Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Separation of Radionuclides of Silver and Antimony from Low-Level Liquid Waste of Research Reactor by Using Iron(II) Hydrous Oxide Coprecipitation

Farooq Jan[a]; M. Aslam[a]; S. D. Orfi[a]; M. Hussain[a]
[a] Radioactive Waste Management Group, Health Physics Division, Pakistan Institute of Nuclear Science & Technology (PINSTECH), Islamabad, Pakistan

To cite this Article Jan, Farooq , Aslam, M. , Orfi, S. D. and Hussain, M.(2005) 'Separation of Radionuclides of Silver and Antimony from Low-Level Liquid Waste of Research Reactor by Using Iron(II) Hydrous Oxide Coprecipitation', Separation Science and Technology, 39: 5, 1021 — 1036

To link to this Article: DOI: 10.1081/SS-120028569

URL: http://dx.doi.org/10.1081/SS-120028569

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 5, pp. 1021–1036, 2004

Separation of Radionuclides of Silver and Antimony from Low-Level Liquid Waste of Research Reactor by Using Iron(II) Hydrous Oxide Coprecipitation

F. Jan,* **M. Aslam, S. D. Orfi, and M. Hussain**

Health Physics Division, Pakistan Institute of Nuclear Science &
Technology (PINSTECH), Islamabad, Pakistan

ABSTRACT

After upgrading the Pakistan Research Reactor-1 from 5 MW (Th) to 10 MW (Th), increased inventory of ^{100m}Ag and ^{124}Sb in the waste stream demanded some sort of treatment to bring the radioactivity levels within the disposal limits. A chemical treatment, making use of scavenging precipitation of the radionuclides with hydrous oxides of iron, was studied. Fe(II) hydrous oxide coprecipitation by using green vitriol provided complete removal of silver activity and an acceptable decontamination factor (DF) for antimony. Coagulant doses and other parameters for decontamination of the bulk of the waste were studied and

---

*Correspondence: Dr. Farooq Jan, Radioactive Waste Management Group, Health Physics Division, Pakistan Institute of Nuclear Science & Technology (PINSTECH), P.O. Nilore, Islamabad, Pakistan; Fax: 92 51 9290275; E-mail: shafiq@pinstech.org.pk; pinstech@panknet1.ptc.pk; or fjan@pinstech.org.pk.

DOI: 10.1081/SS-120028569 0149-6395 (Print); 1520-5754 (Online)
www.dekker.com

optimized. Various parameters and results of the process are presented. High DFs for silver and antimony radionuclides have been achieved.

Key Words: Scavenging; Coprecipitation; Chemical treatment; Silver; Antimony; Decontamination factor; Low level liquid waste.

INTRODUCTION

Minimizing the volume of liquid radioactive wastes for their subsequent disposal is an important step in radioactive waste management. The total mass of radioatoms in these waste substances may usually be very small, and the spectrum of the radioactive elements and their separation conditions are so broad and varied that its manipulation calls for special, and expensive, techniques. The degree of decontamination of the waste effluents achieved is another important aspect. Decontamination factors (DFs) of the order $>10^2$ are required for the treatment of low and intermediate level radioactive liquid waste, therefore, the concentration of active ions will have to be reduced to very low levels.[1] Various treatment processes are being operated for this purpose. Precipitation methods, particularly hydrous oxide precipitates of metal ions like Mn^{4+}, Fe^{3+}, Al^{3+}, Ti^{4+}, etc., which exhibit sorption affinity for other ions,[2] are often used[3] as scavengers for trace amounts of unwanted elements in large volumes of liquid waste.[1]

The value of a given precipitate as a scavenger depends upon its ability to remove a sizable portion of the contaminants. Iron and lanthanum hydrous oxides are very effective scavengers on many radioactive tracers.[1,4] Most of the radiochemical separation work, particularly in the practice of radioactive waste management, is ascribed to ferric hydrous oxide precipitation. Hydrous oxides of iron have a high surface activity and are easily flocculated. When formed under alkaline conditions, the floc is negatively charged due to OH^- ions and will thereby adsorb positive ions.

Iron–hydrous oxides cover a large length of the pH scale, and the solubility product of many hydrous oxides would have already exceeded that which would provide growth points as nuclei and would adsorb on their surface those which will precipitate later. The knowledge of solubility products of metallic hydrous oxides sometimes becomes a little obscure, so that exact theoretical calculations are not always possible, and, for practical purposes, quite a number of bench-top and jar tests are required.

