



Treatment of low level radioactive liquid waste containing appreciable concentration of TBP degraded products

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ABSTRACT

The acidic and alkaline low level radioactive liquid waste (LLW) generated during the concentration of high level radioactive liquid waste (HLW) prior to vitrification and ion exchange treatment of intermediate level radioactive liquid waste (ILW), respectively are decontaminated by chemical co-precipitation before discharge to the environment. LLW stream generated from the ion exchange treatment of ILW contained high concentrations of carbonates, tributyl phosphate (TBP) degraded products and problematic radio nuclides like ^{106}Ru and ^{99}Tc . Presence of TBP degraded products was interfering with the co-precipitation process. In view of this a modified chemical treatment scheme was formulated for the treatment of this waste stream. By mixing the acidic LLW and alkaline LLW, the carbonates in the alkaline LLW were destroyed and the TBP degraded products got separated as a layer at the top of the vessel. By making use of the modified co-precipitation process the effluent stream ($1\text{--}2\ \mu\text{Ci/L}$) became dischargeable to the environment after appropriate dilution. Based on the lab scale studies about $250\ \text{m}^3$ of LLW was treated in the plant. The higher activity of the TBP degraded products separated was due to short lived ^{90}Y isotope. The cement waste product prepared using the TBP degraded product was having good chemical durability and compressive strength.

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1. Introduction

Classification of waste is very important from safety as well as process consideration point of view. In India apart from IAEA categorization, the radioactive liquid waste is broadly classified into three categories based on the radioactivity concentrations, low ($<1\ \text{mCi/L}$), intermediate ($1\ \text{mCi/L}\text{--}1\ \text{Ci/L}$) and high level ($>1\ \text{Ci/L}$) waste [1]. As a waste management practice, vitrification, ion exchange treatment and chemical co-precipitation are the conditioning processes adopted for high, intermediate and low level waste, respectively with the objective of safeguarding the health of present and future generations [2].

Reprocessing of spent fuel from reactor generates broadly two categories of radioactive liquid waste streams viz high level liquid waste (HLW) and intermediate level radioactive liquid waste (ILW). HLW in acidic conditions is stored in stainless steel tanks. Vitrification process based on sodium borosilicate glass matrix [3,4] has been accepted and adopted for immobilisation of HLW using induction heated metallic melter and joule heated ceramic melter at Trombay and Tarapur, respectively [5]. Prior to vitrification, the HLW is concentrated with respect to salt content and activity.

During the concentration operation of HLW, nitric acid is recovered through fractionator and subsequently the off gases are condensed to collect as condensate stream. The condensates obtained during concentration operation have activity in the range of LLW. Major radionuclides present in this stream are ^{137}Cs , ^{90}Sr , ^{125}Sb and ^{106}Ru .

ILW is generated during U/Pu purification cycles and waste evaporation in PUREX process flow sheet. At Tarapur site this ILW is made alkaline using sodium carbonate and sodium hydroxide prior to storage in carbon steel tanks. This IL radioactive liquid waste contains carbonates and large amount of salts. It also contains radiation degradation products of TBP like Na-dibutyl phosphate, Na-monobutyl phosphate etc. Major radionuclide present in this stream is ^{137}Cs . Other radio nuclides present are ^{90}Sr , ^{106}Ru , ^{125}Sb , ^{99}Tc and trace concentration of actinides. A treatment process using resorcinol formaldehyde polycondensate (RF) resin with iminodiacetic chelating group is followed for the effective removal of Cs and Sr from this ILW at Tarapur [6,7]. The alkaline effluent from the RF column is LLW in nature and has high salt content mainly in the form of sodium nitrate. Carbonates and TBP degraded products are getting removed during the pretreatment step prior to ion exchange. The effluent comprises of small amount of ^{137}Cs , ^{90}Sr , ^{125}Sb , ^{106}Ru and ^{99}Tc which are not retained by the RF column.

LLW generated from the concentration operation of HLW and ion exchange treatment of ILW are managed by chemical co-precipitation [8]. The radio nuclides in the LLW are removed from

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Table 1
Characteristic of the low level radioactive liquid waste.

