marine origin and also wind transported salt. The transport of solutes (dissolved substances, mainly salts) into, and within, the clay barrier is expected to have special relevance for the clay surface properties. The arrangement of clay particles is changed, and the intracrystalline swelling capacity can be deteriorated, by high saline concentrations[14] As a consequence, the permeability may increase in compacted natural clays. In addition, salinity is an accelerating factor in

the processes of corrosion of the metallic components of the canister, and of degradation of interfaces between bentonite and cement. As a cement plug is planned as cap on the disposed overpack in Indian geological repository, such studies are vital. It is therefore important to describe the process of migration of salts in compacted bentonite, to assess the risks for salt accumulation in specific areas, particularly at the canister walls, and to obtain transport parameters for the conditions of the thermal gradient imposed in the compacted bentonite.

Future areas of research in Indian Context

Implications of various parameter and processes of bentonite clays for EBS design, repository operation and performance need to be assessed . This should also focus on feasibility of constructing engineered barriers for the horizontal/vertical storage of canisters placed in disposal tunnels including insitu compaction of buffers. Though Indian programme currently envisages disposal of overpack in vertical pit mode but the final lay out will depend on site characteristics. Thus both the modes need to be analyzed with respect to Indian overpack and bentonite clays. At this stage, it is also essential to demonstrate that the manufacturing and handling of bentonite blocks is feasible at industrial scale and that the clay barrier may be constructed with a specified average dry density, in order to achieve the permeability and swelling pressure required for the effective barrier. This type of research will also provide highly useful information for the design of a repository, in relation to the size of the disposal tunnels, the specifications and procedures for the manufacturing and handling of the bentonite blocks and the basic characteristics of the equipment for construction of the clay barrier and insertion of the waste canisters. The focus of research on laboratory as well as Underground Research Laboratory scale should be specifically on the following aspects of EBS.

1. Impact of petromineralogical characteristics of clays on its mechanical behavior
2. Evaluation of pore water chemistry in clays
3. Gas flow mechanism in compacted clays

4. Establishment of pore network connectivity by X ray microtomography
5. Moisture movement in clays using geoelectrical tomography
6. Temperature effect on water retention properties of compacted clays
7. Dissolution of smectite and precipitation kinetics of secondary minerals in hyperalkaline conditions at 75-150°C.
8. Experimental study on changes of bentonite mineralogy and physical properties as a result of exposure to high Ph.
9. Thermal conductivity improvement in compacted clays
10. Metal iron-smectite interactions and newly formed minerals at low temperatures
11. Bentonite colloid diffusion through rocks
12. Determination of tortuosity of diffusion paths in saturated compacted bentonite clays
13. Experiments modeling of sorption of radionuclides on clays
14. Geochemical codes for dissolution, nucleation and growth of clay minerals
15. Assessment of other material like argillite, reduced clayey sandstones, olivinitite etc as buffer material
16. Chemical degradation of concrete under clay physicochemical conditions
17. Experimental study on change of bentonite mineralogy and physical properties due to high Ph solutions
18. Erosion, generation and stability of clay colloids at bentonite granite interface
19. Conversion of Na-bentonite to Ca bentonite/illite and impact on barrier functions
20. Experimental studies on microfracturing in Clay buffers induced by gas and water pressures.
21. Impact of organic matter on near barrier functions
22. Cement-bentonite interactions

Conclusions

The bentonite buffer around the HLW canister has a key role for repository safety. It must hold the canister in place in the centre of the bore hole. The buffer will also have to conduct the heat emitted by radioactive material decays. The bentonite will hinder groundwater, possibly containing various corrosive substances, from flowing freely to the canisters' surface. A crucial prerequisite for the repository will avoid oxygen encroachment during its' operational lifetime. In an oxidizing environment, corrosion processes would be accelerated and the solubilities of fuel components would be enhanced. Bentonite thus has an important role to play in preventing corrosive oxidizing agents from reaching the canister. One of the purposes of the bentonite packing material is, in such a situation, to limit the rate of water transport to the canister, again to prevent corrosion. The buffer will also prevent leakage of radioactive gases and water soluble compounds to the surrounding bedrock.

In India, systematic studies on naturally occurring bentonite deposits of different parts of the country mainly Rajasthan has been initiated. Initial studies suggest that Na- Smectite rich bentonite clays of Barmer has good potential for use in deep geological repository. However, their testing in insitu underground experiments are yet to begin.

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Radionuclide Migration in Aquatic Environment



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The pathways of radionuclides in the aquatic environment (which is composed of both aqueous and solid phases and includes rivers, lakes, estuaries, shelf seas, deep oceans, ice sheets, glaciers, groundwater and ground-ice) are of importance since a major fraction of the earth's surface is occupied by this compartment. The transfer of radionuclides present within the aquatic environment is affected by both nonliving and living components. Radionuclide behavior in the aquatic environment is determined by transport of the solution and solid phases, the chemical interactions between phases and their biological cycling, importance in determining radionuclide behaviour and its solid/solution distribution are the chemical characteristics (i.e. the radiobiological response).

Radionuclides in the environment can be present in many forms, depending on the nature of the surrounding environment. They complex with natural organic ligands as humic substances. The solubility of these complexes varies with the pH of the natural aquifers. For example, compounds with hydroxides are common at high pHs. Radionuclides also can form complexes with inorganic materials

such as carbonate and sulfate. Some radionuclides are associated with colloids [1-4]. At multidisciplinary nuclear sites, radionuclides such as uranium, plutonium, and strontium were found in some cases to be disposed of with organic substances such as organic acids, complexing agents (such as EDTA), and solvents, all of which can influence radionuclide geochemical behavior and subsurface transport. Traces of Uranium and strontium have been reported in groundwater worldwide around nuclear facilities, and along with tritium are the most frequent radioactive constituents of groundwater. The major radionuclides of concern in the aquatic environment as per Indian Nuclear Power Programmes are H-3, Sr-90, Cs-137, Pu-239+240, and Am-241, whereas some attention needs to be paid towards Ru-103, Ru-106, I-131, I-129 and Co-60. In Indian context, uranium, plutonium, and cesium have been cited as the most common radioactive waste components of soil and sediment [5-6].

Radionuclide transport in surface water bodies

Radionuclide in a water body is transported by the water flow (advection processes) and its

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concentration is altered by the simultaneous influence of turbulent diffusion processes. The radionuclides can also interact with suspended sediments and bottom depositions. The radionuclide transfer between the river water and suspended sediments can be described as an adsorption-desorption process. The transfer between river water and the upper layer of the bottom deposition is determined by adsorption-desorption and diffusion processes. The sedimentation of contaminated suspended sediments and the bottom erosion are also important pathways of the "water column-bottom" exchange of radionuclides. As mentioned also for the surface runoff, two different types of processes can be identified. These are the hydrological ones, which describe water, suspended sediment and bottom dynamics, and the radio-chemical processes, which govern the fate of radionuclides in those different phases driven by the hydraulic forces like

- advective-diffusive transport of water flow
- suspended sediment transport, and
- sedimentation, resuspension and erosion.

The fate of radionuclides in aquatic environment is in general driven by:

- dissolved contaminant transport by the river/reservoir flow,
- particulate contaminant (pollution absorbed by sediment)
- transport by the river/reservoir flow (this includes a separate description of the contaminant transported by clay, silt, mud and sand with different grain size), and
- contamination dynamics in the upper active layer of bottom sediments.

The main physical exchange mechanisms are the sedimentation of contaminated suspended matter into the river bed and re-suspension of the sediments into water. They are controlled by hydraulic factors (e.g. river flow, sediment transport), and depend strongly on the sediment size fractionation (e.g. clay, silt, sand and gravel). Radionuclide diffusion through interstitial water is a process which accounts for migration phenomena not related to sediment transport. Adsorption and desorption of radionuclides by the surface bed sediment are the main chemical exchange processes. These processes are not always completely reversible and are

controlled by geochemical reactions of the dissolved radionuclides with the sediment. Uptake and subsequent excretion of radionuclides by aquatic biota and, in general, perturbation of sediments due to the action of living organisms represent biological processes which are responsible for the exchange of radionuclides between water and the bed sediment.

Mathematical models describing the radionuclide transport and dispersion in rivers and reservoirs can be classified according to two different approaches - (1) spatial averaging of the variables and (2) the individual treatment of variables describing radionuclides in different physico-chemical forms. Various model pertaining to migration of radionuclides in surface water available with their major characteristics are given in the Annexure-1 [7-8].

Speciation of Radionuclide in aquatic environment

For micro-pollutants (concentration less than 10^{-5} M solution), trace chemistry phenomena occur; and reaction directions and mechanisms known from macro-chemistry may change as micro-chemical processes, such as chemistry at phase boundaries, or chemistry of colloidal systems may become predominant. Furthermore, reaction rates may decrease as the probability of effective collisions decreases. Thus, relevant micro-chemical processes including sorption dynamics due to changes in pH, Eh, ionic strength and temperature as well as colloidal transport and kinetics involved should be included in dispersion, transport or impact assessment models.

In natural waters, most trace elements and radionuclides are present in different physico-chemical forms varying from low molecular mass (LMM) ions or molecules, via hydrolysis products and polymers to colloids and pseudo-colloids, or incorporated in inorganic or organic particles (Fig. 1). The borderline between categories is difficult to establish and transformation among categories occurs gradually. As natural waters are dynamic systems, the distribution of species exhibits spatial and temporal variations due to ongoing transformation processes. Owing to sorption to available surfaces, complexation with available inorganic as well as organic naturally occurring ligands, polymerisation and aggregation

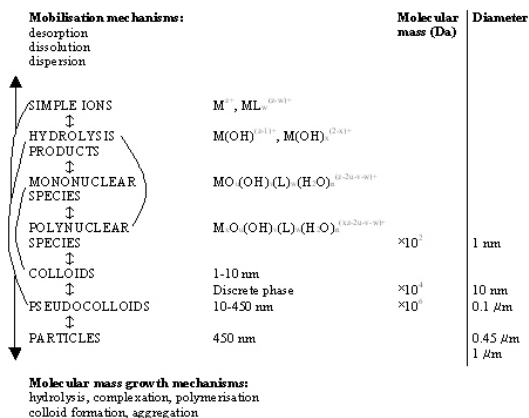


Fig. 1 Size classes for the different physico-chemical forms of pollutants in aquatic systems. transformation processes changing the distribution of species are indicated

of colloids, LMM species are transformed to high molecular mass (HMM) species, while desorption, dissolution, displacement and dispersion processes may mobilise LMM species from surfaces of solids. Thus speciation models should not only focus on the distribution of species but also utilise kinetic information on transformation processes influencing the speciation. Information on kinetics and reversibility of transformation processes is, however, scarce in literature.

