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Removal of some Fission Products from Low Level Liquid Radioactive Waste by Chemical Precipitation

E.H. Borai, M.F. Attallah, F.A. Shehata*, M.A. Hilal and M.M. Abo-Aly**

Analytical Chemistry and Control Department, Hot Laboratories, Atomic Energy Authority, P.No.13759, Egypt

*** Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt*

ABSTRACT

In Egypt, liquid radioactive waste has been generated from various uses of radioactive materials. Presence of cesium demonstrated a major problem from the removal point of view even by conventional and advanced technologies. Selective chemical precipitation has been oriented for removal of some fission products including ^{137}Cs from low level liquid radioactive waste (LLRW). The aim of the present study was focused to investigate the effectiveness of various phosphate compounds that improved the precipitation process and hence the decontamination factor. The results showed that, maximum removal of ^{137}Cs reaching 46.4 % using di-sodium hydrogen phosphate as a selective coagulant. It was found that significant enhancement of co-precipitation of ^{137}Cs (62.5 %) was obtained due to presence of Nd^{3+} in the LLRW.

Key Words: Cesium Separation / Liquid Radioactive Waste / Co-precipitation / Phosphate Coagulant

INTRODUCTION

Radiocesium and radiostrontium are the most environmentally significant radionuclides of liquid radioactive wastes (LRW) ⁽¹⁾. Total world-wide cumulative inventory of ^{137}Cs was estimated to be around 3.7×10^{14} kBq (10^4 kCi)^(2,3). On the other hand, it has a potential application as an excellent source for gamma irradiators which are in use for environmental pollution control, food preservation and sterilization of medical accessories⁽⁴⁾.

Phosphate coagulation is the most efficient precipitation process for di- and polyvalent radionuclides ⁽⁵⁾, and precipitation with *d*-metal ferrocyanides, are used for separation of cesium radionuclide⁽⁶⁾. However, these are unconfident processes where no more than 15% of ^{137}Cs could be removed by phosphate coagulation⁽⁷⁾. Kulyukhin et al⁽⁶⁾ studied the behavior of microamounts of ^{137}Cs , ^{152}Eu , ^{22}Na ,

*Corresponding author e-mail: fatasr@yahoo.com

and ^{85}Sr co-precipitation on mixed potassium neodymium ferrocyanide. It was found that ^{22}Na and ^{85}Sr do not noticeably co-precipitate with potassium neodymium ferrocyanide, in aqueous medium, depending on cesium concentration, from 80 to 98% of ^{137}Cs co-precipitate toward potassium neodymium ferrocyanide. Experiments on co-precipitation of ^{152}Eu toward solid potassium neodymium ferrocyanide in its formation from homogeneous solution showed that up to 98-99.9% was removed.⁽⁶⁾

Kulyukhin et al⁽⁸⁾ investigated the co-precipitation of trace amounts of ^{137}Cs and ^{85}Sr with $[\text{Na}(18\text{-Crown-6})]\text{BPh}_4$ from neutral and alkaline solutions. The co-crystallization coefficient of ^{137}Cs and ^{85}Sr from aqueous solutions are 2.6 ± 0.5 and 3.3 ± 0.3 , respectively. For aqueous-ethanolic solutions, the corresponding values are 4.4 ± 0.5 and 3.4 ± 0.4 . In the alkaline solutions,

0.1 and 1 M NaOH, 54-74 % of ^{137}Cs and 37-51 % of ^{85}Sr pass into $[\text{Na}(18\text{-Crown-6})]\text{BPh}_4$ solid phase, depending on the crown ether concentration in the system⁽⁸⁾.

Volkovich et al⁽⁹⁾ studied the treatment of molten salt wastes by phosphate precipitation removal of fission product elements after pyro-chemical reprocessing of spent nuclear fuels in chloride melts. The behavior of solutions of a variety of metal chlorides was studied in LiCl-KCl eutectic at 550°C in presence of solid Li_3PO_4 and in NaCl-KCl melts at 750°C in presence of Na_3PO_4 . The cations investigated were Cs(I), Mg(II), Sr(II), Ba(II), Zr(IV), Cr(III), Mo(III and V), Mn(II), Re(V), Fe(II and III), Ru(III), Ni(II), Cd(II), Bi(III), Te(IV) and lanthanides (La to Dy(III)). The distribution coefficient of most of these elements between chloride melts and precipitates were determined. Cesium can not be removed completely from chloride melts by the phosphate precipitate technique. Lanthanides and some transition metals (e.g., Zr) could be removed completely from both systems, LiCl-KCl and NaCl-KCl based melts. The behavior of some metals is solvent dependent: Cd could be precipitated in NaCl-KCl melts and Bi from LiCl-KCl melts, but not vice versa. Strontium and barium could be removed from NaCl-KCl melts, where as the reverse in case of magnesium⁽⁹⁾.

