



## Study on the Temperature Effect on Regeneration of Cesium Form of Resin into Ferric Form

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### ABSTRACT

The pressurized heavy water reactors which are used for power production make use of heavy water in moderator and in primary heat transport system. The cationic fission products produced during the reactor operation such as cesium, strontium, cobalt, palladium, ruthenium and anions iodide, iodate, ruthenate, etc. contaminate the heavy water and hence the need for purification of the moderator and primary heat transport system to nuclear grade to achieve the desired efficiency arises. Columns containing ion exchange resins in online are used for purification. Also ion exchange resins are used in purification of fuel storage pond water. In this purification process, the resins pick up activity and ionic impurities. The activity-loaded resin so formed is called spent resin. It is imperative to treat the spent resin into innocuous form, highly inert towards exchange with any external radioactivity. Hence, an attempt has been made to convert the Cs-containing spent resin into ferric form and to study the role of temperature in the exchange reactions. Results show that the spent resin of Cs form could be completely converted into ferric form in batch study. Also the extent of exchange to ferric form was found to come down with temperature resulting in the release of -59.46 KJ/mole with cesium form of resin.

### INTRODUCTION

Spent resins are generated in purification of primary heat transport system, moderator system, and spent fuel storage pond water. Plecas & Paviovic (2003) reported that the spent resin is disposed off in the radioactivity disposal area without treatment or fixed in cement or in thermosetting polymer. Direct immobilization in thermosetting resin, cement, etc. results in final product whose volume is more than that of the original waste form. Incineration of spent resin involves burning at higher temperature (700°C), problem of handling off gasses, corrosive fumes of NO<sub>x</sub>, SO<sub>2</sub>, etc. and radioactivity from the resin. Also, it does not result in complete burning, and therefore, results in tarry residue.

Miriam (1982) has reported that the other alternate method, acid digestion, generates new kind of waste solutions and complicates the final disposal. Also, it needs handling of concentrated mineral acids and handling off gasses viz., NO<sub>x</sub>, SO<sub>2</sub>, etc. Kuobota (1983) has investigated wet oxidation and reported that it did not completely oxidize organic carbon to carbon dioxide gas.

Hence, an attempt was made to convert the spent resin into multivalent ionic forms. Regeneration of spent resin into multivalent ionic forms renders the handling of the almost non-active resin easy which can be fixed in cement or polymer safely.

Not much literature is available on the regeneration of

spent resin into multivalent ionic forms but it has been reported (Vogel 1978) that there is literature on the feasibility and conditions of conversion of one form of resin into another form. Batch experiments carried out under conditions favouring film diffusion controlled show that the spent resin could be completely regenerated into inactive form. It is imperative to treat the resin into innocuous form highly inert towards exchange with any external ion. Hence, an attempt has been made to convert the spent resin of cesium form into ferric form and to study the role of temperature in the exchange reactions.

Cesium form of the ion exchanger was equilibrated with ferric ion containing solutions of various strengths corresponding to 100-500% stoichiometry with respect to exchange capacity at four different temperatures, 303, 323, 343 and 363 K. Results indicate that the percentage conversion of the resin into ferric form and the equilibrium constant for the exchange reactions come down with temperature favouring the conversion to the ferric form of the resin at lower temperature.

### MATERIALS AND METHODS

H<sup>+</sup> form of cation exchanger (Make Tulsion 46) was used for the experiment. AR grade cesium chloride was used for conversion of the resin into cesium forms of the resin. Radioactive cesium procured from Isotope Division of BARC, Trombay was used for loading the resin with radioactive cesium.

AR grade ferric chloride, iron powder, sodium thiosulphate and iodine procured from M/s Merck were used for the experiment. Single channel analyser was used for estimation of radioactive cesium.

The unexchanged ferric ion was analysed volumetrically. The exchanged cesium was estimated from the analysis of radioactive cesium in the solution phase.