Sorption of radionuclides species

In principle two different approaches are used to describe the partitioning of micro-components between solids and solutions at equilibrium conditions:

1. Empirical partitioning relationships (such as K_d) i.e. conditional constants derived from experimental field data or laboratory experiments.
2. Conceptual models based on theoretical considerations describing interaction processes individually or in combination:
 - physical sorption
 - reversible electrostatic sorption
 - irreversible chemisorption

Because of the complexity of natural systems, the empirical approach has been widely used in describing the partitioning of solutes between mineral and water phases in geochemical applications, especially in transport models and engineering applications. Surface complexation models on the other hand, have been used primarily by aquatic scientists interested in developing a thermodynamic understanding of the coordinative properties of mineral surface ligand groups via laboratory investigations [9 -12].

Empirical sorption models

Distribution coefficients

Sorption is often described in terms of equations or partitioning relationships that relate the activity of a solute in water to the amount of the solute sorbed at constant temperature. The simplest of these expressions is the distribution coefficient (K_d) derived from the association reaction:



where M represents solute dissolved in the aqueous phase (e.g. g/l), and SM is solute M sorbed (e.g. g/kg). The K_d is usually defined as:

$$K_d = \frac{[SM]}{[M]}$$

The K_d is highly dependent on the conditions under which it is measured, e.g., pH, temperature, background electrolyte composition and concentration, concentration of $CO_2(aq)$, concentrations of competing adsorbates, etc. Thus, the distribution coefficient has little value in predicting the response of solute sorptive behavior that may result from changes in either the aqueous or mineralogical composition of a system. Furthermore, the K_d approach gives no information on binding mechanisms and equilibrium is assumed.

Langmuir isotherm

The Langmuir adsorption model is applicable for electrostatic sorption and chemisorption reactions (mono-layer model). The number of surface sites available for sorption is limited and must be specified at the outset. The surface reaction can be written:



where M is the solute, S is the surface site, and SM represents the species of sorbed solute M. Assuming that all surface sites have the same affinity for solute M, the following mass law equation can be written

$$K_L = \frac{[SM]}{[M][S]}$$

where K_L is the conditional Langmuir equilibrium constant. Making the further assumption that the density of all adsorptive sites on the surface, S_T , is fixed and that M is the only adsorbing solute, the mass balance law can be combined with the mass balance for surface sites:



to yield the expression commonly known as the Langmuir isotherm:

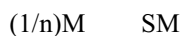
$$SM = S_T \frac{K_L[M]}{1 + K_L[M]}$$

The K_L isotherm is an improvement over the K_d concept since the introduction of total surface sites takes saturation effects into consideration. However, like the distribution coefficient equilibrium conditions are assumed and K_L is dependent on constant solution conditions and is very sensitive to changes in pH. Thus, the application of K_L is questionable for variable ecosystem conditions.

Freundlich isotherm

In contrast to Langmuir monolayer model, the Freundlich isotherm is a consecutive layer model (unlimited sorption sites) and is useful for describing physical sorption. It is frequently observed that a plot of K_d versus SM results in a curve that is convex to the SM axis instead of the straight line expected from the homogeneous site Langmuir expression. In these cases the data must be fitted to a multiple-site Langmuir expression or a generalised exponential isotherm, such as the Freundlich isotherm.

The mass action equation representing the Freundlich model can be written:



$$K_F = \frac{[SM]}{[M]^{1/n}}$$

where $1/n$ is the mass action stoichiometric coefficient pertaining to M and K_F is the conditional Freundlich stability constant. Like the K_d model, an unlimited supply of un-reacted sites is assumed. For the special case where $n = 1$, the Freundlich and activity K_d mass action equations are identical. Thus, the fitting of experimental data to Langmuir or Freundlich isotherms elucidates binding mechanisms.

General partitioning equation

Because sorption of many ionic species is highly dependent on the concentration of H^+ , it is important that sorption models are capable of predicting sorptive behaviour as a function of pH. The empirical relationships that relate sorption density to sorbate concentration are valid only for constant conditions, and thus, these models are generally insufficient for modelling processes in environmental systems. Honeyman and Leckie [13] have considered a modified form of the distribution coefficient which describes the sorption of ion M in terms of the macroscopic observations of proton (or hydroxyl) exchange:

$$K_{part} = \frac{[SM][H^+]}{[M][S]}$$

where is the apparent ratio of moles of protons released per mole of solute adsorbed. Despite the conditional nature of the constants, the approach has been useful in examining specific issues of adsorptive behaviour [10-,14-16].

Complexation (chemisorption) models

Two different types of models based on defined surface sites are commonly used, i.e., the three state (2 pK) and two state (1 pK) models. The surface of a metal (hydr)oxide can be considered as a combination of oxide, hydroxide, and water groups. These surface O^- , OH , and OH_2^+ groups can be coordinated to one or more metal ions in the solid. The different surface groups will each have their own distinct proton affinity and charging characteristics. This complicated situation can be

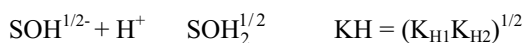
TABLE 1. Equations defining the 1 pK and 2 pK Models [17-18].

1 pK model $\text{SOH}^{1/2-} + \text{H}^+ \rightleftharpoons \text{SOH}_2^{1/2} \quad \text{KH} = (\text{K}_{\text{H1}}\text{K}_{\text{H2}})^{1/2}$	2 pK model $\text{SO}^- + \text{H}^+ \rightleftharpoons \text{SOH} \quad \text{K}_{\text{H1}}$ $\text{SOH} + \text{H}^+ \rightleftharpoons \text{SOH}_2 \quad \text{K}_{\text{H2}}$
1. Species $\text{SOH}^{1/2-}, \text{SOH}_2^{1/2}$	$\text{SO}^-, \text{SOH}, \text{SOH}_2$
2. Mass Action $n_{\text{SOH}_2^{1/2}} K_{\text{H}} = n_{\text{SOH}^{1/2}} a_{\text{H}}(w) \exp(-F/RT)$	$n_{\text{SOH}_2} K_{\text{H1}} = n_{\text{SOH}} a_{\text{H}}(w) \exp(-F/RT)$ $n_{\text{SOH}} K_{\text{H2}} = n_{\text{SO}} a_{\text{H}}(w) \exp(-F/RT)$
3. Mass Balance $2N_s = n_{\text{SOH}_2^{1/2}} + n_{\text{SOH}^{1/2}}$	$N_s = n_{\text{SOH}_2} + n_{\text{SOH}} + n_{\text{SO}}$
4. Surface Density of Exchange Protons $N_H = n_{\text{SOH}_2^{1/2}}$	$N_H = 2n_{\text{SOH}_2} + n_{\text{SOH}}$
5. Surface Density of Proton Charge $q_H = \frac{e n_{\text{SOH}_2^{1/2}} - n_{\text{SOH}^{1/2}}}{2} - e N_H + N_s$	$q_H = -e n_{\text{SOH}_2} + n_{\text{SO}} - e N_H + N_s$

simplified by use of a one-step or a two-step surface protonation.

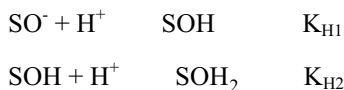
Two state model (1 pK)

Each surface group can exist in either a protonated or a deprotonated state



Three state model (2 pK)

The surface group can exist in a positive, neutral, or negative state



The 1 pK and 2 pK models are defined mathematically by the species, mass action, and mass balance equations as shown in Table 2 (1-3). To solve the chemical model in Table 2 an additional equation is required to relate the surface density of proton charge (q_H) and surface potential (ψ); this equation is derived from an interface (electrostatic)

model (Westall 1987) which has been described above.

Conclusions and recommendations

Migration of radionuclides in aquatic environment is a very complex process which depends on an array of environmental variables such as pH, Eh, concentration and composition of both solvent and surfaces, time and temperature. Traditionally, these complex processes have been modeled from a macro perspective (e.g. K_d), not taking these variables fully into account. It has been shown that the K_d value is highly dependent on the underlying variables, and therefore is only applicable under static equilibrium conditions. Due to increased understanding of how many of the underlying processes affects sorption, an alternative, more fundamental approach has emerged (i.e. SCMs incorporated into aqueous speciation codes), that unfolds the K_d into its basic parameters. This approach gives a much more versatile tool in modeling sorption in dynamic aqueous environments such as estuaries and surface waters. The SCMs have been very successful in describing

sorption on pure metal-oxide surfaces but have not been extensively used on natural heterogeneous particles. Furthermore, some metals (like the important radionuclides Cs and Sr) must be modeled using ion exchange processes instead of surface complexation. Even if some speciation computer codes (e.g. PHREEQC) contain algorithms for ion exchange, thermodynamic data are scarce in literature and difficult to obtain experimentally [19]. Even if the speciation computer codes describing important natural sorption processes are not yet fully matured, they are destined to serve as a much more flexible modeling tool, and would probably generate lower uncertainties, than the use of static K_d values in risk assessment models.