Sr. No.	Property	LLW from IX process	Condensate LLW from concentration of HLW	MW (1:1 mixing)
1	Colour	Yellow	Colourless	Pale yellow
2	pH	12.5	0.43M acidic	<1
3	TBP degraded products as DBP, g/l	1.8	BDL	NA
4	Gross β (mCi/L)	0.20	0.43	0.30
4	Gross α (mCi/L)	5×10^{-3}	BDL	2.0×10^{-4}
Isotopic constituents				
5	^{137}Cs (mCi/L)	0.12	0.18	0.14
6	^{134}Cs (mCi/L)	5×10^{-4}	8×10^{-3}	4.1×10^{-3}
7	^{90}Sr - ^{90}Y (mCi/L)	2×10^{-3}	0.25	0.11
8	^{106}Ru (mCi/L)	7.5×10^{-3}	4×10^{-2}	2.1×10^{-2}
9	^{125}Sb (mCi/L)	1.5×10^{-3}	2.86×10^{-3}	2.0×10^{-3}
10	^{99}Tc (mCi/L)	5.1×10^{-2}	BDL	2.4×10^{-2}
11	^{154}Eu (mCi/L)	BDL	3.04×10^{-4}	BDL
Elemental analysis				
12	Sodium (g/L)	56	0.10	28
13	Uranium (g/L)	1.8	0.05	0.85

BDL, below detection limit; NA, not analysed. Minimum detectable conc. for $\beta = 3 \times 10^{-5}$ mCi/L and for $\alpha = 5 \times 10^{-6}$ mCi/L.

the bulk solution as sludge by co-precipitation or adsorption, using insoluble compounds like hydroxides, sulphate, phosphates and ferrocyanides [9]. Subsequent to precipitation, liquid phase is discharged after providing necessary dilution, in order to meet the regulatory limits for radioactive discharge. The sludge containing bulk of the radioactivity is conditioned by immobilizing in cement matrix before disposal. Fig. 1 shows the schematics for this process.

Presently a modified flow sheet has been adopted for this process of ILW where the pretreatment step is avoided to improve the processing capacity of the plant [10]. In addition to high salt content the effluent LLW from this process have carbonates, degraded TBP products and relatively high concentrations of ^{106}Ru and ^{99}Tc . The presence of carbonates and TBP degraded products caused interference in the chemical co-precipitation process during the effective removal of radionuclides.

The present study details the formulation of a modified chemical treatment scheme for the LLW, containing carbonates, TBP degraded products and relatively higher concentrations of ^{106}Ru and ^{99}Tc . The performance of this modified scheme in the plant scale treatment of about 250 m³ of LLW was also assessed. Conditioning of the separated TBP degraded products in cement matrix was also studied.

2. Experimental

2.1. Material

As this chemical treatment method is to be adopted on plant scale, all the chemicals used for the treatment process were of

technical grade. All experiments were carried out in triplicate and the average values are presented.

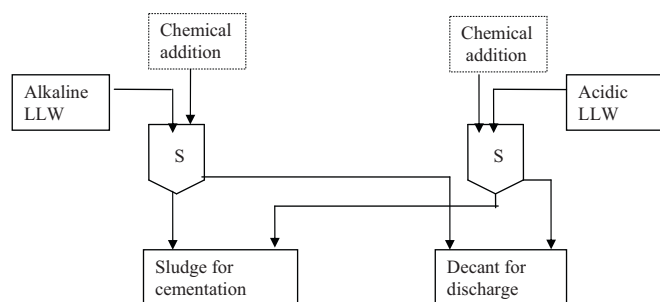
2.2. Characterization of the radioactive waste

The LLW streams generated from concentration cycle of the HLW and from modified ion exchange treatment process of ILW were characterized for radiochemical nature and isotopic constituents. The values are given in Table 1. The activity spectrum of the waste streams was determined using GM counter (Nucleonix, GM tube 72314) for gross β , ZnS detector based scintillation counter (Para Electronics Pvt. Ltd. India) for gross α and HPGe detector coupled with 4K MCA (GMBh Germany) for γ - spectrum. Na was analysed using flame photometer (Elico CL361). U and Fe were analysed by ammonium thiocyanate method at wavelengths 360 nm and 565 nm, respectively [11] using spectrophotometer (Chemito, UV2600).

The acidic and alkaline LLW streams were mixed to get pH <2 and kept for 5–6 h to separate the TBP degraded products. The characteristics of this mixed waste stream (MW) are also given in Table 1. The MW was further taken up for its treatment using chemical co-precipitation for removal of various radionuclides.

2.3. Lab scale co-precipitation experiments

Large numbers of co-precipitation experiments were carried out with the MW. Various combinations and concentrations of the precipitating chemicals were tried. The optimum chemical combination and concentration selected for further studies is given in Table 2. All the experiments were performed on 25 ml batch size.



S - MS Settlers

Fig. 1. Schematics for chemical co-precipitation of alkaline and acidic LLW.

