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Treatment of ^{106}Ru Present In Intermediate Level Radioactive Liquid Waste With Nickel Sulphide

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Abstract: ^{106}Ru is one of the major radionuclides of concern in the aqueous radioactive waste generated during the reprocessing of the spent fuel. Intermediate level radioactive liquid waste (ILW) stream is generated during reprocessing of spent fuel and is neutralised with alkali to enable it to be stored in carbon steel tank. The waste is initially treated for ^{137}Cs recovery using a specific resorcinol formaldehyde (RF) ion exchange resin. The effluent stream from the ion exchange treatment process has significant activity due to ^{106}Ru. The present paper deals with a chemical treatment study for removal of ^{106}Ru in the effluent using sulphides of cobalt and nickel. The decontamination factor of 250 obtained using NiS (at 2500 ppm concentration of Ni^{2+}) is distinctly better than that obtained using CoS (at 7200 ppm concentration of Co^{2+}).

Keywords: Intermediate level waste (ILW), ion exchange, nickel sulphide, resorcinol formaldehyde (RF) resin, ruthenium

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INTRODUCTION

Reprocessing of the spent fuel from reactor generated broadly two categories of radioactive liquid waste streams viz. high level liquid waste (HLW) and intermediate level radioactive liquid waste (ILW). HLW in acidic condition is stored in Stainless steel (SS) tanks for its subsequent vitrification, while ILW is neutralized by alkali and stored in Mild steel (MS) tanks for suitable treatment. Due to neutralization large salts are introduced in the waste. Major radionuclides present in the ILW are ^{137}Cs, ^{90}Sr, ^{106}Ru, and trace concentration of actinides.

The chemical characteristics of ruthenium are quite complicated, because ruthenium possesses many oxidation states and related compounds. In acidic waste stream Ru exists as a complex nitrosyl ruthenium (Ru-NO) species. This can be represented by general formula (1).

$$[\mathrm{Ru(NO)(NO_3)_x(NO_2)_y(OH)_z(H_2O)_{5-x-y-z}}]^{3-x-y-z}$$

The nature of the complex may be cationic, neutral or anionic depending on the number of ligands attached to RuNO group.

When the acidic waste is neutralized, the ruthenium species in alkaline conditions may exist as ruthenate ion ($\mathrm{RuO_4^{2-}}$) or perruthenate ion ($\mathrm{RuO_4^{-}}$) (2); however, the exact nature of the ruthenium species in alkaline condition is not understood properly hence most of the work related to ruthenium removal is performed with actual liquid waste solutions.

Major quantities of ^{90}Sr and actinides present in ILW are removed by precipitation, in which carbonates present in the waste are destroyed by acidification followed by alkaline precipitation. The resultant supernatant is passed through a column containing resorcinol formaldehyde (RF) resin to specifically remove ^{137}Cs (3). However, the resin does not provide any decontamination for ^{106}Ru and this radionuclide finds its way in the resin column effluent. Therefore the radioactive effluent stream of the ion exchange treatment process, which is low active in nature (with gross beta value of 2.05 mCi/L), needs further chemical treatment for removal of residual ^{137}Cs and ^{90}Sr as well as specific chemical treatment for ^{106}Ru prior to dilution and discharge.

^{106}Ru can be removed from such waste streams by using $\mathrm{Fe^{2+}}$ as carrier in reduced atmosphere (4,6). However, this method provides a poor decontamination factor, which is not adequate for effective removal of ^{106}Ru. Use of zinc charcoal mixture as adsorbent has been explored for the removal of ^{106}Ru from the radioactive waste stream (4–7). This method was found to be useful in acidic conditions and provides an overall decontamination of about 10 which was not sufficient for the effective removal of ^{106}Ru from the present waste stream. Polyaniline has been used for the removal of ^{106}Ru from the aqueous waste stream at pH 5.0 and above (8–10). However, this was found to be useful for the radioactive waste having lower ruthenium concentration (10^{-2} to 10^{-3} mCi/L) and lower dissolved salt content (upto 1–2 gm/L). Precipitation of copper ferrocyanide with the help of sodium ferrocyanide and copper sulphate was also reported for the removal of ^{106}Ru from radioactive liquid waste stream at pH 4–6.0 (11). Use of sulphide precipitates of Fe^{2+}, Co^{2+} has been reported earlier (4,12). An attempt was made in the present work to remove ^{106}Ru from such waste using S^{2-} precipitation of Co^{2+} and Ni^{2+}. The study was carried out to optimize the experimental parameters for the quantitative decontamination of ^{106}Ru. Further conditioning in cement matrix of the chemical sludge obtained during the chemical treatment of the effluent waste with respect to ^{106}Ru using NiS precipitation was also studied.