Based on Fe(II) hydrous oxide scavenging precipitation, a procedure was studied and selected for the removal of radionuclides of silver and antimony from low-salt low-activity liquid waste of the Pakistan Research Reactor-1 (PARR-1), a low-enriched uranium-fuelled reactor and a major research facility at the Pakistan Institute of Nuclear Science and Technology (PINSTECH), Islamabad. The selection was made after a series of experimentations by using different classical reagents and techniques in a bid to arrive at a cheap, single reagent/single step process with reasonable DFs for silver and antimony. Real PARR-1 waste samples were used throughout this work. Certain aspects of this treatment process are being described in this paper.

EXPERIMENTAL

Method and Materials

Wastewater samples were collected periodically, in shielded 2.5-L amber glass bottles, from the reactor sump room and underground tanks. Low activity samples were collected from storage tanks in a disposal area, last in the collection system, and also receiving from other streams, to eliminate dilution of the sample liquid and to see the effect of fungal growth on coagulation/flocculation. In a few cases, samples were preconcentrated to increase activity range. Activity content of samples depended on the regeneration time of the demineralizer in the primary coolant circuit and on the sample collection point, and varied generally in the range of 1.0×10^2 up to 1.0×10^5 Bq/L for Ag and from a few Bq up to 2.5×10^5 Bq/L for Sb.

Initially, a few tests, pH, alkalinity, turbidity, and radioisotopes concentrations, were made on the piled-up waste effluents. Common anions and cations profiles and other characteristics of PARR-1 waste samples were worked out beforehand. Many anions in low concentrations could not have been detected because of sample dilution for lowering the activity level for nonactive instrumental analysis of the samples. After these preliminary tests, scavenging precipitations by using different reagents and techniques such as removal by ion-exchange resins, cation and isotopic exchange, radiocolloids removal through a membrane filter, and removal of the activity by charcoal were examined. These preliminary studies lead us to in the end, use a Fe(II) hydrous oxide scavenging precipitation that exhibited the highest selectivity for the silver as compared with Fe(III) hydrous oxide precipitation by using ferric chloride or other scavengers studied. The process provided a reasonably high DF for silver and comparable values for antimony cost-effectively in a single reagent, single-step manner. Precipitation of the Fe(II) hydrous oxide was effected in a basic medium by using commercial ferrous sulphate by flash mixing and thorough shaking of the sample matrix. It was followed by gentle agitation for some time to allow for proper floc buildup. Precipitation and coagulation steps were followed by clarification of the effluent. Activity in solid component was removed by decantation, filtration, or centrifugation.

A number of process parameters, such as the optimum dose of reagents, order of mixing the reagents, best pH range, shaking time/speed of the precipitation matrix, flocculation, sedimentation optimums, etc., were studied. Besides other aspects, the difference in the removal efficiency by decantation, filtration, and centrifugation was studied. Though digestion has little effect upon amorphous or gelatinous precipitates, tests were made for any considerable amount of radionuclides resuspension upon aging the precipitate in contact with the supernatant. The pH also was changed during aging to see its effect. The effect of shaking during aging also was observed. As the order of addition of reagents is of utmost importance in chemical reactions, this factor also was checked for efficiency changes; $FeSO_4$ was added to a pre-alkalized sample and vice versa. Reagents were prepared as:

$FeSO_4 \cdot 7H_2O$: Initially analytical reagent (A.R.) grade was used; but, for subsequent analysis, commercial product in plastic bags was purchased. The product had an "insoluble" content of about 2–5 wt% and a Fe(II) content of about 90% of the soluble portion. A complete assay was, however, not needed. Dilute (2–4%) sulfuric acid solution of the $FeSO_4$ reagent of various concentrations was used within days.

pH adjusting reagents: Different bases were studied but finally NaOH, in the form of 50% commercial lye or A.R. grade pellets were used.

To prepare a solution of the coagulant, first, concentrated H_2SO_4 was mixed in distilled water to make it 0.025% (20–30 mL). Solid $FeSO_4 \cdot 7H_2O$ then was dissolved in it. This was prepared preferably on the same day or a day before its use, in plastic or stainless steel container. Sodium hydroxide can be used as such, but, if desired, it can be diluted to an equal volume or double its volume. This added a little more to the dilution factor when used in conjunction with the bracketed values in the following paragraph.

The process optimized for the treatment of PARR-1 waste is outlined below. The optimum values of the reagents worked out with the help of bench-top tests on 0.5–5.0 L samples are given per liter of a typical waste sample. By using these parameters, very high decontamination of the waste effluents was achieved, giving us a wide margin of further reduction in the precipitant doses for practical application.

