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Flotation of Cesium Coprecipitated with Nickel Hexacyanoferrate(II) from Aqueous Solutions and Radioactive Waste Simulants

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Abstract: The coprecipitate flotation of ^{137}Cs from dilute aqueous solutions and simulated radioactive wastes using nickel hexacyanoferrate(II) as a coprecipitant and sodium lauryl sulfate, cetyltrimethylammonium bromide, or dodecyl amine as a collector was extensively investigated to establish the best conditions for cesium removal. Under the optimal conditions, removals exceeding 99% and decontamination factors higher than 110 could be achieved for the radioactive waste simulants. The results are compared with those obtained by conventional removal methods and are discussed in terms of the collector properties and the electrical state of the coprecipitate.

Keywords: Flotation, coprecipitate flotation, Cesium-137, nickel hexacyanoferrate(II), radioactive waste, collector

INTRODUCTION

Nuclear reactors and research centers as well as radioactive isotope production laboratories generate liquid wastes of various radioactivity levels. ^{137}Cs, one of the major long lived ($T_{1/2} \sim 30y$) and the most biologically hazardous radionucleides, is usually present in such wastes at activity levels which considerably exceed the permissible values allowed by the concerned regulatory authorities. Therefore, such wastes have to be adequately treated before discharge into the environment. Conventional processes for cesium removal from radioactive wastes include:

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(i) ion-exchange utilizing both of organic and inorganic materials (1–8);
(ii) precipitation as sodium tetraphenylborate (9), phosphotungestate (10), or phosphomolybdate (8, 11); and
(iii) coprecipitation with ferrocyanides of Cu(II), Ni(II), Co(II), etc. (12).

Ion-exchange exhibits a complicated flow-sheet (13) which involves many operational steps: absorption, back flush, regeneration, washing, and periodic replacement of the bed. Chemical precipitation and flocculation techniques are the least expensive but they also are less effective. Gravitational sedimentation of the flocculated precipitate is relatively slow, hence large vessels are required. Besides, in many instances the process suffers from difficulties in separating the precipitate, especially when present in the form of colloid or slimes. To overcome this difficulty, expensive and laborious separation techniques, e.g. centrifugation, high speed centrifugation, or ultrafiltration have to be used. Therefore, much attention has been directed towards foam separation techniques, of which coprecipitate flotation seems to be the most appropriate for cesium decontamination.

Coprecipitate flotation combines the benefits of both coprecipitation and foam separation and has proved to be effective, simple, and well suited for the removal of trace amounts of metal ions from large volumes of solution (14–19). In coprecipitate flotation the ionic species to be removed is first coprecipitated with an appropriate agent. A surfactant (the collector) is then added to the suspension with continuous stirring whereby it coats the precipitate particles rendering them hydrophobic. The coprecipitate-collector product is then levitated to the surface of the bulk solution by means of a gentle stream of fine gas bubbles.

For cesium, the best coprecipitation properties have been shown by hexacyanoferrate(II)s of the transition bivalent metals. These compounds are known to have strong ion-exchange properties and can be easily prepared by mixing a solution of alkali metal hexacyanoferrate(II) with soluble transition metal salts. They have been widely used for cesium decontamination from radioactive waste solutions by coprecipitation and separation of the cporecipitate by filtration or sedimentation, or by adsorption on preformed hexacyanoferrate salts (7, 8, 20–25). One of the most effective of these compounds is nickel hexacyanoferrate(II) (abbreviated NiHCF). It has a high efficiency and exceptionally strong affinity for cesium over a large pH range (12).

Like other hexacyanoferrate(II)s, NiHCF can be easily prepared by mixing a solution of alkali metal ferrocyanide with a soluble nickel salt, but simple precipitation leads to colloidal precipitates or slimes (7, 24) which are very difficult to separate from the suspension and are insuitable for conventional column processes. Based on previous investigations in this laboratory (15–17) and other work (26), flotation provides a most effective method of hexacyanoferrate precipitate separation. It also offers several advantages over the current conventional processes (e.g. sedimentation), such as faster separation, higher flexibility, and production of more concentrated sludge occupying smaller volumes (15–17, 27).

This work is a part of a research program on the application of foam separation techniques for decontamination of radioactive process waste water (PWW) and low-level liquid radioactive waste (LLLW) generated by research laboratories of the Nuclear Research and the Hot Laboratories Centers at Inshas, Egypt. Radioactive process waste water is ordinarily tap water contaminated with small quantities of radionuclides. The water is usually produced at high rates (about 5000 gal/day in large nuclear plants) and has to be properly treated to remove the hazardous radioactive isotopes prior to its release to the environment. The objectives of the present research work were: first, to investigate the major parameters that might control coprecipitate flotation of ^{137}Cs from aqueous solutions using nickel hexacyanoferrate(II), prepared in situ, as a coprecipitant and the anionic surfactant sodium lauryl sulphate (NaLS) or the cationic ones: cetyltrimethylammonium bromide (CTAB) and dodecylamine(DA) as collectors, and to establish the best conditions for cesium removal, and second to test the feasibility of applying the developed process for ^{137}Cs removal from liquid radioactive waste simulants.

EXPERIMENTAL

Apparatus and Reagents

The flotation system, shown in Fig. 1, has been described before (14, 15, 28) and generally it consisted of a pure nitrogen gas cylinder connected to a flotation column through a fine pressure reduction unit, manometer, filter flask, and gas humidifier.

The flotation experiments were carried out in a Pyrex glass column 45 cm in height and 4.5 cm in diameter to which a G4 sintered glass disc was fused. A tap was sealed at a distance of 1 cm above the fritted disc to enable the removal of samples from the bulk suspension. Nitrogen gas was introduced through the fritted disc at a rate of 29 cm^3/min, except where the effect of gas-flow-rate was studied. All experiments were batch type. The initial volume of each feed solution was 250 ml.

The collectors: sodium lauryl sulphate (NaLS) and cetyltrimethylammonium bromide (CTAB) were purchased from Aldrich Chemical Co. Dodecylamine (DA) was provided by Fluka. The collector solutions were freshly prepared daily. Absolute ethanol was used as a solvent for DA and CTAB as well as a frother at a rate of 1 ml of alcohol per 250 ml of aqueous suspension. Because NaLS is not soluble in absolute ethanol it was dissolved in a 50% (v/v) solution of ethanol and water to allow the simultaneous addition of collector and frother.

The radionuclide, carrier-free ^{137}Cs, was obtained from the Radiochemical Center, Amersham, and was used as a tracer.