EXPERIMENTAL

Chemical Treatment of Intermediate Level Radioactive Liquid Waste (ILW)

ILW was decontaminated with respect to alpha radionuclides and ^{90}Sr after elimination of carbonates by acidification. The carbonates, present in the waste, form soluble complexes with alpha radionuclides and affect the decontamination factor. Hence prior to the alkaline precipitation of alpha radionuclides, the carbonates are destroyed by the addition of nitric acid. This is followed by alkaline precipitation at pH 13.0 and settling. The clear supernatant thus obtained was passed through resorcinol formaldehyde (RF) resin column for removal of ^{137}Cs (3). The characteristic properties of the alkaline radioactive liquid waste and effluent are presented in Table 1. The effluent obtained from the column was further

Table 1. Properties of the alkaline radioactive liquid waste before and after resorcinol formaldehyde ion exchange treatment

Properties	Initial waste	Effluent waste
pH	12.07	11–11.5
Total solids, % (wt/vol)	22.1	22.1
Gross beta, mCi/L	38.0	2.05
Gross alpha, mCi/L	0.1–0.2	$<2.0 \times 10^{-4}$
^{137}Cs, mCi/L	28.04	0.45
^{106}Ru, mCi/L	1.3	0.8

taken up for ^{106}Ru removal using S^{2-} precipitation of Co^{2+} and Ni^{2+}. The details of the three sets of experiments are as follows.

1. Set – I: Co-precipitation of ^{106}Ru with CoS was carried out using cobalt nitrate and sodium sulphide at pH 10.0. The clear supernatant obtained from the first step of precipitation was taken for second step precipitation.
2. Set – II: Co-precipitation of ^{106}Ru with NiS was carried out using nickel nitrate and sodium sulphide at pH 10.0. The clear supernatant obtained from the first step of precipitation was taken for the second step precipitation. Different sets of experiments were conducted to optimize the concentration of Ni^{2+} and S^{2-} required for achieving maximum decontamination of Ru^{106}. The concentration of Ni^{2+} was varied from 200–6000 ppm and corresponding equimolar quantity of S^{2-} was added. The NiS precipitation study was also conducted at pH 13.
3. Set – III: Further study was carried out to visualize the repeated/cascade manner use of NiS precipitate/sludge obtained from above experiment. For this purpose the experiments were conducted on 100 ml batch size. The sludge of NiS obtained from first set of experiment was recovered by decantation of the upper clear supernatant. In this sludge fresh 100 ml effluent waste was added and the solution was stirred for one hour. After one hour, the sludge was allowed to settle, a clear supernatant was removed, and its ^{106}Ru content was monitored. Such reuse of the sludge was performed repeatedly five times.

All the above sets of experiments were repeated for four to five times and average results are indicated in the table and figures given below. The results are within ±5 % variation.

Cementation of the NIS Sludge

The sludge obtained after five steps of equilibration was found to contain major proportion of ^{106}Ru. In order to check the compatibility of NiS sludge with high ^{106}Ru content in the cement matrix, a cementized waste product was prepared using ordinary Portland cement (13) and vermiculite. The cement block was cured for a period of 28 days.

Leaching of the Cement Block

The cured cement blocks were subjected to leaching in distilled water media at room temperature. The leachant was replenished periodically and its ^{106}Ru activity was monitored using high purity germanium (HPGe) 8K multichannel analyser. Details of the cement block and the leaching parameters are given in Table 3. The leach rate was calculated on ^{106}Ru loss basis.

$$\text{Leach Rate} = \frac{\text{Fraction of activity leached} \times \text{wt. of cement block (gm)}}{\text{Surface area (cm2)} \times \text{Time in days}}$$

RESULTS AND DISCUSSION

CoS precipitation with Co^{2+} concentration of 7200 ppm and S^{2-} concentration of 4000 ppm gives a decontamination factor (DF) of about 185 with respect to ^{106}Ru and about 64 with respect to ^{137}Cs in two steps (Table 2). Table 3 shows the DF value of 250 with respect to ^{106}Ru and about 34 with respect to ^{137}Cs in two steps using 2500 ppm of Ni^{2+} and 1326 ppm of S^{2-}. The DF values in case of NiS precipitation are lower with respect to Cs but are higher with respect to Ru as compared to CoS co-precipitation, even though the concentration of NiS is about one-third. Consequently, the sludge volume generated also is less during NiS treatment as compared to CoS treatment. The chemicals nickel nitrate and sodium sulphide were added in stoichiometric proportion for precipitation. However, cobalt nitrate was added slightly more than the stoichiometry. This was based on the practically DF achieved.