Recovery of ammonium and cesium ions from aqueous waste streams by sodium tetra phenyl borate was reported by Ponder et al⁽¹⁰⁾. Cesium or ammonium salts precipitated by mixing aqueous sodium tetra phenylborate with the waste stream dissolved in acetone. Recovery of ammonium ions was shown to be quantitative, whereas recovery of cesium ions was about 90 %⁽¹⁰⁾. Removal of cesium from aqueous solutions and radioactive waste simulates by co precipitate flotation was investigated by Shakir et al⁽¹¹⁾. Co-precipitate flotation (CPF) investigations showed that cesium can be efficiently separated from aqueous solutions by co-precipitation with zinc hexacyanoferrate(II) (ZnHCF) and subsequent flotation of the precipitate. Collectors of different types were tested but acetyl pyridine chloride showed the best performance. Before undertaking the flotation investigations, co-precipitation of Cs with ZnHCF was studied to determine the optimal co-precipitation conditions. The developed CPF process was applied successfully for ^{137}Cs removal from process wastewater and low level liquid radioactive waste simulates⁽¹¹⁾.

The present work was directed to study the prospects efficient of five phosphate coagulants for separation of cesium and some fission products such as ^{137}Cs , ^{60}Co , $^{152+154}\text{Eu}$ from low level liquid radioactive waste by chemical precipitation. The effect of presence of some alkaline metal salts on removal of ^{137}Cs was investigated and discussed.

EXPERIMENTAL

Chemicals and Reagents

All chemicals and reagents used in this work were of analytical grade purity and used without further purification. Two types of liquid wastes were collected. The first waste sample includes a mono-radionuclide (^{137}Cs only) was collected from the storage tank in liquid radioactive waste treatment facility (LRWTF) while the second waste sample includes mixed radionuclides ^{134}Cs , ^{65}Zn , ^{60}Co and $^{152+154}\text{Eu}$ was collected from some research laboratories in Hot Laboratories Center, located at Inshas site, Sharkia government, Egypt.

Instrumentation

Measurements of gamma radioactivity of the different radionuclides in the tested samples were identified and determined using a typical non-destructive γ -ray spectroscopic technique equipped with a high purity germanium (HPGe) detector model 2201-Oxford (USA) with a relative efficiency of 30%.

Chemical Precipitation Process

0.1M of each of five phosphate coagulants under investigation and 0.1M of calcium chloride were prepared by dissolving the suitable weight of each in double distilled water. Fixed volume of calcium chloride and different phosphate coagulants were added with stirring the waste solution at the ambient room temperature ($25\pm 1^\circ\text{C}$). The desired pH value was adjusted by sodium hydroxide and phosphoric acid solutions. The precipitate formed was separated by centrifugation and filtration. The clear solution was analyzed radiometrically. The removal percent (R %) was calculated from the following equation:

$$R(\%) = \frac{C_i - C_f}{C_i} \times 100$$

(1)

where: C_i and C_f is the initial and final counts per unit time per unit volume.

RESULTS AND DISCUSSION

Physical and Radiochemical Characterization of the Waste

Separation and removal of some hazardous fission products from low level liquid radioactive waste (LLRW) containing individual ^{137}Cs and mixed radionuclides (^{134}Cs , ^{65}Zn , ^{60}Co and $^{152+154}\text{Eu}$) by chemical precipitation was investigated. Some physical properties of these liquid wastes include, pH, total dissolved salts (TDS) and electric conductivity (EC) were determined, Table (1). Also, the radiochemical characterization of individual and mixed radionuclide wastes are presented in Table (1).

Table (1): Some physico-chemical and radiochemical properties of LLRW.