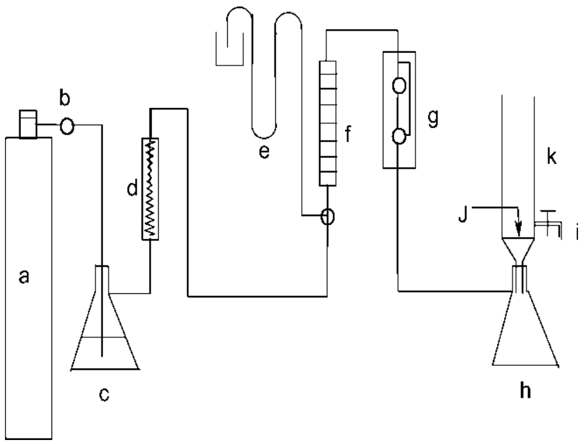

Figure 1. A schematic diagram of the foam separation apparatus. (a) nitrogen gas cylinder, (b) fine gas flow rate regulator, (c) distilled water, (d) glass wool filter, (e) manometer, (f) rotameter, (g) low-flow-rate controller, (h) filter flask, (i) tap at a distance of ~1.0 cm above the fritted disc, (j) fritted disc (sintered glass G4), (k) flotation cell (diameter 4.5 cm, length 45 cm).

Stock solutions of $K_4Fe(CN)_6$ and $NiCl_2$ were prepared from the corresponding Analar salts and were used to prepare the coprecipitating agent, NiHCF. The $K_4Fe(CN)_6$ solution was prepared weekly and was preserved in a dark reagent bottle to minimize any possible photochemical effects. Dilute working solutions were prepared, just prior to experimentation, from the concentrated stock solutions. The $NiCl_2$ solution was standardized by titration against a standard EDTA solution using pyrocatechol violet as an indicator (29). Hydrochloric acid, sodium hydroxide, and sodium chloride solutions at various concentrations, prepared from reagent grade chemicals, were used to adjust the pH and/or the ionic strength. Double distilled water was used throughout all the experimental work.

General Procedure of Flotation

For each experiment, CsCl solution of the required strength was spiked with ^{137}Cs, and the pH of the solution was then adjusted with sodium hydroxide or hydrochloric acid to the desired value. The NiHCF was produced -in situ- by adding the calculated amount of $K_4Fe(CN)_6$ to the CsCl solution to be treated. The precalculated volume of standard $NiCl_2$ solution was then added while stirring the bulk solution. The pH of the resulting suspension was measured and, if necessary, a final pH adjustment was made. Unless otherwise stated, the suspension was left to age for 15 minutes (the induction time) before vigorous shaking and transferring to the flotation cell. Gas flow was started and an appropriate volume of the suspension was withdrawn from the cell for pH measurement and for the initial radioactivity determination. The solution of the collector was then injected in one injection while vigorously stirring the suspension in the cell. At the end of the experiment, samples of the suspension were withdrawn for radioactivity and pH measurements. Unless otherwise specified, the initial pH of the suspension was maintained at 5.0 ± 0.2, the ageing time (induction time) of the suspension was 15 minutes. Under all of the investigated conditions the ultimate removal was reached in less than 15 minutes. This time period was, therefore, chosen for presenting the flotation results shown in the accompanying figures.

Analysis and Data Presentation

For ^{137}Cs determination, samples of the suspension before and after flotation were treated with concentrated hydrochloric acid in order to dissolve any precipitate. The activities of the samples were then determined radiometrically using a well type NaI(Tl) scintillation detector connected to Ortec EG&G single channel analyzer.

The flotation results are presented as removal percent (R%) of ^{137}Cs, volume reduction (VR), decontamination factor (DF) and enrichment ratio (ER), where:

R% = (initial count rate) − (count rate after flotation)/(initial count rate),

VR = original volume of the suspension/volume of the collapsed foam,

DF = initial concentration of cesium/its concentration in the residual liquid phase, and

ER = concentration of Cs(I) in the collapsed foam/its concentration in the residual liquid phase.

The results presented for cesium removal from the radioactive waste simulants investigated are averages of 3–5 experiments. An overall experimental error is estimated to be not greater than 3%.

RESULTS

Effect of Ni(II)/$[Fe(CN)_6]^{4-}$ Molar Ratio on Cs(I) Removal with NaLS or CTAB

The effect of initial $Ni^{2+}/[Fe(CN)_6]^{4-}$ molar ratio (abbreviated Ni/Fe) on Cs(I) removal and volume reduction was investigated at initially constant collector (Cc) to $[Fe(CN)_6]^{4-}$ molar ratio (Cc/Fe), two different $[Fe(CN)_6]^{4-}$/Cs(I) molar ratios (Fe/Cs) and varying doses of $NiCl_2$. The results obtained with either NaLS or CTAB are respectively depicted in Figs. 2 and 3. As observed in the figures, removal with CTAB can successfully take place at Ni/Fe ratio 1/1 or even less, but removal with NaLS starts increasing only at significantly higher Ni/Fe ratio. Under comparable experimental conditions, the percentage removal generally increases with increasing the initial $NiCl_2$ concentration to reach a maximum which depends not only on the collector type (Figs. 2 and 3) but also on the initial collector/Ni/Fe molar ratio (Cc/Ni/Fe). That is, the percentage removal is a function of the initial Cc/Ni/Fe ratio and not a function of the initial collector/coprecipitate ratio (Fig. 3 curves B and C). The data presented in Fig. 2 (curve a) indicate that the removal with NaLS becomes nearly quantitative at a higher initial Ni/Fe ratio as compared to the removal with CTAB (Fig. 3). Generally, the volume reduction is adversely affected by increasing the initial Ni/Fe ratio. It decreases abruptly by NaLS (Fig. 2), but gradually by CTAB (Fig. 3).

Effect of the Initial Cs(I) Concentration on its Removal with NaLS or CTAB

Using initially constant $[Fe(CN)_6]^{4-}$ and collector concentrations and Ni/Fe ratio, the effect of increasing the initial Cs(I) concentration on its removal with each of NaLS and CTAB was investigated. The obtained results (Fig. 4) indicate that, under the experimental conditions, removals >99%

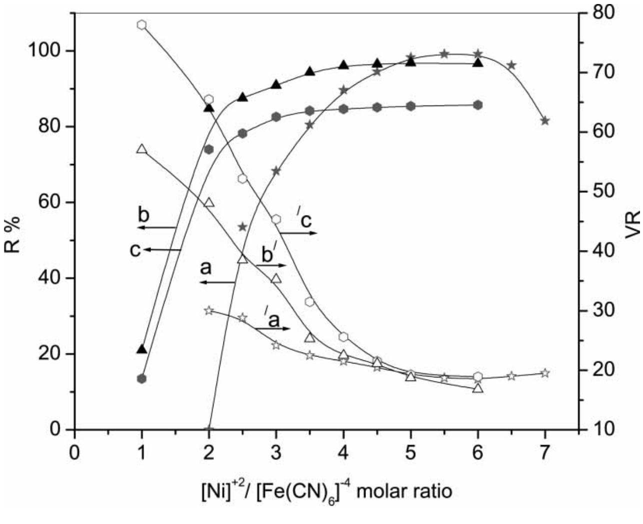

Figure 2. Effect of the molar ratio of Ni/Fe on Cs(I) removal and VR obtained by NaLS. Cs(I), $[Fe(CN)_6]^{4-}$ and NaLS concentrations: (a, a′): 1×10^{-5} M, 5×10^{-5} M and 5×10^{-5} M; (b, b′): 1×10^{-5} M, 1×10^{-4} M and 1×10^{-4} M; (c, c′): 1×10^{-4} M, 1×10^{-4} M and 1×10^{-4} M.