As it is observed from Fig. 1, with increase in concentration of Ni^{2+} and S^{2-}, the decontamination factor for ^{106}Ru also increases. It ranges from 4 to 58. However, concentration of Ni^{2+} as 2500 ppm and that of S^{2-} as 1326 ppm was found to be optimum. Further increase in concentration of Ni^{2+} as well as S^{2-} does not result in appreciable increase in DF. Hence, this concentration of Ni^{2+} and S^{2-} was selected for the subsequent work.

Table 2. Details of CoS precipitation experiment

Dosing : Co^{2+} : 7200 ppm & S^{2-} : 4000 ppm

Initial activity, (mCi/L)		Final activity (mCi/L)		Decontamination factor		
		First step	Second step	First step	Second step	Cumulative
Gross beta	2.05	0.075	0.022	27.3	3.41	93.1
^{137}Cs	0.45	0.022	0.007	20.4	3.14	64.1
^{106}Ru	0.8	0.024	0.0044	33.3	5.58	185.8

Table 3. Details of NiS precipitation experiment

Dosing : Ni^{2+} : 2500 ppm & S^{2-} : 1326 ppm

		Final activity (mCi/L)		Decontamination factor		
Initial activity, (mCi/L)		First step	Second step	First step	Second step	Cumulative
Gross beta	2.05	0.12	0.02	17.1	6.0	102.6
^{137}Cs	0.45	0.072	0.0132	6.25	5.45	34.1
^{106}Ru	0.8	0.015	0.0032	53.3	4.68	249.4

With these concentrations of Ni^{2+} and S^{2-}, the first step treatment gives a DF of 53.3 and 6.25 for Ru^{106} and Cs^{137} respectively. The second stage treatment gives a DF of 4.68 and 5.45 for ^{106}Ru and ^{137}Cs respectively. Thus the overall DF achieved after the two-step treatments with respect to ^{106}Ru is 250 and for ^{137}Cs is 34.0. Lower DF observed in the second the step may be attributed to the lower concentration of ^{106}Ru present in the solution obtained after the first step precipitation.

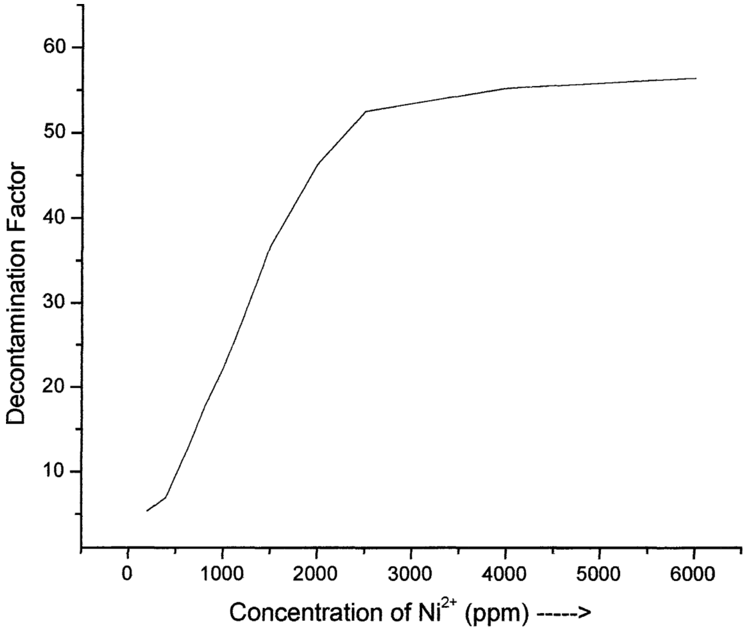

Figure 1. Variation of decontamination factor with conc. of Ni^{2+}.