Table 2
Concentration and sequence of chemicals for 1st and 2nd step treatment.

Chemicals added	Concentration (ppm)	
	1st step	2nd step
Initial pH	2.0	–
Na ₂ SO ₃	1260	–
Fe ²⁺ as Fe(SO ₄) ₇ ·H ₂ O	600	300
(PO ₄) ₃ [–] as Na ₃ (PO ₄) ₁₂ ·H ₂ O	–	400
S ^{2–} as Na ₂ S	300	–
NaOH to adjust pH to	7–7.5	–
Cu ²⁺ as CuSO ₄ ·5H ₂ O	40	–
[Fe(CN) ₆] ^{4–} as K ₄ Fe(CN) ₆ ·3H ₂ O	60	–
Ba ²⁺ as BaCl ₂	400	800
Fe ³⁺ as Fe(NO ₃) ₃ ·9H ₂ O	150	100
NaOH to adjust pH to	7–7.5	9.5–10

Table 3
DF obtained in lab scale chemical co-precipitation of MW.

Properties	Initial values	With organics			Without organics		
		1st step	2nd step	DF	1st step	2nd step	DF
pH	<1	7–7.5	9.5–10		7–7.5	9.5–10	
Gross β (mCi/L)	0.30	1.6×10^{-2}	8.5×10^{-3}	35	5.6×10^{-3}	1.5×10^{-3}	200
Gross α (mCi/L)	2.0×10^{-4}	BDL	BDL	50	BDL	BDL	50
^{137}Cs (mCi/L)	0.14	4.5×10^{-4}	1.5×10^{-4}	1000	2.6×10^{-4}	3.1×10^{-5}	5000
^{106}Ru (mCi/L)	2.1×10^{-2}	8.6×10^{-3}	6.8×10^{-3}	7	1.1×10^{-3}	6.5×10^{-4}	40
^{125}Sb (mCi/L)	2.0×10^{-3}	4.2×10^{-4}	BDL	220	BDL	BDL	220
^{90}Sr – ^{90}Y (mCi/L)	0.11	6.3×10^{-3}	1.1×10^{-3}	120	2.8×10^{-3}	6.1×10^{-4}	215
^{99}Tc (mCi/L)	2.4×10^{-2}	1.4×10^{-3}	3.2×10^{-4}	80	4.8×10^{-4}	1.4×10^{-4}	185

BDL, below detection limit. Minimum detectable conc. for $\beta = 3 \times 10^{-5}$ mCi/L and for $\alpha = 5 \times 10^{-6}$ mCi/L.

Table 4
DF obtained in plant scale chemical co-precipitation of MW (average of 10 batches).

	Initial activity of MW	Activity and DF after two step chemical treatment			
		1st step	DF	2nd step	Overall DF
pH	<1	7–7.5		9.5–10	
Gross β (mCi/L)	0.38	4.2×10^{-3}	90	1.6×10^{-3}	238
Gross α (mCi/L)	2.5×10^{-4}	BDL	50	BDL	50
^{137}Cs (mCi/L)	0.11	3.3×10^{-4}	333	5.4×10^{-5}	2040
^{106}Ru (mCi/L)	9.2×10^{-2}	1.0×10^{-3}	92	6.6×10^{-4}	140
^{125}Sb (mCi/L)	1.8×10^{-3}	BDL	180	BDL	180
^{90}Sr – ^{90}Y (mCi/L)	0.12	2.1×10^{-3}	57	5.2×10^{-4}	230
^{99}Tc (mCi/L)	2.6×10^{-2}	4.8×10^{-4}	54	1.2×10^{-4}	216

BDL, below detection limit. Minimum detectable conc. for $\beta = 3 \times 10^{-5}$ mCi/L and for $\alpha = 5 \times 10^{-6}$ mCi/L.

To see the effect of the TBP degraded products on the co-precipitation of radionuclides from the MW two different sets of experiments were carried out. For the first step chemical precipitation, 25 ml of the clear decant of the MW with out any organic content was taken in a beaker. Similarly in another beaker 25 ml of the MW was taken after mixing the solution thoroughly with separated organic mass. Required concentrations of the chemicals were then added in the sequence as given in Table 2 step-1. During addition of each chemical the content was mixed thoroughly using magnetic stirrer. The pH of the solution was adjusted to 7–7.5 using NaOH solution. After complete settling of the sludge the activity spectrum of the clear decants was determined and the decontamination factor (DF) was calculated using the equation:

$$DF = \frac{A_i}{A_f} \quad (1)$$

where A_i and A_f are the initial and final specific activity (activity per volume), respectively.

