DEVELOPMENT OF IMPROVED LIQUID RADIOACTIVE EFFLUENTS TREATMENT TECHNOLOGY BY PRECIPITATION AND ION EXCHANGE AND THE RELATED ANALYTICAL CONTROL SYSTEM

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Abstract

Chemical precipitation method for treatment of LLW and ILW by co-precipitation of caesium with nickel ferrocyanide was employed. High decontamination factors were observed in the pH range of 9 to~11. The percentage removals of ^{137}Cs from 37 kBq, 370 kB and 3.4 MBq per litre of simulated effluents were ~ 90%, 99.7% and 99.8% respectively. Liquid radioactive wastes generated from radioisotope production facilities of AERE, Savar were found to contain ^{134}Cs and ^{60}Co with the average activity levels of 13.23 kBq/L and 5.3 kBq/L, respectively. Test runs for removal of ^{134}Cs from the wastes varied from ~ 90% to 99%. The radioactive concentrates (sludges) were conditioned by cementation and safely stored in interim storage room.

1. INTRODUCTION

Low and intermediate level radioactive wastes are produced from diverse applications of radionuclides and radioactive materials in industry, medicine, agriculture and research and from operation and maintenance of research and power reactors, radioisotope production facilities, fuel processing/re-processing plants, etc. Many of the liquid wastes need treatment for safe management. Chemical precipitation processes are well established for the removal of radioactivity from LLW & ILW. These processes are suitable for the treatment of a large volume of liquid waste and may be employed to treat a wide variety of waste streams including large amounts of particulates and/or salts. This report aims at the development of low-cost and simple precipitation technology for the treatment of LLW and ILW.

2. DESCRIPTION OF RESEARCH

2.1. INVESTIGATION OF IDEAL PRECIPITATION CONDITIONS FOR CAESIUM

With a view to concentrating and separating the caesium radionuclides, ideal precipitation conditions based on precipitation of nickel ferrocyanide were investigated according to the following reaction:

$$K_4[Fe(CN)_6] + NiSO_4 \rightleftharpoons Ni\text{-ferrocyanide} + K_2SO_4$$
$$\text{(aq)} \qquad \text{(aq)} \text{(ppt.)} \qquad \text{(aq)}$$
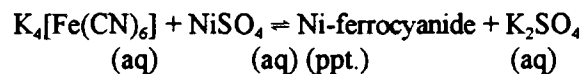
The caesium in low concentration is likely to co-precipitate with the metal ferrocyanide under favourable pH condition.

2.1.1. Effect of pH

The precipitation was conducted at different pHs but at the Ni^{2+} to $[Fe(CN)_6]^{4+}$ mole ratio of 1.5:1 and using stable CsCl as a carrier at a concentration of ~ 2×10 mole/L and ^{137}Cs (aq.soln.) as simulated effluent. Addition of chemicals was done under fast stirring condition. After 1 min. of thorough mixing, the speed was reduced and continued for ~ 5 min. The aqueous systems were allowed to settle for ~ 24 h, then the clear aqueous layers were taken by filtration and counted for residual Cs-137 by gamma spectrometry. The DFs were calculated from initial and final counts. Variation of DF as a function of pH is shown in Table I. The pH corresponding to the maximum DF is shown in Figure 1.
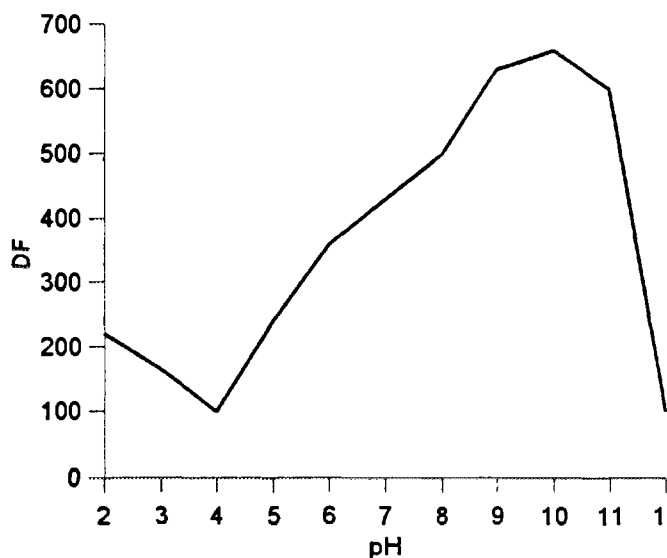
FIG.1. pH versus DF

TABLE I. VARIATION OFs DF AT DIFFERENT pHS (^{137}Cs activity of the simulated effluent - 3.7 kBq)

