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Decontamination of ^{106}Ru and ^{99}Tc bearing effluents by chemical treatment

Dayamoy Banerjee*, Manjula Anand Rao, Annie Joseph, Ajay Manjrekar, Inderjit Singh, Piaray Kishen Wattal

Process Development Division, Bhabha Atomic Research Centre, Trombay, Mumbai-85, India
Tel. +91 22 25594106; Fax: +91 22 25505150; email:dayabanerjee@gmail.com

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ABSTRACT

Ion exchange separation of ^{137}Cs and ^{90}Sr from alkaline intermediate level waste (ILW) generated at back-end of nuclear fuel cycle results in downstream effluent containing substantial amounts of ^{106}Ru and ^{99}Tc activity. Efforts were made to develop suitable chemical treatment based processes for decontamination of these effluents. Feasibility of using various metal sulphides alone or in combination was examined for simultaneous removal of ^{106}Ru and ^{99}Tc. Based on these studies, a formulation involving precipitation of CoS in conjunction with FeS has been proposed for effective decontamination of the effluent. Presence of dibutyl phosphate (DBP) in some of the streams of ILW interfered with decontamination of ^{106}Ru. A process involving removal of DBP as Fe-DBP complex followed by CoS and FeS precipitation developed in this study was found to be effective in decontamination of the effluent containing gross beta activity of 5550 to 37 Bq ml^{-1}. It is inferred that the process is promising for practical application.

Keywords: Chemical treatment; Removal; Decontamination; Radioactive waste; ^{99}Tc; ^{106}Ru

1. Introduction

The intermediate level waste (ILW) generated at the back end of nuclear fuel cycle is alkaline in nature and characterized with high salt loads. The waste has gross β activity in the range of $1.5 \times 10^5 - 1.5 \times 10^6$ Bq ml^{-1} with ^{137}Cs as the major radionuclide and traces of ^{90}Sr, ^{106}Ru etc. This alkaline ILW is treated by ion exchange based process using resorcinol formaldehyde polycondensate resin for removal of Cs and Amberlite IRC-718 for Sr^{2+} [1–3]. This treatment scheme has been demonstrated earlier in an industrial scale campaign, comprising of a mobile ion exchange facility with in-built self shielded columns and filters on a 40*t* trailer, where 2100 m^3 of the ILW was treated successfully [4,5]. The same facility has recently been used to treat stored ILW generated from the reprocessing of power reactor spent fuel. This treatment resulted in a low level effluent which contained substantial amounts of ^{106}Ru and ^{99}Tc activity. Because of the presence of these radioelements, further decontamination of the effluent by conventional chemical treatment was found to be ineffective. In order to develop a suitable process for effective decontamination of the effluent, studies were therefore undertaken using the actual downstream effluents.

It is known that the effective separation of ^{106}Ru from the aqueous waste of reprocessing plant origin is difficult mainly because of its complex aqueous chemistry involving nitrosyl ruthenium (Ru-NO) species [6]. Kochetkov et al. reported that ferrous and titanium hydroxides, among the various metal hydroxides, have significant potential for separation of the complex ruthenium species [7]. Further improvement of ^{106}Ru decontamination performance by these hydroxides is noted

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*Corresponding author.

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in the presence of reducing agents [8]. Investigations carried out earlier from this laboratory have shown that the precipitation of $Fe(OH)_2$ in the presence of sodium sulphite is promising for removal of ^{106}Ru from alkaline reprocessing waste [9]. This process has been found useful for industrial scale application [10]. Precipitation of transition metal (Co, Ni) sulphide under acidic as well as basic condition is known to be effective for removal of Ru species from high salt-loaded reprocessing wastes [11–13]. In the Cogema waste treatment facility at La Hague (France), precipitation of cobalt sulphide is used for removal of ^{106}Ru from medium level reprocessing waste under alkaline condition [11].

The ^{99}Tc in reprocessing waste is present mostly as TcO_4^- anion. Because of its higher solubility in water, separation of this anion requires highly selective coagulants. For analytical purposes, precipitation of TcO_4^- anion is carried out by using tetraphenyl arsonium chloride [14]. Use of the reagent for waste treatment has not been adopted possibly from economic point of view. In some rare instances, the use of an isomorphic coagulant, tetraphenyl phosphonium bromide for decontamination of waste from TcO_4^- ions has been reported [15]. Ellwood et al. showed that precipitation of FeS is one of the promising candidates for removal of $^{99}TcO_4^-$ ion from low level waste [16].

Keeping these in mind, efforts have been made to find a suitable formulation for decontamination of the ^{99}Tc and ^{106}Ru bearing effluent. Detailed evaluation of formulations and their performance are reported here.