For the second step precipitation, the clear decant from the first step was given chemical treatment as per the scheme given in Table 2 step-2. The pH of the final solution was adjusted to 9.5–10 using NaOH solution. Here also the activity spectrum of the clear decants was determined and the DF was calculated. The DF values achieved in both steps are given in Table 3.

2.4. Plant scale chemical treatment

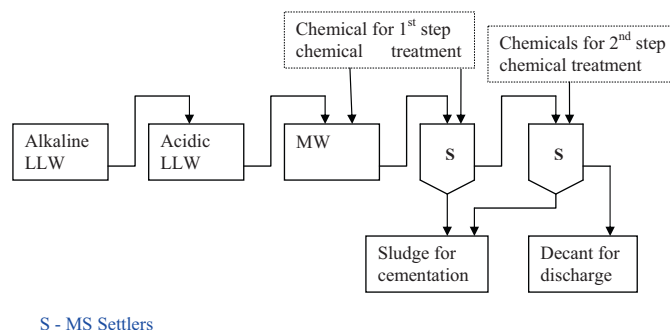
Based on the lab scale treatment results, about 250 m³ of MW was treated in the plant. The batch size of the plant scale treatments was 12 m³. Acidic LLW was mixed with alkaline LLW in a SS tank till pH 1–2 was obtained and kept for about 5–6 h. The degraded products of TBP got separated and were floating on the top of the tank. The clear decant below the organic layer was transferred to another SS tank and chemicals such as Na₂SO₃, FeSO₄ and Na₂S as given in Table 2 step1 were added and pH was adjusted to 7. The total mass was then transferred to a MS settler and remaining chemicals for first step treatment were added and allowed to settle overnight. During the addition of chemicals thorough mixing was

done by recirculation. The decant solution was analysed for activity spectrum and was transferred to another MS settler. There, chemicals for second step treatment as given in Table 2 step 2 were added and allowed to settle overnight. Decant was analysed for activity spectrum and DF was calculated. The details are given in Table 4. The schematic for this MW treatment in plant scale is given in Fig. 2.

Further batches of treatment were carried out in the same tanks and settlers without removing the organic mass/sludge from them. This was based on the lab scale multiple batch precipitation studies (Table 5). After about 10 batch treatment the sludge from the settlers was cleared and fresh batches were received. However in the carbonate destruction tank the organic mass was removed only after completing the treatment campaign of the LLW from the particulate waste storage tank.

2.5. Analysis of the organic mass separated

Solubility of the separated organic mass in acid and alkali medium were tried. The clear decant of the alkali dissolved solution was analysed. The reddish precipitate of ferric hydroxide was dissolved in acid and analysed. The activity spectrum of the organic mass calculated from these analysis are presented in Table 6.



S - MS Settlers

Fig. 2. Schematics for plant scale treatment of MW.

Table 5
DF obtained during lab scale multiple batch treatment.

Chemical Treatment	DF with respect to initial activity					
	Batch I	Batch II	Batch III	Batch IV	Batch V	Batch VI
Ist step SR		10	12	13	12	11
Ist step CT	9	40	45	40	37	50
IInd step SR		130	120	115	110	125
IInd step CT	160	220	230	190	180	200

Initial gross β activity of the waste solution = 0.30 mCi/L. CT, chemical treatment; SR, sludge recycle.

Table 6
Analysis of organic solid mass dissolved in Na_2CO_3 .

Sl.No	Properties of organic mass	Value calculated from		
		Supernatant (1)	$\text{Fe}(\text{OH})_3$ residue (2)	Total (1 + 2)
1	Gross β ($\mu\text{Ci/g}$)	57	4.260	61.260
2	Gross α ($\mu\text{Ci/g}$)	0.012	0.063	0.075
3	^{137}Cs ($\mu\text{Ci/g}$)	0.693	0.282	0.975
4	^{106}Ru ($\mu\text{Ci/g}$)	0.670	0.687	1.357
5	^{125}Sb ($\mu\text{Ci/g}$)	0.072	0.766	0.838
6	^{90}Sr ($\mu\text{Ci/g}$)	4.401	BDL	4.401
7	^{154}Eu ($\mu\text{Ci/g}$)	BDL	0.102	0.102
8	$(\text{PO}_4)^{3-}$ (mg/g)	240	NA	–
9	U (mg/g)	<10	NA	–
10	Fe (mg/g)	NA	58	58

NA, not analysed; BDL, below detection limit. Minimum detectable conc. for $\beta = 3 \times 10^{-5}$ mCi/L and for $\alpha = 5 \times 10^{-6}$ mCi/L.