Exp. No.	Volume of simulated effluent (mL)	Volume of CsCl 10^{-3} Molar (mL)	pH	Volume of $K_4[Fe(CH)_6]$ 0.5 Molar (mL)	Volume of $NiSO_4$, 0.75 Molar (mL)	DF
1	50	10	2	1	1	220
2	50	10	4	1	1	98
3	50	10	6	1	1	347
4	50	10	8	1	1	497
5	50	10	9	1	1	618
6	50	10	10	1	1	654
7	50	10	11	1	1	598
8	50	10	12	1	1	93

TABLE II. VARIATION OF DFs FOR DIFFERENT AMOUNTS OF $K_4[Fe(CN)_6]$ AT pH10 (^{137}Cs activity of the simulated effluent - 3.7 kBq)

Exp. No.	Volume of simulated effluent (mL)	Volume of CsCl 10^{-3} Molar (mL)	Volume of $K_4[Fe(CH)_6]$ 0.5 Molar	Volume of $NiSO_4$, 0.75 Molar (mL)	DF
1	50	10	10 µL	1	60
2	50	10	50 µL	1	95
3	50	10	100 µL	1	140
4	10	10	500 µL	1	160
5	50	10	1 mL	1	280
6	50	10	2 mL1	1	275

TABLE III. VARIATION OF DFs FOR DIFFERENT AMOUNTS OF NiSO$_4$ AT pH10 (^{137}Cs activity of the simulated effluent - 3.7 kBq)

Exp. No.	Volume of simulated effluent (mL)	Volume of CsCl 10^{-3} Molar (mL)	Volume of K$_4$[Fe(CH)$_6$] 0.5 Molar (mL)	Volume of NiSO$_4$, 0.75 Molar (mL)	DF
1	50	10	1	10 μL	45
2	50	10	1	50 μL	80
3	50	10	1	100 μL	130
4	50	10	1	500 μL	180
5	50	10	1	1 mL	296
6	50	10	1	2 mL	293

TABLE IV. VARIATION OF DFs FOR DIFFERENT AMOUNTS OF CsCl AT pH10 (^{137}Cs activity of the simulated effluent - 3.7 kBq)

Exp. No.	Volume of simulated effluent (mL)	Volume of CsCl 10^{-3} Molar (mL)	Volume of K$_4$[Fe(CH)$_6$] 0.5 Molar (mL)	Volume of NiSO$_4$, 0.75 Molar (mL)	DF
1	50	2	1	1	88
2	50	4	1	1	110
3	50	6	1	1	130
4	50	8	1	1	215
5	50	10	1	1	310
6	50	12	1	1	308

2.1.2. Effect of stoichiometric amounts of K$_4$[Fe(CN)$_6$]

The experiments were conducted as under 2.1.1. at pH10 but using different amounts of K$_4$[Fe(CN)$_6$]. The results are shown in Table II.

2.1.3. Effect of stoichiometric amounts of NiSO$_4$

The experiments were conducted as under 2.1.2. but using different amounts NiSO$_4$. The results are shown in Table III.

2.1.4. Effect of different amounts of the carrier (CsCl)

The experiments were conducted under optimum conditions as derived from the experiments 2.1.1. to 2.1.3, but using different amounts of the carrier (CsCl). The results are shown in Table IV.

2.2. OPTIMUM CONDITIONS

The results are summarized. The optimum conditions are shown in Table V.

TABLE V. OPTIMUM CONDITIONS FOR TREATMENT OF THE SIMULATED EFFLUENTS

No.	Parameter	Values
1	Volume of the simulated effluent	50 mL
2	Volume of stabile CsCl, 10^{-3} Molar	10 mL
3	Volume of aq. NaOH or acid, 1 Normal	as needed for pH adjustment
4	pH	10
5	Volume of $K_4[Fe(CH)_6]$, 0.5 Molar	1 mL
6	Volume of $NiSO_4$, 0.75 Molar	1 mL

TABLE VI. RADIOMETRIC MEASUREMENTS ON THE REAL LIQUID RADIOACTIVE WASTES (on 31.05.94)

Waste ID	Date of interim storage	Volume of waste (L)	Container surface dose rate (μSv/h)	Specific activity (kBq/L)	
				Cs-134	Co-60
RW1	07.03.89	24	2.5	15.02	2.69
RW2	16.05.89	23	3.5	21.74	13.39
RW3	24.09.89	7	1.5	16.43	1.51
RW4	16.11.89	18	2.3	10.79	9.57
RW5	25.07.89	15	0.9	2.81	0.80
RW6	22.09.92	10	1.8	12.62	3.86