It would be preferable to use the speciation computer code as a separate module which computes the chemical speciation at each node and time interval via calls from an external transport code. This gives the speciation and transport modules an independent internal structure, and considerably increases the codes maintainability. The main consideration when using speciation computer codes are their extensive thermodynamic (and kinetic data) requirements. Good thermodynamic data for many surface reactions are still missing, and for kinetic reactions the availability of data is even more scarce. The situation has, however, improved over recent years and is expected to continue doing so in the future.

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Actinide Speciation by Spectroscopic Methods



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Introduction

Modelling and prediction of the release or transport rate of actinides in aquatic environment requires knowledge of the form, “physical or chemical” in which they are present in the environment.

Actinides in aquatic environment can follow one of the four routes [1].

1. Precipitation: If sufficient concentration of actinides exists in the solution to exceed the

solubility product (K_{sp}), e.g. Pu(OH)₄, then there is a retarding effect on release and migration rate.

2. Complexation: Inorganic (CO₃²⁻, SO₄²⁻, OH⁻, Cl⁻ etc.) and organic (humate, fulvate, citrate, etc.) anions present in the natural water may complex actinides. This will result in the increase in release and migration rate.

3. Sorption: Actinides may attach themselves to mineral or rock surfaces in contact with aqueous phase. It tends to reduce the amount of

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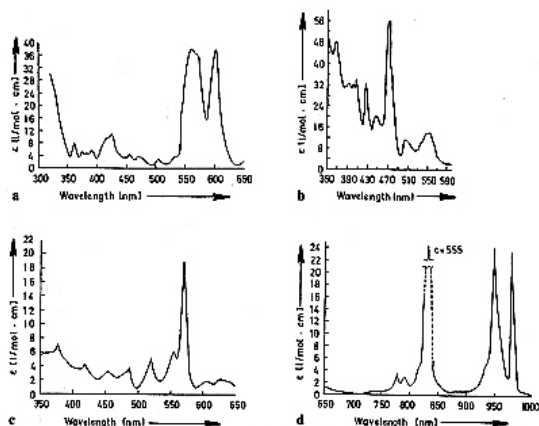


Fig. 1 Optical absorption spectra of (a) Pu^{3+} , (b) Pu^{4+} , (c) PuO_2^+ , and (d) PuO_2^{2+} ions.

actinide ions in solution and thus has a retarding effect on migration process.

- Colloid formation: Higher valent actinides, such as, Pu(IV), upon their release from the immobilized waste form may undergo hydrolysis in the aquatic environment and subsequently form colloids, which are called intrinsic or true colloids. This type of phenomenon was observed in the site close to the Nevada test site in United States [2]. Alternatively, actinides may get sorbed onto the colloidal particles (made of inorganic oxides of Si, Al, Fe, etc.) present in the natural water. These are called pseudo colloids. Actinides in the form of true colloids or pseudo colloids may exhibit considerably different migration behaviour than dissolved species. Depending upon the nature of colloids and solution condition, this process may enhance or retard actinide migration.

For understanding and predicting the chemical behaviour and transport properties of actinides in environment, all the above four processes must be considered. Detailed knowledge of actinide species and charges are essential because the nature and extent of precipitation, complexation, sorption and colloid formation and strongly dependent upon them. Conventionally, partition of a radionuclide in different phases is carried out by counting its radioactivity using the suitable radiation detectors. These nuclear counting methods are sensitive

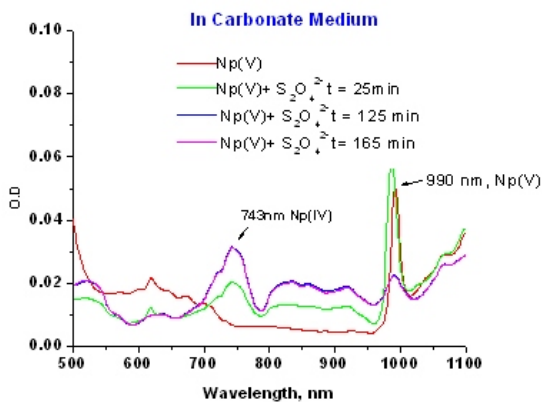


Fig. 2 Kinetics of Np(V) reduction to Np(IV) by dithionate in carbonate media, $[\text{Np}] = 2 \times 10^{-4} \text{ M}$

methods for determining the amounts, but do not give any information about the nature of species. Spectroscopic methods provide valuable information about the oxidation state, coordination number, coordination geometry (inner and outer sphere) and nature of binding of ligands to actinides. During the last decade, spectroscopic methods have been extensively applied to study the speciation of actinides in aquatic environment [3-4].

The spectroscopic methods can be classified into absorption (optical and X-ray) spectroscopy and fluorescence spectroscopy.

Optical Absorption Spectroscopy

Actinides, in aqueous solution, show optical absorption spectra due to f-f electron transitions, which are weak and have low molar extinction coefficients. The spectra are narrow, having full width at half maximum (FWHM) of the order of a few nanometers. The wavelength of maximum absorption (λ_{max}) is characteristic of the oxidation state of the metal ion. Typical absorption spectra of different oxidation states of plutonium are shown in Fig. 1 [5].

The speciation of redox sensitive actinides, such as, Np, Pu, very much depends upon the Eh and pH of the aqueous solution. A typical example of the kinetics of redox reaction of Np(v) with sodium dithionite in carbonate medium is given in figure 2

[6]. The figure clearly shows the disappearance of the peak due to Np(V) (990nm) and appearance of that due to Np(IV) (743 nm) as a function of time.

One of the drawbacks of optical absorption spectroscopy is that its detection limit is low (10^{-5} to 10^{-6} M). With the solubility of actinides in aqueous solution of near neutral pH being 2 or 3 orders of magnitude less (10^{-7} to 10^{-8} M).

Laser Induced Photoacoustic Spectroscopy

Following absorption of light by the species, non-radiative de-excitation of the excited states results in local heating of the volume illuminated by the laser pulse and hence the solution expands. This generates a sound wave with an amplitude proportional to the laser pulse energy (E). Sound waves are detected by microphones or piezoelectric transducers. The photoacoustic signal intensity is proportional to the concentration C of the absorbing species as given by the following equation.

$$\text{Pulse amplitude } V = (\epsilon) C E(\lambda) \quad (1)$$

Where ϵ is the molar extinction coefficient of the absorbing species. By use of the laser excitation source the detection limit of LIPAS technique can be brought down to 10^{-7} to 10^{-8} M. The major background in the PAS spectra is due to absorption of light by water, which limits the sensitivity. Table 1 gives the sensitivity of LIPAS for various actinide ions [1].

TABLE 1. Sensitivity of LIPAS for various actinide ions

Ion	λ_{max} (nm)	$(\text{M}^{-1} \text{cm}^{-1})$	Sensitivity (M)
U ⁴⁺	650	58	1×10^{-7}
UO ₂ ²⁺	415	8	1×10^{-6}
NpO ₂ ⁺	980	395	1×10^{-7}
Pu ³⁺	600	38	1×10^{-7}
Pu ⁴⁺	470	55	5×10^{-7}
PuO ₂ ⁺	568	19	1×10^{-7}
PuO ₂ ²⁺	830	550	1×10^{-7}

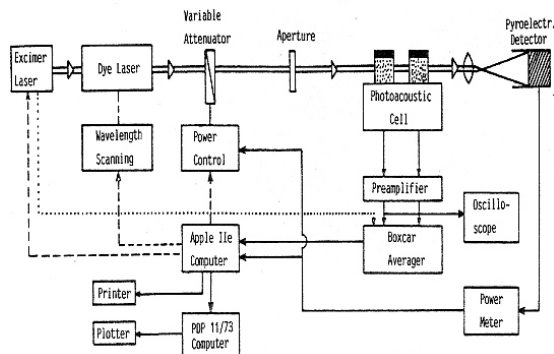


Fig. 3 Instrumentation for LIPAS

Am ³⁺	503	380	1×10^{-8}
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The instrumentation for LIPAS is shown in figure 3 [7]. It consists of an excimer laser pumped dye laser (typical energy ~40mJ, pulse width ~10 ns, range 320 – 970 nm) as an excitation source with a variable attenuator filter to control laser intensity which varies with λ and dye efficiency. A pyroelectric detector is used to measure laser pulse energy. The sample is kept in quartz cuvette mounted on a quartz plate glued to a piezo ceramic disc. The scattered light is deflected from detector by coating the quartz plate with aluminium. The cuvette is contacted on quartz plate by a drop of glycerol. The piezoelectric detector converts acoustic signal to electric signal which is amplified by a charge sensitive preamplifier and then further processed by a box car integrator + band pass filtering to enhance the signal to noise (S/N) ratio. The box car signal is normalised to the pulsed laser power and averaged automatically from over 60 repetitions for recording each spectral point.

Figure 4 shows a typical LIPAS spectrum of Am in carbonate medium. This study was carried out to understand the behaviour of Am under repository conditions [8]: $[\text{CO}_3^{2-}] \sim 10^{-5}$ M to 1M, pH 7-11. Am(III) solution in HCl was added to cement equilibrated with water and pH was adjusted with HCl and Na₂CO₃ solution. LIPAS spectra of filtrates showed Am(CO₃)₃²⁻ and Am(CO₃)₃²⁻ as well as mixed complexes Am(OH)(CO₃)₂⁻.

