

Optimization Of Treatment Of Cs¹³⁷ Bearing Radioactive Effluent By Chemical Precipitation

Ajay Kumar Mishra, B S Panigrahi, S K Khandelwal, K Ravichandran

Abstract: An attempt to remove Cs from radioactive effluent was made by chemical precipitation. Chemical precipitation using insitu precipitation with CuSO₄ and K₄Fe(CN)₆ under optimized condition in the removal of Cs¹³⁷ is in vogue. In the present work insitu precipitation of Cu₃(PO₄)₂ using Na₃PO₄ and CuSO₄ as precipitant and FeCl₃ as flocculent was carried out. The optimized condition was found to be 189 ppm Copper with 477ppm CuSO₄ 190 ppm PO₄ with 328 ppm Na₃PO₄ corresponding to 120% stoichiometry of the precipitation reaction, at pH 7.5 with 70 ppm ferric with 198 ppm ferric chloride as flocculent. The Copper phosphate powder of mesh size-20+40,-40+60,-60+80, -80+100 ASTM was used as column material for removal of cesium at different flow rate. The optimised size is found to be -80+100 ASTM and optimized flow rate as 15 bed vol/hr. The Cu₃(PO₄)₂ powder was heated to different temperatures and so obtained powder was subjected to XRD study to analyze the crystallinity and SEM study to find the change in morphology. The heated and unheated Cu₃(PO₄)₂ loaded with Cs was subjected to FTIR study to elucidate the type of bonding of Cs with Cu₃(PO₄)₂ powder.

Keywords: Co precipitation, agglomeration, particle size, Zeta potential

1 INTRODUCTION

In the nuclear fission for generating current using uranium as fuel, fission products like Cs, Sr, Co, Ru etc are produced. Because of long half life comparable to man's life and high fission yield, Cs¹³⁷ and Sr⁹⁰ are of more concern in the treatment of radioactive effluent. Radioactive liquid effluents generated are categorized into low, medium and high level depending on the specific activity [Panikar et al, 1990] Even though several methods which are, chemical precipitation, ion exchange, evaporation, membrane process are in practice for treatment of these effluent to make them innocuous [IAEA-TRS-236,1983], chemical precipitation has its own advantage for its feasibility of precipitation in bringing down radio nuclide having isomorphous structure. Also the technique is well known to scale up to pilot plant to plant level. Other alternate methods like ion exchange, evaporation, membrane process (electrodialysis, reverse osmosis, ultra filtration etc.) have also been used for waste treatment even though they have merits they have some demerits also. Some of the merits using ion exchange process are their adequate exchange capacity which is sufficient for pickup of activity, needless to choose a suitable matrix for fixing the spent resin, needless to add extra chemical externally etc. some of the demerits of ion exchange process are that they are not applicable for effluent of high salt content, since ion exchange column is exhausted by the salt before taking up activity. Also dealing with spent resin treating as solid waste besets with problems. Evaporation is suitable for effluent with high chemical contents but it is cost intensive since huge amount of liquid has to be removed. Also since volatile radio element escapes during evaporation efficient off gas treatment is mandatory. Also soap and detergent present in laundry water cause a 'foaming' over in the evaporator.

Membrane process are two types, electrically driven and pressure driven. Electro dialysis process requires suitable ion selective membranes and pressure derived reverse osmosis and ultra filtration process require porous membrane with small and large pores respectively. Choosing proper membrane, installation cost, Membrane replacement costs etc are highly discouraging to adopt those techniques. Hence an attempt has been made to remove activity from effluent by chemical precipitation which is simple (since chemistry of chemicals used is well known) easy adoptability and handling the sludge with activity (immobilization of activity in sludge with suitable matrices).

2 MATERIALS AND METHODS

AR grade CuSO₄, Na₃PO₄, Radioactive Cs¹³⁷ of source activity (1mCi/ml), Peristaltic pump of make, Miclins pp-20 was used for controlling the flow rate. IR lamp was used for heating the material, XRD of make PAN analytical, Netherlands for finding out the crystallinity, FTIR of make SHIMADZU, IRTRACER 100 to find out type of bonding of Cs with precipitant, SEM of make FEI, Quanta 200 was used for finding out morphology of the material and pH meter of make Elico, for adjusting the pH were used. Radioactive Cs was analyzed by NaI (TI) scintillation counter, Zeta meter of make Malvern was used for finding out the Zeta potential of the precipitate to optimize the pH at which maximum removal of radioactive Cs¹³⁷ takes place.