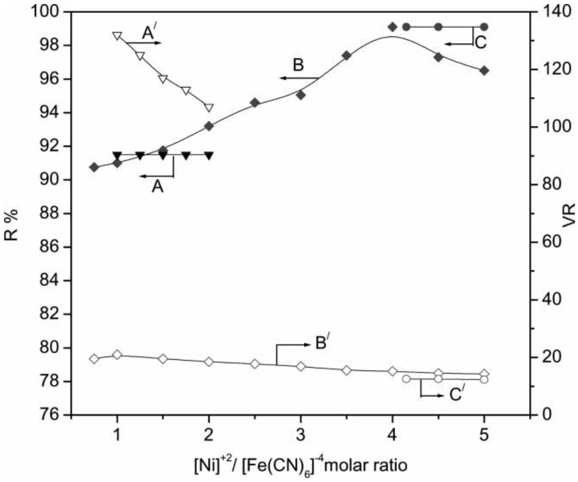

Figure 3. Effect of the molar ratio of Ni/Fe on Cs(I) removal obtained by CTAB. Cs(I), $[Fe(CN)_6]^{4-}$ and CTAB concentrations: (A, A′): 1×10^{-4} M, 1×10^{-4} M and 1×10^{-4} M; (B, B′): 1×10^{-5} M, 5×10^{-5} M and 5×10^{-5} M; (C, C′): 1×10^{-5} M, 5×10^{-5} M and 2×10^{-4} M.

are achieved with any of the tested collectors at initial Cs(I) concentrations up to 4 ppm ($\sim 2.5 \times 10^{-5}$ M) then decreases as the initial Cs(I) concentration is further increased. In contrast, the amount of Cs(I) removed increases as its initial concentration is increased. The VR(s), not shown for abbreviation, were significantly affected by Cs(I) concentration and sharply decreased with increase in its initial dosage.

Effect of NaLS and CTAB Concentrations

The results for the effect of the initial collector concentration on the efficiency of removal from solutions 1×10^{-5} M in initial Cs(I) concentration are given in Fig. 5 for each of NaLS and CTAB, curves a and A respectively. As shown in the figure, by increasing the collector concentration up to a certain value, which depends on the collector type, the removal increases sharply to form a plateau of maximum removal approaching 100%. Under the experimental conditions, the minimum collector concentrations required for optimum Cs(I) removal with NaLS and CTAB are about 1×10^{-4} M and 8×10^{-5} M respectively. Figure 5 also shows that increasing the collector dosage results into a corresponding reduction in the VR. Therefore, the use of collector concentrations much higher than the minimum amount required for optimum Cs(I) removal is not recommended. Generally, the volume reductions achieved with CTAB are distinctly greater than those obtained by NaLS.

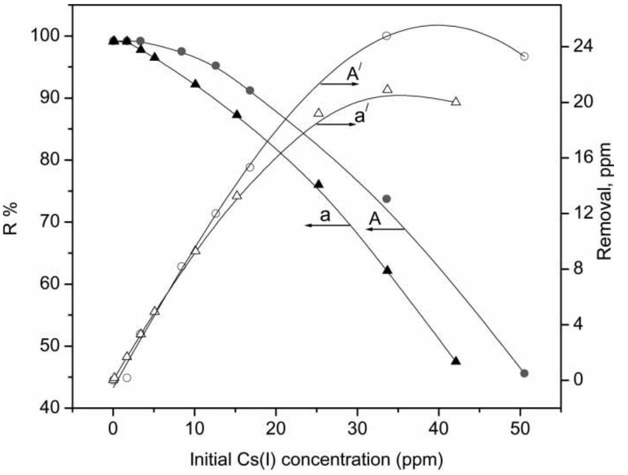

Figure 4. Percentage and ppm removals obtained by NaLS (curves a, a′) and CTAB (curves A, A′) from solutions of initial different cesium concentrations. Collector and $[Fe(CN)_6]^{4-}$ concentrations and Ni/Fe ratio: (a, a′): 1.25×10^{-4} M NaLS, 1×10^{-4} M and 4.5; (A, A′): 1×10^{-4} M CTAB, 1×10^{-4} M and 1.5.

Effect of pH on Cs(I) Removal with NaLS, CTAB, or DA

To study the effect of pH on Cs(I) removal, several series of solutions of initially constant Cs(I) concentration and varying pH values in the range 2–10, were subjected to flotation with NaLS, CTAB, or DA, under the

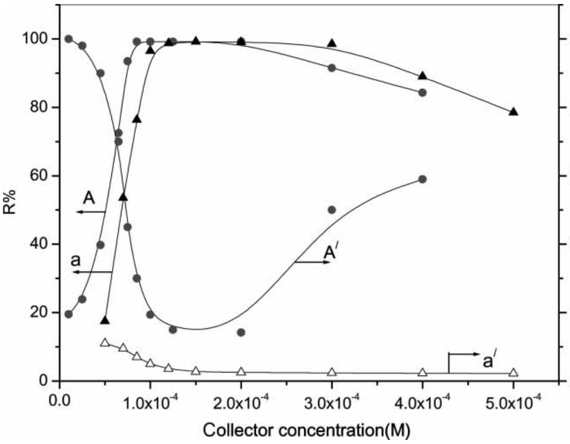

Figure 5. Effect of NaLS (curves a, a′) and CTAB (curves A, A′) concentrations on the percentage removal and VR of Cs(I). Cs(I), $[Fe(CN)_6]^{4-}$ concentrations and Ni/Fe ratio: (a, a′): 1×10^{-5} M, 1×10^{-4} M and 4.0; (A, A′): 1×10^{-5} M, 1×10^{-4} M and 1.5.

above optimum experimental conditions. The obtained removals and decontamination factors are plotted on Figs. 6, 7, and 8 as functions of initial pH of the suspension. As seen in the figures, the removal curves obtained with the three collectors tested exhibit very similar removal patterns with maxima exceeding 99% in the pH range 3–9 for NaLs (Fig. 6) and CTAB (Fig. 7). The removal curve achieved by DA (Fig. 8) is slightly displaced towards the acidic pH side. Preliminary investigations indicated that both NaLS and CTAB are not efficient for Cs(I) removal from solutions of ionic strength higher than 0.008. Therefore, and because high molecular weight amine collectors are reported (18) to be effective at a somewhat high ionic strength, it was decided to study the effect of using DA on the removal efficiency.

