

PRESENT PRACTICES AND INNOVATIVE TREATMENTS DEVELOPED IN SOLID AND LIQUID WASTE MANAGEMENT IN INDIA

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ABSTRACT

The nuclear program in India encompasses the entire nuclear fuel cycle. This paper briefly mentions the current waste management practices and various developmental activities in progress in India. The innovative treatments under development are in the following areas of waste management:

- copper hexacyanoferrate and phenol-formaldehyde based sorbents for the removal of cesium and strontium from low and intermediate level wastes
- improved slag containing cement formulations for the fixation of intermediate level wastes
- wet oxidative destruction of spent ion exchange resins with hydrogen peroxide
- Solvent extraction of actinides from high level liquid wastes
- ceramic melter for the vitrification of high level liquid wastes.

These processes are at various stages of development and after pilot scale demonstration, appropriate changes in the waste management practice will be incorporated.

INTRODUCTION

It is recognized that the success of a nuclear program depends on the safe management of various types of radioactive wastes generated by the nuclear facilities in such a manner as to ensure minimum long term effects to the members of the public and the environment. The Indian waste management policy and program lays emphasis upon demonstrating that all radioactive wastes can be safely isolated for the required period of time from man and the environment in order to meet the above objective. Atomic Energy (Safe Disposal of Radioactive Wastes) Rules promulgated by the Government of India in 1987 stipulates the guidelines for the safe management of nuclear wastes in the country. All waste management operations are governed by these guidelines and are in conformity with the general principles of radiation protection as formulated by ICRP from time to time.

THE INDIAN NUCLEAR WASTE MANAGEMENT POLICY AND PROGRAM

The nuclear program in India includes facilities like uranium mining, milling, fuel fabrication, nuclear power production, spent fuel reprocessing and waste immobilization. In a highly populated and developing country like India where there exist logistical transportation and infrastructural constraints, a decision has been taken at the National level to set up nuclear facilities at different locations, notwithstanding certain economic penalties and increased surveillance commitments. Therefore, as a matter of policy, the management of radioactive wastes is carried out at the site where waste is generated to avoid transshipment of these wastes. Because of widely varying environmental features at different nuclear sites, different norms had to be adopted after evaluating the specific characteristics of each site from the point of view of discharge of radioactivity to the environment as well as containment of wastes that cannot be discharged.

CURRENT PROCESSES AND ADVANCEMENTS

Liquid Wastes

Nuclear facilities generate large quantities of low level liquid wastes (LLW) which need segregation at source. Chemical treatment and ion exchange are the processes that are being currently practiced for treatment of low level waste effluents.

Intermediate level liquid wastes (ILW) are generated during the operation of power reactors and spent fuel reprocessing plants. Wastes from reprocessing plants are alkaline in nature and are characterized by high salt content and specific activity levels of up to 3700 MBq/L. They are stored in underground carbon steel tanks located in specially designed concrete storage vaults. Such wastes are subjected to immobilization using bitumen. A bituminization plant is operational at the Waste Immobilization Plant (WIP) at Tarapur (1). Cementation process as an alternative to bituminization has been investigated (2). Improvements in the leach resistance of cement-waste matrix and other desirable characteristics have been achieved using blended cements with additives. Table I summarizes the characteristic properties of this improved cement matrix. The leach rates observed for these products containing actual ILW are of the order of $7 \times 10^{-6} \text{ g.cm}^{-2}.\text{d}^{-1}$. The cumulative percentage of activity released over a period of about 2 years was seen to be as low as 0.14% only. The improved cementation process is planned to be adopted in future for immobilization of these ILW effluents.

India has two fuel reprocessing plants which are operational. The high level liquid waste (HLW) generated from these plants are acidic in nature and are stored in underground stainless steel tanks located in specially designed concrete vaults. R&D work on the immobilization of this waste in alkali borosilicate matrix was started in the late sixties and several useful glass formulations were identified for adoption in WIP at Tarapur. It is planned to store the vitrified high level waste in stainless steel containers in air-cooled vaults for an interim period of 20 to 30 years before their ultimate disposal

TABLE I
Properties of Cement Waste Forms

	Blended Cement	OPC
Waste/cement ratio	0.48	0.48
Macropore volume (cm ³ /g)	0.008	0.065
Setting time (minutes)	212	330
Fluidity index	252	140
Compressive strength (kg/cm ²)	355	125

in a deep geological repository. Efforts are already on to identify suitable repositories in the country for this purpose.