TABLE VII. PHYSICO-CHEMICAL CHARACTERISTICS OF THE REAL LIQUID RADIOACTIVE WASTES

Waste ID	Physical appearance (colour, turbidity, etc.)	Density (g/mL)	Dry extract	Fixed residue (g/L)	pH	Electrical conductivity (mS/cm)
RW1	Almost colourless, slightly turbid	1.03	96.1	85.1	10.43	67.7
RW2	Colourless to slightly yellowish, slightly turbid	1.04	89.2	88.3	10.98	58.5
RW3	Almost colourless, slightly turbid	1.05	105.3	90.8	10.24	75.4
RW4	Almost colourless, slightly turbid, dirty sediment	1.04	168.2	114.2	10.59	108.2
RW5	Brownish, turbid, dirty sediment	0.99	128.0	108.1	10.87	91.7
RW6	Almost colourless, turbid, dirty	1.01	118.2	96.5	10.67	45.3

2.3. CHARACTERIZATION OF LIQUID RADIOACTIVE WASTES

The selection of a chemical treatment process for liquid radioactive waste depends upon its radiological and physico-chemical properties and the quantity of arising waste. Therefore, in order to know the pertinent properties, the wastes generated from radioisotope production facilities of the Institute were studied as follows:

- surface dose rates (μSv/h) of liquid waste stored in plastic drums in the interim storage room were measured by a calibrated beta-gamma survey meter, Berthold LB-1200, Germany;
- the waste samples were analysed by gamma spectroscopy using HPGe detector (Vol:74 cc, resoln.:2.1 keV at 1332 keV for ^{60}Co), MCA (Canberra 40+ series 4096 channel) and the associated electronics;
- colour and turbidity of the wastes were ascertained by eye estimation as usual;
- a certain volume of the wastes was weighed to measure density;
- pHs of the wastes were measured by pH meter, Philips PW9432; electrical conductivities of the wastes were measured by digital conductivity meter, Philips PW9526;
- dry extract and fixed residue of the wastes were determined following standard procedures [2].

The results are shown in Tables VI and VII.

2.4. TEST RUNS WITH THE ^{134}Cs SEPARATION FROM THE LIQUID WASTES

The ^{134}Cs separation was conducted under optimum conditions (shown in Table V) as follows:

- the liquid wastes containing ^{134}Cs were used in the experiments (specific activity is shown in Table VI);
- twenty mL of the wastes were taken in 100 mL beaker, pH was adjusted accordingly;
- requisite amounts of carrier and precipitating agents, etc. were added and the volume adjusted to 100 mL;
- mixing was carried out at 160 rpm for ~2 min., subsequently at 120 rpm for 20 min;
- the system was allowed to stand for ~24 h;
- after the settling period, 50 mL of clear liquid layer was transferred to another 100 mL beaker and analyzed for ^{134}Cs by gamma spectrometry;
- DF was calculated from initial and final counts.

The results are shown in Table VIII.

TABLE VIII. REMOVAL OF ^{134}CS FROM THE REAL LIQUID RADIOACTIVE WASTES

Waste ID	Volume of waste (mL)	Final volume (mL)	% removal
RW!	20	100	98.26
RW2	20	100	99.11
RW3	20	100	90.98
RW4	20	100	94.25
RW5	20	100	96.17
RW6	20	100	98.13

TABLE IX. EFFECT OF ^{137}Cs ACTIVITY OF SIMULATED EFFLUENT ON % REMOVAL AT pH10

Exp. No.	Vol. of simulated effluent (mL)	^{137}Cs-activity (kBq)	Vol. of CsCl 10-2 Mol. (mL)	Vol. of NaOH 1 Normal (pH adj.)	Vol. of K$_4$[Fe(CH)$_6$]	Vol. of NiSO$_4$ 0.75 Mol. (ML)	Final volume	% removal of ^{137}Cs
1	500	18.5	10	5	10	10	606	89.9
2	500	186.0	10	4	10	10	564	99.7
3	500	1690.0	10	4	10	10	609	99.8

2.5. EFFECT OF ^{137}Cs OF SIMULATED EFFLUENT ON (%) REMOVAL AT pH10

The experiments were conducted at different concentration levels of ^{137}Cs of the simulated effluents. The results are shown in Table IX.

3. CALCULATIONS

The following equations were used :

$$Sp.activity=\frac{(A-B)100}{EVT}Bq/L$$

where

A   is the average counts for sample,
B   is the average counts for background,
E   is the efficiency of the detector,
V   is the volume of sample (L), and
T   is the time of counting (S).

B. Percentage removal of radionuclide

$$removal=\frac{original\ activity-final\ activity}{original\ activity}100$$

C. Decontamination factor (DF)

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