Name	Individual LRW	Mixed LRW
pH	8	7.5
TDS (mg l^{-1})	2844	809
Conductivity ($\mu\text{S cm}^{-1}$)	6460	1716
Activity concentration (Bq l^{-1})		
^{137}Cs	25397 \pm 715	ND
^{134}Cs	--	128549 \pm 1399
^{60}Co	--	8320 \pm 971
^{152}Eu	--	71921 \pm 2667
^{154}Eu	--	9707 \pm 489
^{65}Zn	--	5175 \pm 200

ND: Not detected

Effect of Hydrogen Ion Concentration

The effect of hydrogen ion concentration $[H^+]$ on the chemical co-precipitation of ^{137}Cs was investigated in the pH range of 8 to 12.5. The effect of pH on the degree of removal of ^{137}Cs by different phosphate namely ammonium di-hydrogen phosphate $(\text{NH}_4)_2\text{H}_2\text{PO}_4$, di-sodium hydrogen phosphate $(\text{Na}_2\text{HPO}_4)$, tri-sodium phosphate (Na_3PO_4) , sodium hexameta phosphate $(\text{NaPO}_3)_{12-13}\text{NaO}$ and phosphoric acid (H_3PO_4) as coagulants of precipitation was studied and the obtained data was represented in Fig. (1). It is clear that, the degree of removal of cesium was increased by increasing the pH value from 8 to 10, followed by a steady state by increasing the pH more than 10 in case of tri- sodium phosphate, di-sodium hydrogen phosphate and phosphoric acid. On the other hand, approximately no effect of pH value on the co-precipitation of ^{137}Cs using ammonium di-hydrogen phosphate, but in case of sodium hexameta phosphate the degree of removal increased by increasing of pH value till pH= 12.5. Maximum removal values of ^{137}Cs 46.4, 41.5, 37.1, 46 and 32.5 % was obtained using di-sodium hydrogen phosphate (pH=10), tri-sodium phosphate (pH=11), ammonium di-hydrogen phosphate (pH=10), sodium hexameta phosphate (pH=12.5) and phosphoric acid (pH=10) as coagulants of precipitation, respectively. From these data, di-sodium hydrogen phosphate was chosen as a more efficient for removal of ^{137}Cs than the other phosphate coagulants under study, which gives the highest degree of cesium removal; 46.4 % , at the pH range 10-12.5.

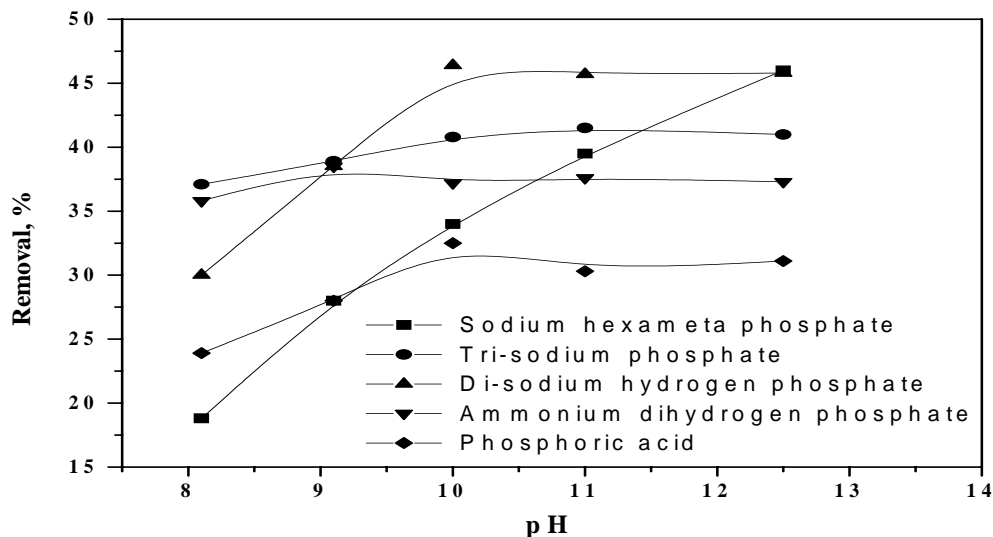


Fig. (1): Effect of pH on removal of ^{137}Cs by different phosphate compounds as coagulants of precipitation.