Sump water	1000 mL
Activity range	
(Ag)	Up to 5×10^4 Bq/L
(Sb)	Up to 2.5×10^5 Bq/L

$FeSO_4$, commercial	1.4–1.6 g
NaOH, 50% lye	3.2–4.0 mL
H_2SO_4 A.R. grade	0.3–[0.4] mL
Distilled water to make	20–[30] mL
DF values obtained	
(Ag)	>450
(Sb)	>290

The values in brackets if used, will also give an additional small dilution factor for a plant-scale treatment process.

Radiometric Analysis

Radioactivity measurements were performed either by NaI(Tl) crystal detector or by HPGe detector coupled with a multichannel analyzer (MCA) Series-85 from M/S Canberra, using a ^{166m}Ho source for calibration purpose[5,6]. All the measurements were carried out in either 250-mL or 300-mL glass beakers under similar conditions for reference and test samples. Beakers were identical to detect a cross-sectional active area and were washed frequently with dilute acids. Because the reference samples were to be counted in liquid form and the precipitate carried the bulk of activity that would greatly increase the detector's dead time, more accurate results were obtained by counting the supernatant or filtrate rather than the precipitate. Counting was done for an appropriate time in 2π geometry.

DISCUSSION

Radioactive liquid waste generated at the institute generally falls in the low level category, with mixed β, γ-activity. Allowance for decay to allowable limits and shallow ground disposal has been the prime practice prevailing at PINSTECH.[7] Some time back, PARR-1 was upgraded from 5 MW to 10 MW (Th). Immediately after upgrading the reactor, when the waste management system was not yet enhanced, increased inventory of ^{110m}Ag and ^{124}Sb in the waste stream and the exhaustion of storage capacity demanded some sort of treatment to increase the disposal rate and to ensure smooth reactor operations and flow of radiopharmaceuticals to medical centers. Another objective in perspective was to gather data for a technical scale chemical treatment facility to be used for demonstration and teaching purpose.

The waste contained a number of short-lived radionuclides of which only ^{110m}Ag has been of radiological significance and was present in radioactive waste of the institute in appreciable amounts. Antimony also is encountered as a contaminant element worth interest in the waste. Its short-lived isotopes posed no significant problem from waste management point of view; however, ^{124}Sb, having a half-life of about 60 days, had some worth because of its relatively higher production abundance in PARR-1. Tables 1 and 2 depict common ions and radionuclides profiles of a typical PINSTECH wastewater sample. Results obtained for various parameters of the process are presented in Tables 3 through 7.

In some previous studies, scavenging precipitation with other reagents and electrolytic removal was carried out. Fe(III) hydrous oxide as a scavenger using ferric chloride was not found very effective against silver. While ferrous sulfate did well for both silver and antimony,[2,8] ferric chloride gave a partial DF and needed a second precipitation step for more complete removal of the silver activity. It, however, provided a better DF for antimony as compared with other reagents studied. Thus a procedure based on ferrous sulfate scavenging precipitation was optimized for the removal of Ag and Sb. With added tracers of ^{60}Co and ^{137}Cs, reasonably high DFs also were shown for cobalt-60, while removal efficiency for ^{137}Cs was under 50% in the range of $1500-3000\,\mathrm{Bq\,L^{-1}}$, with a little higher reagent concentration than used for Ag and Sb. The process is expected to be applicable, with minor adjustments, for radionuclides such as Cr, Sr, Ru, Tc, Zr, Nb, Ce, Pu, Am, Np, rare earth, and transuranic elements. Various parameters of the process are discussed in the following paragraphs.

Table 1. Common ions profile of a typical PINSTECH wastewater sample.

Ionic species	Conc. range (ppm)	Ionic species	Conc. range (ppm)
Bromide	bd	Lead	bd
Chloride	314–754	Magnesium	4.2–7.6
Carbonates	357–671	Mercury	bd
Nitrate	1–70	Potassium	0.5–1.4
Phosphate	bd/0.8–94	Silicon	bd–0.8
Sulfate	3–109	Sodium	154–539
Calcium	bd–53	Strontium	bd
Cobalt	bd	Sulfur	bd
Iron	0.02–0.08	Zinc	0.01–0.04

Note: bd, below detection limit.

Table 2. Common radionuclides profile[a] of a typical PINSTECH wastewater sample.