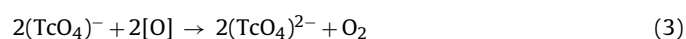
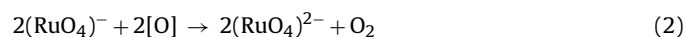
The NaOH dissolved organic mass was further cementised to see the feasibility of fixation in cement matrix [12]. For this, ordinary Portland cement and alkaline solution of the organic mass was mixed in 1.3:1 w/w ratio and the cement block formed was cured for a period of 28 days in humid condition. Chemical durability study of the cement block was carried out by conventional leaching method at ambient temperature using distilled water as leachant [13]. The details of the cement block and leaching conditions are presented in Table 7. The leachant was replenished periodically and the leachate was analysed for gross beta activity. Compressive strength of the cement block was also determined using Compression testing machine provided by Lawrence & Mayo (India) Pvt. Ltd.

3. Results and discussion

In the new scheme for co-precipitation, mixing of acidic and alkaline LLW was considered to minimise the use of concentrated acid and alkali for the neutralization of these waste streams. It was observed that during carbonate destruction, the degraded products of TBP is getting separated as solid mass and floats on the top of the liquid. Since the waste was containing relatively higher concentrations (0.02–0.03 mCi/L) of ^{106}Ru and ^{99}Tc , TBP degraded products

and carbonates, normal chemical co-precipitation method [10] followed for the treatment of LLW streams did not provide required DF with respect to gross beta activity. Hence a new scheme with two step chemical treatment as given in the Table 2 was formulated after extensive experimental trials in the laboratory. The precipitation of Ru, Tc and Cs are effective in acidic/neutral pH and that of Sr and Sb in alkaline pH. Therefore a two step chemical treatment was carried out at two different pH conditions.

Ru and Tc form various anionic, cationic and neutral species in aqueous medium. Due to the complex chemistry of these ions the mechanism of the reductive co-precipitation of them is not clearly known. However it may be explained as follows. Na_2SO_3 is reducing the perruthenate and pertechnate ions (VII) to ruthenate and technate ions (VI) [14]. These ions are then co-precipitated along with FeS and $\text{Fe}(\text{OH})_2$.



Cs is precipitated along with potassium copper ferrocyanide and Sr with barium phosphate. Sb is precipitated as hydroxide along with ferric hydroxide.

Co-precipitation of ^{106}Ru , ^{99}Tc , $^{134,137}\text{Cs}$, ^{90}Sr and ^{125}Sb occurred during first step treatment. In the second step treatment co-precipitation of remaining ^{106}Ru , ^{90}Sr and ^{125}Sb was there (Table 3). Separation of the TBP degraded products and reductive co-precipitation of ^{106}Ru and ^{99}Tc at acidic pH improved the DF values. However the DF for Ru is low compared to other nuclides. This may be due the inefficient co-precipitation of Ru ions because of its complex chemistry in aqueous medium. The effluent after the two step chemical treatment is dischargeable to environment.

Table 3 shows that the DF obtained is high for MW with out TBP degraded product compared to that with TBP degraded products. The TBP degraded products are soluble in alkaline medium and hence interferes with the co-precipitation process.

Table 4 shows the average DF obtained in ten batches of plant scale treatment of MW. The values are comparable or better than

Table 7
Details of cement block and leaching conditions.

Details of cement block	
Weight of waste (organic mass dissolved alkali)	21.924 g (1.924 g organic mass)
Cement (~1.3 time waste)	26 g
Height of cement block	2.0 cm
Diameter	3.8 cm
Weight	47.51 g
Surface area (S.A.)	46.56 cm^2
Leaching conditions	
Leachant	Distilled water
Temperature	Ambient
Volume of leachant	600 ml
S.A./vol. of leachant	~0.1 cm^{-1}



Fig. 3. Organic layer separated at the top of the SS tank in the plant.

the lab scale values. The better value may be the advantage of large scale treatment. During multiple batch treatment, the sludge obtained in the previous batch operation was giving advantage to the next batch operation (Table 5). This is due to the ion exchange property of the precipitate formed for the uptake of different radionuclides.

At the end of treatment of ten batches of MW, a thick layer of solid organic mass was observed at the top of the carbonate destruction SS tank (Fig. 3). The total organic mass separated was about 0.2–0.3% of the total waste treated. Though the volume of the organic mass is very less, treatment of the same is of concern due to its organic nature. In view of this detailed analysis of the organic mass was carried out.