Solid Wastes

Volumes of low active solid wastes generated by nuclear facilities are very high. Segregation, compaction and incineration are the practices followed for handling such wastes. After appropriate conditioning, disposal of low level solid wastes is done in shallow land repositories having institutional control. In addition to conditioning of the wastes, intrusion barriers and chemical barriers in the form of backfill are incorporated in the disposal system.

The containment adopted at shallow land repository consists of earth trenches, reinforced concrete trenches and specially engineered "tile-holes".

Chemical sludges, spent ion exchange resins and incinerator ash form the bulk of the intermediate level solid waste. Chemical sludges are dewatered, immobilized in cement in standard drums and are disposed of in RC trenches. Other assorted solid wastes are conditioned and packaged before disposal in RC trenches or tile-holes. Spent ion exchange resins are temporarily stored either in specially designed stainless steel lined concrete vaults or in steel lined concrete tile-holes depending upon the activity content. Based on the extensive R & D work carried out on the fixation of spent resins in polymer matrices, a resin fixation plant based on polyester styrene as the immobilization matrix has been commissioned at the reactor waste management site, Narora.

INNOVATIVE APPROACHES

In view of the new challenges posed by environmental and regulatory concerns, considerable stress is laid by various countries for the development of improved treatment and conditioning processes for radioactive wastes. Some of the developmental work carried out by us in this direction is briefly mentioned below:

Removal of Cs and Sr from Low Level Liquid Wastes

Methods based on the sorption of these radionuclides on inorganic ion exchangers have been evaluated. Following published information (3, 4), procedures for preparing bulk quantities of copper hexacyanoferrate impregnated organic anion exchange resin and synthetic zeolite have been standardized. These materials along with other samples of zeolite have been tested on laboratory scale using actual LLW solutions. Results are given in Table II. It may be seen from the Table that materials impregnated with copper hexacyanoferrate and the locally available Zeolite AR-1 seem to be effective in remov-

TABLE II
Removal of Cesium and Strontium from Low Level Waste Solution by Various Sorbents

Feed			
Dissolved solids		550 mg/L	
pH		9.5	
Activity		3.7 to 37 kBq/L (¹³⁷ Cs + ¹³⁴ Cs/ ⁹⁰ Sr + ⁸⁵ Sr)	
Sorbent			
Particle size		0.3 to 1.2 mm	
Bed diameter		1.2 cm	
Bed volume (BV)		5 mL	
S.No. Sorbent	Bed volume passed	Flow rate (BV/hr)	Cumulative DF
Part A : Cesium			
1. R.-CuF ^a	2600	18 -20	63
2. MS-AR1 ^b	"	"	166
3. MS-13X ^c	"	"	1.4
4. MS-13X-CuF ^d	"	"	200
Part B : Strontium			
1. T-42 ^e	1100	8 -10	4.5
2. MS-4A ^f	"	"	11.2
3. MS4A + AR1 ^g		"	4.8

^acopper hexacyanoferrate impregnated anion exchange resin

^bsynthetic zeolite of Indian origin containing mordenite

^csynthetic zeolite of Indian origin containing faujasite

^dMS-13X impregnated with copperhexacyanoferrate

^estrongly acidic sulfonic acid resin

^fsynthetic A-type zeolite of Indian origin

^ga 1:1 mixture of MS-4A and MS-AR1.

ing cesium from LLW solutions having a pH of 9.5. The locally available Zeolite 4A is found to be suitable for the removal of strontium from the solution.

The impregnated material R.-CuF has been subjected to further investigation with respect to cesium uptake in the presence of acid and salts and also pilot scale testing with actual LLW solutions. Results of this investigation have been published elsewhere (5). Results of pilot scale experiment are reproduced in Table III. It may be seen from the Table that decontamination factors (DF) in the range of 15 to 120 were obtained. A more clearer indication of the effectiveness of the system comes from the dose build-up at the top of the column. After a throughput of 994L, the dose had gone up to 77×10^{-4} mCi/kg/hr equivalent to 30 mR/hr. Further increase was small because of the decreased feed activity. At the time of termination of the run, the dose was 90×10^{-4} (35 mR/hr) indicating that the column had effectively removed all the cesium activity from 3400L of LLW. This material has also been tested for the removal of cesium from spent fuel storage pond water. Results show that a DF of about 1000 is obtainable using this resin. Efforts are underway to carry out tests on these sorbents on