Radionuclide	Half-life	Radionuclide	Half-life
^{24}Na	14.96 hr	^{108}Ag	2.41 m
^{27}Mg	9.46 m	^{110m}Ag	249.9 d
^{51}Cr	27.7 d	^{113}Sn	115.1 d
^{54}Mn	312.2 d	^{122}Sb	2.7 d
^{121}Te	16.8 d	^{123m}Te	119.7 d
^{124}Sb	60.3 d	^{131}I	8.02 d
^{56}Mn	2.58 hr	^{134}Cs	2.06 a
^{60}Co	5.27 a	^{141}Ce	32.5 d
^{65}Zn	244.3 d	^{198}Au	2.69 d

[a] The inventory of the commonly encountered radionuclides varies with the run of the reactor operation and the associated radioisotopes production and other laboratories. Certain very short-lived and/or very low concentration or seldom-encountered radionuclides are not indicated in the list.

Order of Mixing of Reagents

By providing relative supersaturation in terms of Fe^{2+} ions concentration, by mixing the coagulant to alkaline solution or reversing the mixing order, i.e., adding NaOH following the coagulant addition, the precipitate is formed under different pH and coagulation environments. This fact did not bring any worthwhile change in the overall DF values. However, a brown tint persisted even after filtration when $FeSO_4$ was mixed before NaOH, indicating occurrence of some oxidation of Fe(II) to Fe(III). The effect of the order of mixing the reagents also can be seen in Table 3.

Characteristics of the Sludge

Pale green precipitate of Fe(II) hydrous oxide was more slimy and flocculent and was more cleanly handled than the brown precipitate from Fe(III). The former deposited less on the containers, but easily changed to the brown variety in contact with air. There is a great tendency of the precipitate to become red-brown “rust”, which is difficult to filter after a long aging period. The end product sludge when dewatered and dried completely after filtration turned into a flaky material of red-brown rusty nature, amenable to blow away by air current but cleanly manageable. It was hard to dissolve in dilute mineral acids and was magnetic. When dispersed in distilled water at various pH, it lost some bulk at a lower pH value (Table 6). Redissolution of the freshly formed sludge by acid and reprecipitation tests also were carried out to see any

Table 3. Precipitant ($FeSO_4$) concentration vs. decontamination factors.

Coagulant concentration ($g\,L^{-1}$ of sample)	Order of mixing (× = first)			Activity range (Bq per 100 mL sample)		DF	
	$FeSO_4$	NaOH	pH	Ag	Sb	Ag	Sb
0.6	×		10	3,767	na	>4	na
0.7	×		9	150	310	>7	na
0.7		×	9	150	310	>8	>5
0.8	×		9	150	310	>11	na
0.8		×	9	150	310	>18	na
0.9	×		9	150	310	>19	>9
1.0	×		9	150	310	>24	na
1.2	×		9	150	310	>31	>22
1.2		×	9	150	310	>27	na
1.4	×		9	270	595	>100	>62
1.5	×		9	270	595	>331	>118
1.6		×	9	270	595	>530	>292
1.7	×		9	270	595	>710	na
1.8	×		9	183	na	→∞	>300
2.0	×		10	6,360	na	>850	>305
2.2	×		10	6,360	na	>905	na
2.4	×		10	1,579	2,000	>934	>286
2.6	×		10	1,579	2,000	→∞	>290
3.0	×		10	4,260	11,109	1,000	na
4.0	×		~8	4,260	11,109	1,000	>295
6.4	×		~8	4,260	11,109	→∞	>300

Note: These observations were carried out by simple decantation of the samples that contained no flocculated particles. Because, in most of the cases, if the decantate was allowed to settle overnight, some material was sedimented out. The decontamination factors would be higher should centrifugation or filtration be used.

Key: na, Data not available; →∞, DF tends to infinity as the Activity term in the denominator ($A_{\text{INFLUENT}}/A_{\text{EFFLUENT}}$) approaches zero.

effect on the retention of activity should a need arise for this operation. No deleterious effect was shown.

Clarification of Treated Effluent

Immediate filtration through either filter paper or a cloth bag after precipitation with $FeSO_4$ was more effective than when the sample was simply

Table 4. Scavenging precipitation when using various bases for pH adjustment.

							Activity range (Bq per 100 mL)		DF	
Coagulant concentration	A	B	C	D	E	pH	Ag	Sb	Ag	Sb
	×					~8	7,474	3,400	1,000	5.6
$4.0\,g\,L^{-1}$		×				~8	7,474	3,400	1,000	7.7
				×		~8	7,474	3,400	5.6	1.1
					×	~8	7,474	3,400	Lost	Lost
$1.6\,g\,L^{-1}$			×			~8	4,260	11,109	500	5.0
Excess NH_3[a]										

Note: A = NaOH, B = KOH, C = NH_4OH, D = $Ca(OH)_2$, E = Na_2CO_3.