The separated solid mass was off-white in colour and was fluffly in nature. Dissolution of this mass in boiling concentrated nitric acid resulted in hazy solution with finely distributed fine particle. Perchloric acid digestion also gave a hazy solution. In both these cases the organic part is only partially getting destroyed. With 1 M NaOH solution the organic part was almost soluble and there was some reddish precipitate of $\text{Fe}(\text{OH})_3$ at the bottom, which was soluble in dilute nitric acid. Dissolution of the organic mass with 1 M

Na_2CO_3 solution resulted in a clear solution. Here also reddish precipitate was observed. In alkali medium the TBP degraded products namely DBP, MBP and butyl alcohol form respective soluble sodium salts.

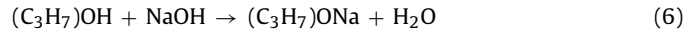
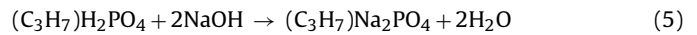
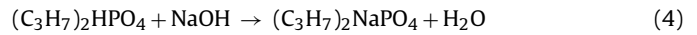


Table 6 shows the activity spectrum of the supernatant and residue of Na_2CO_3 dissolved organic mass. Fig. 4 shows the gamma ray spectra of the supernatant and residue. From Table 6 it can be seen that there is appreciable concentration of ^{154}Eu in the organic mass whereas in the MW solution its concentration was below detection limit (Table 1). This may be due to the extraction of trace levels of ^{154}Eu by the organic mass. The source of ^{154}Eu is the acidic LLW.

The gross β activity of the sample is much more than the sum total of all individual isotope activities (Table 6). This shows that there are unknown isotopes. The unknown isotopes have to be pure β emitters as there is no unknown line in the γ spectrum. It was also observed that the gross beta activity of the organic solid mass was fast decreasing with time. The fast decrease in beta activity shows that the pure beta emitting isotope is short-lived. To identify the unknown isotope, a fresh sample of organic mass was dissolved in sodium carbonate and its activity trend with respect time was followed (Fig. 5). (Activity of the unknown isotope was taken as 'gross beta activity – sum total of activity of other isotopes'). The initial activity of the unknown isotope was 110 mCi/g. After 28 days the activity got decreased to 5.7 mCi/g. Considering the presence of ^{90}Sr in the waste solution, the short lived beta isotope may be ^{90}Y ($T_{1/2} = 64 \text{ h}$).

The activity decay of an isotope is represented by the equation:

$$A = A_0 e^{-\lambda t} \quad (7)$$

$$\lambda = \frac{0.693}{T_{1/2}} \quad (8)$$

where A_0 is the initial activity, A is the activity after a time period of t , λ is the decay constant and $T_{1/2}$ is the half life of the radioactive isotope.

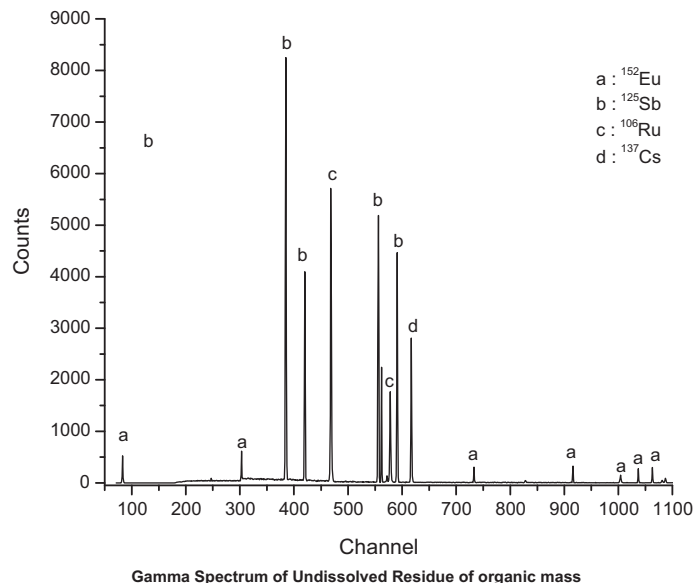
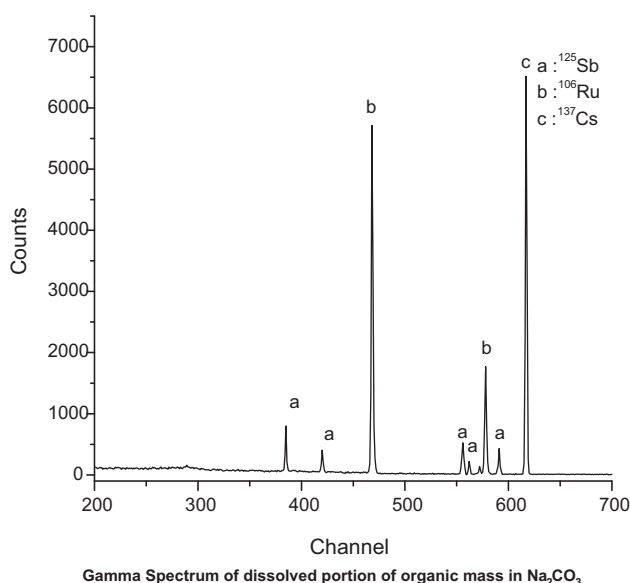