Effect of Phosphate /Calcium- Ratio

Various volume ratios of phosphate and calcium from 1:1 to 5:1 were chosen to investigate their effect on the removal of cesium. About 50 ml of LLLRW containing ^{137}Cs were taken and mixed with 5 ml of 0.1 M CaCl_2 then different volumes of di-sodium hydrogen phosphate (0.1 M) were added drop by drop with stirring and the pH was adjusted at 10 by NaOH. The obtained results of the removal values of ^{137}Cs were plotted against the different volumes ratios of $\text{PO}_4^{3-} / \text{Ca}^{2+}$, Fig. (2). It is observed that there is an increase in the removal values of ^{137}Cs from LLLRW with increasing the volume ratio till about 2:1, to reach a constant removal

values of ^{137}Cs (46 %). Therefore, 10 ml of di-sodium hydrogen phosphate (0.1 M) to 5 ml of 0.1 M CaCl_2 were chosen as a suitable volume ratio for treatment of 50 ml of LLLRW, i.e., $\text{PO}_4^{3-} : \text{Ca}^{2+} = 2:1$.

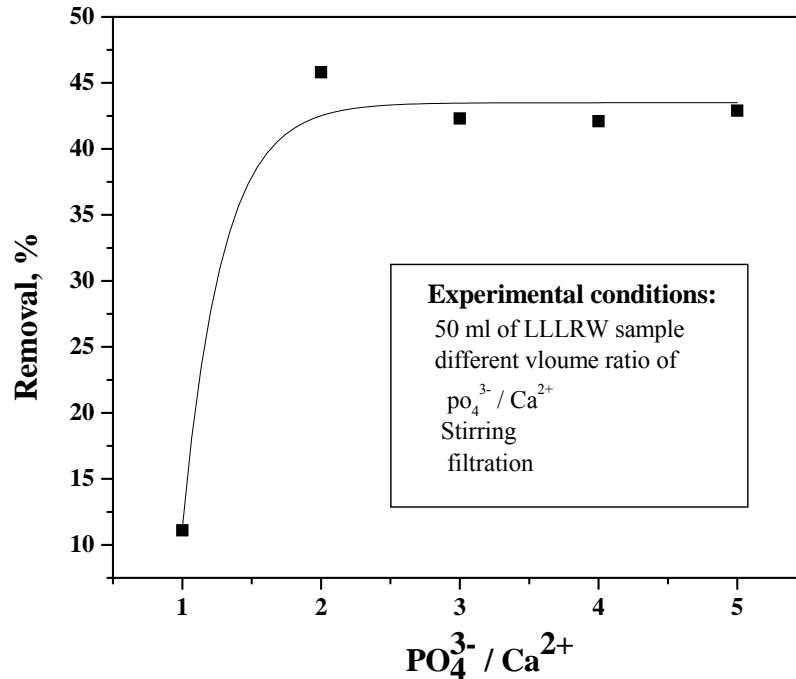


Fig. (2): Effect of volume ratio of phosphate and calcium on removal of ^{137}Cs by di-sodium hydrogen phosphate as a coagulant.

Effect of Phosphate Concentration

This experiment was carried out to study the effect of di-sodium hydrogen phosphate concentration on the removal of ^{137}Cs content in LLLRW. Different concentrations of di-sodium hydrogen phosphate ranged between 0.05 and 0.5 M were prepared and used as coagulants for the co-precipitation of cesium to investigate the removal of ^{137}Cs from LLLRW. The obtained results were represented in Fig. (3), as a relation between the removal percent of ^{137}Cs present in the investigated LLLRW versus the different concentrations of di-sodium hydrogen phosphate used for co-precipitation of cesium. The obtained results showed a rapid increase in removal of Cs with increasing the concentration of sodium hydrogen phosphate till 0.1 M. At concentration higher than 0.1 M of di-sodium hydrogen phosphate, a constant removal of ^{137}Cs (~ 46 %) was obtained at pH ~ 10 till 0.5M. The optimum concentration of di-sodium hydrogen phosphate is 0.1 M was therefore chosen as a suitable concentration for co-precipitation of cesium from LLLRW.

Based on the obtained results, the optimum conditions required for removal of ^{137}Cs present in LLLRW with co-precipitation as phosphate can be obtained as, the volume ratio of

phosphate and calcium is 2, (i.e., $\text{PO}_4^{3-} : \text{Ca}^{2+} = 2:1$), with 0.1 M of di-sodium hydrogen phosphate and calcium chloride at $\text{pH} \geq 10$.

