Separation of Cs-Sr through Ultrafiltration

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Abstract: ***Complexation - ultrafiltration is a new technique which can be used for the absolute separation of trace elements. We have attempted to separate a mixed metal system to their individual components using the technique. The isotopes (Cs-137 and Sr-90) are required to be isolated from the discharge streams for safe discharge. Chemical co-precipitation is presently practised but the method has many challenges. Ultrafiltration has been demonstrated to be effective but not much work has been reported. The first in the series of proposed studies, reported here aims at the demonstration of the potential of UF not only in the isolation of the trace contaminants but also in separating them. The results indicate that Cs can be effectively separated at pH6.5 as a ferrocyanide colloid and Sr as carbonate at pH9. The relative advantage of using UF over the chemical co-precipitation has been discussed.***

Keywords: Ultra-filtration, Complexation-UF, Separation, Cs-Sr

1. Introduction

Membrane processes such as reverse osmosis (RO) and nano-filtration (NF) have been deployed for many separations particularly for the removal of trace heavy metal species from the industrial and nuclear effluents. They could not however be adopted on large scale because of the inherent limitations of high pressure operation and limited volume reduction of contaminated streams [1]. Almost all the aqueous effluents are large in volume and contain relatively low concentration of the metal ions, which frequently makes the operation of traditional separation techniques difficult [2]. Most of the traditional methods such as sorption, co-precipitation etc are equilibrium controlled and requires large foot print area besides being operationally cumbersome[3]. Ultra-filtration is a pressure driven process and the controlling mechanism is size driven. It has relatively larger pore-sizes (at least a few orders of magnitude higher) compared to reverse osmosis. Consequently the net osmotic pressure to be overcome is relatively negligible permitting the operations to be carried out at much lower pressures say about 1-2 bars. As the separation mechanism is size based it is felt that if the size of the metal ion is increased either by complexation or converting it to the colloidal form then one can isolate them. Already several workers have reported the separation of heavy metals through complexation ultrafiltration or by colloidal formation. Complexation Ultrafiltration uses water-soluble complexing agents to complex easily interesting metallic ions and gives them a macromolecular size. Binding of metal ions to water soluble polymers enables us to separate them from solution and retain them when they are pumped through an ultrafiltration membrane. It is also well known that the complexation or the colloidal conversion of different metal ions vary with reference to the conditions such as nature of complexing agent, pH etc.

Cs -137 and Sr-90 the two long lived isotopes (of the nuclear fission products) often are encountered together in nuclear discharge streams [4]. The removal of cesium radioisotopes from liquid waste, including handling during nuclear accidents, has recently become a major concern due to their long half-life and biological hazards [5]-[6]. In order to address the environmental concerns, these two species are concentrated and isolated. Separation of these isotopes would allow the use of them independently and would add value to overall operations. Hence it was decided to take up the studies on the separation Cs and Sr using ultrafiltration process.

It is known that transition metal hexacyanoferrate (II) selectively adsorb Cs among alkaline and alkaline earth elements, and they are often used to decontaminate Cs for treatment of radioactive liquid waste from nuclear fuel recycling facilities. Transition metal ferrocyanide exhibit good adsorption properties for cesium because they have a high affinity for cesium over a wide pH range [7]. Strontium can be removed as a carbonate or phosphate.

The aim of this study was to investigate the efficiency of Cs and Sr removal using complexation ultrafiltration. Initially the efficiency of co-precipitation of cesium using potassium ferrocynide and copper sulphate was established. The optimum pH and ratio (Cs: $CuSO_4$:K_4 [Fe (CN) $_6$]) were established. A possible chemical consumption reduction was checked. Secondly, the removal of strontium using sodium carbonate was studied and establishment of optimum pH. The last part involved the study of the separation efficiency of both the metals (cesium and strontium) in solution at respective optimum operating pH.

2. Materials and Methods

2.1 Chemicals and synthetic waste water

All chemicals involved were of analytical reagent grade. Cesium and strontium solutions were prepared by dissolving cesium nitrate ($CsNO_3$) and strontium nitrate (Sr $(NO_3)_2$) respectively in pure water. Copper sulphate ($CuSO_4.5H_2O$) and potassium ferrocynide (K_4 [Fe (CN) $_6$].$5H_2O$) were used for preparing solutions for co-precipitation of cesium ions. Sodium carbonate (Na_2CO_3) was used to precipitate strontium ions. The pH values of the solutions were adjusted using 0.05M HCl and 0.1M NaOH.