**Estimation of exchange capacity of resin:** The exchange capacity of the ion exchanger was found out by equilibrating 10 g of the H<sup>+</sup> form of the resin in 500 mL of 3 N sodium chloride solution and estimating the exchanged H<sup>+</sup> titrimetrically using phenolphthalein indicator.

**Preparation of non active and radioactivity loaded resin:** 50 g of H<sup>+</sup> form of ion exchange resin was soaked in 500 mL solution containing non active cesium corresponding to 300% stoichiometric amount of exchange capacity. It was kept overnight, the supernatant drained and the resin was dried under IR lamp. The so prepared nonactive Cs loaded resin was used for studying the effect of temperature on the exchange of Cs loaded resin with ferric ion. 50 g of H<sup>+</sup> form of resin was equilibrated with 500 mL of radioactive Cs solution of specific activity  $1.2 \times 10^{-5}$   $\mu\text{Ci/mL}$ . The so prepared cesium loaded resin with radioactive cesium of total activity  $1.2 \times 10^{-4}$   $\mu\text{Ci/g}$  was used for verifying the experimental findings on the effect of temperature on the conversion into ferric form.

**Effect of temperature:** One gram of the cesium form of the resins was equilibrated with 100 mL of ferric chloride solution of strength 22 mN, 44 mN, 66 mN, 88 mN and 110 mN corresponding to 100, 200, 300, 400 and 500% stoichiometric amount with respect to exchange capacity, at 303 K, 323 K, 343 K and 363 K by thermostating for 1 hour.

The strength of the unexchanged ferric ion was estimated volumetrically from which quantity of exchanged cesium in to the solution phase and the exchanged ferric into the resin phase were estimated knowing the exchange capacity as 2.2 meq/g. The % conversion into ferric form of the cesium form of the resin was plotted against strength of ferric ion solution at various temperatures (Fig. 1).

The apparent equilibrium constant at various temperatures ( $K_{app}$ ) were estimated from the strength of the unexchanged ferric ion in the solution phase, exchanged cesium ion in the solution phase and the remaining cesium and ferric in the resin phase obtained from the exchange capacity of the resin. Fig. 2 shows the plot of variation of  $\log K_{app}$  of the exchange reaction with ferric ion concentration.

Table 1 gives the thermodynamic equilibrium constants for the exchange reactions obtained by extrapolating the

equilibrium constant against concentration of ferric ion to zero ferric ion concentration.

Also the enthalpy of the exchange reaction ( $\Delta H$ ) was calculated using Gibbs Helmholtz equation based on the relation between the variation of  $K_{ther}$  with temperature and the enthalpy of the reaction. Fig. 3 shows the plot of  $\log K_{ther}$  against  $1/T$  to obtain the enthalpy of exchange reactions between cesium form of the ion exchanger with ferric ion.

To verify the effect of temperature on the exchange of ferric ion with cesium form of resin with temperature, 1 g of radioactive Cs form of resin with activity  $1.2 \times 10^{-4}$   $\mu\text{Ci/g}$  was equilibrated with 100 mL ferric solution of 300% stoichiometry with respect to exchange capacity and thermostated at 303, 323, 343 and 363 K. The extent of conversion into ferric form was studied by analysing the activity of Cs exchanged into solution phase at each temperature. Table 2 shows the % conversion as function of temperature.

## RESULTS AND DISCUSSION

**Extent of regeneration:** The exchange capacity of resin was found out to be 2.2 meq/g. The % regeneration was found to vary from 83.5-87.36 at 303K, 76.13-83.63 at 323K, 68.63-78.86 at 343K and 60.86-72.04 at 363K using the ferric solutions of strength corresponding to 100-500% stoichiometry with respect to exchange capacity. The respective line equations are  $y = 0.0096x + 82.614$ ,  $y = 0.0191x + 73.682$ ,  $y = 0.0259x + 65.909$  and  $y = 0.0292x + 57.291$  for 303 K, 323 K, 343 K and 363 K.