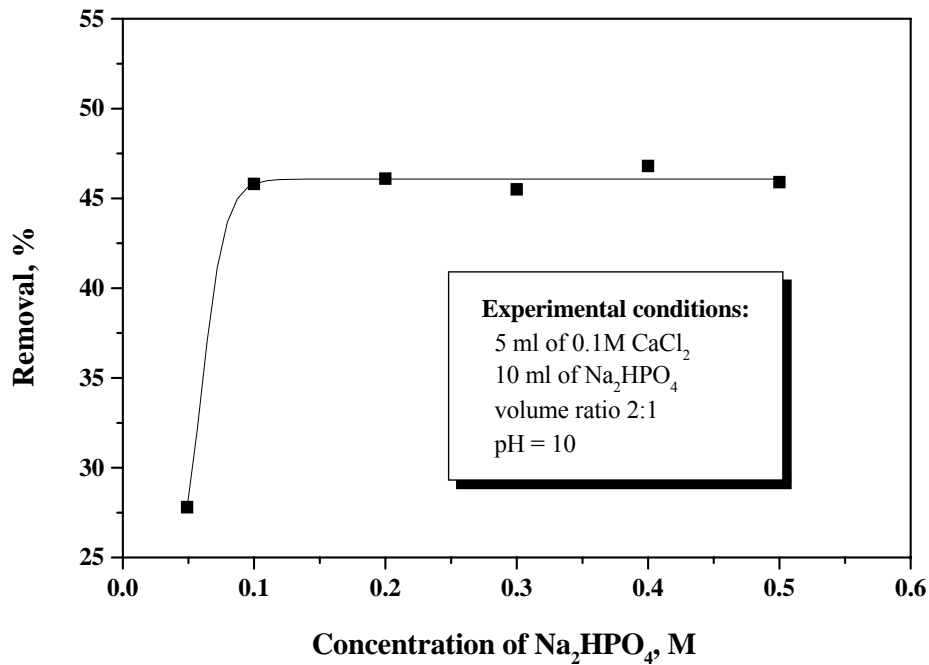


Fig. (3): Effect of di-sodium hydrogen phosphate concentration on removal of ^{137}Cs .

Effect of Cesium Concentration

In this concern, different concentrations (5-25 mg l^{-1}) of stable cesium solutions were used to study their effect on removal of ^{137}Cs from LLLRW. The obtained results were represented in Fig. (4), as a relation between the removal percent of ^{137}Cs present in the investigated LLLRW versus concentrations of stable cesium carrier. This experiment was carried out under the optimum conditions mentioned above. The obtained results indicated that the removal of ^{137}Cs increases slowly by increasing the stable cesium carrier till $\sim 20 \text{ mg l}^{-1}$, followed by no effect on the co-precipitation of cesium by increasing the concentration more than 20 mg l^{-1} . It was observed that the maximum removal of ^{137}Cs is 51 % using 20 mg l^{-1} of stable cesium carrier. It is clear that, low enhancement of removal of ^{137}Cs (5 %) was obtained when introducing stable cesium over the obtained removal without stable cesium carrier (46 %).

Effect of Nd^{3+} and La^{3+} Addition

Different concentrations of Nd^{3+} and La^{3+} solutions ranged from 5 to 20 mg l^{-1} were mixed with 50 ml of LLLRW and 5 ml of 0.1 M CaCl_2 with a drop wise adding of 10 ml of 0.1 M di-sodium hydrogen phosphate for co-precipitation of ^{137}Cs . Fig. (5), showed the effect of concentration of Nd^{3+} and La^{3+} on the removal of ^{137}Cs . It is observed that no significant change of removal of ^{137}Cs with low concentration (5 mg l^{-1}) of La^{3+} , followed by a gradual decrease of the removal of ^{137}Cs by increasing the concentration of La^{3+} more than 5 mg l^{-1} . On the other hand, significant enhancement of the removal of ^{137}Cs with low concentration (5 mg l^{-1})

l^{-1}) of Nd^{3+} , followed by a gradual decrease in removal of ^{137}Cs . The highest degree of co-precipitation of ^{137}Cs (62.5 %) was obtained by introducing 5 mg l^{-1} of Nd^{3+} to the LRW under the optimum conditions for treatment of LLLRW by di-sodium hydrogen phosphate.