Effect of Ionic Strength on the Removal with NaLS or CTAB plus DA

The results obtained for Cs(I) removal with NaLS or CTAB/DA from 1×10^{-5} M Cs(I) solutions initially containing constant concentrations of $NiCl_2$ and $K_4Fe(CN)_6$ and varying concentrations of NaCl are presented in Fig. 9. As shown in the figure, the percentage removal and volume reduction are slightly affected by increasing the NaCl concentration up to about 0.0075 M. More NaCl deleteriously affects R% but favorably influences VR. Increasing the initial collector concentration does not significantly affect the removal efficiency (Fig. 9, curve a $\neq$ b).

Figure 10 shows data obtained for the effect of CTAB concentration on Cs(I) removal from solutions 0.05 M in initial NaCl. The obtained results indicate that CTAB (Fig. 10), like NaLS (Fig. 9. curve b) fails to effectively

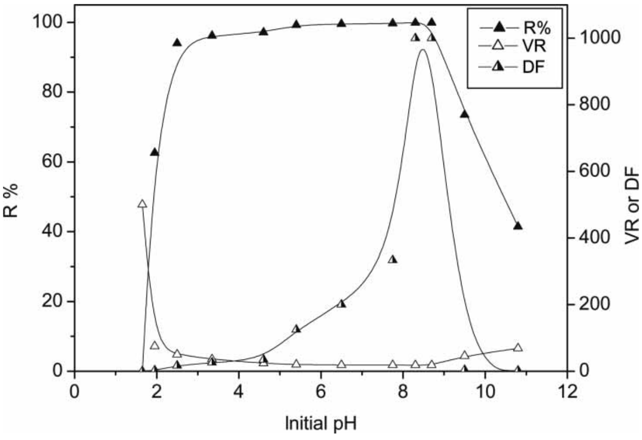

Figure 6. Cs(I) removals, VR(s) and DF(s) obtained with 5×10^{-5} M NaLS at different initial pH values. $[Fe(CN)_6]^{4-}$: 5×10^{-5} M; Cs(I): 1×10^{-5} M; Ni/Fe: 5.6.

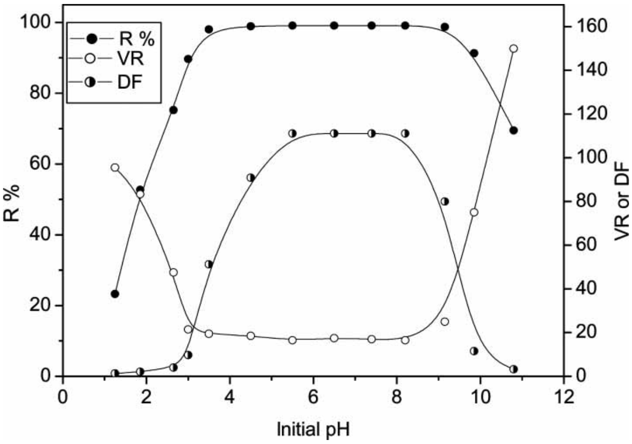

Figure 7. Cs(I) removals, VR(s) and DF(s) obtained with 5×10^{-5} M CTAB at different initial pH values. $[Fe(CN)_6]^{4-}$: 5×10^{-5} M; Cs(I): 1×10^{-5} M; Ni/Fe:4.

float the coprecipitate from solutions relatively high in ionic strength. With CTAB, the maximum removal of only 41% is achieved from solution 0.05 M in NaCl (Fig. 10) as compared to removal >99% from 0.001 M NaCl solution (Fig. 9 curves a, b).

Preliminary studies on Cs(I) removal from solutions 0.05 M in NaCl using varying concentrations of DA indicated considerable reduction in removal efficiency, even in the presence of frothing agents of different types, apparently due to improper foaming properties. However, this difficulty could be overcome by the addition of an adequate amount of CTAB. As shown

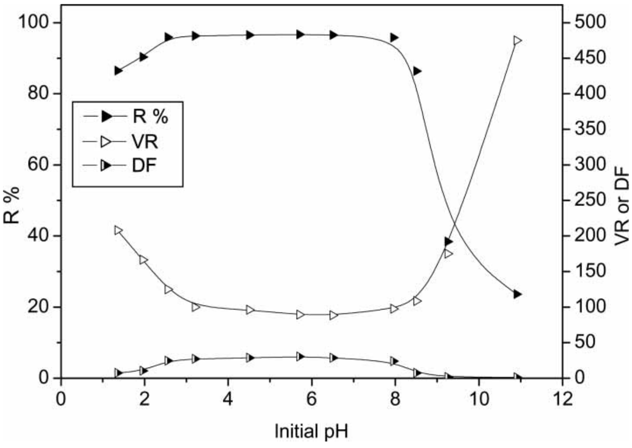

Figure 8. Cs(I) removal, VR(s) and DF(s) obtained with 5×10^{-5} M DA at different initial pH values. $[Fe(CN)_6]^{4-}$: 5×10^{-5} M; Cs(I): 1×10^{-5} M; Ni/Fe:4.

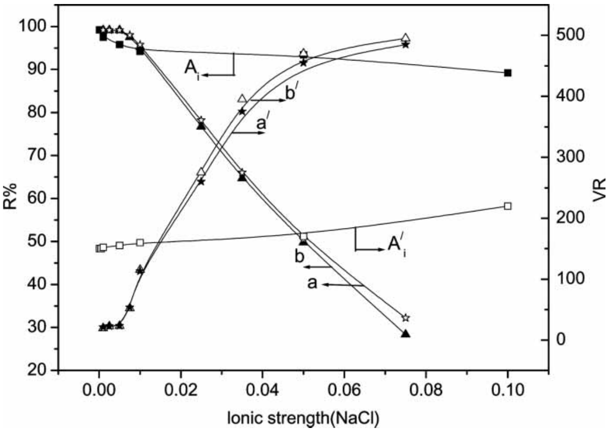

Figure 9. Cesium removals and VR(s) obtained by NaLS and CTAB/DA combination as functions of ionic strength. Collector and $[Fe(CN)_6]^{4-}$ concentrations and Ni/Fe ratio: (a, a′): 2.5×10^{-4} M NaLS, 1×10^{-4} M and 4.0; (b, b′): 1.25×10^{-4} M NaLS, 1×10^{-4} M and 4.0; (A_i, A'_i): 2×10^{-4} M/5×10^{-5} M CTAB/DA, 5×10^{-5} M and 4.0.

in Fig. 11, the removal increases with elevation in the initial molar ratio of CTAB/DA to reach maximum at ratios ≥3.0. Under comparable conditions, optimum removals exceeding 93% could be achieved, with CTAB/DA, from solutions of initial ionic strength 0.05 (Fig. 11) as compared to about 50% and 41% optimum removals achieved by NaLS (Fig. 9 curve b) and CTAB (Fig. 10) respectively. Furthermore, the VR(s) obtained by CTAB/DA are

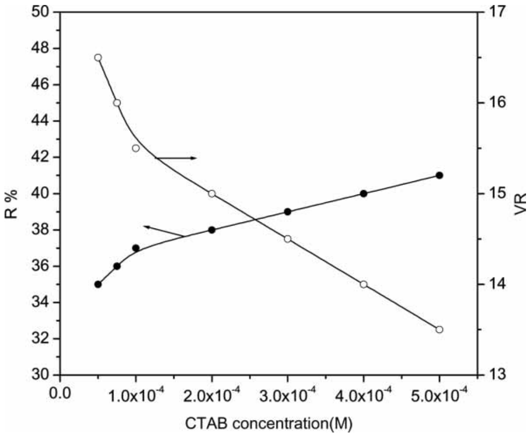

Figure 10. Percentage removals and volume reductions obtained by CTAB from solutions 0.05 M in NaCl. Cs(I): 1×10^{-5} M; Ni/Fe: 4.0; $[Fe(CN)_6]^{4-}$: 5×10^{-5} M.

much higher than those achieved by either NaLS or CTAB solely. Therefore, CTAB/DA was used as the collector in all of the following experimental work.