From Fig. 1, we found that the percentage regeneration of cesium form of the resin into ferric form increases with increase in the strength of the ferric ion solution. Also, the percentage regeneration was found to come down with temperature. As the strength of the ferric ion increases from 22 mN to 110 mN, the available ferric ion in 100 mL of the solution increases from 2.2 meq to 11 meq. As the exchange capacity was found to be 2.2 meq/g, the amount of ferric ions needed for 100% conversion of 1 g of the resin is 2.2 meq. Since the availability of ferric ion was more with concentration of ferric ion, the percentage regeneration was found to increase with strength of the ferric solution.

Even though the ionic potential (ionic size to charge ratio) of cesium is less than that of ferric as the strength of the ferric ion solution is more, the Cs from the resin is pulled out by ferric depending upon the availability of the ferric ion.

**Effect of temperature on equilibrium constant:** From the Fig. 2, we observe that the equilibrium constant of the ex-

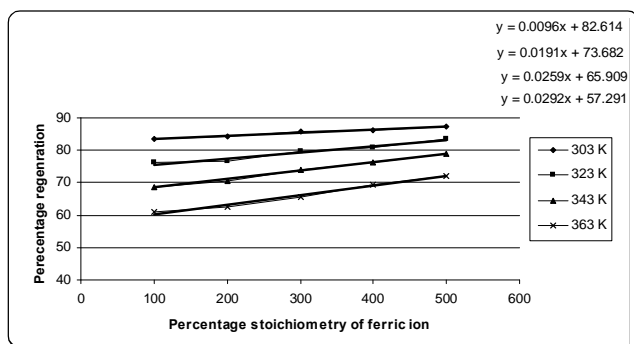


Fig. 1: Regeneration of cesium form of resin into ferric form as function of temperature.

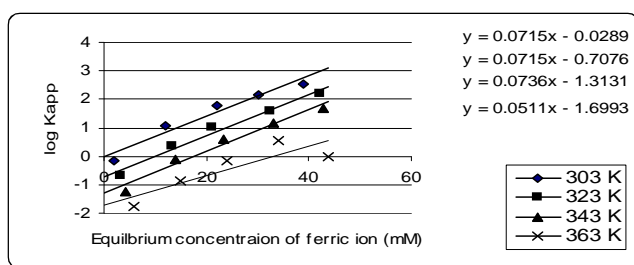


Fig. 2: Equilibrium studies on the exchange of ferric ion with cesium form of resin.

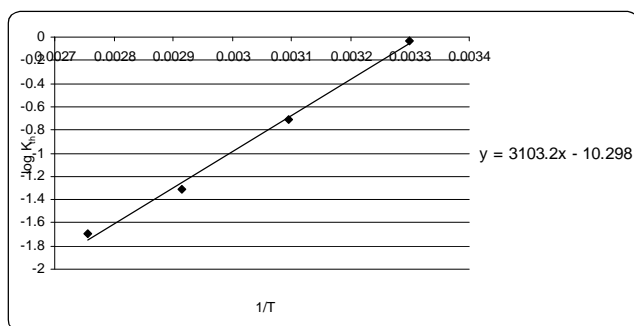
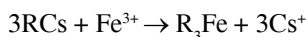


Fig. 3: Estimation of enthalpy of exchange reaction of Cesium loaded resin with ferric.

change reaction was observed to be less with temperature. More rigorous calculations were made by including the activity coefficients of the counter ions in the solution to compute the thermodynamic equilibrium constant (Lokande & Singare 1999, Vanselow 1932, Myers & Boyd 1956, Argersinger & Davidson 1952). The ion exchange reaction at equilibrium may be represented as



The apparent equilibrium constant was calculated using the equation:

$$K_{app} = [R_3Fe][Cs^+]^3 [f_{Cs^+}]^3 / [RCs]^3 [Fe^{3+}][f_{Fe^{3+}}]$$

Where, RCs refer to amount of Cs<sup>+</sup> in the resin phase

Table 1: Thermodynamic equilibrium constants of equilibrium reactions of ferric ion with cesium loaded resin at various temperatures.