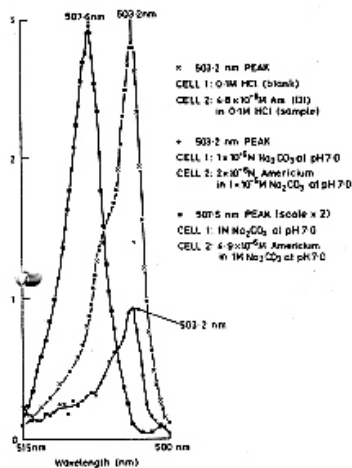


Fig. 4 Am speciation in $Am^{3+}/OH^{-}/CO_3^{2-}$ medium

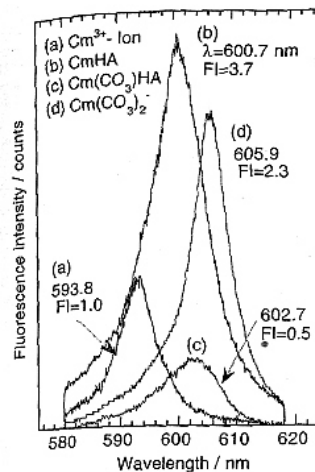


Fig. 5 TRLFS spectra of Cm(III) species under 1% CO_2 .

Time Resolved Laser Fluorescence Spectroscopy (TRLFS)

The technique is based on the laser excitation followed by temporal resolution of the fluorescence signal. It provides the advantage of triple resolution, namely, (i) Excitation resolution: proper choice of laser wavelength, (ii) emission resolution: fluorescence is characteristic of each species and (iii) life time resolution: fluorescence life time is characteristic of the environment of the element (complexation, quenching). Actinides amenable for TRLFS include: U, Cm and Am with detection limits (U ~ 1 ng/l, Cm ~ 10 ng/l, and Am ~ 1 g/l). Lanthanides amenable for TRLFS include: Eu, Sm, Dy, Tb, Gd, Ce, and Tm.

TRLFS Instrumentation consists of an excitation source, which is usually a Nd-YAG or excimer pumped dye laser. It is necessary to change dyes several times to cover visible and NIR region. Now a days optical parametric oscillator (OPO) system using pure barium borate crystals is being used in place of dye laser. The OPO provides continuous spectrum scanning from UV to NIR possible. Typical energy of the laser pulse is around 1.5 mJ in 5 ns pulse with a repetition rate of 10-20 Hz. Laser output energy is measured by a Pyroelectric joule meter. Detection of fluorescence detector is carried out by PMT or optical multi channel analyzer (MCA), which provides

simultaneous detection of whole spectrum. It consists of a pyrochromator with 1200 lines/mm grating and a time gatable photodiode array with 1024 Si photodiodes. A time delay of 1.2 s is usually given after laser pulse to discriminate fluorescence from Rayleigh and Raman scattering.

A typical TRLFS study of curium speciation in presence of HA, OH^{-} and CO_3^{2-} was carried out by Panak et al. [9] using the simulated water of Gorleben site in Germany. Experiments were carried out with CO_2 free water, pH 6-9.5. Continuous shift of λ_{max} from 600.7 at pH = 6 to 605.3 at pH = 9.5 was observed which was attributed to the formation of Cm(OH)HA and Cm(OH)₂HA. On the other hand, experiments with 1% CO_2 showed distinct peaks at 600.4, 602.7 and 605.7 nm corresponding to CmHA, Cm(CO₃)HA, and Cm(CO₃)₂⁻ respectively. The stability constants of the complexes were also determined from the TRLFS spectra. Typical TRLFS spectra are shown in Fig. 5.

At Radiochemistry Division, BARC, the time resolved fluorescence studies were initiated recently, wherein complexation of Eu(III), an analogue of trivalent actinides, with humic acid and its model compounds, such as, alpha hydroxyl isobutyric acid, phthalic acid, succinic acid, etc were carried out [10]. The fluorescence spectra of Eu(III) show multiple emission peaks at 580, 592, 616, 650 and 700 nm due to de-excitation of ⁵D₀ state of ⁷F₁

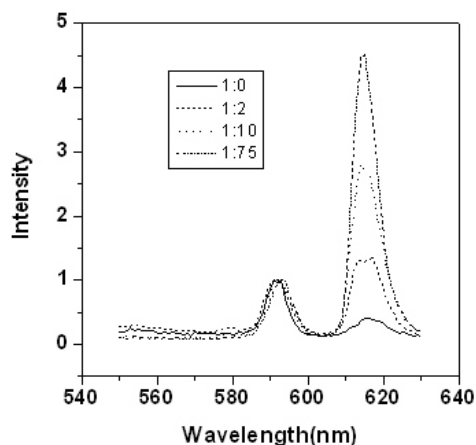


Fig. 6 Fluorescence emission spectra of solutions with different Eu : HIBA ratio

with $i = 0, 1, 2, 3, 4$ respectively. Out of these peaks, the one at 616 nm was found to be hypersensitive, that is, its intensity with respect to 592 nm peak increased with increasing ligand to metal ion concentration (L/M) ratio as shown in Fig. 6. This fact was used in determining the stability constant of the Eu(III) complexes with model compounds. The life time of the emission peaks was found to increase with increasing L/M, due to replacement of the coordinated water molecules by ligand molecules. Using an empirical relation, the number of water molecules coordinated to Eu(III) was also obtained from the life time data.

Chung et al. [11] carried out the TRLFS study of Cm sorption by silica colloids as a function of pH using ^{248}Cm . Concentration of Cm and silica was $= 7 \times 10^{-7} \text{M}$, and 0.5g/l silica respectively. At low pH, the fluorescence spectra showed the peak at $\lambda_{\text{max}} = 593.8 \text{nm}$ with life time (τ) around 65 ns corresponding to Cm^{3+} aquo complex, indicating negligible sorption of Cm by silica. With increasing pH, the intensity of the peak at 593 decreased with the appearance of new peaks at 602.3 and 604.9 nm. These peaks were found to be associated with large τ , which were attributed to sorbed Cm species, namely, $=\text{SiOCm(I)}$ $\tau = 220 \text{ ns}$ and $=\text{SiOCm(II)}$ $\tau = 740 \text{ ns}$. Increase in τ with complexation reflects stepwise exclusion of water molecules from Cm coordination sphere. Typical fluorescence spectra are shown in Fig. 7.

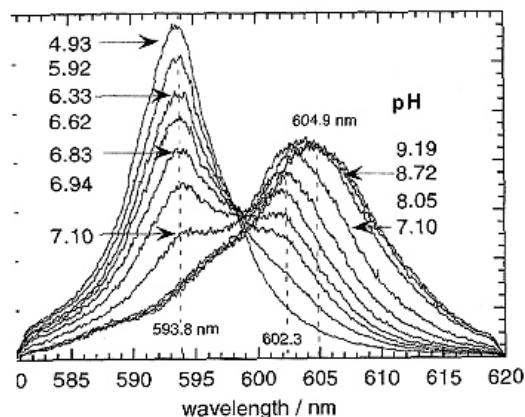


Fig. 7 TRLFS spectra of Cm-Silica system

X-ray Absorption Spectroscopy

X-ray interact with any matter by photoelectric effect. At photon energy greater than the binding energy of electron, the electrons from inner core states are excited into empty outer lying states. The intensity of the incident photons decreases as,

$$I = I_0 e^{-d} \quad d = \ln(I_0/I) \quad (3)$$

The sharp rise in d occurs at ionisation energy (E_0) of the K, L, ... shell.

Fine Structure in X-Ray Absorption Spectra

X-ray absorption spectrum above E_0 for any shell has oscillatory structure due to constructive and destructive interference between outgoing photoelectron wave and that scattered from neighboring atoms. These oscillations in the absorption spectrum contain information about the type of atoms around the central atom, their number and distance from the central atom. Depending upon the region of X-ray energy, different type of information is obtained from the absorption spectra. Extended X-ray absorption fine structure spectroscopy (EXAFS) deals with the X-ray absorption spectrum $E_0 + 50 \text{ eV}$ and X-ray absorption near edge spectroscopy (XANES) deals with that from $E_0 - 30$ to $E_0 + 30 \text{ eV}$ [12]. Typical EXAFS/XANES Spectra are shown in Fig. 8.

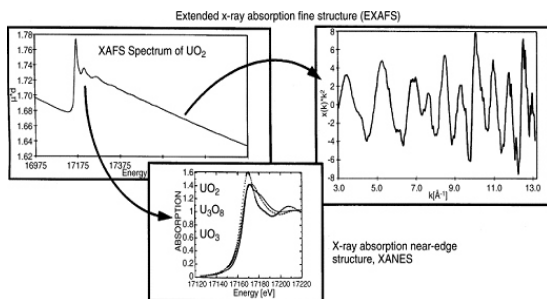


Fig. 8 Typical EXAFS/XANES Spectra

TABLE 2. Absorption edges (eV) of important actinides

Element	E(K)	E(L ₁)	E(L ₂)	E(L ₃)
U	115,596	21,736	20,946	17,165
Np	118,689	22,438	21,615	17,608
Pu	121,790	23,112	22,270	18,060
Am	124,986	23,808	22,952	18,086

EXAFS and XANES studies are carried out using synchrotron sources, which provide 3-4 orders of magnitude higher photon intensities than X-ray tubes. Measurement time is thus reduced from few days to few minutes.

Extended X-ray Absorption Fine Structure Spectroscopy

The wave function of the excited photoelectron in the core region is modulated by the interference of the outgoing wave function with a fraction which has been backscattered on the neighboring atoms. EXAFS oscillatory pattern is thus an interferogram of the atomic arrangement surrounding the absorbing atom. It contains the information about the number and type of neighboring atoms and their distance to the absorbing atom. Due to the higher energy of electron, backscattering from single neighbouring atom is dominant.

Final EXAFS equation [12]

$$(k) \frac{m}{2 \hbar^2 k^2} \sum_i N_i \frac{t_i(2k)}{R_i^2} \exp(-2k^2 \sigma_i^2) \exp\left[-\frac{2R_i}{\lambda} \sin[2kR_i - \delta_i(i)]\right] \quad (4)$$

Where N = number of atoms of type i in one coordination shell, R_i = Average distance of atom i from the scattering atom, σ_i = rms deviation from R_i . It is also called as the Debye Waller Term. The above equation is for one coordination shell. If there are different atoms at same distance, each type of atom would constitute a separate coordination shell.