[a] Iron-hydroxides do not completely precipitate with ammonia. Excess ammonia, however, yielded sufficient precipitate to remove bulk of the activity.

decanted, while centrifugation (around 2500 rpm) was most effective for the removal of activity in the solid phase. However, decantation overnight was absolutely sufficient for our process.

Optimization of the Reagents and Effect of pH on the Removal of Activity

Amounts of reagents were optimized wholly on experimental observations. Drastic variations in the composition of the waste were foreseen; therefore, enough margins had to be kept if a least number of bench tests were to be performed for a reliable process.

Economic use of reagents can be effected by holding the pH at 9–10 during precipitation step with the controlled addition of NaOH while the coagulant is being added. The fact that activity in the liquid phase is decreased on aging (discussed later) can be used to further economize the reagent doses to some extent. A bit of excess of precipitants is needed, however, to assure completeness of the reactions and fair coagulation and to give bulk to the precipitates from the low-salt wastewater to improve the flocculation and sedimentation characteristics of the solid phase. A colloid formation due to insufficient reagents, if it occurs, can be remedied by the addition of a little more reagent. Small amounts of reagents may be used if centrifugation could be used. Decontamination factors obtainable are directly proportional to the amount of reagents used, up to $10^4\,Bq\,L^{-1}$. Activity greater than this approximate range required the use of an additional reagent or called for a two-step scavenging. A second precipitation in every case removed the last traces of activity. The

Table 5. Settling rate and sediments volume of a well-formed floc under different conditions.

Coagulant concentration	pH	Time (T)	Starting volume (V)	Settling rate ($\mathrm{cm\,min^{-1}}$) [volume reduction rate ($\mathrm{mL\,min^{-1}}$)]	Settled volume	
					Settled at T	Percentage of V
$5.0\,\mathrm{g\,L^{-1}}$	9	4 min	1,000 mL[a]	0.58 [50.00]	800	80
		5 min		0.60 [60.00]	700	70
		7 min		0.66 [57.10]	600	60
		9 min		0.64 [55.50]	500	50
		14 min		0.49 [42.86]	400	40
		28 min		0.29 [25.00]	300	30
		36 min		0.23 [20.14]	275	28
		24 hr				—[c]
$5.0\,\mathrm{g\,L^{-1}}$	10	2 min	1,000 mL[b]	1.80 [25.00]	950	95
		4 min		3.60 [25.00]	900	90
		6 min		5.40 [25.00]	850	85
		10 min		7.20 [20.00]	800	80
		12 min		9.00 [21.00]	750	75
		15 min		10.80 [20.00]	700	70
		17 min		12.60 [21.00]	650	65
		19 min		14.40 [21.00]	600	60
		22 min		16.20 [20.00]	550	55
		28 min		18.00 [18.00]	500	50
		30 min		19.81 [18.00]	450	45
		34 min		21.60 [18.00]	400	40
		42 min		23.40 [15.00]	350	35
		58 min		25.20 [15.00]	300	30
		24 hr			85	8.5
Optimum	10	24 hr	1,000[b]		42	4.2

[a] In 11.5-cm × 10.5-cm beaker.

[b] In 36-cm × 6-cm cylindrical column.

[c] Could not be measured because of the round bottom of the beaker and the thin layer deposits.

amounts reported are, however, quite reasonable. The results are recorded in Table 3, and the variation of DF with the coagulant concentration is shown in Fig. 1. Effects of various bases on the removal of silver and antimony is depicted in Table 4. However, this feature was not thoroughly studied.

The pH control in wastewater treatment has marked effects on the selection and output of the process,[2] but, for the scavenging precipitation with ferrous

Table 6. Effect (approx.) of pH on sedimentation and flocculation of floc.

Coagulant concentration	pH	Time (min)	Settling rate (cm min^{-1})	Volume settled
1.6 g L^{-1}	10	10	32.40	50 mL
		13	32.20	
		15	34.60	
	8	10	34.60	40 mL
		13	37.70	
		15	34.80	
	6.5	10	34.50	32 mL
		13	31.50	
		15	35.20	

Note: 30 cc of the ppt (settled slurry) was transferred to distilled water having different pH.

sulfate, the effect of pH on the fraction of activity removed was not obvious. The largest fraction of Ag and Sb activity removed was in the pH range of 8–10 [this also was true for Ag and Sb when using Fe(III) chloride as a coagulant]. Very little effect was observable outside this range, down to pH 7 and up to pH 11. A pH lower than 7 had, however, an adverse effect on activity removed while, higher than pH 10 had something to do with the characteristics of precipitate.