Effect of Aging of Cs(I) Coprecipitate Suspension

Several series of cesium coprecipitate suspensions, prepared under the above optimum conditions, and adjusted with NaCl to 0.05 M, were aged for varying durations (the induction time) before transferring to the flotation cell and subjecting to flotation. The results obtained with NaLS and with CTAB/DA are depicted in Fig. 12 which shows that removal with NaLS strongly depends on the induction time; one hour or more is required to attain the maximum removal ~80%. But with CTAB/DA, only 15 minutes aging is sufficient to achieve the optimum removal, ~93%. An increase of the induction time deleteriously affects the VR obtained by any of the tested collectors.

Effect of Foreign Salts

The effect of the presence of metal salts, other than those of Ni(II), on the percentage removal and DF obtained by CTAB/DA, is shown in Fig. 13. At foreign ion concentrations less than a certain value, which depends on the type of salt added, the flotation results are not significantly affected. However, when the salt content is further increased, the percentage removal decreases. The adverse effect caused by the tested cations on removal increases according to the series: Na(I) < Ca(II) < Co(II) < Mn(II) < Fe(III) < Al(III). As regards the tested anions, the SO_4^{2-} anion is less deleterious than the Cl^- or the NO_3^- anion (Fig. 13).

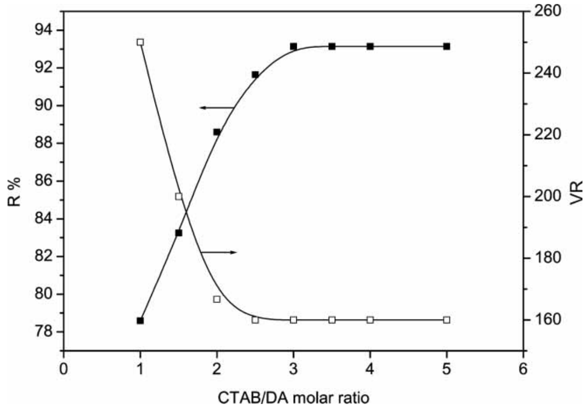

Figure 11. Effect of the molar ratio of CTAB/DA on the volume reduction and percentage removal of Cs(I) from solutions 0.05 M in NaCl. Cs(I): 1×10^{-5} M; Ni/Fe: 4.0; $[Fe(CN)_6]^{4-}$: 5×10^{-5} M; DA: 5×10^{-5} M.

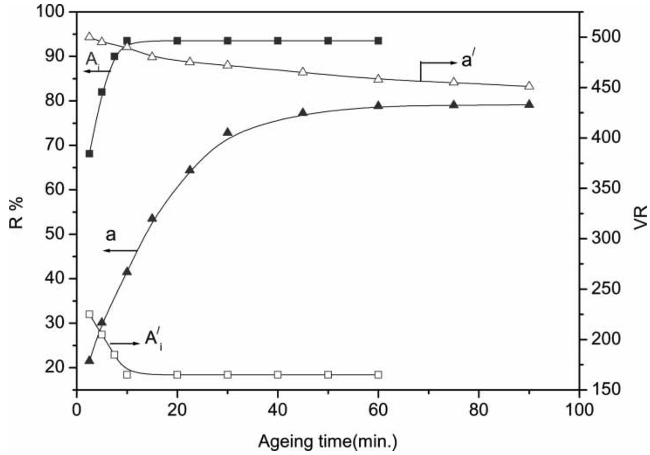

Figure 12. Effect of aging period on Cs(I) removal and VR obtained by NaLS and CTAB/DA from solutions of 1×10^{-5} M in CsCl and 0.05 M in NaCl. Collector and $[Fe(CN)_6]^{4-}$ concentrations and Ni/Fe ratio: (A_i, A_i'): 2×10^{-4} M/5×10^{-5} M CTAB/DA, 5×10^{-5} and 4.0; (a, a′): 1.25×10^{-4} M NaLS, 1×10^{-4} M and 4.0.

Effect of Gas-Flow-Rate and Bubbling Duration

The effect of gas-flow-rate on cesium removal with CTAB/DA was investigated at three levels: 29 cm^3/min, 50 cm^3/min and 72 cm^3/min. The results (Fig. 14) indicate that at a gas-flow-rate 29 cm^3/min, a maximum or steady

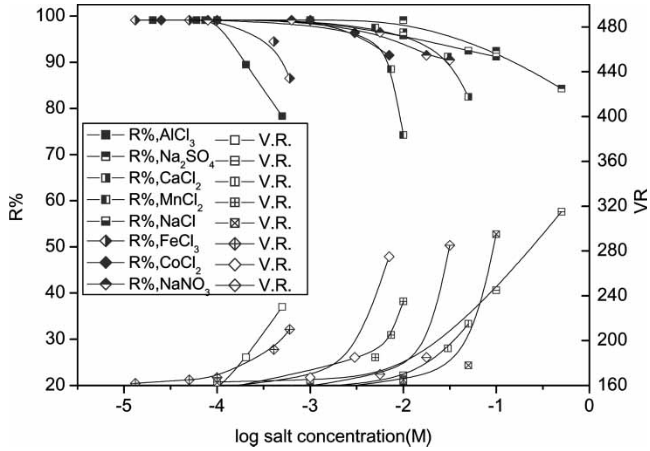

Figure 13. Effect of foreign salts on Cs(I) removals and VR(s) using CTAB/DA. Cs(I): 1×10^{-5} M; DA: 5×10^{-5} M; CTAB/DA: 4; $[Fe(CN)_6]^{4-}$: 5×10^{-5} M; Ni/Fe: 4.0.

state removal is reached in less than 15 minutes. Increasing the gas-flow-rate does not significantly affect the maximum removal though it considerably results in increase in the rate of removal as indicated by the steepness of the initial slopes of the removal curves. The amount of liquid entrained in the foam was observed to increase by increasing the gas-flow-rate. Therefore, the gas-flow-rate 29 cm^3/min was selected for use in the present work so as to minimize liquid entrainment while maintaining a reasonable rate of removal.