X-ray Absorption Near Edge Spectroscopy (XANES)

At lower energies near E_0 the outgoing photoelectron is not simply backscattered on neighbouring atoms, but is scattered in all directions. The scattering function for photoelectrons with low E_{kin} has significant value at all angles. This fact along with the longer wavelength of X-ray leads to multiple scattering. After repeated scattering from neighbouring atoms the photoelectron returns to absorbing atom. XANES region contains information about coordination geometry of absorbing atom, including inter atomic distances and angles. However, this information is not easily extracted. XANES features depend on more parameters than EXAFS. Usual practice is to compare XANES spectra with known compounds, perform theoretical calculations. Interestingly the valence state can also be inferred from XANES.

Experimental set up for EXAFS/XANES

These studies are carried out using an electron/positron storage ring, that is, synchrotron radiation source. It provides intense, highly collimated, polarised beam of electromagnetic radiations with continuous band of λ from IR (μm) to hard X-ray (pm) range. A monochromator is used to select $[n \lambda = 2d \sin \theta, n=1,2,\dots]$ and vary λ around E_0 of element of interest. Typical monochromators are Si(111) $d=3.135\text{\AA}$, Si(311) $d=1.638\text{\AA}$, Ge(220), $d=2.000\text{\AA}$, Ge(422), $d=1.155\text{\AA}$. The photon energy (keV) is related to the wavelength as $12.398/\lambda(\text{\AA})$. Double crystal monochromator (DCM) has advantage that it suppresses the higher harmonic reflections ($n>1$) by detuning slightly the parallel alignment of crystal pair. A typical experimental set up for EXAFS/XANES is given in Fig. 9 [13].

To record a spectrum, the photon intensity in front of the sample (I_0) and behind the sample (I_i) are measured at specified energies.

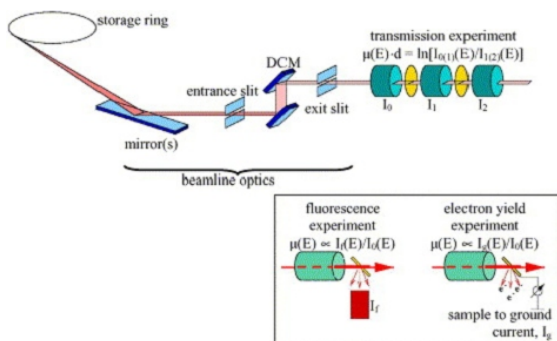


Fig. 9 Experimental set up for EXAFS and XANES

$$(E) \cdot d = \ln[I_0(E)/I_1(E)] \quad (4)$$

Absorption of a reference with known E_0 placed upstream from sample and measured simultaneously. $\ln[I_1(E)/I_2(E)]$ is used for energy calibration. For actinide L_3 edge Y or Zr foil with $E_0 = 17.038$ and 17.998 keV respectively are used. The mode of measurement is either transmission or fluorescence (for dilute <1% or totally absorbing samples).

The sample should be homogeneous. It can be solid or liquid

Liquid samples: Sealed containers, capped vials with windows for incident and transmitted beam and known path length, $\sim 65\text{-}50 \text{ cm}^2/\text{g}$ for L_3 edges of Th-Cm, Absorption by solvent has to be taken into account

Solid samples: Finely ground, neat thin layer between two adhesive polycarbonate, mylar or similar tapes or dispersed in a diluent such as polyethylene, Teflon or boron nitride powder or pressed into pellets.

EXAFS of the complexes of humic acid (HA) and its model compounds with U was studied by Denecke et al. [13] using the synchrotron facilities at HASYLAB, and Stanford. The model uranyl carboxylate complexes included those having bi-dentate or mono-dentate coordination to uranyl ion, such as, uranyl benzoate and acetate, as shown in Fig. 10. The humic acid from Fluka and natural HA (Gorleben) were used. The EXAFS spectra showed bond lengths of axial and equatorial U-O bonds as, $U-O_{ax} = 1.77\text{-}1.79 \text{ \AA}$, and $U-O_{eq} =$

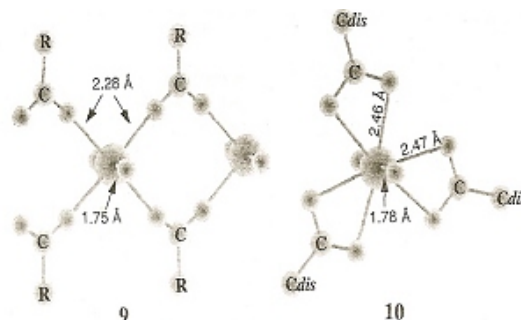


Fig. 10 Structures of Uranyl complexes with model compounds of humic acid

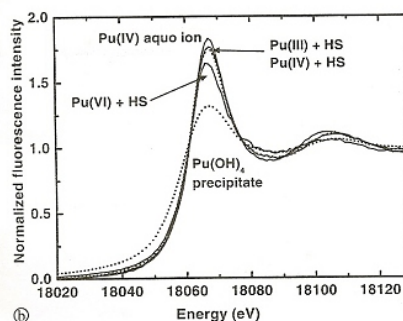


Fig. 11 Pu-speciation in humic rich ground water

$2.37\text{-}2.39 \text{ \AA}$. Uranium coordination was found to be similar in all samples. It was also observed that humic acid binds uranium as mono-dentate, suggesting that additional neutral ligands must be coordinated in order to satisfy the C.N. $= 5 + 0.7$.

Pu-speciation in humic rich ground water was studied by C.M. Marquardt et al., using the synchrotron facility at Karlsruhe, Germany [14].

The XANES spectra (Fig.11) showed that Pu(VI) and Pu(V) are reduced to Pu(IV) and even to Pu(III) under reducing conditions in presence of HA. The inference for Pu colloid formation was drawn from the observed variation in white line intensity, Pu - Pu (3.8 \AA) distance and ultrafiltration experiments.

Indian scenario: The synchrotron facility INDUS-2 will be commissioned shortly at Raja Ramanna Centre for Advanced Technology (RRCAT). The facility can be used for EXAFS/ XANES studies on complexation of actinides and long lived fission

products with inorganic and organic anions, Sorption of actinides on inorganic colloids in absence and presence of natural organic matter, such as, humic acid and fulvic acid. These studies in conjunction with other spectroscopic techniques, such as, LIPAS and TRLFS will provide complete understanding of the molecular level speciation of actinides in aquatic system.

Acknowledgement

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Modeling of Geological Repository Related Processes



Dr. D. N. Yadav graduated from Indian School of Mines, Dhanbad in 80s in Applied Geophysics stream and subsequently earned Ph.D. degree from Physical Research Laboratory, Ahmedabad in 90s. He has wide range of expertise in environmental geochemistry such as establishment of chronology of coastal marine sediments from eastern Arabian sea, fate of redox sensitive trace elements in regulating marine biogeochemistry at sediment-water interface and between coastal to open ocean environments. At PRL, he has also studied chemical and isotopic evolution of Sambhar Salt lake, Rajasthan from various end-member of lake waters for constraining the origin of salt in the lake basin. Later, Dr. Yadav worked as PRL PDF and CSIR Research Associate and studied high anomalous helium/radon concentrations in soil-air and groundwaters from Nal Sarovar, Gujarat and reconstructed late-Quaternary palaeo-climatic sequence in eastern Rajasthan and central India (M.P.). Currently, Dr. Yadav's research interest lies in areas of temporal and spatial modeling of fission product radionuclides (^{137}Cs and ^{90}Sr) in surface waters and groundwater media for post-closure safety assessment of Near Surface Waste Disposal Facility, hydro-geological characterization of groundwaters in terms of recharge and groundwater movements with application of conservative tracers and migration of radionuclides through colloidal phase of groundwaters for hydro-geological investigation of geological repository.

Shri R.K. Bajpai obtained his Master of Technology degree from Center of Advanced Studies in Geology, University of Sagar (MP) in 1987 . Sri Bajpai a recipient of prestigious VS Prabhakar Rao Gold Medal of Sagar University, served its Applied Geology department as Assistant Professor before joining Regional Center for Exploration & Research, AMD , Shillong in 1990 .He carried out extensive uranium exploration in Meghalaya, Assam and Arunachal Pradesh. He later joined Repository Projects Section of Nuclear Recycle Group Bhabha Atomic Research Center, Mumbai. His expertise lies in the field of geological disposal of radioactive wastes, stability assessment and remote sensing and geographic information systems . Currently Sri Bajpai, holds the responsibility of site selection and characterization for radioactive waste disposal facilities ie near surface as well as deep geological repositories, reactor sites and geotechnical evaluation of other nuclear establishments besides setting up Underground Research Facilities.



Abstract

Safety of environment and biosphere due to radionuclide release and transport from high-level waste emplacement in deep geological repository depends much on safety and integrity of waste containment, waste disposal site and prevailing hydro-geological conditions. The time frames of safety in the case of deep geological disposal are of the order of tens of thousands of years. There is no

direct approach to assess the performance of such disposal facilities and their components over these time scales. Laboratory based short duration experiments to evaluate degradation of components of engineered barrier system ie glass, canisters, overpacks and backfill do provide insight into possible behavior of such material under the geochemical environments in near field region of a deep geological repository, but their extrapolation of

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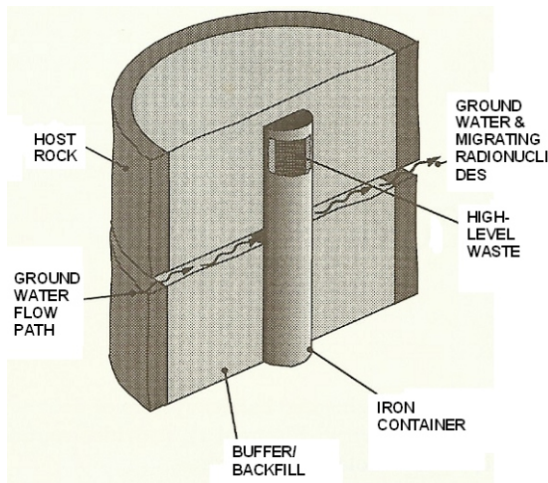


Fig. 1 Schematic diagram of an engineered barrier system (EBS) for radioactive waste repository

such results to long duration is achieved mainly using numerical modeling. The main issues addressed through this approach include engineering design of waste disposal modules, optimal distance between two successive layers of over pack canisters and integrity and corrosion rates of canisters and radiological impact to biosphere components etc. These models also form the basis of all long term safety assessment related to deep geological repositories. Though, this is a very vast and developed aspect of deep geological repositories, nevertheless few important processes and material modeling is discussed in this article.