Table 7. Effect of aging/digestion on activity removed.

pH	Range (Bq per 100 mL)	DF after 1 hr contact time	DF after 24 hr contact time	DF after 48 hr contact time	Remarks
9.5	300	104 (90, after precipitation)	119	→∞	Reagent was added first
9.5	300	100	158	→∞	Low reagent conc., added last
9.5	300	27	50	353	
8.5	300	54	69	→∞	
8.5	300	73	107	→∞	
8.5	300	20	33	107	Low reagent conc.

Note: →∞, DF tends to infinity as the Activity term in the denominator ($A_{INFLUENT}/A_{EFFLUENT}$) approaches zero.

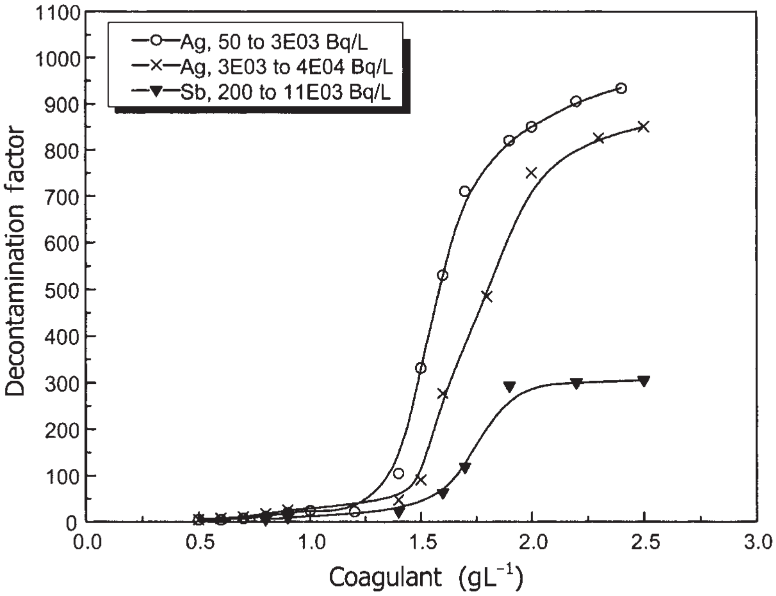

Figure 1. Decontamination factor as a function of coagulant concentration.

Decontamination Factors

Decontamination factors obtained with different coagulant doses at different activity ranges for both silver and antimony are recorded in Table 3. In either case, the DFs increased linearly with the coagulant concentration through a very steep rise at optimum doses and up to certain maximum value where, after this, no increase in DF was made. The behavior is shown in Fig. 1.

Flocculation and Sedimentation and Effect of pH

Under the optimum conditions, the tendency for the floc formation is tremendous. Sufficient but gentle shaking must be done after flash mixing (during flocculation, commencing just after precipitation and till floc fragments were clearly seen during gentle agitation) and before the periods of poor flocculation that follow.

Rather vigorous shaking at the time of flash mixing the reagents must be performed to bring more Ag-containing solution in contact with the precipitating agent. Once the precipitation was complete, very gentle shaking was performed to affect proper flocculation and bring more and more substrate in contact with the maturing floc. One minute of continued good shaking after reagents were mixed, however, had no deleterious effect on DF or flocculation characteristics on bench scale (2- or 5-L process).

Settling rate and sediments volume of a well-formed floc from minimum and maximum reagent concentrations (beyond which there was no appreciable change in any parameter observed) were recorded against time intervals and are presented in Table 5. The observations were made in glass cylinders and also in beakers for diameter-to-height ratio vs. settling time. Initial settling rates were high, therefore, a time interval of 1 min through 2, 10, 30, and 60 min were used for measurements. The results are plotted in Fig. 2. Maximum sludge volume reduction after 24 hr was about 98% at optimum coagulant concentration and 8–9% of the total volume at some maximum 5 g L^{-1} concentration of the coagulant. A little self-compaction was observed in cylindrical vessel. Sedimentation rate was worked out by using a graduated cylindrical column of 36 cm height and 6 cm inner diameter (very slight constant turbulence would reduce the settling rate). Under the observed rate,