2.2 Cross-flow Ultrafiltration model

The laboratory ultrafiltration model was designed to test and check performance of hollow fiber ultrafiltration membrane modules and is a compact table top made of stainless steel consisting of: feed and backwash pump (both diaphragm type, 48V DC with suitable 230V AC adaptor), storage and backwash tank (both 1.5 liters capacity), lab model of hollow fibre membrane element, feed and reject pressure gauges (both 0-4kg/cm^2), and necessary valves for operation (needle valves). The membrane was made from polyvinylidene fluoride (PVDF). The membrane had molecular weight cut off (MWCO) of 100KD with effective membrane area of 0.2m^2, and flow direction from out to in (out-in). The membrane had a pure water permeate flux of 50lph.

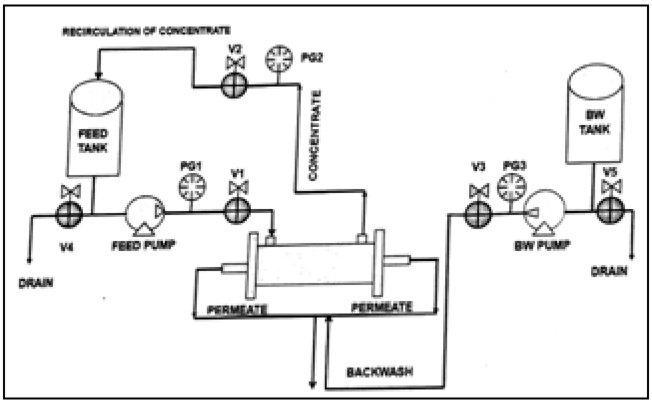

Figure 1: Schematic of Lab UF model

2.3 Method

Ultrafiltration experiments were performed using a cross flow laboratory scale ultrafiltration model. The desired filtration conditions were maintained by manually operating valves. For cesium co-precipitation trial runs were done to establish the precipitate giving ratio of potassium ferrocynide and copper sulphate. The effect of acidity and alkalinity of the solution was also observed. Solution of 25ppm cesium and respective solutions of copper sulphate and potassium ferrocynide were prepared. The three solutions were mixed and stirred gently for thirty minutes [7]. In order tocontrol and correct the solution pH, pH meter and neutralizing agents (HCL and NaOH) were employed. The resulting solution was placed into the feed tank and the ultrafiltration process started. At the beginning of the filtration, both permeate and retentate were returned to the feed tank (run in a cycling mode) for ten minutes to achieve steady-state operation. After circulating the solution (cycle mode) for 10 minutes at constant pH and pressure (2kg/cm^2), permeate samples were taken for cesium analysis. The runs were done from pH=5.5 to 9.5 and optimum pH established. Decreasing cesium concentration solutions were run at optimum pH to check if the rejection rate was affected significantly. A possible chemical consumption reduction was checked by decreasing the ratio of potassium ferrocynide and copper sulphate. Solutions of strontium and sodium carbonate were also run from pH=8 to 12 and optimum pH established. The two metal solutions (Cs and Sr) were mixed with the respective complexing agents and run at respective optimum pH and separation efficiency analyzed.

The rejection rate *R*, which measures the membrane's separating capabilities is defined as:

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad (1)$$

where C_p and C_f are permeate and feed concentrations respectively.

2.4 Concentration Analysis

Cesium analysis was done using x-ray fluorescence analyzer (XRF). Quantitative XRF analysis fundamental parameter method was used which does not need a standard solution.The intensity of each fluorescent X-ray can be derived theoretically through sophisticated computer programs and the composition of unknown sample can be extrapolated by its fluorescent X-ray intensity of each element [8].

Strontium analysis was done using complexometric titrations as XRF could not detect the very low ppm levels. Ethylenediaminetetra-acetic (EDTA) - 0.01M was the titrant with thymolphthalein as the metal indicator. Thymolphthalein contains a stable lactone ring and reacts only in an alkaline medium with acolour change from blue to colorless (or a slight pink) [9].

3. Results and Discussion

3.1 Hydrodynamic performance of membrane

The behavior of membrane is reported in Fig. 2, flux was found to be increasing with applied pressure even in the presence of working fluid from which it was evident that membrane pores were not clogged. After backwash the flux did not significantly change from the pure water flux.

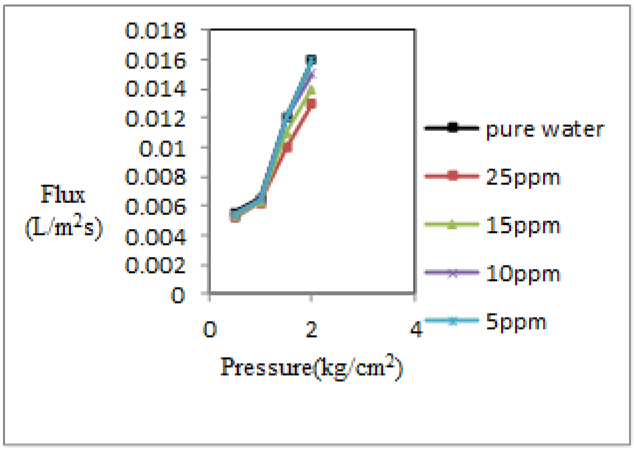

Figure 2: Permeate flux

3.2 Complexing agents-metal ratio

The simulated solutions of $[Cs^+]$: $[Cu^{2+}]$: $[K_4 [Fe (CN)_6]$ = 1:1:1 and 1:2:1 showed apparent no change. The solution of 1:3:1showed a red brown colour and this suggested that formation copper hexacyanoferrate (II) had occurred. Potassium ferrocyanide precipitates red-brown copper (II) ferrocyanide from Cu^{2+} solutions:

$$2Cu^{2+} (aq) + [Fe (CN)_6]^{4-}(aq) \Longleftrightarrow Cu_2 [Fe (CN)_6] (s)$$

It is realized that metal hexacyanoferrate (II) was generated and Cs was decontaminated as $K_nCs_mCu_{2-(n+m)/2}[Fe (CN)_6]$ Cesium was trapped along with copper.

3.3 Cesium XRF Results-effect of pH on Rejection rate

During the trial runs the precipitate intensity decreased as acidity increased (below pH=4) as well as alkalinity increased (above pH=11). The concentration of Cs in the solutions and the removal rate after ultrafiltration process are shown in Table 1.

Table 1: Effect of pH on removal rate

Feed (ppm)	Permeate (ppm)	Ratio	pH	Removal %
25	1.1878	1:1:3	5.5	95.25%
25	0.8180	1:1:3	6.5	96.73%
25	1.2222	1:1:3	7.5	95.11%
25	1.2589	1:1:3	8.5	94.96%
25	1.3627	1:1:3	9.5	94.55%

The concentration of Cs decreased for all the simulated solutions with maximum rejection of 96.73% achieved at pH=6.5. Fig 3.0 shows the effect of pH on rejection rate (%).

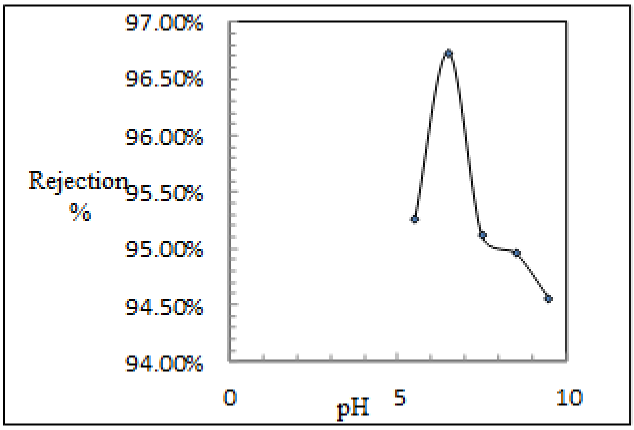

Figure 3: Effect of pH on Rejection rate

A decrease in rejection as we move away from pH=6.5 is observed.The reason being that if a metal hexacyanoferrate (II) was generated and Cs was decontaminated as a complex:

Cs^{+} $+2Cu^{2+}$ (aq) + $[Fe\ (CN)_6]^{4-}$(aq) <==>$K_nCs_mCu_{2-(n+m)/2}[Fe\ (CN)_6]$ (s)

The donor atoms of complexing agents react with metal and hydrogen ions. Metal ions compete with hydrogen ions for the available donor atoms and hydroxyl ions may react with metal ions. Therefore, hydrogen and hydroxyl ions will affect the co-precipitation of Cs from the chemical reaction. Acidic conditions will increase competition for metal ions and alkaline condition will cause the metal ions to react with hydroxyl ions thus limiting forward reaction.

3.4 Cesium XRF Results-effect of initial metal concentration

Fig 4.0 shows the effect of decreasing Cs concentration in the feed on rejection rate. From a feed concentration of 25ppm to 5ppm the corresponding rejection percentages were 96.73%, 94.78%, 89.01%, 88.42%, and 81.56%.
This suggests the process can be extended to very low Cs ppm levels.

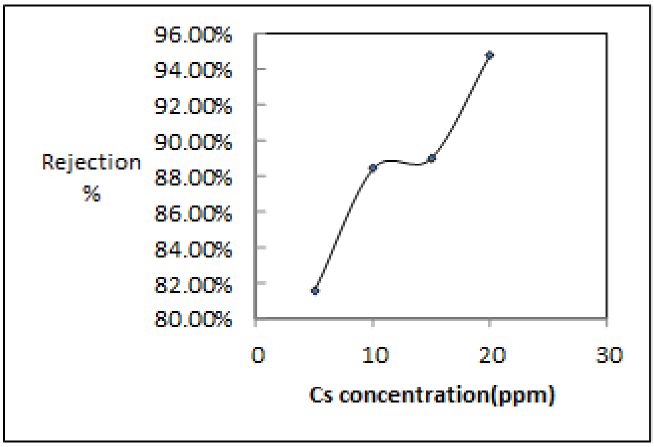

Figure 4: Effect of initial metal concentration

3.5 Cesium XRF Results-Chemical Consumption Check

The molar ratio of cesium to complexing agents, $[Cs^{+}]$: $[Cu^{2+}]$: $[K_4\ [Fe\ (CN)_6]$, in the feed solutions and the removal rate after ultrafiltration process are shown in Table 2