Introduction

The concept of safe disposal of high-level radioactive waste in deep geological environment is worldwide accepted as viable option; however, methodology of site selection, site characterization, construction and operation of repository tunnels and chambers is complex process. It requires multi-disciplinary approach ranging from mining, geological, geophysical, civil and chemical engineering at different stages of repository development. Modeling of repository related processes has become an integral part of essential exercise which must be taken up for any given site for long-term protection of geo-sphere and

bio-sphere. The various processes can be broadly grouped under four major headings:

- Environment (Near field, Far field and biosphere)
- Containment
- Radionuclide release, and
- Migration and transport of radionuclides

Near-field of repository comprises the engineered barrier system (EBS) of waste form, backfill/buffer and canister as shown schematically in Fig. 1.

Near Field Environment (Thermal, Mechanical, Chemical, and hydro-geological conditions)
Vitrified waste product degradation and leaching from waste form i.e. source term modeling

Far Field Environment (Geological environment/Host rock, Hydrological and Hydro-geochemical processes, Groundwater and water-rock reactions, Retardation processes, Disturbance due to excavation/EDZ, Groundwater flow and contaminant transport modeling, generation of colloids and migration of radionuclides)

Biospherical modeling (Migration and accumulation of radionuclides, radiological impact of radionuclide release and transport to Critical Group and environment)

Near-Field Environment

Nuclear waste emplaced in geological host rock brings out changes in ambient natural environmental conditions and further continues to evolve, and thus, it affects the long-term performance of near-field. The near-field environmental conditions are:

- thermal,
- mechanical
- chemical, and
- hydro-geological characteristics

The above environmental conditions are linked and coupled to each other. For example, perturbation in temperature may lead to changes in additional changes in chemical, hydro-geological and/or mechanical conditions.

2.1 Thermal Conditions

Temperature and temperature gradients are important parameters for HLW (heat producing waste) which may influence hydro-geological, mechanical and chemical conditions in near-field repository environments. Emplacement of HLW in host rock will generally raise temperature of surroundings to about 100°C. In case of saturated repository condition, fluid pressure in depressurized region (excavated portion of rock mass) of near-field increases and with elevated temperatures water-vapor conditions may prevail. Due to this, EBS is subjected to heated vapor conditions leading to corrosion/erosion of waste containments. However, in case of unsaturated site, the fluid pressure will be nearly at atmospheric pressure (1 bar) and with decrease in heat-generation rate, the temperature gradient will stabilize at 100°C and 1 bar atmospheric pressure.

There are three notable consequences of groundwater vaporization: (i) restriction in aqueous transport of radionuclides, (ii) chemical composition of groundwater entering EBS gets significantly altered from the natural condition, and (iii) secondary mineral precipitation at vaporization front causing changes in porosity and hydraulic conductivity of rock as well as changes in groundwater chemistry.

Of the three heat conducting mechanisms, conduction is dominating factor followed by convection and radiation depending on site-specific hydro-geological conditions and EBS design considerations. For modeling purpose, the repository heat-transfer calculations are typically performed at large number of scales depending on individual waste package, emplacement drift panel and repository as a whole system.

2.2 Mechanical Conditions

In the process of nuclear waste emplacement in deep geological formations, the mechanical conditions of near field rocks gets perturbed due to induced stresses and structural damage caused during excavation. The various excavation techniques followed in repository construction phase create damage in rock zones of variable extent around the rock openings. Also, the mechanical

tangential stress is distributed around the boundary of openings. Due to rise in temperature from heat generating waste, the thermal tangential compressive stress is produced in the rock mass. Depending on the elastic, expansive and strength properties of rock formation (i.e. in-situ stress), the formation of cracks/fractures may either remain intact, creep or fail. Failure of rock will result in reduction in life expectancy of nuclear waste containers. In addition to induced changes in host rock stresses due to waste emplacement, EBS also experiences variable loads ranging from hydrostatic pressure to lithostatic pressures in deep geological repository. The fluid pressure of excavated rock formation can vary between the hydrostatic (equivalent to height of water column) and lithostatic (column rock of same height) pressures depending on the degree of load transfer from rock to groundwater medium. In a repository environment, the fluid pressure should not exceed in any case more than the yield strength of rock. If it is so, then it will result in fracturing of the rock, thereby reducing the fluid pressure.

2.3 Chemical Conditions

With the emplacement of HLW in geological repository, the chemical condition of the Near Field environment is bound to change with time. Major changes will be reflected in groundwater chemistry. The three most important factors that influence groundwater chemistry are: (i) pH, (ii) Eh and (iii) concentration of anions in pore water of interacting material. As a result of following combinations of different interaction mechanisms, the chemical environment of repository will evolve as a function of time soon after decommissioning of facility. Some of the salient points related to these processes are described below.

- EBS interaction with intruding groundwater
- Interaction of waste container (Iron or Copper) with groundwater
- Interaction of cement/bentonite backfill with groundwater
- Interaction of organics present in HLW with groundwater
- Temperature and Pressure effects in repository environment
- Microbiology and radiolysis

Generation of gas in repository

The abundance and concentration of polyvalent aqueous species (e.g. Fe, S and C) in pore fluid of EBS materials plays major role in maintaining particular Eh/pH conditions of intruding groundwater, which in turn control the stability and corrosion mechanism of container material. Coupled to this, release of several multi-valent radionuclides from EBS may take place depending on redox and pH conditions of groundwaters.

The groundwater in contact with bentonite backfill material (Na or Ca- montmorillonite clay) in the near-field region will result in increase in pH between 9 and 10, which may further rise to values up to 13 in case of cement backfill. Such alkaline groundwater will have adverse effects in terms of reactivity to waste containers. The chemical evolution of groundwater (Eh-pH change) as a function of time in near-field environment of a hypothetical repository is modeled and calculated for both iron container/cement backfill and copper container with bentonite backfill as shown in Fig.2.

In addition to Na/Ca montmorillonite, bentonite consists of minor amounts of quartz, feldspar, kaolinite, carbonates, sulphides, sulphates and organic matter. Interaction of these constituents with groundwater is chemically important and also complex in nature. The basic interaction processes of bentonite fluids with groundwater can be outlined in three major heads:

- (i) rapid ion-exchange of alkali and alkaline earth cations,
- (ii) relatively slower dissolution of carbonates, sulphates and organics,
- (iii) slow dissolution-precipitation reactions of montmorillonites and other silicates.

The alteration of bentonite and associated change in chemical composition of pore fluid take place at exceedingly slow rate on geological time scales, however, they do influence the near-field chemical environment of repository.

The groundwater movement with time through EBS with cement/concrete as backfill material will result in leaching of alkali hydroxides causing increase in pH as high as 13. Such hyper-alkaline

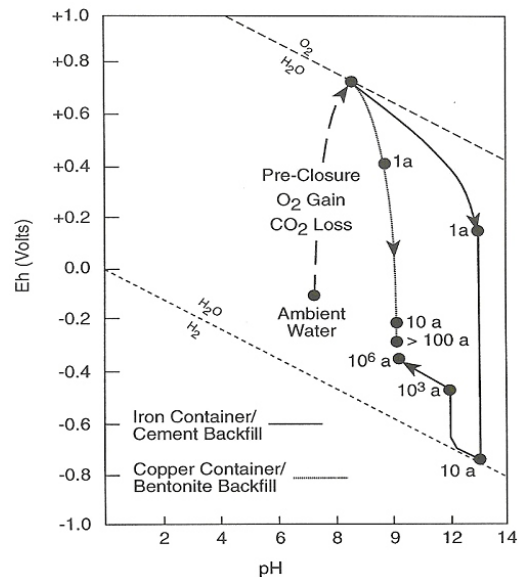


Fig. 2 Evolution of near-field chemistry for hypothetical repository of HLW (Savage, 1995)

condition of groundwater will restrict canister corrosion and radioelement solubility, however, suitability of cement/concrete as a choice of construction material is still a matter of concern in geological disposal system.

The thermal and pressure gradients, as mentioned in Sec. 2.1& 2.2, near EBS in deep geological repository will influence solubilities of hydroxides, carbonates and silicates minerals differently as compared to the near earth surface low temperature aqueous geochemistry. Due to depressurization of water in near field, the groundwater will experience degassing of CO₂ resulting in precipitation of calcite (CaCO₃) in open pore spaces. Also, the soluble Fe²⁺ may change to insoluble Fe⁺³ amorphous oxides and hydroxides in the repository environment. Coupled with these chemical changes as a result of thermal and pressure gradients, the hydro-geological properties (e.g. porosity, hydraulic conductivity) of near-field environments may change. Modeling of some of these processes is important in evaluating performance assessment of deep geological repository.

In deep geological environments microbes also influence chemical condition, mainly Eh, pH and concentration of anions and organic complexants. Microbially-mediated degradation of organics and corrosion of waste containers and concrete may occur. In such process considerable amount of gas may also be generated (e.g. anaerobic corrosion of steel/iron, degradation and volatilisation of organics, helium production by alpha decay, release of gas from host rock), which may pose physical disruption in near-field. Radiolysis (either α or β) of groundwater may produce variety of reactive radiolytic radical species, which will convert to more stable and inert species. Attempts are being made to carry out model based studies which can be implemented in design and construction stage of repository to reduce or minimize deleterious radiolysis effects on near-field performance.