Decontamination of Simulated Radioactive Waste Solutions

In order to demonstrate the efficiency of applying the developed coprecipitate flotation process for radioactive waste decontamination, simulants of two varieties of radioactive waste solutions, generally produced in nuclear research institutes, were examined:

1. Radioactive process waste water (PWW) simulating the waste water generated at radiochemical laboratories of the Hot Laboratories Center, at Inshas, and
2. A synthetic aqueous solution similar to the low-level liquid radioactive waste (LLLW) generated in the Nuclear Research Center at Inshas.

The chemical composition of the PWW and LLLW simulants are listed in Tables 1 and 2 respectively and the flotation results obtained for PWW at different pH values and for LLLW at initially varying Cs(I) concentrations are summarized in Table 3 and Figs. 15 and 16. The pH of the waste

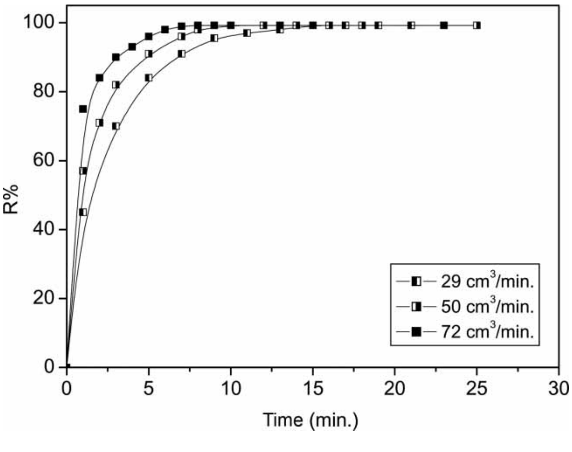

Figure 14. Effect of gas flow rate and bubbling duration. Cs(I): 1×10^{-5} M; CTAB/DA: 2×10^{-4} M/5×10^{-5} M; $[Fe(CN)_6]^{4-}$: 5×10^{-5} M; Ni/Fe: 4.0, pH ~ 5.2.

solution, to be tested, was adjusted with hydrochloric acid or sodium hydroxide to the desired value and the precipitate was then floated with CTAB/DA under the optimum removal conditions. The obtained results (Table 3 and Figs. 15 and 16) indicate that removals $>99\%$ could be achieved for both the PWW and LLLW in the pH range 9.2 down to 5.5 and probably lower. As shown in Fig. 16, under the experimental conditions, the percentage removal of Cs(I) depends on its initial concentration in the system, being $>99\%$ up to initial Cs(I) concentration of about 2.5×10^{-5} M and decreases as the initial metal ion concentration is further increased.

DISCUSSION

The data presented in Figs. 2 and 3 indicate that cesium could be successfully removed by either an anionic or a cationic collector. The extent of removal is markedly affected by the initial Ni/Fe ratio. With the strong anionic collector, NaLS, cesium removal starts suddenly at an initial molar ratio of Ni/Fe slightly higher than 1 (Fig. 2 curves b and c) indicating the formation of easily floated compound. Previous investigations in our laboratory (30) have shown that under experimental conditions of pH and of nickel concentrations similar to those of the present work $Ni(OH)_2$ is not formed. Therefore, the observed increase in the removal efficiency with increase in the initial nickel concentration cannot be attributed to adsorption of Cs(I) on $Ni(OH)_2$ precipitate and subsequent flotation, but should be ascribed to enhancement of flotation of precipitated NiHCF (with the incorporated cesium).

Coprecipitate flotation involves two consecutive processes: coprecipitation of the ion to be removed by a suitable agent, followed by flotation of the coprecipitate with a surfactant collector usually of a charge opposite to that of the coprecipitate. The efficiency of the collector is principally determined by:

(i) The sign and magnitude of the initial charge of the precipitate surface and the characteristics of the ions present thereon, and
(ii) The type and state of ionization of the active groups of the collector.

Table 1. Chemical composition of the simulated PWW[a].

Ion	Cl^-	SO_4^-	NO_3^-	Fe^{3+}	Mn^{2+}	F^-	CN^-	Na^+	K^+	Ca^{2+}	Mg^{2+}
Concentration (mg/L)	18	17	0.2	0.12	—	0.3	0.028	70	14	24	10

[a] The pH of water is 7.3 and was adjusted to the desired value with either hydrochloric acid or sodium hydroxide.

Table 2. Chemical composition of the simulated LLLW[a]

Ion	Total hardness (g/eq · L)	Ca:Mg ratio	SO_4^-	Cl^-	NO_3^-	PO_4^{3-}	Oxalate
Concentration (mg/L)	18	1:1	0.2	0.12	—	0.3	0.028

[a] The pH of the real waste is 7.0–7.5 and was adjusted to the desired value with either hydrochloric acid or sodium hydroxide.

According to the literature (31), the initial charge of a precipitate is determined by exchange of ions from solution with ions of the outer layer of the crystal and/or with ions of the interior. Since the constituent ions of the crystal fit better in the crystal lattice, the constituent ion present in excess in the solution phase is usually exchanged in preference to the other ions. Hence, the initial charge of a precipitate depends on whether excess cations or anions are present in the solution (32).

Based on the foregoing considerations and on the result that the high removal achieved at Ni/Fe molar ratios > 1 is obtained by the strongly ionized anionic collector, NaLS (Fig. 2 curves a–c), then from electrostatic considerations it is deduced that NiHCF precipitated at initial Ni/Fe molar ratios > 1 should be positively charged. This charge is believed to be acquired by the coprecipitate as a consequence of possible presence, in the solution, of free (non-complexed) Ni(II) ions in excess of the stoichiometric amount required for NiHCF precipitation. Being a constituent of the NiHCF crystal, free Ni(II) cations can preferentially adsorb on the surface of the coprecipitate. Consequently, the precipitate acquires a positive charge and can readily float with anionic collectors. On the other hand, at Ni/Fe molar ratios less than 1 excess free $[Fe(CN)]^{4-}$ would presumably exist in the solution phase. By arguments similar to those mentioned above, it is concluded that NiHCF, under this condition, will be negatively charged. In support of this view, previous work (21) indicates that the zeta potential of NiHCF precipitated at Ni/Fe ratio < 1.09 is negative. Accordingly, precipitates formed at Ni/Fe ratios < 1 cannot be floated by the anionic collector, NaLS, (Fig. 2), but can be readily removed by the cationic one CTAB as illustrated in Fig. 3.

Table 3. Results[a] obtained for Cs(I) removal from PWW and LLLW simulants

Waste solution	pH	R (%)	VR	DF	ER	[Cs(I)], M
PWW	7.2	99.10 ± 1.1	135	~111	14769	1×10^{-5}
LLLW	7.0	99.15 ± 0.9	155	~125	19114	1×10^{-7}

[a] Mean of 5 experiments.