TABLE III

Pilot Scale Removal of Cesium from Low Level Waste^a

<u>Feed</u>			
Dissolved solids		700 to 1400 mg/L	
pH		9 to 9.5	
Flow rate		10 BV/hr	
<u>Sorbent</u>			
Resin		R-CuF	
Particle size		0.3 to 1.2mm	
Bed diameter		10 cm	
Bed volume (BV)		7 L	
Volume (L)	Gamma activity (kBq/L)		Dose on the top of the column (mCi/kg/hr x 10 ⁻⁴)
	Feed	Effluent	
10	15.5	0.13	10
142	9.6	0.10	10
994	1.5	0.10	77
1250	0.9	0.04	77
2100	0.6	0.04	83
3266	0.7	0.04	85
3400	Column operation terminated		90
^a Taken from reference (5)			

larger scale and establish their potential for application on treatment of low level radioactive wastes from different sources. These sorbents are likely to replace the chemical precipitation process currently practiced for the treatment of LLW solutions.

Removal of Cs and Sr from Intermediate Level Liquid Waste

An alternative approach based on the selective removal of cesium and strontium nuclides from ILW streams was investigated. From the known behavior of the variety of sorbents available commercially, phenol-formaldehyde polycondensate resins were identified as the ones capable of giving adequate decontamination of above radionuclides from alkaline salted solutions. These resins containing different combination of phenolic compounds, such as phenol, resorcinol, catechol and gallic acid, with formaldehyde were synthesized under various conditions and their ion exchange characteristics evaluated (6, 7). Among the resins synthesized, the resorcinol-formaldehyde polycondensates gave the highest distribution coefficient (K_d) values of 16000 to 19000 for Cs from a test solution of 1.0M NaNO₃ + 0.1M NaOH. In regard to Sr, high K_d values in the range of 4000 - 7000 were obtained under similar conditions using catechol and gallic acid resins.

The utility of resorcinol-formaldehyde resin was tested with a sample of actual ILW from a reprocessing plant (salt content, 19.5%; ¹³⁷Cs, 54MBq/L) and cesium from 77L of this waste was effectively removed using a 0.45 L bed at a DF of

about 2000. Moreover, it was also possible to elute the loaded cesium quantitatively using a small volume of formic acid. Similar testing of catechol and gallic acid based resins with respect to Sr nuclides are underway.

Based on these developments, a treatment scheme can be envisaged for the removal of cesium and strontium from alkaline ILW. The loaded activities can be eluted into a small volume of acid which can be treated as high level waste whereas the largely decontaminated effluent can be handled as low level waste.

Wet Oxidation of Spent Ion Exchange Resins

A catalytic low temperature wet oxidation process for the destruction of spent ion exchange resins has undergone detailed study. Results of laboratory scale study are presented in Table IV. It may be seen from the Table that both cation and anion exchange resins can be fully oxidized to CO₂ and water at a low temperature of about 100°C using H₂O₂. Efforts are on to test this process on kilogram scale. The residual solution after oxidation of the resin contains all the radioactivity originally present in the resin. Synthetic zeolites have been tested for the removal of cesium from simulated waste solutions and have been found to give DF of the order of about 100. Laboratory studies have indicated that it will be possible to remove the major radionuclides such as cesium or cobalt from the solution such that the effluent can be qualified as low level waste. Alternatively, the resin solution can be evaporated to a low volume and immobilized in a suitable matrix. The wet oxidation process is expected to give high volume reduction factor and may turn out to be a potential alternative to the polymer fixation process.

Wet oxidation process for the destruction of TBP in the spent solvent and recovery of the diluent for possible reuse is being actively pursued.

Ceramic Melter for the Vitrification of High Level Wastes

It has been established that joule-heated ceramic melter has several advantages. Its amenability for continuous operation is a main feature well-suited for plants of larger throughputs. After the initial study in a proto-type model, work is in progress now for setting up an engineering scale facility.