2. Experimental

2.1. Origin and characteristics of the effluent

The procedure followed for characterization of the waste solution and the samples generated therein from precipitation studies were similar to that discussed in detail in our earlier communication [5]. In brief, pH of the effluent sample was measured by a calibrated pH microelectrode (combination glass electrode) coupled with pH meter (model: cyberscan 2100, Eutech Singapore). Total dissolved solid content was determined from the weight of a sample (1 ml) after drying under IR lamp to constant weight. The total radioactivity content of the effluent was estimated in terms of gross β activity. For gross β analysis, 0.1 ml of the effluent was taken in an aluminium planchette containing 1.0 ml of distilled water which was then dried under IR lamp. The planchette was counted using GM counter (Pla, India) and the counts were used to calculate the gross beta activity (Bq ml^{-1}) using known efficiency of the counter. Gamma spectrometry was done for the detection and estimation of the γ-emitting radionuclides present in effluent by counting a 4 ml sample in a HPGe detector coupled to a 8K MCA. Estimation of ^{90}Sr was carried out by radiochemical separation followed by β-counting. The ^{99}Tc was separated as a white precipitate of tetraphenylarsonium pertechnetate and tetraphenylarsonium perchlorate (carrier), then the precipitate was collected by filtration using microfiltration system, dried under IR lamp and counted using GM counter [14]. The composition of the downstream effluents used in the work is shown in Table 1. It can be seen that both the wastes are almost similar chemically and have similar radionuclide profiles, but the concentration of radionuclides are significantly different. Both wastes are ^{106}Ru and ^{99}Tc rich but it can be seen that as compared to waste A, waste B contains almost 20 and 2 times more ^{106}Ru and ^{99}Tc activity, respectively.

2.2. Materials and methods

Stock solutions of the metal ions were prepared by dissolving requisite amount of the analytical grade salts (S.D. fine and Qualigens, India make) in distilled water. Concentration of the salt in stock solution prepared were as follows: cobalt nitrate (0.5 M), sodium sulphide (1.0 M), ferrous sulphate (1.0 M), ferric nitrate (1.0 M), copper sulphate (0.1 M), potassium ferrocyanide (0.1 M), barium chloride (1.0 M) and sodium hydroxide (1.0 M). To ensure minimal increase in waste volume, concentrated nitric acid (16 M) was used for pH adjustment.

2.2.1. Procedure for jar tests

All the jar tests were carried out in glass beakers (batch size: 25 ml), unless otherwise mentioned. The pH of effluent was adjusted to 7 or 2 by adding nitric acid before conducting jar tests. The requisite dosing of metal salt solutions (coagulants) were added sequentially to the waste. Instantaneous mixing of coagulants with waste was done by stirring using magnetic stirrer. The final pH was then adjusted to about 7. After addition

Table 1
Composition of ^{106}Ru and ^{99}Tc bearing effluent

Constituent	Concentration	
	Effluent A	Effluent B
pH	12.8	12.5
TDS, g l^{-1}	140	180
Gross β, Bq ml^{-1}	2220	5550
^{137}Cs, Bq ml^{-1}	1.5	370
^{90}Sr, Bq ml^{-1}	1.0	111
^{106}Ru, Bq ml^{-1}	192	1628
^{99}Tc, Bq ml^{-1}	1887	3330

of all salt solutions, the mixture was stirred for another 15 min and left overnight for settling. Finally, the clear supernatant was drawn from top and analyzed radiometrically.

3. Results and discussion

3.1. Treatment of effluent A

Screening test was conducted with effluent A to evaluate the promising candidates for removal of ^{106}Ru and ^{99}Tc. In these tests, the performance of various metal sulphides, alone as well as in various combinations, were examined by adjustment of effluent pH to 7 followed by addition of coagulant. In the case of a single metal ion, formation of the metal sulphide precipitate under the present experimental conditions was inferred from visual observation of the black colored precipitate which formed immediately after addition of the sodium sulphide solution. As the concentration of sulphide used is equal (molar ratio) to that of the total concentration of the metal ions, it is reasonable to assume that both metal sulphide precipitates were formed in the solution. Results of the screening tests are shown in Fig. 1. Amongst others, the precipitation of CoS in combination with FeS is found to be superior for simultaneous removal of ^{106}Ru and ^{99}Tc and hence was selected for further studies.