Table 2: Chemical consumption check

Ratio	Feed (ppm)	Permeate (ppm)	Removal %
1:1:3	25	0.818	96.73%
1:0.5:1.5	25	1.1734	95.31%
1:0.25:0.75	25	1.3410	94.64%
1:0.125:0.375	25	1.4832	94.10%

As it can be observed the removal rate reached a minimum of 94.10% with a molar ratio of 0.125:0.375(Cu^{2+}]: $[K_4\ [Fe\ (CN)_6]$). This implies that chemical consumption for the removal of cesium can be reduced as long as the $[K_4\ [Fe\ (CN)_6]$: $[Cu^{2+}]$ is kept as 1:3.

3.6 Strontium Complexometric Titrations Results-effect of pH

The effect of pH on the rejection rate is shown in fig 5.0. At pH 8 to 12 with feed concentration of 25ppm Sr the rejection rates were 83.10%, 85.49%, 80.66%, 70.98%, and 63.73%. The maximum rejection rate was experienced at pH= 9.

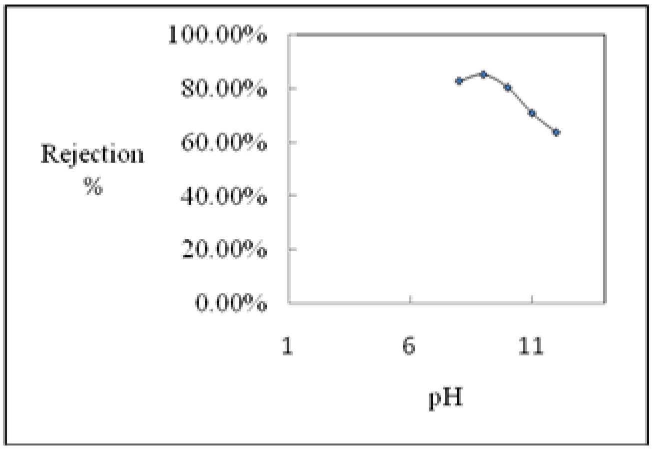

Figure 5: Effect of pH on Rejection rate

This can be explained by the fact that by altering the pH of aqueous solutions will alter the concentration of ions in the precipitation equilibrium by the common-ion effect.

Carbonate precipitation takes place only if carbonate ions ($CO_3^{2-)}$ are present. Free carbonate ions are present only if the pH is high

$$Sr^{2+} + CO_3^{2-} <==> SrCO_3$$
$$H^+ + CO_3^{2-} <==> HCO_3^-$$

Increasing the hydrogen-ion concentration (lowering the pH) decreases the carbonate ion concentration by forming HCO_3^-, which makes the precipitate more soluble. Therefore, decreasing the hydrogen-ion concentration (raising the pH), therefore, aids precipitation. The pH values above 10 promote the formation of metalhydroxyl complexes that can increase the metal solubility and reduce the precipitation effectiveness.

3.7 Cesium and Strontium mixture separation efficiency

Table 3: Mixture of both metals

Metal	pH	Feed (ppm)	Permeate (ppm)	Removal %
Cs	6.5	25	1.1611	95.36%
Sr	9	25	6.6488	73.40%

Separation factor, $\alpha_{sc} = \dfrac{\left(\frac{C_s}{C_c}\right)permeate}{\left(\frac{C_s}{C_c}\right)feed}$

$$= \frac{\frac{6.6488}{1.1611}}{\frac{25}{25}}$$

$$=5.72$$

Runs at pH=7 and 8 for cesium gave rejection of 94.60% and 94.03% respectively and 73.40% at pH=9 for strontium. This suggests the mechanism did not significantly change for the mixture solution.

4. Conclusion

The data summarized in this paper suggest that UF assisted by complexation can be successfully applied for removal of cesium and strontium. Cesium co-precipitation using copper sulphate and potassium ferrocynide proved viable as well as strontium using sodium carbonate. Increase of a carbonate can be investigated if it can affect the strontium removal. Use of a phosphate for the removal of strontium can also be investigated. The development of mathematical models for process simulation and optimization will be useful tool for prediction and understanding further the mechanisms. Before developing a practical COUF process, industrial effluents should be considered to study the effects of other metals and substances on the separation of target metal ions. Membrane fouling characterization and scaling-up should also be investigated.

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