Experiment

Radioactive Cs of specific activity each of 10⁻²μCi/ml to 10⁻⁴μCi/ml were prepared using stock solution of Cs¹³⁷ of specific activity 1mCi/ml. Beakers containing 100 ml of 10⁻²μCi/ml of radioactive Cs were taken. Stock solution of 500 ppm CuSO₄ and 500 ppm Tri Sodium Phosphate (assay cross checked using procedure given in Vogel [Vogel A I(1961)]) were prepared. 189 ppm of CuSO₄, 190 ppm of Tri Sodium Phosphate were added using glass rod stirring continuously precipitating Cu₃(PO₄)₂ in the first beaker corresponding to 100% stoichiometry. Similar procedures were adopted for 110,120,130, stoichiometry. Table 1 shows the strength of copper as copper sulphate and strength of Phosphate as tri sodium Phosphate

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corresponding to 110, 120, 130% of stoichiometry respectively. The beakers were allowed for stirring in stirring unit.

Table1 Strength of chemicals of different % stoichiometry

% Stoichiometry	CuSO ₄	Cu	Na ₃ PO ₄	PO ₄
100	477	189	328	190
110	524.7	207.9	360.8	209
120	572.4	226.8	393.6	228
130	620.1	245.7	426.4	247

The treated effluent will have radioactive ions within the precipitate either in co precipitated form or adsorbed form. If particles don't settle down the activity will be carried along with slurry resulting in less removal of activity. Hence it is imperative to settle down the precipitate or flocculate. Different flocculents like Calcium Chloride (CaCl₂), Ferric chloride (FeCl₃), Stannic nitrate Sn(NO₃)₄ at different strength were attempted. Table 2(a), 2(b), 2(c) shows the flocculating efficiency of the flocculent Calcium Chloride (CaCl₂), Ferric chloride (FeCl₃), Stannic Nitrate Sn(NO₃)₄ of different strength.

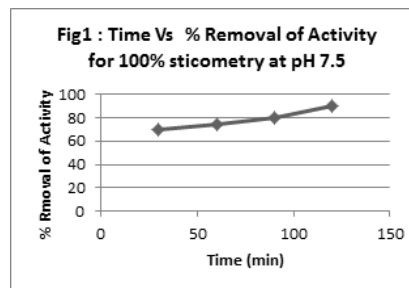


Fig1. shows percentage removal of Cs from the effluent as function of time.

Table 2(a) Effect of Flocculent Calcium Chloride (CaCl₂) in removal of activity of Cesium (7.1 X 10⁻⁵ μCi/ml).

Strength of CaCl ₂ (ppm)	Activity after adding flocculent (μCi/ml).	% Removal of Activity
20	3.9 x 10 ⁻⁵	45.07
40	3.6 x 10 ⁻⁵	49
70	3 x 10 ⁻⁵	57
100	2.6 x 10 ⁻⁵	63

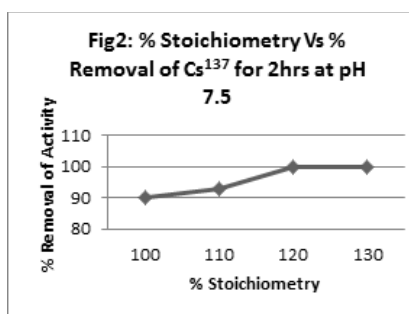
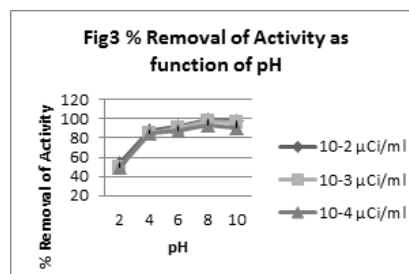


Fig 2. Shows percentage removal of Cs¹³⁷ as function of % stoichiometry of the precipitant using 10⁻³ μCi/ml of Cs¹³⁷.

Table 2(b) Effect of Flocculent Ferric chloride (FeCl₃) in removal of activity of Cesium (7.1 X 10⁻⁵ μCi/ml).

Strength of FeCl ₃ (ppm)	Activity after adding flocculent (μCi/ml).	% Removal of Activity
20	3 x 10 ⁻⁵	57.74
40	0.7 x 10 ⁻⁵	90.14
70	1 x 10 ⁻⁵	85.91
100	0.8 x 10 ⁻⁵	88.73



Optimization of pH-

100ml of radioactive Cs¹³⁷ of specific activity of 10⁻² μCi/ml is taken in five different beakers adjusted to pH 2, 4, 6, 8, 10.

Table 2(c) Effect of Flocculent Stannic Nitrate Sn(NO₃)₄ in removal of activity of Cesium (7.1 X 10⁻⁵ μCi/ml).