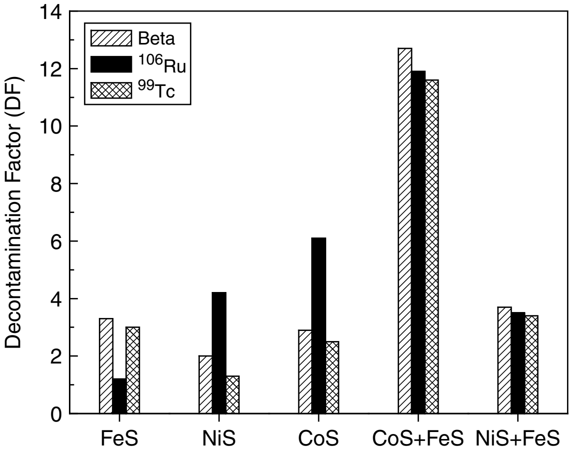

Fig. 1. Screening of formulations for removal of ^{106}Ru and ^{99}Tc from effluent "A" (conc. of each metal ion: 500 ppm, sulphide: equimolar of total metal ion, initial and final pH: 7).

Detailed tests for optimization of the dosing of metal ions involving precipitation with CoS and FeS were carried out by adding metal salt solutions in effluent of pH 7 and the results are shown in Fig. 2. In terms of total activity removal performance, the combination of 500 ppm of Co^{2+} and 1000 ppm of Fe^{2+} is found to be most promising. In other words, precipitation involving 500 ppm of Co as CoS in combination with 1000 ppm Fe^{2+} as FeS is able to reduce the gross β activity from 2220 to 92 Bq ml^{-1} (overall DF = 24). Based on the reported results, it can be inferred that adsorption of $[Ru(NO)]^{3+}$ species on CoS and TcO^{4-} on FeS is the predominant process for separation of the radionuclides [12,16].

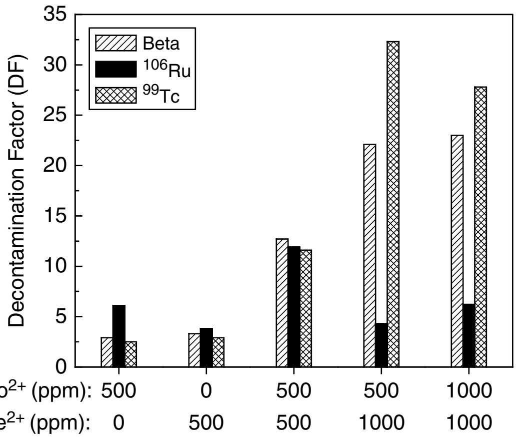

Fig. 2. Effect of metal ion concentration on simultaneous removal of ^{106}Ru and ^{99}Tc from effluent "A" (conc. of sulphide: equimolar of total metal ion, initial and final pH: 7).

The results of earlier experiments from our laboratory show that ^{106}Ru removal by the metal sulphide is more effective in absence of carbonate in solution [12]. In the present study also, significantly improved decontamination of effluent A was noted when the jar tests were carried out with the effluent of pH 2. In this case, the pH of the solution was raised to 5 after addition of Co^{2+} and Fe^{2+} and then S^{2-} was added. The addition of sulphide in acidic pH was avoided to minimize the formation of H_2S gas (pKa of H_2S = 7.05). The final decontaminated effluent obtained after precipitation contained <26 Bq ml^{-1} of gross β activity (overall DF = 85). From the detailed analysis of the decontaminated effluent, it was confirmed that the formulation is effective for complete removal of ^{99}Tc. This remaining activity was due to the presence of ^{106}Ru (20 Bq m l^{-1}) only, as can be seen from the gamma spectrum shown in Fig. 3. It is noteworthy to mention that the reduction of ^{106}Ru activity below 20 Bq m l^{-1} was not achieved under various conditions adopted during the investigation. It has also been established that the adjustment of final pH between 6 and 8 is necessary to get effective decontamination performance.

3.2. Treatment of effluent B

In the case of effluent B, initially above mentioned two processes, that is, after adjustment of pH 2 and 7 were tested. In addition, the precipitation of copper

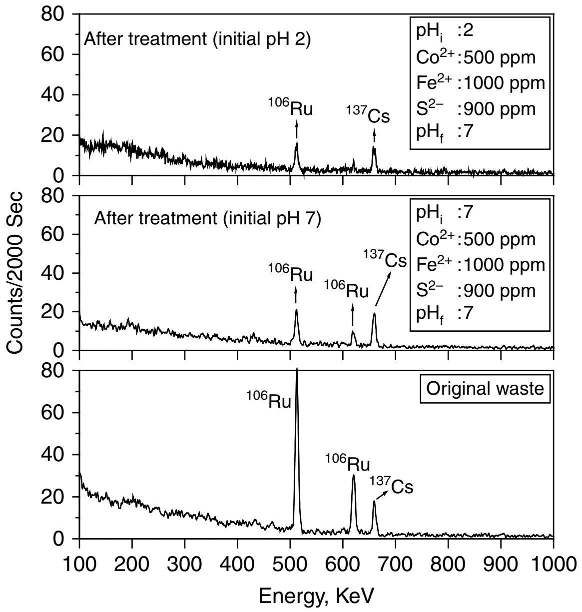

Fig. 3. Gamma spectrum of the effluent "A" before and after decontamination.