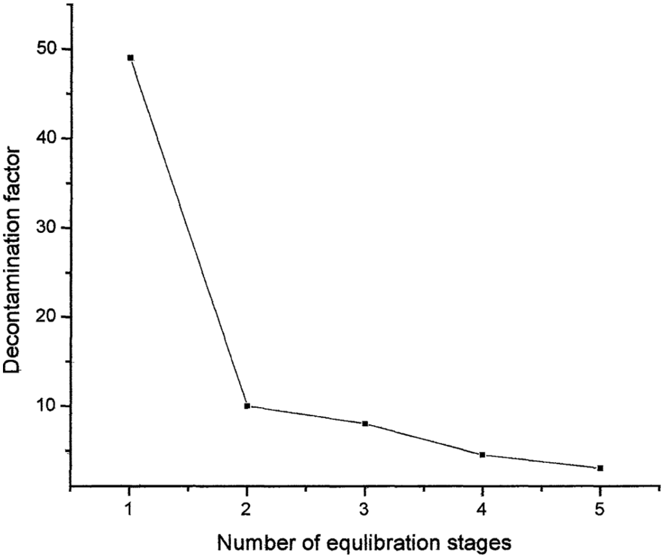

Figure 2. Decontamination factor vs no. of contacts.

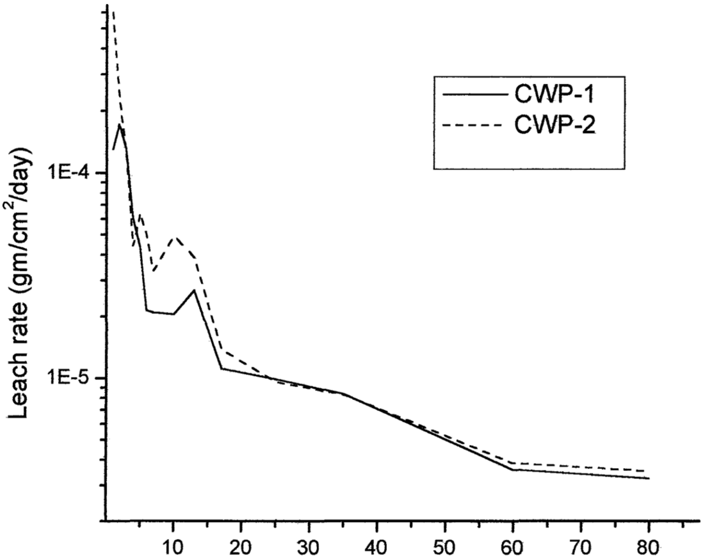

Figure 3. Leaching behavior of CWP on activity loss basis/CWP: Cementised Waste Product, CWP-1: with NiS sludge obtained at pH 10, CWP-2: with NiS sludge obtained at pH 13.

Figure 2 shows that the cascade manner use of NiS sludge generated in one experiment with fresh waste was found to yield removal of ^{106}Ru upto five stage of equilibration. During 5 stage of equilibration with fresh waste, DF decreased from 49 to 3. Though DF is decreasing at each stage, it gives removal of ^{106}Ru without addition of extra chemicals for NiS precipitation. Decant from these experiments can be further polished by second step NiS precipitation.

The DF for ^{106}Ru obtained during insitu precipitation of NiS has indicated a co-precipitation mechanism. However, during cascade manner use of NiS sludge, when fresh waste was equilibrated with sludge obtained in previous experiment, the decontamination of ^{106}Ru observed indicates that the removal of ruthenium from liquid waste is not just a coprecipitation but there is sorption mechanism is also being followed. There are still more active sites are left on the NiS precipitate particles, which provides area for further sorption of ruthenium when fresh liquid waste was equilibrated. The detailed study pertaining to the same is on the way. The same will be addressed in future.

NiS precipitation was carried out at pH 10 and 13.0. It showed that the settling of NiS precipitate was better at pH 10. The time required for bulk settling of NiS precipitate at pH 10.0 was 1.0 hour. However, at pH

Table 4. Details of cement block and leaching parameter

Parameters of cementation		
pH of sludge	10	13
Volume of Sludge	30 ml	30 ml
Cement, gm (1.3 time sludge volume)	39 gm	39 gm
Vermiculite	3 gm	3 gm
Details of cement block		
Height of cement block, cm	3.2	3.2
Diameter, cm	3.8	3.8
Weight, gm	72.99	71.92
Surface Area (S.A), cm^2	60.85	60.85
Leaching conditions		
Leachant	Distilled water	Distilled water
Temperature	Ambient	Ambient
Volume of Leachant, ml	600	600
S.A./Vol. of leachant	0.1	0.1

13.0, the settling time required was more than 24 hours and still equivalent settling was not observed.