Strength of Sn(NO ₃) ₄ (ppm)	Activity after adding flocculent (μCi/ml).	% Removal of Activity
20	2.8 x 10 ⁻⁵	60
40	1.8 x 10 ⁻⁵	74
70	.9 x 10 ⁻⁵	87
100	.7 x 10 ⁻⁵	87

Fig 3. Shows percentage removal of Cs as function of pH using 10⁻² μCi/ml initial activity with chemicals at 120% stoichiometry for precipitation. Similar experiments were conducted at different strength of Cs¹³⁷ of specific activity 10⁻³ μCi/ml and 10⁻⁴ μCi/ml as function of pH.

The beakers were subjected to stirring for precipitation and analyzed for Cs.

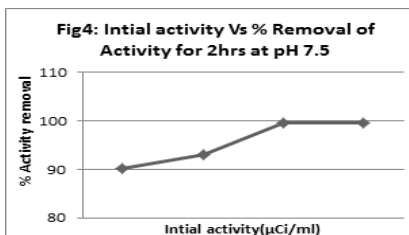


Fig 4, shows % removal of Cs as function of initial activity 10⁻² μCi/ml to 10⁻⁵ μCi/ml respectively

To confirm the optimized pH, Copper phosphate was precipitated and pH of solution was adjusted 2, 4, 6, 8, 10 using pH meter in five different beakers. Zeta potential and particle size of copper phosphate was analyzed as the function of pH. Fig. 5a, shows Zeta potential as function of pH. The point of zero charge coincides with optimized pH for removal of activity by precipitation

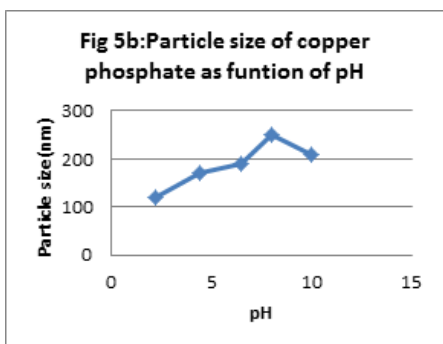
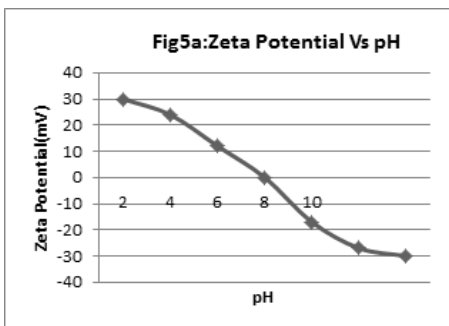
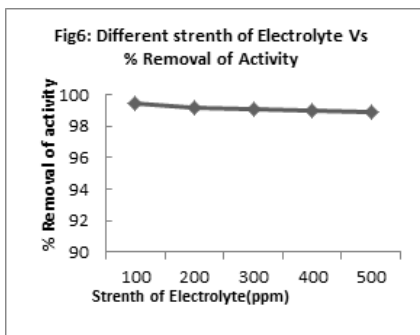


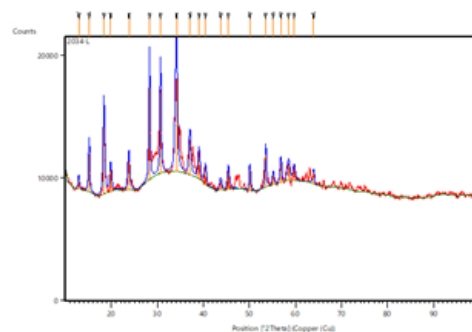
Fig 5b shows the particle size as function of different pH

To study the effect of presence of electrolyte in the coprecipitation of Cs using $\text{Cu}_3(\text{PO}_4)_2$ solutions NaCl solution of strength 100ppm, 300ppm, 500ppm were carried out at pH 7.5 fig 6 shows the % removal of activity at different strength of electrolyte.