Removal of Transuranics from High Level Wastes

High level liquid wastes from spent fuel reprocessing plants contain toxic transuranic elements. Separation and transmutation of transuranics recovered from these wastes will be an advantageous proposition both from the point of view of disposal criteria and public acceptance. We have, therefore, embarked on experimental studies on the removal of transuranics from HLW solutions. Tributyl phosphate in n-dodecane diluent and octyl (phenyl)-N, N-diisobutyl carbamoyl methyl phosphine oxide (CMPO) in TBP have been investigated for this purpose. Multistage counter-current experiments using TBP-dodecane extractant showed that use of salting out agents such as aluminium nitrate, sodium nitrate and ferric nitrate are required to obtain satisfactory K_d values for transuranics. The concentrations of salting out agents were so adjusted that the resulting raffinates could be vitrified to produce durable glass.

Similar studies were carried out on the uptake of actinides from a sample of actual high active waste solution using a mixture of 0.2M CMPO and 1.2M TBP in dodecane at 1:1 ratio (8). About 99.8% of the alpha activities could be

TABLE IV
Wet Oxidation of Organic Ion Exchange Resins

Resin weight	:2g (100 g) ^a					
Temperature	:95-100°C					
Volume of CuSO ₄ taken	:10 mL (200mL) ^a					
Concentration of H ₂ O ₂ used	:35% by weight					
Resin Type	Conc. of CuSO ₄ (M)	H ₂ O ₂ flow rate (mL/min)	pH of residual solution	Volume of H ₂ O ₂ consumed for		
				50% oxidation	75% oxidation	100% oxidation
Cation	0.001	0.75	1.5-2.5	9.5	13.5	21.5
	0.01	0.75	"	9.5	13.5	21.0
	0.01	0.25	"	9.0	13.0	21.0
	0.01	1.25	"	9.0	13.0	21.0
Anion	0.001	0.25	5-6	25.0	37.5	50.0
	0.005	"	"	20.0	28.0	45.0
	0.01	"	"	16.0	21.0	30.0
	0.01	0.8	"	20.0	26.0	40.0
	0.01	1.35	"	22.0	28.5	45.0
^a Mixed bed	0.01	12.5	2.5	-	-	1500

removed in two stages from the waste solution. It was also observed that cerium and other rare earth metal ions (e.g. Pm, Eu) exhibited the same behaviour as that of americium. In the case of high level waste solution, a pre-extraction step with 30% TBP - dodecane to deplete the uranium content in the feed was found to be advantageous. This pre-extraction step was followed by transuranics extraction in four stages by 0.2M CMPO + 1.4M TBP in dodecane. This two step process was found to give a raffinate having about 0.03% of the initial alpha activity (Table V). It was also found possible to recover all the

actinides as a group by stripping the extractant by oxalic acid solution.

CONCLUSIONS

In order to meet the challenges posed by growing concern on the hazards of radioactive wastes, improved treatment and conditioning processes have to be developed. special selective sorbents developed in this study are an improvement in this direction. Peroxide-based oxidative destruction of ion exchange resins is promising and is expected to result in large

TABLE V
Extraction of Alpha Activities From High Level Waste Solution^a

Feed acidity	: ~3M HNO ₃			Contact time:	5 minutes
Extractant	: 0.2M CMPO + 1.4M TBP in dodecane;			Temperature:	25°C
Sample stream	Total	Alpha activity (kBq/mL)		Aq:Org	
		Pu	Am (+ Cm)		
Raffinate of TBP contact	467	19.6	447		
Loaded CMPO (first contact)	217	9.1	207	1:2	
Raffinate	21.1	0.4	21		
Loaded CMPO (second contact)	16.4	0.3	16.1	1:1	
Raffinate	1.68	0.01	1.67		
Loaded CMPO (third contact)	1.38	0.01	1.37	1:1	
Raffinate	0.54	-	0.54		
Loaded CMPO (fourth contact)	0.42	-	0.42	1:1	
Raffinate	0.15	-	0.15		
^a Taken from reference (8)					

volume reduction and environmentally acceptable waste form for storage. Improved cement matrix seems to have the potential to act as a strong barrier against accidental release of radioactivity to the environment. Mixtures of CMPO and TBP seem to be capable of reducing significantly the radiotoxicity of actinides associated with high level liquid wastes. Successful pilot scale demonstrations of these processes are required before their incorporation into the waste management system.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to Mr. M. K. T. Nair, Mr. S. V. Kumar and Mr. T. K. Theyyuni for guidance and encouragement. Thanks are also due to Ms. C. Varghese, Mr. D. S. Deshingkar, Mr. C. Srinivas, Mr. R. R. Chitnis, Ms. Savita Jain, Ms. M. K. Thomas and Ms. M. A. Rao for their contribution towards the making of this manuscript.

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