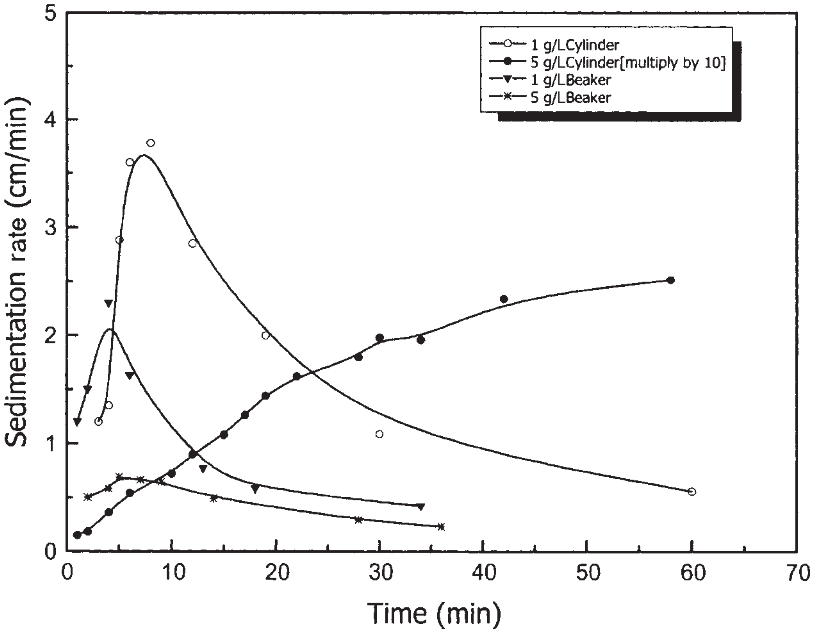

Figure 2. Settling rate of sludge at different width-to-height ratio with different coagulant concentrations.

no adverse effect on the DFs was noticed. The effect of detergents, etc., was not studied; however, lower concentration of detergents was well tolerated in the waste stream. Well-formed floc settled at a rate of $2\,\mathrm{m\,hr^{-1}}$ ($3\,\mathrm{m\,hr^{-1}}$ maximum and $0.75\,\mathrm{m\,hr^{-1}}$ suggested in [2]) and was linearly proportional to the width-to-depth ratio of the vessel. No secondary process to hasten sedimentation, usually required for gelatinous metal hydrous oxide flocs, was needed.

The effects of pH upon the settling rate and settled volume are shown in Table 6. In this experiment, the precipitate obtained was transferred to distilled water and agitated for a constant time (allow a little piptization; variation in the pH in the same precipitated matrix may dissolve the ppt). The settling rate after 10, 13, and, 15 min was observed, and the volume settled after 15 min was recorded at different pH values. A minor increase in settling rate toward lower pH values can be seen from the table, but there is a marked decrease in the volume settled at lower pH values.

Sludge volume reduction (compaction of sludge) followed similar curve-like settling rates. The effect is shown in Fig. 3. At the beginning of each curve, lower rates are due to turbulence in the vessel that retarded the settling of floc for

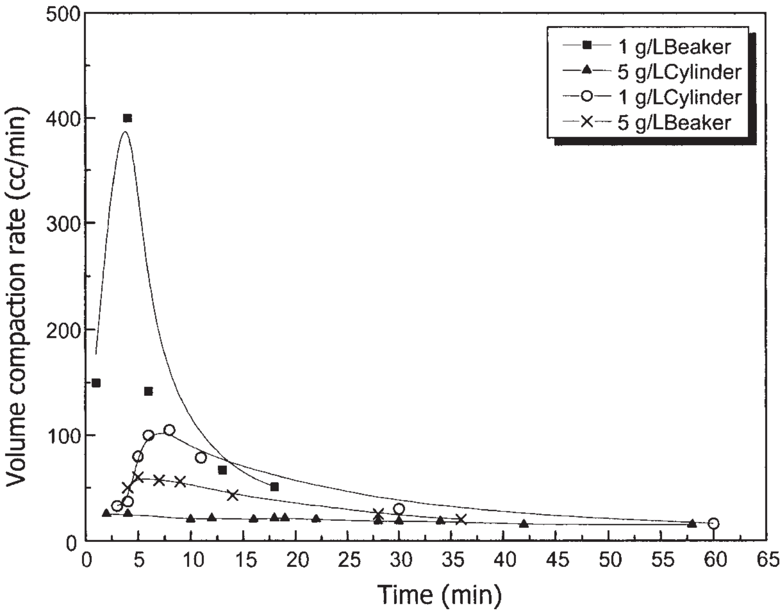

Figure 3. Compaction of sludge volume (reduction) with time at different coagulant concentrations.

some time. Settled volume after 24 hr was 2% of the total volume at 1 g L^{-1} coagulant concentration, 4.2% at the optimum and 8.5% at a maximum 5 g L^{-1} coagulant concentration. Effect of pH on aging was not clear.