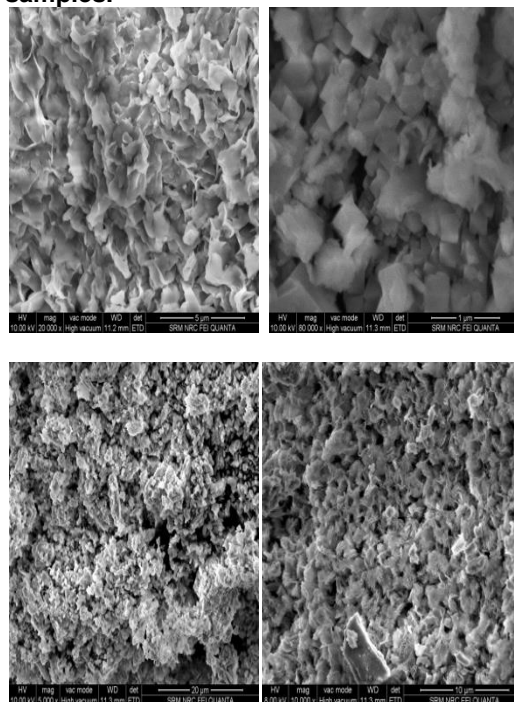


Characteristics of $\text{Cu}_3(\text{PO}_4)_2$ powder

a. XRD and SEM study: XRD and SEM study The $\text{Cu}_3(\text{PO}_4)_2$ was precipitated insitu at optimum pH and optimum stoichiometry without Cs¹³⁷. The precipitate was filtered, dried and heated to different temperatures. Unheated sample was subjected to XRD and SEM analysis. Fig 7. Shows XRD of unheated $\text{Cu}_3(\text{PO}_4)_2$.



b. Fig 9 shows SEM of unheated and heat treated samples.



c. FTIR study 10 ppm solution of non active Cs¹³⁷ was treated with CuSO_4 and Na_3PO_4 at optimized pH and optimized percentage stoichiometry and precipitate containing Cs was filtered dried and subjected to FTIR studies. It was heated to different temperatures and subjected to FTIR study. Fig 9a and 9b Shows the FTIR of heated and unheated samples.

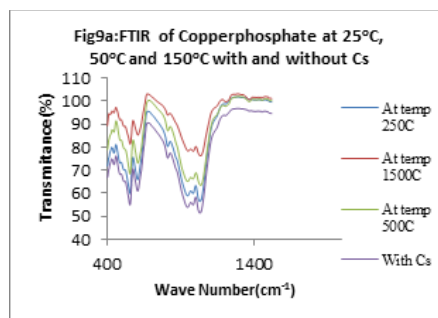
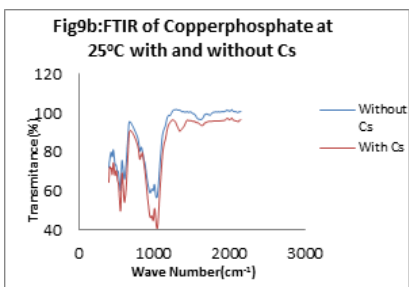
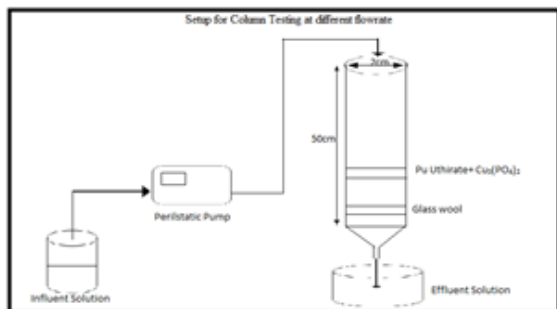


Fig 9 shows FTIR of $\text{Cu}_3(\text{PO}_4)_2$ with and without Cs.



Column Studies

Copper phosphate was precipitated at optimized pH and optimized stoichiometry and so prepared precipitate was filtered and heat treated at different temperatures. The material so prepared was used as column material. Different columns were prepared. At bed volume of 10ml with glass wool support radioactive Cs¹³⁷ of specific activity 10⁻³ μCi/ml was passed through the column at flow rates 10 bed volume per hour corresponding to residence time of 6 min. similar experiments were conducted using the column material at flow rates 15 and 20 bed volume/hr respectively. Sample was collected at 10 min interval. Fig 11 show the setup for column testing. Table 3a to 3d shows percentage removal of Cs¹³⁷ as function of flow rate optimized time.



Flow Rate(bed-vol/hr)	Sample temp °C	Retention Time(min)	% Removal
10	Unheated	60	85
10	60	60	75
10	80	60	67.2
10	90	60	55.6

Flow Rate(bed-vol/hr)	Sample temp °C	Retention Time(min)	% Removal
15	Unheated	60	92
15	60	60	82
15	80	60	73.4
15	90	60	60.5

Flow Rate(bed-vol/hr)	Sample temp °C	Retention Time(min)	% Removal
20	Unheated	60	84.2
20	60	60	73.3
20	80	60	65.2
20	90	60	53.26

Flow Rate(bed-vol/hr)	Sample temp °C	Retention Time(min)	% Removal
25	Unheated	60	72
25	60	60	61.5
25	80	60	52.2
25	90	60	49.1