2.4 Hydro-geological Conditions

The natural hydro-geological conditions are subjected to change due to waste emplacement in the repository. Changes in thermal, chemical and mechanical conditions will contribute to change in near-field hydro-geology. During repository excavation there is creation of low pressure/high-porosity region thereby allowing a change in groundwater regime. Formation of cracks/fractures within the surrounding rock also perturbs natural groundwater flow. Thermal effects induce changes in porosity due to secondary mineral formation in the geological medium. Under both saturated and unsaturated conditions, emplacement of backfill materials surrounding tunnels and waste packages with permeabilities different from host rock will cause differential groundwater movement. Modeling studies help in characterizing groundwater flow lines around EBS and predict in estimation of re-saturation times of clay layers in backfilled materials.

2.5 Containment Failure

After operational lifetime of containment in repository, there would be containment failure in the near-field of which followings are important factors of consideration:

- (i) Meantime of containment failure. Depending on meantime of containment failure, the

radionuclide release is estimated. If it is 300 years, then ^{90}Sr and ^{137}Cs will undergo 10 half-life decays after disposal. The initial inventory would reduce effectively by a factor of 1000. Similarly, if meantime of containment period is 10,000 years, it would be effective in reducing the activity of all radionuclides with half-lives less than 1,000 years to negligible values.

- (ii) Differential containment failure over large range of time arising due to difference in nature of multiple waste packages. This will give rise to differential peak arrival times for radionuclide release from the EBS. If all waste containers fail at a time, then superposition of release may result in very high peak release of radionuclides, the impact of which would be unacceptable.
- (iii) Differential mode of containment failure whereby either local corrosion (e.g. pitting) or general corrosion may take place. Model calculations show that partially failed containers provide a more effective 'barrier' to release of radionuclides than engineered clay layers or impermeable host rock.

2.6 Radionuclides Release

Upon containment failure from EBS, the surrounding groundwaters may come in contact with the nuclear waste whereby radionuclide release may take place. Such release is controlled by a number of physical and chemical characteristics of waste forms and radionuclides concerned. Following factors are important:

- (i) Radionuclide inventory of waste forms
- (ii) Nature of waste forms: Inhomogeneity in radionuclide distribution
- (iii) Chemical property of waste forms (waste form leach/dissolution rate, solubility of radionuclides etc. depend more on environmental conditions such as temperature and groundwater composition)

2.7 Transport of radionuclides from Near-Field

Following processes and factors are important in transport of dissolved as well as colloidal

radionuclides from the near-field to far-field (Pigford and Chambre, 1988):

- (i) Mechanisms of transport (advection and diffusion)
- (ii) Physico-chemical properties of EBS and natural barriers (hydraulic conductivity, porosity, diffusion co-efficient, fractures, etc.,)
- (iii) Retention/retardation properties of EBS and natural barriers (sorption, filtration etc.)
- (iv) Coupling of groundwater flow and chemical reaction (thermo-mechanical, flow and chemical reactions)

The migration and transport of radionuclides is controlled by the transport mechanisms, radioactive decay, groundwater chemistry, and the geometry of source term. The transport mechanisms include advection, diffusion and dispersion. In advection process, the dissolved species is carried by groundwater velocity. In molecular diffusion, the dissolved species migrate due to concentration gradient by colliding with moving water molecules. The concentration of dissolved species also moves as a result of spreading in space due to dispersion effects. There are a number of factors that affect dispersion in porous medium, such as heterogeneity, change in groundwater velocity and chemical effects. Other factors controlling transport of dissolved radionuclides are groundwater flow velocity, diffusion co-efficient of concerned radionuclides and hydraulic conductivities of backfill and host rock materials.

2.8 Source Term Modeling

To simulate near-field radionuclide release and transport, mathematical models are developed in which a set of partial differential equations represent mass-transfer properties of constituents from and within system. For this, one has to solve coupled equations for:

flow (Darcy's law and continuity of fluid flow),
mass-conservation of radionuclide in transport region,
mass-conservation inside canister (including dissolution and diffusion),
energy-conservation, and
chemical reactions.

The conservation equations are second-order partial differentials of spatially independent variables which are solved by use of three boundary conditions: (i) by defining dependent variable (e.g. concentration of radionuclide) on the boundary, (ii) by defining normal derivative of dependent variable (e.g. radionuclide diffusive flux) on the boundary, and (iii) by defining combination of dependent variable and normal derivative on the boundary (Zwillinger, 1992). The solution of mathematical models is usually obtained by either analytical or numerical techniques. The analytical method is accurate and fast but limited to system where number of processes is reduced and geometry of source is too simple. On the other hand, numerical technique is capable of handling more complex system with model results more close to reality. Whatever be the choice of solving mathematical model, the results should be able to simulate actual processes occurring in repository near field environments. To check the accuracy of model calculations, it is essential to validate and calibrate the models with experimental data and natural analogues for confidence building process.

There are several source-term modeling codes available worldwide, however, they have been developed for different sites or the same site with different approaches. Recent review on this topic (Apted, 1993; NEA, 1993) has brought out 4-types of source-term models:

1. Simple model with complete solution: Model is based on simple system (e.g. reduced number of processes and simple geometry. Complete solution of governing equations is obtained by either analytical (e.g. AREST code: Apted et al., 1989) or numerical (e.g. SOTEC code: Sagar et al., 1992).
2. Comprehensive model with approximate solution: Model is based on complete and realistic picture of the system and some approximations are made to solve the governing equations (e.g. SYVAC code: AECL, 1991; STAG code: Robinson, 1992, etc.).
3. Comprehensive, coupled models with complete solution: Models simulate a system as closely as possible and numerical methods

are followed to solve the governing equations (e.g. MARNIE code: Martens et al., 1993).

4. Screening or scoping type models: Models use simple solution methods with complex geometry. Computation is fast but results are not accurate and reliable (e.g. SKB compartmental model code: Romero et al., 1991).

In fact, choice of model codes should be based on the performance assessment criteria, physical, chemical and hydro-geological conditions of specific site and waste form. Also, analytical method should be used to benchmark a numerical code which can model a more complete system.

2.9 Coupled Thermo-mechanical (TM) modeling in case of Indian granite host rock repository system: a case study

A finite difference numerical code (Goel, R. K. et al., 2003) was used for granite rocks from one of the potential site of repository to study the coupled behaviour of mechanical and thermal stresses produced by excavation and waste emplacement. The HLW canister in over packs will be emplaced in disposal holes vertically downward as shown in shown in Fig. 3. After emplacement of HLW in over packs along disposal holes, these holes as well as tunnels will be filled with bentonite buffers. A quarter symmetry model was used involving one disposal tunnel and one disposal hole section of 4m x 4m size . In this study, following sequence of simulation was adopted:

- simulation of excavation of disposal tunnel
- simulation of excavation of disposal holes
- analysis of static stability of tunnel
- disposal hole filled with waste and tunnel backfilled
- thermal loading of tunnel
- analysis of stability of tunnel

A disposal depth of 450 m was used in TM modeling along with the properties of rocks, waste pack and model parameters as shown in Tables 1&2. In the absence of actual field measurements of stress, the in-situ stress was used from the relationship established for earth's medium. The static stability of tunnel was analysed by estimation of major

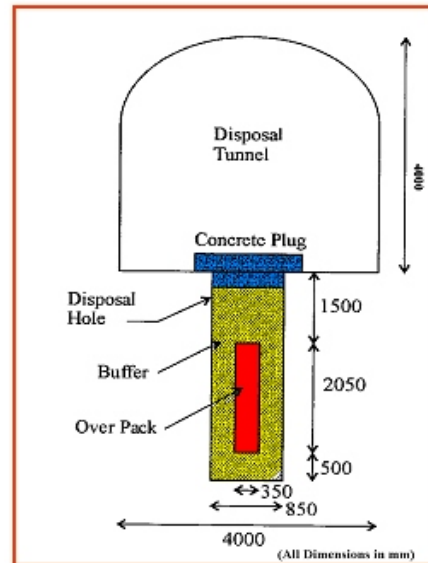


Fig. 3 Proposed vertical placement of over packs in Indian geological repository

principal stress (σ_1) and minor principal stress (σ_3) respectively. In the analysis temperature effect was initialized and continued for calculation up to 1000 years of heating. Factor of safety (i.e. failure criterion of rock) was calculated from induced stresses σ_1, σ_3 around excavation by relation:

The factor of safety model contours at different time intervals was obtained as a function of heating. It was observed that factor of safety was less than unity in the region surrounding the rim of disposal hole after 5 years of heating indicating instability and heaving phenomena whereas in first year of heating the factor of safety around tunnel was more than 1.5 indicating a stable condition. After 50 years of heating, the factor of safety was less than 1.0 in the roof indicating failure . Based on these results, the repository design modifications have been suggested. The temperature distribution profile as a function of distance and time from canister was also obtained as shown in Fig.4.