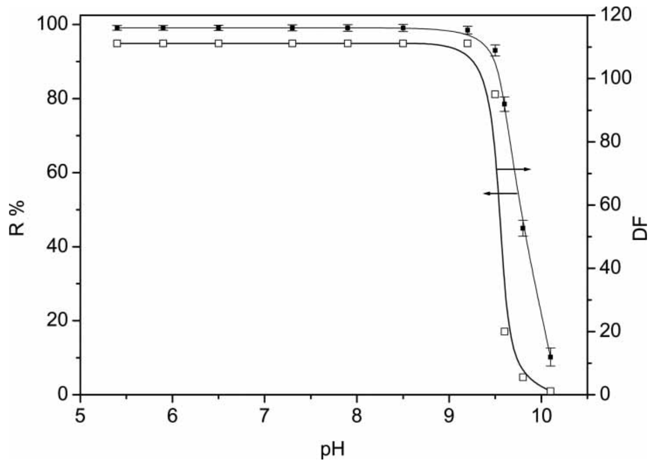

Figure 15. R% and DF(s) obtained for Cs(I) removal from PWW at different values of pH using CTAB/DA. Cs(I): 1×10^{-5} M; CTAB/DA: 2×10^{-4} M/5×10^{-5} M; $[Fe(CN)_6]^{4-}$: 5×10^{-5} M; Ni/Fe: 4.0.

It might be expected that the magnitude of the positive charge on the precipitate surface increases as the concentration of the free Ni(II) cations in the solution is increased with the result enhancement of coprecipitate-collector attachment. Therefore, removal with NaLS is seen to increase with increasing the initial Ni/Fe ratio as seen in Fig. 2. Because coprecipitate-and mineral-

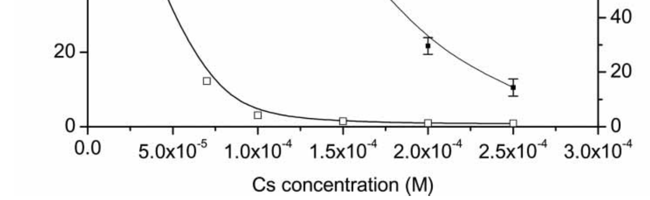

Figure 16. R% and DF(s) obtained for Cs(I) removal from LLLW of different initial cesium concentrations using CTAB/DA. $[Fe(CN)_6]^{4-}$: 5×10^{-5} M; Ni/Fe: 4.0; CTAB/DA: 2×10^{-4} M/5×10^{-5} M.

flotation are alike, in that both may be activated with certain ionic species, Ni(II) in the present case; these species have been called activators (15) in analogy with the mineral flotation terminology.

Unexpectedly, the cationic collector CTAB could remove not only the negatively charged NiHCF precipitate but could also float the positively charged precipitate formed at $Ni/Fe > 1$ (Fig. 3). However, in systems where charge effects are minimum or nil coordination between ionic species present in precipitate and collector may be so strong so that the precipitate can be floated by a collector of the same charge (33). Since Ni(II) is known to be a nitrogen coordinator, removal of the positively charged precipitate with the cationic collector might be attributed to coordination effects.

Results obtained by either NaLS or CTAB (Fig. 4 curves a and A) indicate that increasing the initial Cs(I) concentration, and keeping constant the other experimental conditions, results into decrease of cesium removal. In contrast, the mass of Cs(I) removed is simultaneously increased. For example, the percentage removal and mass of Cs(I) removed by CTAB (Fig. 4 curve A) were ~99% and 4 ppm ($\sim 2.5 \times 10^{-5}$ M) when the initial Cs(I) concentration was 5 ppm ($\sim 3 \times 10^{-5}$ M) and were ~62.5% and 25 ppm ($\sim 1.5 \times 10^{-4}$ M) when the initial Cs(I) concentration was 40 ppm ($\sim 2.4 \times 10^{-4}$ M). In the light of these observations it could be concluded that the decrease in the extent of cesium removal with elevation in its initial concentration cannot be attributed to either reduction in flotation efficiency or exceeding the incorporation capacity of NiHCF for Cs(I). It could be due to formation of NiHCF product of varying composition and consequently of different cesium contents. According to the literature (20, 21, 24, 25), NiHCF has no definite formulae and its chemical composition and physical characteristics can vary over wide ranges depending on the precipitation conditions. However, NiHCF is best represented by the formula $M_{2-x}\,Ni_{x/2}\,[Ni\,Fe(CN)_6] \cdot H_2O$ (20, 24, 25) where M represents a metal cation. For K(I) the value of x ranges between 0.05 to 1.2 (24). Accordingly, the composition (and consequently the incorporation capacity for Cs(I)) of NiHCF formed in the present work is expected to vary considerably with variation in the initial Cs(I) concentration in the solution.

The obtained results (Figs. 9 and 10) indicate that the ionic strength of the solution (adjusted with NaCl) deleteriously affects the removal efficiency obtained by either the anionic collector NaLS (Fig. 9 curve b) or by the cationic ones, CTAB/DA (Fig. 9 curve A_i). As shown from Fig. 3 (curves B and C), the reduction in removal could be partly remedied by increasing the initial collector concentration. Therefore, the deleterious effect of ionic strength cannot be attributed to decrease in the incorporation capacity of NiHCF for Cs(I) by reason of increasing competition of the electrolyte cations. This conclusion is supported by the fact that the affinity of NiHCF for Cs(I) is much stronger than for the other alkali metal cations (20).

Generally, in flotation only the collector is removed directly by gas bubbles; the coprecipitate is removed indirectly by attraction to collector ions. In the present work, the collector concentration changes during flotation were not monitored. However, according to the literature (34, 35), the removal of the collector by foaming increases with increasing electrolyte concentration. Therefore, the reduction in cesium removal observed with increasing ionic strength (Fig. 9) cannot be ascribed to decreased collector flotation and consequent reduction in coprecipitate removal. It should be due to alteration of the attraction between the coprecipitate and collector as a result of increase in the ionic strength; that is, increase of the electrolyte concentration. The deleterious effect of ionic strength on the efficiency of precipitate flotation also has been observed and discussed by different investigators (14, 16, 18, 36–39); the effect being more pronounced for bi-charged than for uni-charged ions. However, the reduction in removal observed in the present case (Fig. 9) may be attributed to one or more of the following: first, as the ionic strength is increased, the Na(I) and Cl^- ion concentrations increase too. Consequently, the attraction between the collector ions and the counter ions of the electrolyte becomes more probable. Hence, the possibility of interaction between the precipitate and the collector decreases and the removal efficiency is correspondly reduced; second, in the presence of electrolyte (NaCl in the present case), Na(I) will compete with Ni(II) cations for adsorption on the precipitate surface. As a result, the magnitude of positive surface charge (necessary for attachment of the anionic collector, NaLS) and the amount of adsorbed Ni(II) cations (required for adequate coordination with the cationic collector, CTAB) might be affected; and third, reduction in the foam stability by reason of increased concentration of anions on the outer and inner surfaces of the bubble film (36).