3 RESULTS AND DISCUSSION

From Table 1, we find that removal of activity is facilitated by flocculation. As per Hardy Schulz rule flocculation increase with the increase the valence of flocculent. Removal of activity from the slurry followed the order Sn⁴⁺ > Fe³⁺ > Ca²⁺ Since ferric is commonly used as flocculent in waste treatment and since there is not much difference between Ferric and stannic in the extent of flocculation as reflected in the removal of activity, Ferric has been used as flocculent for our experiment. Table2 shows the amount of diff chemical to be added for different % stoichiometry. From Fig 1. We find that percentage removal of activity increases with increase in time. It is because with increase in residence time contact with radio nuclide with the precipitate increases resulting in maximum removal. From Fig 2, we find that percentage removal increase with increase in stoichiometry to 110% and remain steady. Therefore optimum % stoichiometry is fixed at 110%. From fig 3 we find that percentage removal of activity increase with initial activity. It is because removal being partially absorption and partially chemical reaction rate of reaction is proportional to the initial concentration. From Fig.4. We find that percentage removal increase with increase in pH up to pH 8 and attains max at pH 8. Similar trend was seen at different initial activity also establishing the optimum pH as 8. Therefore further experiments were carried out at pH 8. Fig.5(a) shows the Zeta potential as function of pH. Zeta potential comes down with pH and attains zero value at pH=8. (Fig. 5(a)) and then comes to negative Zeta potential. Therefore point of zero charge was fixed pH 8 Corroborating the conclusion drawn earlier on the optimization of pH of 8 for maximum removal of Cs. Fig 5b shows that particle size increases due to fusing and agglomeration which reduces surface area. (J Sol-Gel Sci and Tech. 2003, Volume 28, Issue 3, pp 327–333) From Fig.6, we find that presence of electrolyte does not have much influence on the percentage removal of Cs¹³⁷ at different pH. Fig.7. Shows the XRD pattern of unheated sample. It shows peak positions corresponding to 2 Theta 28,32,38,48,53,55,57.59,67 showing the d-spacing A of 3.11,2.77,2.33, 1.86, 1.71, 1.65,1.55 and 1.38 respectively. The XRD pattern of heat treated Cu₃(PO₄)₂ are broad indicating gradual loss of crystallinity with increase in temperature. The removal of Cs activity was reduced correspondingly. (R Hepzi Pramila devamani et al 61 (2013) pp 16917-16921) Activity removal using heat treated sample is found to be less and so it is concluded that treatment by co precipitation at room temperature itself is preferable for max removal of activity. Fig. 8 shows SEM analysis of heated and un heat treated samples. Morphology of the material shows that particle agglomeration increases with temperature resulting in less surface area. Therefore heat treated sample have less influence in the removal of radioactive samples. The average particle sizes of particles were found to be 1micron, 5micron, 10 micron and 20 micron at temperatures of 323K and 423K respectively. This shows that with increase in temperature particle comes closer, coalesce and formed bigger particles. FTIR shows peaks for the bonding Cs with Cu₃(PO₄)₂ precipitate probably of co precipitated Cu₃(PO₄)₂ and Cs₃(PO₄)₂. Bands at 1060 and 992 cm⁻¹ corresponds to asymmetric and symmetric stretching vibration of PO₄⁻³ and the bands at 629 and 560 cm⁻¹ are out of phase

bending vibrations of PO_4^{3-} in the XRD of $\text{Cu}_3(\text{PO}_4)_2$. The respective frequencies were slightly reduced as evidenced from FTIR of $\text{Cu}_3(\text{PO}_4)_2$ bonded with Cs^{137} by coprecipitation/ adsorption. Fig.11 shows the set up for column testing. Table 3(a)-3(d) shows that percentage removal of Cs increase with flow rate from 5 bed volume/hour to 10 bed volume/hour and it comes down with increase in flow rate. The increase in percentage removal with increase in flow rate was due to more number of Cs ion coming in contact with column material $\text{Cu}_3(\text{PO}_4)_2$ and further decrease is due to decrease in residence time with increase with flow rate. At any flow rate, the percentage removal increases with time as expected, since more Cs^{137} ion come in contact with column material. With the heat treated sample, the percentage removal of Cs^{137} was found to be less than the unheated samples.

4 CONCLUSION

The treatment of radioactive effluent containing Cs^{137} by insitu precipitation $\text{Cu}_3(\text{PO}_4)_2$ has been found to be very successful. The optimized condition for the % stoichiometry of the chemicals, pH, particle size and flow rate in the batch study and flow rate and bed volume were established in the column study.

5 REFERENCES

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