Fig. 4. Gamma ray spectra of organic mass dissolved in Na_2CO_3 .

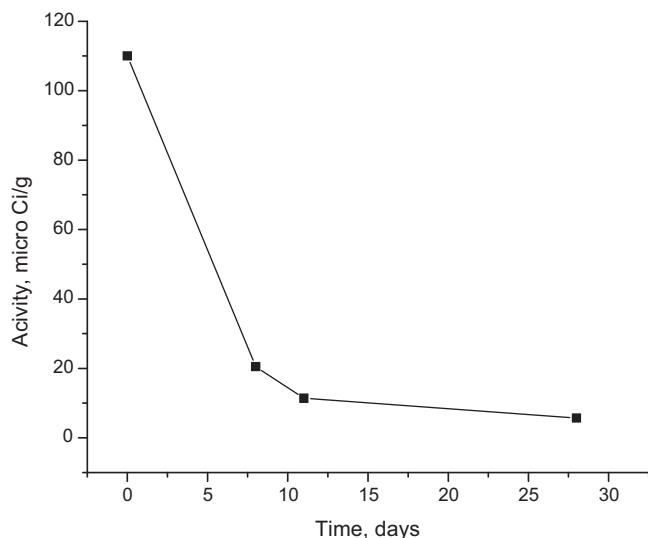


Fig. 5. Decrease in β activity of the organic mass with time.

The decay pattern of the unknown beta isotope was tested by plotting the logarithm of activity of unknown isotope against time of decay (Fig. 6). The $T_{1/2}$ of the unknown beta isotope calculated from the slope of the straight line in Fig. 5 (70 h) matches with the $T_{1/2}$ of ^{90}Y with in the error limits and hence confirms the presence of ^{90}Y . This shows that yttrium is behaving similar to ^{154}Eu and is getting extracted from the waste solution in to the degraded TBP products.

The high beta activity of the organic mass was mainly due to the short lived isotope ^{90}Y present in it. After about one month time the activity got decreased to about twenty times less. Fig. 7 shows the leaching behaviour of the cementised product of organic mass. As seen from Fig. 6, the stabilized leach rate with respect to gross beta for the cementised waste product after a period of 100 days is $4.80 \times 10^{-5} \text{ gm cm}^{-2} \text{ day}^{-1}$ and the cumulative activity leached from the cement block is around 2.4%, which is below the internationally accepted leach rate for cementised waste product [5,15]. The compressive strength of the cement block (15–20 MPa) was also with in the acceptable limit of cement waste products [16]. Hence fixation of organic mass in cement matrix can be adopted for its conditioning and shallow land disposal. The alpha burden of

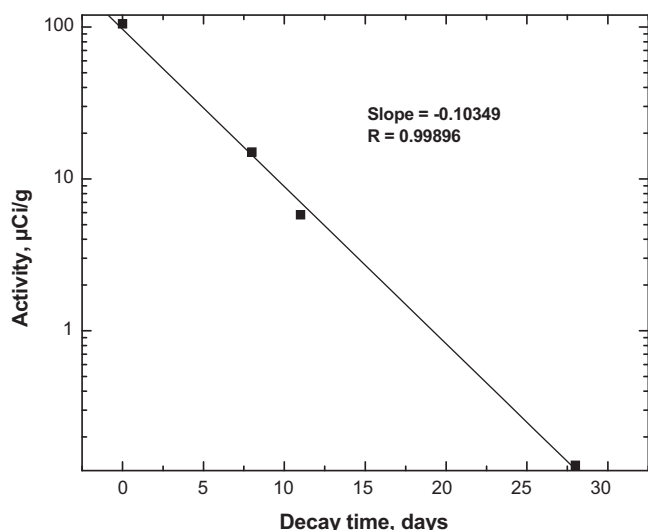


Fig. 6. Plot of β activity (log scale) versus decay time.