Effect of Aging on Sediments

Aging of precipitate had very pronounced effect on the fraction of activity removed. As can be seen from Table 7, DFs increased considerably with increasing contact time of the precipitate with mother liquor, regardless of the order of mixing the reagents and pH changes. The precipitate though remained settled at the bottom, still it adsorbed more and more radioactivity from the supernatant with time (in some of low-activity samples, extra activity added to the supernatant was also adsorbed by the precipitates).

There was no release of activity from the sludge even after prolong aging of more than two months, indicating a very firm lodging of the positive radiocations on the negatively charged floc particles. This behavior not only assures a secure embodiment of the activity onto the sediments but also can be exploited for further reduction of the reagent doses on a large-scale operation. This effect was recognized at a later stage of the work and, as a consequence, some scatter was seen in the data on reagent concentration vs. DFs obtained because certain samples were not filtered promptly and got delayed.

CONCLUSION

Fe(II) hydrous oxide scavenging precipitation was effectively applied for the removal of radioactivity due to silver and antimony radionuclides from the bulk of low-salt low-level radioactive waste effluents generated at a 10 MW research reactor. Selectivity of the Fe(II) hydrous oxide for silver was greater than that of Fe(III) hydrous oxide. While for antimony, Fe(III) hydrous oxide was more selective. However the DFs obtained for antimony by using ferrous hydrous oxide scavenge was still better and acceptable. Excellent DF values for ^{60}Co and about 50% removal of ^{137}Cs at some specific activity range also was shown when certain samples were spiked with these moieties. The process also can be applied for the removal of many other radionuclides indicated as removable by hydrous oxides of iron in the literature. Along with the optimum doses of the reagents, detailed behavior of the process is described. Several parameters such as the effect of pH on certain unit operations, flocculation and sedimentation behavior, aging of the sludge, and sludge characteristics were studied. These are reported, along with some experimental details.

ACKNOWLEDGMENT

The authors gratefully acknowledge the cooperation of Mr. M. Shafiq, Principal Scientific Officer, Mr. Imtiaz Hussain, Senior Scientific Assistant, Mr. Ibrar Hussain, Scientific Assistant-II, and Mr. Tanveer Akhter, Laboratory Attendant.

REFERENCES

1. *Advances in Technologies for the Treatment of Low and Intermediate Level Radioactive Liquid Wastes*, Technical Report Series No. 370; International Atomic Energy Agency: Vienna, 1994.
2. *Chemical Precipitation Processes for the Treatment of Aqueous Radioactive Waste*, Technical Report Series No. 337; International Atomic Energy Agency: Vienna, 1992.
3. *Advance Management Methods for the Medium Active Liquid Waste*, Rep. EUR-7037, Commission of the European Communities, CEC/UKAEA Harwood Academic Publishers: London, 1981. In *IAFA*, Technical Report Series No. 287: Vienna, 1988.
4. Rustamov, S.; Ehl'nazarov, S. Nitrite method for the separation of silver from base metals (In Russian). Radiokhimiya **1989**, *39* (5), 83–87.
5. Khan, H.M.; Khan, K.; Atta, M.A.; Jan, F.; Perveen, N. Gamma spectrometry of some vegetables of Peshawar, Mardan and Charsada area. Physical Chemistry **1992**, *11*, 151–158.
6. Khan, H.M.; Khan, K.; Atta, M.A.; Jan, F. Measurement of gamma activity in soil samples of Charsadda District in Pakistan. Jour. Chem. Soc. Pak. **1994**, *16* (3), 183–185.
7. Hussain, M.; Orfi, S.D.; Wahid, A.; Aslam, M.; Jan, F.; Iqbal, T. In Management of low and intermediate level radioactive wastes at Pakistan Institute of Nuclear Science and Technology (PINSTECH). *Proceedings of the International Conference on Management of Radioactive Waste from Non-Power Applications-Sharing the Experience*, Malta, November 5–9, 2001; IAEA-CN-87/57 (IAFA CN8757):IAEA-CN-87, 2001; 62 pp.
8. Commission of the European Communities, Luxembourg, 1982, Report EUR-8272.

Received January 2003
Revised August 2003

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Downloaded At: 10:09 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/ Order Reprints" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Request Permission/Order Reprints

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SS120028569