2.10 Modeling of glass alteration for assessing the long term performance of vitrified nuclear waste

Synthetic glass is considered as one of the viable option for immobilization of high level

TABLE 1. Thermal properties of rock, waste pack and model parameters

Properties	Rock	Over pack	Waste	Parameters	
Thermal conductivity (W/m °K)	3.3	0.78	1.2	Geothermal gradient	0.024°C/m
Specific heat (J/kg °K)	1000	590	960	Ground surface temperature	35°C
Co-efficient of linear thermal expansion (°C)	1.4E-05	1.0E-06	1.0E-06	Heat intensity	500 W/ over pack
				Decay constant ()	7.32496E-10 sec ⁻¹

TABLE 2. Mechanical properties of rocks

Young's modulus (GPa)	29
Poisson ratio	0.23
Rock density (kg/m ³)	2581
Uni-axial compressive strength _c (MPa)	118
Tensile strength _t (MPa)	11

nuclear waste in geological repository. To assess long-term performance of such glass, it is necessary to carry out leaching/dissolution experiment in laboratory, the results of which will validate geochemical modeling of glass alteration. It is well recognized that weathering of glass produces micro-gel layer on the surface in contact with water releasing alkali and alkaline earth cations in aqueous phase. These processes need to be quantified by experiments and model based studies. The geochemical modeling is generally performed to simulate chemical evolution of solution phase and formation of alteration product i.e. altered gel layer and mineral precipitates during glass dissolution as well as in evaluating the kinetics of glass dissolution (Munier et al., 2004). A number of geochemical model codes are available such as EQ 3/6, GLASSOL and KINDIS which could be used to study simulation of dissolution of vitrified nuclear waste glass in contact with water medium. For example, the code KINDIS was used to simulate French reference SON68 glass (French confinement matrix for light water reactor high level nuclear

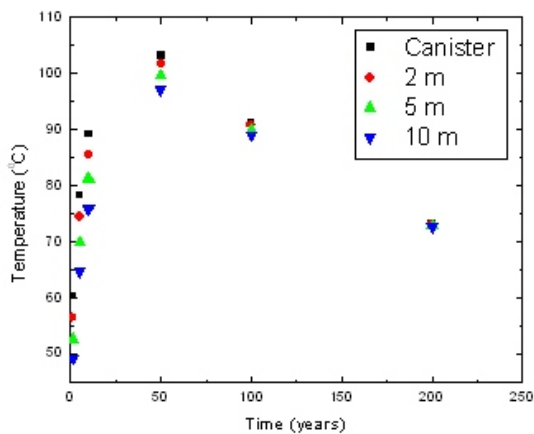


Fig. 4 Calculated temperature distribution as a function of time and distance from the disposal point in repository

waste) dissolution (Munier et al., 2004). The formation of altered layer gel composition was simulated in two model glasses (Si-Al-B-Na and Si-Al-B-Na-Ca-Zr) having the same molar ratios as that of reference glass by precipitation of an ideal solid solution and compared with alteration experiments carried out in parallel at 363K in pure water at two different S/V ratios (1 and 80 cm⁻¹) for 1-6 months period of time. By suitable selection of precipitation of end-member (amorphous silica, chalcedony or quartz and oxides, hydroxides and metasilicates), it was possible to simulate the chemical evolution of solution with respect to the experimental observation for the two model glasses. Such studies are important as they bring out relative importance of various processes such as diffusion of alkali metal ions, ion-exchange process, hydrolysis

of glass surface region and secondary mineral precipitates at different stages of glass dissolution.

3. Far-Field Environment Modeling

The far-field environment of a repository consists of sub-surface geology of area, type and nature of host rock, geo-hydrology of area such as groundwater occurrence in different types of aquifers (confined, unconfined, aquitard, fractures/fissures/joints etc.), groundwater movement and direction, groundwater chemistry and rock-water interaction, recharge and discharge of groundwater system and sorption properties for potential radionuclides (e.g. ^{90}Sr , ^{137}Cs , ^{60}Co , ^{93}Zr , ^{90}Y , etc). All these components of far-field environments are highly complex in nature and needed to be characterised during extensive site selection process while locating the site for deep geological repository. The important issues of far-field environment modeling relate to groundwater flow modeling and contaminant transport in sub-surface medium either through saturated/unsaturated porous media or through fractured network depending on geological conditions of site.

3.1 Migration and transport through saturated porous media

The mathematical model for general groundwater flow in anisotropic, heterogeneous and porous medium is represented by following partial differential equation (Freeze and Cherry, 1983):

$$\frac{\partial}{\partial x} k_x \frac{h}{x} + \frac{\partial}{\partial y} k_y \frac{h}{y} + \frac{\partial}{\partial z} k_z \frac{h}{z} - R - S_s \frac{h}{t} \quad (3)$$

Where k_x , k_y and k_z represent components of hydraulic conductivities of aquifer in x, y and z direction respectively, h the hydraulic head (discharge potential), R the source/sink term and S_s is the specific storage of aquifer (i.e. volume of water released from storage per unit change in head per unit volume of porous material). The source could be recharge rate (volume of water added per unit time per unit area of aquifer) and sink could be rate of water withdrawal such as pumping rate (volume of water removed per unit time per unit area of aquifer). In Eqn. (1), the term under parenthesis is Darcy

velocity or specific discharge in x, y and z directions respectively.

Similarly, the general governing equation for dissolved solute transport in groundwater along x-axis is advection-dispersion equation given by (Anderson and Woessner, 2002):

$$\frac{\partial}{\partial x} D_x \frac{C}{x} + \frac{\partial}{\partial y} D_y \frac{C}{y} + \frac{\partial}{\partial z} D_z \frac{C}{z} - v \frac{C}{x} - C.R_d - R - R_d \frac{C}{t} \quad (4)$$

Where C is solute concentration (ML^{-3}), D_x , D_y and D_z the three components of dispersion co-efficient (L^2T^{-1}), v the groundwater velocity in x- direction (LT^{-1}), the decay constant of radionuclide (T^{-1}), R the source/sink term ($\text{ML}^{-2}\text{T}^{-1}$) and R_d is the retardation factor of solute (i.e. sorption on aquifer). The retardation factor R_d is defined by:

$$R_d = \frac{V_w}{V_c} + 1 + \frac{k_d \cdot b}{\phi} \quad (5)$$

Where V_w is linear groundwater velocity, V_c is the velocity of solute, k_d is the distribution co-efficient, b is the bulk density of aquifer and ϕ is the porosity.

Both the governing equations (3 & 4) of groundwater flow and solute transport are solved by either analytical or numerical methods with proper initial and boundary conditions and also with suitable aquifer and source geometry representing more or less actual field conditions. The solution of Eqn. (3) will provide spatial and temporal distribution of groundwater head and Eqn. (4) will provide distribution of solute concentration as a function of time and space in groundwater system. Modeling groundwater flow and contaminant transport in far-field region is a vast topic of research and requires separate treatment which is beyond the scope of this article. Now-a-days, due to availability of fast computers, numerical method is generally followed to solve the above equations. Also, numerical methods can be applied in case of complex system of aquifers which is not possible with the analytical methods. The most widely used numerical methods are Finite Difference Method (FDM) and Finite Element Method (FEM). All these methods have their own advantages and disadvantages with respect to cost, user friendliness

and required knowledge of user. The commonly used commercial numerical code for groundwater flow model is MODFLOW which is a 3-D model originally developed by U. S. Geological Survey (McDonald and Harbaugh, 1988). The list of other commercially available software codes is very long (Kumar, 2006) however, to name a few are FEFLOW (Finite element package for 3-D and 2-D simulation of flow in saturated/unsaturated zones), GMS (comprehensive code for groundwater simulation, model development, calibration, post-processing and visualization, supports Finite difference and Finite element models and contaminant transport), FLOWNET/TRANS (2-D cross-sectional flow and transport using FEM), MT3D (comprehensive 3-D numerical model for solute transport in complex hydro-geologic settings), Visual Groundwater (3-D visualization and animation of site data and modeling results) and Visual MODFLOW (integrated modeling environment using MODFLOW, MODPATH and MT3D).

3.2 Fracture flow modeling

The worldwide consensus is to emplace high level nuclear waste in crystalline rocks such as granite, basalt or volcanic tuffs. These rock formations are often encountered with fractures, fissures and joints which form groundwater conduits for movement. In such environment, modeling for groundwater flow and contaminant transport requires approach other than conventional porous media approach. However, the Darcy law of fluid flow is still applicable in fracture systems. The fractured rock systems flow is generally modeled using one or more of the conceptual models such as: (a) equivalent porous medium; (b) discrete fractures and (c) dual porosity. For detailed description of each of these models reference is made to Thangrajan (2000); Anderson and Woessner (2002). The data needed to model flow through fractured rock media are fracture location, fracture apertures, fracture intensity and fracture orientation in addition to site pumping test data such as transmissivity (T) and storativity (S). Because of limited data by direct observation of fracture properties from few borehole logs and few from indirect geophysical surface surveys, statistical treatment of data are needed to be done to arrive at values that would represent broader

scale of modeling. Some of the commercially available software computer codes applicable for fracture flow are (Thangrajan 2000): (a) NAPSAC; (b) FracMan; (c) Frac3 DVS, and (d) FEFLOW. The contaminant transport models sometimes have to involve geochemical modeling for aqueous speciation of metals and radicals, mineral equilibria, surface complexation etc. for which the most widely used code is PHREEQC (Parkhurst and Appelo, 1999). Integrated modeling approach is required to understand natural as well as induced hydro-geological conditions of repository as a function of time and distance due to waste disposal in deep geological environment.

4. Biospheric Transport Modeling

The other important issue of repository processes is biospheric modeling, the input of which is derived from the geo-spherical i.e. far-field modeling. Such modeling is required for post-closure long-term performance assessment of radioactive waste disposal in repository. For biosphere models following points are important (Smith, 1989):

- estimation of annual individual dose of potential radionuclides to man (i.e. critical group)
- estimation of arrival of time and distance of dose
- estimation of annual individual risk to members of critical group
- estimation of dose rates to biota
- assessment of non-radiological environmental impacts of radioactive waste disposal

In biosphere modeling, the accumulation and uptake of potential radionuclides in each compartment (such as atmosphere, sediments, groundwater, seawater etc.) is calculated which is finally converted in dose form by suitable multiplication factor involving consumption rate and dose conversion factor for ingestion, inhalation and exposure pathways. Examples of such models are BIOMOV5 (1991, 1994) and recently developed code such as AMBER (AMBER5, 2006). In Indian scenario, biosphere model calculation has been done for safety assessment of Near-surface waste disposal facilities, NSDF (Rakesh et al., 2004 & 2007). The concept, philosophy and approach remain the same

for deep geological repository, as applicable to NSDF.

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