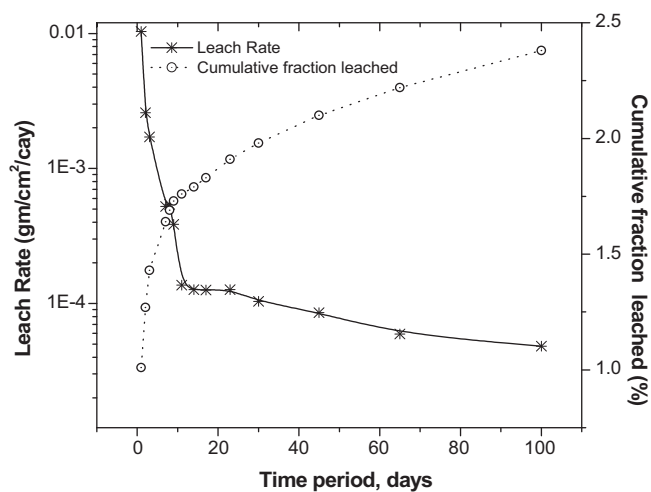


Fig. 7. Leaching behaviour of the cement product.

the solid mass is also well with in the permissible range for NSDF disposal.

4. Conclusion

In the new scheme for chemical treatment of low level effluent stream, separation of TBP degraded products provided very good DF with respect gross beta activity. The reductive co-precipitation of ^{106}Ru and ^{99}Tc resulted in effective removal of these radio nuclides to get sufficient decontamination of the effluent stream for its discharge into environment. Based on the lab scale treatment results of the new chemical treatment scheme, about 250 m³ of LLW was successfully treated in the plant.

As the leach rate data and compressive strength of the cement product are with in the internationally accepted value, fixation of organic mass in cement matrix can be adopted for its conditioning and shallow land disposal.

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References

- [1] IAEA Technical Reports Series no. 101, IAEA, Vienna, Austria, 1970.
- [2] IAEA Safety Series 111- F, 1995.
- [3] R.G. Yeotikar, M.S. Sonavane, J.G. Shah, R. Kanwar, Development of vitrified matrix for high level waste and its characterization – experience at WIP, Tarapur, SMART-93, 1993.
- [4] R. Kanwar, M.T. Samuel, Modified pot glass process for vitrification of high level radioactive waste – process engineering aspects, in: XIV International Congress on Glass, vol. II, 1986, pp. 399–409.
- [5] K. Raj, K.K. Prasad, N.K. Bansal, Nucl. Eng. Des. 236 (2006).
- [6] Y. Kulkarni, S.K. Samanta, S.Y. Bakre, K. Raj, M.S. Kumra, Process for treatment of intermediate level radioactive waste based on radionuclides separation, WM-96, 1996.
- [7] R.G. Yeotikar, C.P. Kaushik, J. Gabriel, R. Kanwar, Treatment of alkaline intermediate level radioactive waste, NUCAR 95 (1995).
- [8] IAEA, Tech. Report. Series No. 222 (1983) b.
- [9] L. Berak, E. Uher, M. Marhol, At. Energy Rev. 13 (1975).
- [10] P.D. Ozarde, S.K. Samanta, K. Raj, Proceedings of the IAEA international conference on issues and trends in radioactive waste management – IAEA-CN-90/51, Vienna, Austria, 2002.
- [11] G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney, Vogel's Text Book of Quantitative Chemical Analysis, sixth ed., p. 452.
- [12] U.S. Singh, A. Mishra, R.G. Yeotikar, R. Kanwar, Immobilisation of intermediate level alkaline radioactive liquid waste in cement matrix, NUCAR 95 (1995).

- [13] United State Department of Energy, Nuclear Waste Management Material Handbook (test methods), Rep. DOE/TIC-11400 (1981).
- [14] F.A. Cotton, G. Wilkinson, *Advanced inorganic chemistry. A Comprehensive Text*, Third ed.
- [15] N.K. Bansal, S. Kumar, C.P. Kaushik, R.R. Rakesh, S.M. Galande, Safety assessment of radioactive waste packages for disposal in near surface disposal facilities, long term behaviour of low and intermediate level waste packages under repository conditions, IAEA-TECDOC-1397. pp. 101–118 (2004).
- [16] C. Verghese, A.K. Govindan, P.K. Wattal, T.K. Theyyanni, Cementitious matrices for intermediate level aqueous radioactive wastes BARC report BARC/1995/E/004 (1995).