ferrocyanide and barium sulphate was also carried out to remove ^{137}Cs and ^{90}Sr activity, respectively. Because of the higher ^{106}Ru and ^{99}Tc activity in effluent B, effective decontamination was not achieved in step-I (Table 2). Therefore, further precipitation with the supernatant of step-I (pH 8) was carried out using same dosing. Results of this study clearly showed that the precipitation after adjustment of pH 2 is better. The remaining gross β activity in effluent (after step II) is due to ^{106}Ru only. It is noteworthy to mention that reproducibility of the performance could not be established during repeated trials and this necessitated further investigation.

Table 2
Chemical treatment of Effluent B effluent

Batch size : 25 ml
Formulation : 500 ppm Co^{2+} + 1000 ppm Fe^{2+} + 900 ppm S^{2-} + 50 ppm Fe(CN)$_6^{4-}$ +50 ppm Cu^{2+} + 1000 ppm Ba^{2+}
Gross β activity before treatment : 5550 Bq ml^{-1}

pH before dosing of chemicals	Gross β activity (Bq m l^{-1}) after	
Step I	Step I	Step II[a]
7	518	148
2	170	63

[a] Effluent (pH 8) of Step I as generated is used for treatment in Step II.

Table 3
Decontamination of effluent "B" by combined chemical treatment as a function of ageing of the solution

Batch size : 50 ml
pH before precipitation : 2
Gross β activity before treatment : 5550 Bq ml^{-1}

Batch no	Period of ageing (h)	Activity after treatment[a] (Bq ml^{-1})			
		Gross β	^{137}Cs	^{106}Ru	^{99}Tc
1	3	137	3.7	111	30
2	24	96	3.7	85	30
3	48	89	3.7	67	25
4	72	63	3.7	55	11

[a] Treatment formulation: same as given in Table 2.

During our detailed investigation it was observed that a thin cream colored layer appeared at the bottom of the beaker when the solution was left standing after adjustment of its pH to 2. Further, good decontamination performance of the process was obtained when precipitation was carried out after separation of this layer. From application point of view, the effect of ageing of the solution (after pH adjustment) was investigated. In this study, pH adjustment was done in a stainless steel container and then left standing. Periodically, mixture was stirred, a portion of the mixture withdrawn and used for precipitation. Results of the study are shown in Table 3. Decontamination performance of the process was found to improve with increase of ageing time, even though precipitation was carried out along with the cream colored layer. Based on our earlier experience, it is inferred that layer formation due to presence of DBP in waste and formation of ruthenium DBP complex is possibly responsible for lower decontamination performance [17]. In acidic solution (pH 2), HDBP is separated as oily layer. The reduced interference of separated HDBP resulted in good decontamination performance. However, identification of the organic matter as DBP could not be done because of practical difficulties. Nevertheless, an indirect approach was adopted to further substantiate the above inferences as described below.

About 250 ppm of Fe^{3+} was added in waste after pH adjustment to 2. Addition of Fe^{3+} resulted in light yellow colored spongy type precipitate, confirming the presence of DBP [17,18]. Settling characteristics of the precipitate is very peculiar as a part was found to be floating and a little settled at the bottom. The precipitate could easily be removed by filtration using whatman 41 paper. Combined chemical treatment as per above mentioned dosing with this filtrate resulted in very good decontamination performance as can be seen from Table 4. It can

Table 4
Decontamination of effluent "B" by combined chemical treatment after separation of DBP

Batch size : 50 ml

Process : Effluent pH was adjusted to 1, Fe^{3+} was added and mixture left standing overnight. After filtration, combined chemical treatment as per dosing given in Table 2 was carried out.

Gross β activity before treatment : 5550 Bq ml^{-1}

Batch No	Activity after treatment (Bq ml^{-1})			
	Gross β	^{137}Cs	^{106}Ru	^{99}Tc
Batch I	52	8	41	8
Batch II	37	8	33	4

therefore be concluded that removal of DBP as Fe-DBP complex followed by chemical treatment is promising for decontamination of the effluent B.

4. Conclusions

A process involving precipitation of CoS and FeS is developed for simultaneous removal of ^{106}Ru and ^{99}Tc bearing effluent. Effective decontamination performance of effluent A is obtained when precipitation is carried out after adjustment of initial pH to 2. In case of effluent B, the presence of traces of DBP was found to be responsible for poor decontamination of ^{106}Ru by CoS precipitation. Removal of the DBP could be achieved as Fe-DBP complex in acidic condition. After removal of DBP, effective decontamination of the effluent B is established. The process is simple and easy for adaptation in plant scale treatment.

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