The leaching data with respect to the cementized waste product after a period of 90 days shows that the leach rate is 3.2×10^{-6} gm/cm^2/day on ^{106}Ru loss basis. From Fig. 3, it was observed that though the cement blocks were made using NiS sludge obtained at pH 10.0 and 13.0, the leach rate of both the cement blocks are almost the same. This demonstrates the compatibility of the sludge with the cement matrix and can be immobilized in ordinary portland cement with a sludge to cement ratio of 1:1.3.

CONCLUSIONS

The effluent from the ion exchange treatment process can be effectively decontaminated with respect to ^{106}Ru using NiS coprecipitation. It also provides decontamination of the waste with respect to ^{137}Cs. Cascade manner use of NiS precipitation helps to reduce the sludge volume generated during precipitation. The cascade manner use of NiS precipitate has also indicated the sorption mechanism for decontamination of ^{106}Ru from the liquid waste. Use of the two-step treatment gives better decontamination. The NiS sludge waste obtained can be immobilized in ordinary portland cement with good chemical durability characteristics.

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REFERENCES

1. Siczek, A.A.; Steindler, M.J. (1978) The chemistry of ruthenium and zirconium in the PUREX solvent extraction process. *Atomic Energy Review*, *16* (4): 575–618.
2. El-Absy, M.A.; El-Amir, M.A.; Mostafa, M.; Abdel Fattah, A.A.; Aly, H.M. (2005) Separation of fission products ^{106}Ru and ^{137}Cs from aged uranium targets by sequential distillation and precipitation in nitrate media. *Journal of Radioanalytical and Nuclear Chemistry*, *266* (2): 295–305.
3. Yeotikar, R.G.; Kaushik, C.P.; Johnson, G.; Raj, K. (1995) Treatment of alkaline intermediate level radioactive waste. *Nuclear and Radiochemistry Symposium NUCAR 95–IGCAR*, Kalpakkam, Feb 21–24, 429–430.
4. Berak, L.; Uher, E.; Marhol, M. (1975) Sorbents for the purification of low and medium level radioactive waters. *Atomic Energy Review*, *1*: 325–367.

5. IAEA – TECDOC – 337 (1984) Inorganic ion exchangers and adsorbents for chemical processing in the nuclear fuel cycle. Radioactive Ruthenium removal from liquid wastes of $M0^{99}$ production process using Zinc and charcoal mixture, 63–74.
6. Samanta, S.K.; Theyyunni, T.K. (1994) Removal of radioruthenim from alkaline intermediate level radioactive waste solution: A laboratory investigation. BARC Report : BARC/1994/E/012.
7. Samanta, S.K. (1992) Studies on the removal of ruthenium from radioactive waste. *Nuclear and Radiochemistry Symposium, (NUCAR–1992)* Andhra University, Vishakhapatanam, Dec 21–24.
8. Syed, A.A.; Dinesan, M. (1992) Polyaniline: A conducting polymer as a novel anion – exchange resin. *Analyst*, *117*: 61–66.
9. Syed, A.A.; Dinesan, M. (1991) Polyaniline: A novel material–review. *Talenta*, *38*: 815–837.
10. Balarama Krishna, M.V.; Arunachalam, J.; Prabhu, D.R.; Manchanda, V.K.; Kumar, S. (2005) Removal of Ru^{106} from actual low – level radioactive waste solutions using polyaniline as anion – exchanger. *Separation Science and Technology*, *40*: 1313–1332.
11. Gandon, R.; Boust, D.; Bedue, O. (1993) Ruthenium complexes originating from the Purex process: Coprecipitation with copper ferrocyanides via ruthenocyanide formation. *Radiocheim Acta*, *61*: 41.
12. Singh, U.S.; Sonar, N.L.; Kore, S.G.; Mishra, P.K.; Sonavane, M.S. (2005) Development of method for treatment of Ru^{106} rich radioactive liquid waste with high salt content. *NUCAR 2005*, Gurunanak Dev University, Amritsar, March 15–18, 371–372.
13. Singh, U.S.; Mishra, A.; Yeotikar, R.G.; Raj, K. (1995) Immobilisation of intermediate level alkaline radioactive liquid waste in cement matrix. *NUCAR95–IGCAR*, Kalpakkam Feb 21–24, 426–427.