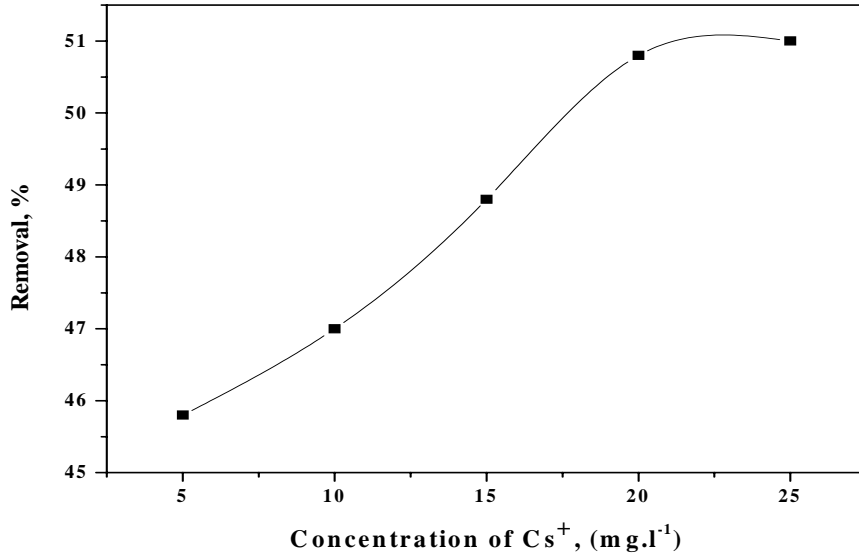


Fig. (4): Effect of concentration of cesium carrier on removal of ^{137}Cs by di-sodium hydrogen phosphate as a coagulant.

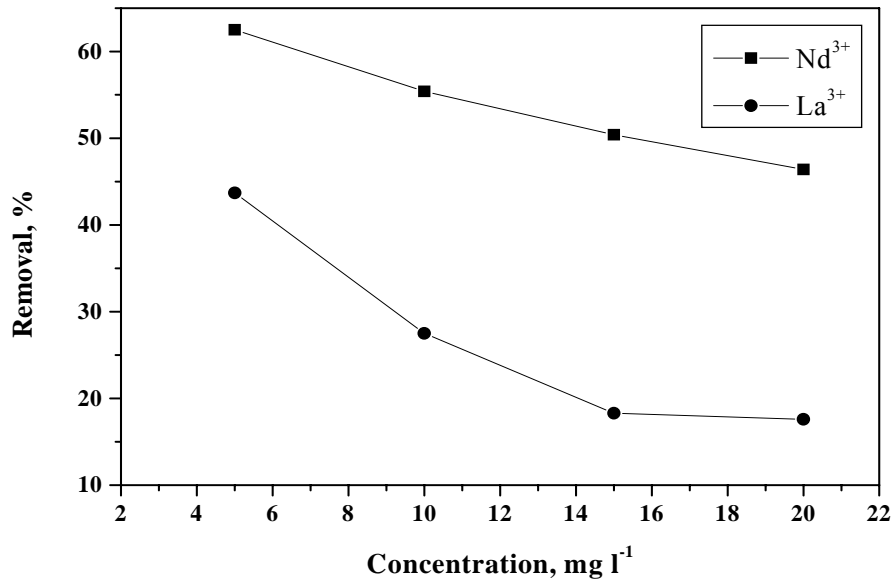


Fig. (5): Effect of Nd^{3+} and La^{3+} concentration on removal of ^{137}Cs by di-sodium hydrogen phosphate as a coagulant.

Effect of Alkaline Metal Salts

For this purpose, some alkaline metal salts of barium, calcium, magnesium and strontium were used as carriers to phosphate precipitation to investigate their effect on removal of ^{137}Cs from LLLRW. The study was performed under the same optimum conditions previously mentioned. 5 ml of 0.1M Ba^{2+} , Ca^{2+} , Mg^{2+} and Sr^{2+} mixed together with 50 ml of LLLRW containing ^{137}Cs , followed by a drop wise addition with stirring at ambient room temperature ($25\pm 1^\circ\text{C}$) of 0.1M di-sodium hydrogen phosphate (10 ml) and the pH was adjusted at 10. The formed precipitate was separated by centrifugation and filtration. The obtained data were presented in Table (2). The results indicated that the removal of ^{137}Cs are 40, 46.4, 49 and 52.4 % obtained using Ba^{2+} , Ca^{2+} , Mg^{2+} and Sr^{2+} respectively, as a carrier for phosphate precipitation.