Because the efficiency of removal by either the anionic collector, NaLS, or the cationic quaternary ammonium surfactant, CTAB, has been found to be deleteriously affected by ionic strength, attention was directed to the use of dodecyl amine (DA), a weakly ionized cationic collector. Aminic collectors are reported (18) to be more effective for precipitate flotation from solutions of high ionic strength. Under the present experimental conditions, when the ionic strength of the medium exceeded 0.01 (NaCl), the removal efficiency decreased considerably. This seems to be due to thin, unstable, collapsing foam resulting in redispersion of floated precipitate. A similar behavior has been reported for coflotation of metal ions with octadecylamine (18) and laurylamine (40). However, a combination of DA and CTAB, of adequate concentrations, has been found to give proper foam and can effectively float NiHCF from solutions of relatively high ionic strength. Therefore, the use of a combination of DA and CTAB was intensively investigated.

The induction time required for maximum removal of cesium differs according to the collector type (Fig. 12). For CTAB/DA, the induction time apparently does not depend on the ionic strength; only 15 minutes aging is sufficient to achieve the maximum removal from either water suspensions (~zero μ) or solutions 0.05 in ionic strength. On the other hand, the induction time required for optimum removal with the anionic collector, NaLS, strongly depends on the ionic strength of the suspension; being less than 15 minutes and more than 50 minutes for solutions of ionic strength ~zero and 0.05 respectively. Since the extent of removal obtained by CTAB/DA from solutions of different ionic strengths is not significantly affected by the induction time, the longer duration required for NaLS to attain maximum removal from solutions of high ionic strength cannot be ascribed to decreased incorporation of Cs(I) by NiHCF. It might, therefore, be attributed to modification of the surface charge on the precipitate particles through equilibration with the bulk solution and the consequent increase of the collector adsorption onto the surface of the precipitate.

Foreign ions usually deleteriously affect the extent of removal by flotation techniques mainly due to affecting the ionic strength and competition with the precipitate for the counter part of the collector. However, in the present case, it has been found that the addition of significant concentrations of different foreign anions and metal cations to the system does not affect the percentage removal. This result may be attributed to: first, possible coagulation effect of the increased electrolyte concentration which renders the precipitate more dense and consequently more accessible to flotation thus partly compensating for the adverse effect of the presence of foreign ions; second, it is probable that foreign metal cation (M) and Ni(II) ion react together with hexacyanoferrate(II) anion to form CsMNiHCF coprecipitate of higher flotation tendency than NiHCF; and/or third, affecting the zeta potential of NiHCF precipitate. However, as shown in Fig. 13, excessive amounts of salt are detrimental to flotation, most probably due to increased attraction between added anions and surfactant cations. Unexpectedly, the obtained results (Fig. 13) suggest that the divalent $SO_4^=$ anion has a lower deleterious effect than the monovalent Cl^- ion. This lower adverse effect of the $SO_4^=$ anion may be ascribed to that adsorption of the sulphate anion on NiHCF precipitate results into significant reduction in the magnitude of the net positive surface charge on the precipitate, hence its flotation tendency increases as a direct result of decrease in the magnitude of electrostatic repulsion between the positively charged precipitate and the collector (CTAB/DA) cations.

From the waste management point of view, the efficiency of a decontamination process depends on its capability to segregate radioactive wastes into: a concentrate containing most of the radioactive nuclei whose volume is as small as possible, and a relatively large volume of decontaminated effluent appropriate for direct release to the environment. Thus, the ultimate objective of a developed decontamination process is to achieve both high VR and DF.

As shown from the results (Table 3) proper VR(s) could be obtained for Cs(I) removal from both simulated PWW and LLLW, ~135 and 155 respectively. For comparison, the decontamination factors reported in the literature for Cs(I) removal by different techniques are summarized in Table 4. Though these values cannot be correlated directly to the DF(s) achieved by the proposed coprecipitate flotation process (Table 3), due to differences in solution composition, yet they reveal that the present flotation results

Table 4. Absorbers[a], processes, and DF values reported in literature for Cs(I) removal from aqueous media

pH	DF	Compound	Comments	Reference
6–11	1.4	Ferric hydroxide	Floc gravity, settled overnight	(9)
6–10	1.4	Sodium diuranate	Floc gravity, settled overnight	(9)
11	1.9	Sodium diuranate	Floc gravity, settled overnight	(9)
7–11	10	Zeolites	Gravitational sedimentation	(13)
~13	12	Sod. NiHCF	Filtration	(21)
~13	35	Granular Pot. Cobalt (II) hexacyanoferrate (II)	Centrifugation	(21)
8–9	$\geq$100	Sod. Tetraphenylborate	Decantation and filtration	(27)
8–9	$\geq$100	Hexacyanoferrate of Cu(II), Ni(II), Co(II), ...	Decantation and filtration	(4)
6–10	$>$100	Hexacyanoferrate of Cu(II), Co(II), Ni(II). . .	Gravitational sedimentation	(13)
Alkaline	10 & 23	Different zeolites	24 hr contact and centrifugation at 12,000 rpm	(41)
7.7	1.0	Dodecyl benzene sulphonate surfactant	Foam fractionation	(28)
11.3	21.0	$NaOH + Na_2CO_3 +$ ferric + Grundite clay	Scavenging precipitation	(42)
2.5–6	9–27	Copper hexacyanoferrate(II) and α-sulphanilic acid collector	Precipitate flotation	(26)
8	40	Cobalt(II)hexacyanoferrate(II) and cetyl pyridinum chloride	Coprecipitate flotation	(43)
4–5.5	21–52	Copper hexacyanoferrate(II) and sodium lauryl sulphate surfactant	Coprecipitate flotation	(16)
5.5–7	34–123	Copper hexacyanoferrate(II) and sodium lauryl sulphate surfactant	Coprecipitate flotation	(16)
9.5–10.5	32–45	Mixture of polyethyleneoimine, chitosan and Cu(II)cyanoferrate	Complexation and ultrafiltration	(44)

(*continued*)

Table 4. Continued

pH	DF	Compound	Comments	Reference
11.5	12	Ferric sulphate + organic polymer + NaNiFC	(Process wastewater) scavenging precipitation	(45)
10.7–13	35	Potassium cobalt hexacyanoferrate(II) (KCoFC)	(LLLW), 30 centerifugation at 5000 rpm & filtration through 0.2 mμ membranes	(45)

[a] In this table the term absorber refers to adsorbents, ion-exchangers, or precipitating agents.

compare favorably with those obtained (Table 4) by conventional precipitation and adsorption processes, and by previously reported foam separation techniques as well. Besides, coprecipitate flotation seems to have many advantages as compared to other conventional processes. The advantages include:

(i) simplicity and ease of manipulation since there is no moving parts, no filter presses or screens which require frequent replacement and continual decontamination,
(ii) the ability to remove colloids and insoluble matter, hence filtration and sedimentation steps may be reduced or even omitted,
(iii) moderate capital and operational costs, and
(iv) possible simultaneous removal of multielements.

The present process has the further advantage that the effective pH range of optimal removal is much wider than those for most of the other removal processes (Table 4). Thus, a pH adjustment step could be avoided.

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