S.No.	Temp., K	Thermodynamic equilibrium constant	
		Log K	K
1	303	-0.0289	0.9356
2	323	-0.7076	0.1960
3	343	-1.3131	0.0486
4	363	-1.6993	0.0199

Table 2: Regeneration of active Cs loaded resin at various temperatures.

Temp.	Activity loaded (μCi/g)	Total Activity exchanged	% exchange of activity
303 K	1.2 × 10 <sup>-4</sup>	0.387 × 10 <sup>-4</sup>	32.3
323 K	1.2 × 10 <sup>-4</sup>	0.361 × 10 <sup>-4</sup>	30.0
343 K	1.2 × 10 <sup>-4</sup>	0.352 × 10 <sup>-4</sup>	29.4
363 K	1.2 × 10 <sup>-4</sup>	0.298 × 10 <sup>-4</sup>	24.8

and [Cs<sup>+</sup>] refers to the amount of cesium concentration in the solution phase respectively. The fs represent the activity coefficients of the ions in the solution phase.

logK<sub>app</sub> was plotted against equilibrium concentration of ferric ion in the solution which was extrapolated to zero equilibrium concentration of ferric ion to get K<sub>th</sub> for the exchange reactions of cesium forms of the resin (Figs. 3 and 4). The activity coefficient of the ions (f) in the solution phase was computed from the Debye Huckel limiting law.

$$\log f = -A\sqrt{\mu} Z^2$$

Where, μ is the ionic strength given by:

$$\mu = 1/2 \sum CiZi^2,$$

where Zi and Ci are the charge and concentration of the ion and A is the Debye Huckel constant.

The plot of log K<sub>app</sub> vs. equilibrium strength of ferric ion at different temperatures give rise to straight lines with equations y = 0.0751x - 0.0289, y = 0.0715x - 0.7076, y = 0.0736x - 1.3131, and y = 0.0511x - 1.6993 showing the thermodynamic equilibrium constants as 0.9356, 0.19607, 0.04863 and 0.019985 at 303, 323, 343 and 363 K.

The apparent equilibrium constant was found to come down with temperature indicating that the equilibrium is more favoured at lower temperatures. The extrapolated equilibrium constant (K<sub>ther</sub>) at zero equilibrium concentration of ferric ion in the external solution (Table 1) also corroborates the same.

**Enthalpy of ion exchange reactions:** In order to get the enthalpy of the exchange reaction, use is made of the Gibbs Helmholtz relation between the variation of equilibrium constant with temperature and the enthalpy of the reaction given by:

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$$

Which in the integrated form gives:

$$\log K = -\Delta H/2.303RT + C$$

The line equations in the plot of  $\log K_{th}$  Vs.  $1/T$  are  $y = 3103.2x - 10.298$ . Where  $K_{th}$  refers to the thermodynamic equilibrium constant,  $T$  is the temperature in K,  $R$  is the universal gas constant and  $C$  is the integration constant. Results indicate that the exchange of cesium form of the resin with ferric entails release of heat showing that the exchange is more favoured at lower temperatures. Bonner and Pruett also found in all uni and bivalent exchanges, equilibrium constants decreased with temperature and the reactions are exothermic.

From the slopes of the line (Fig. 3), the exchange reactions were found to be exothermic with 59.43KJ/mole, in the exchange reactions, Cs-Fe. The experiment using resin loaded with active Cs of activity  $1.2 \times 10^{-4}$   $\mu\text{Ci/g}$  resulted in almost  $0.387 \times 10^{-4}$ ,  $0.361 \times 10^{-4}$ ,  $0.352 \times 10^{-4}$  and  $0.298 \times 10^{-4}$  resulting in 32.3%, 30%, 29.4% and 24.8 % removal of activity from the resin at 303, 323 343 and 363 K respectively.

## CONCLUSION

Ion exchange reactions between cesium form of resin with Ferric ion was carried out. Results indicate that the reactions

are exothermic favouring the exchange reactions at lower temperatures.

## ACKNOWLEDGMENTS

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