On the other hand, the introduction of 5 mg l^{-1} of Nd^{3+} in the liquid radioactive waste under investigations led to a significant enhancement in removal of ^{137}Cs . The results showed that the removal values of ^{137}Cs are 57.7, 57.6, 61.1 and 62.5% using Ba^{2+} , Sr^{2+} , Mg^{2+} and Ca^{2+} , respectively, as carriers for phosphate precipitation.

Table (2): Removal of individual ^{137}Cs from LLLRW by 0.1M di-sodium hydrogen phosphate using some alkaline metal salts as carriers.

Alkaline metal	Degree of removal, R (%)	
	Without Nd^{3+}	With 5 mg l^{-1} of Nd^{3+}
Ba^{2+}	40.0	57.7
Ca^{2+}	46.4	62.5
Mg^{2+}	49.0	61.1
Sr^{2+}	52.4	57.6

Removal of some Hazardous Fission Products from LLLRW

The removal of some hazardous fission products ^{134}Cs , ^{60}Co , $^{152+154}\text{Eu}$ and ^{65}Zn from LLLRW by chemical precipitation was studied to investigate the effectiveness of phosphate precipitation on the decontamination factor (DF). Some alkaline metal salts of barium, calcium, magnesium and strontium were used as carriers to phosphate precipitation. The study was performed under the same optimum conditions previously mentioned. Table (3) represents the obtained data of removal of some fission products by di-sodium hydrogen phosphate as a coagulant. The results indicated that Ba^{2+} and Mg^{2+} are more efficient than other alkaline metal salts under investigation as carriers to phosphate precipitation.

In case of barium, the removal values are 32.6, 99.1, 95, 99.1 for ^{134}Cs , ^{60}Co , ^{65}Zn and $^{152+154}\text{Eu}$, respectively. On the other hand, when using magnesium as a carrier to phosphate precipitation the removal values are 32.5, 98, 98.4, 96.4% for ^{134}Cs , ^{60}Co , $^{152+154}\text{Eu}$ and ^{65}Zn , respectively. The effect of adding 5 mg l^{-1} of Nd^{3+} to the mixed liquid radioactive waste under

investigation was studied for the decontamination factor of ^{134}Cs , ^{60}Co , $^{152+154}\text{Eu}$ and ^{65}Zn from LLLRW by chemical precipitation. It is observed that the removal values of the hazardous fission product under study decreased by introducing 5 mg l^{-1} of Nd^{3+} to the mixed liquid radioactive waste.

Table (3): Removal of some hazardous fission products from LLLRW by phosphate precipitation using some alkaline metals as carriers.

Alkaline metal salts of	Degree of removal, R (%)							
	Without Nd^{3+}				With 5 mg l^{-1} of Nd^{3+}			
	^{134}Cs	^{60}Co	$^{(152+154)}\text{Eu}$	^{65}Zn	^{134}Cs	^{60}Co	$^{(152+154)}\text{Eu}$	^{65}Zn
Ba^{2+}	32.6	99.1	99.1	95.0	22.0	93.6	95.6	84.0
Ca^{2+}	20.4	96.8	98.3	93.9	2.3	98.2	98.9	93.0
Mg^{2+}	32.5	98.0	98.4	96.4	0.0	98.1	96.7	93.0
Sr^{2+}	22.8	98.0	99.4	92.7	0.0	94.3	94.3	92.1

CONCLUSION

Phosphate precipitation process is developed for monovalent radionuclides. The process includes calcium addition, providing precipitation of cesium along with phosphates of di- and polyvalent ions as poorly soluble salts $\text{CsCaPO}_4 \cdot (6\text{H}_2\text{O})$. The effect of different phosphate coagulants were investigated for removal of monovalent cesium radionuclide. Introduction of 0.1 M calcium chloride as a carrier and the equivalent amount of phosphate coagulants in LLLRW containing ^{137}Cs provides 62.5 % removal of ^{137}Cs when LLLRW containing about 5 mg l^{-1} . It can be conclude that di-sodium hydrogen phosphate is more efficient to remove cesium from low level liquid radioactive waste than other phosphate coagulants under investigation at $\text{pH} \geq 10$.

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