

TREATMENT OF Cs-137 BY ZEOLITE IMPREGNATED WITH VARIOUS METALIC IONS AND ZINC FERROCYANIDE

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ABSTRACT

Zeolite was pretreated either with various metallic ions or impregnated with zinc ferrocyanide and used to remove Cs-137 from the simulated High Level Liquid Waste (HLLW). Usually the exchange capacity of ordinary Na-form zeolite for Cs-137 in HLLW was rather poor (0.04 m.eq./g). However, the exchange capacity of Na-form zeolite can be improved by replacing the sodium ion of zeolite with various metallic ions. It was found that the exchange capacity of Zinc-form zeolite increased to 0.23 (m.eq./g.) (ca. 6 times that of the Na-form zeolite). Further studies revealed that the exchange capacity was improved to 0.76 (m.eq./g.) which is ca. 19 times that of the Na-form zeolite, when the zeolite was impregnated with zinc ferrocyanide. After the exchange reaction was completed, all forms of zeolite were pressed to standard shape and ignited to 1000°C. Leaching rates were determined according to standard method and the results showed that Na-form zeolite was fastest, Zn ferrocyanide impregnated zeolite the second, and Zn-form zeolite the slowest.

INTRODUCTION

The composition of High Level Liquid Waste (HLLW) solution which is obtained by reprocessing of spent fuel from nuclear power generation is rather complex. It is estimated that more than 90% of total radioactivity emitted by HLLW comes from the activities of Cs-137 (T_{1/2} = 20.8 yrs) and Sr-90 (T_{1/2} = 28.8 yrs) present in the HLLW during the cooling periods between 10 to 100 years (1). Thus, from the point of view of HLLW management Cs-137 and Sr-90 are the most hazardous radionuclides, and it is preferred to remove them from the bulk of HLLW solution before any further treatment is attempted.

Zeolite has been used to remove Cs-137 from the HLLW Solution. however, it was found that the exchange capacity of Na-form Zeolite was rather poor due to the high concentration of sodium ion in the HLLW solution, which competed with Cs ions during exchange reactions (2). It is the purpose of this study to improve the exchange capacity of the zeolite by replacing the sodium ion in the Na-zeolite with various metallic ions for removal of Cs-137 from HLLW Solution. On the other hand, another study revealed that various metal ferrocyanides showed high selectivity for the exchange reaction of cesium in the HLLW solution (3,4). However, the metal ferrocyanides showed poor mechanical properties, which fact prevented it from the chromatographic column type application for the separation of cesium from HLLW (5). In this work Zn-zeolite will be impregnated with potassium ferrocyanide under various conditions to obtain Zn ferrocyanide zeolite for the removal of Cs-137 from the HLLW solution. After completion of exchange with Cs-137 all forms of zeolite will be pressed and

ignited at the high temperature (1000°C). Leaching rate will be determined by standard procedure.

EXPERIMENTAL

Chemicals

All chemicals used in this work are the analyzed reagent grade. Cesium nitrate, potassium ferrocyanide and zinc sulfate are the products of E. Merck. Na-form zeolite was a synthetic zeolite, Molecular sieve 4A supplied by the Union Carbide of U.S.A. Deionized water was redistilled before use in this work. This HLLW Simulated solution used throughout this study was prepared according to the literature (3). This main compositions are shown below :

Cs+	$3.8 \times 10^{-3} \text{M}$
Na+	1.98 M
Fe ²⁺	0.115 M
Al ³⁺	0.107 M

The simulated solution was spiked with Cs-137.

Preparations of various forms of zeolite.

Na-form zeolite (80-150 mesh) was washed several times with distilled water, dried at 110°C for 24 hrs. and stored in the decicator. M-form zeolite where M is metallic ions other than Na is prepared as follows : 5 g. of Na-form was placed in 250 ml. Erlenmyer flask to which an appropriate metal nitrate solution was added. After saking for 24 hrs. at room temperature the supernatant was decanted. Repeat this process for 4 times. The resultant zeolite was washed with distilled water many times until the respective

metallic ion never appear in the washing. Dry at 110°C for 24 hrs. and stored in desiccator before use. Zinc ferrocyanide-form zeolite was prepared as follows (7): 0.5 g. of Zn-form zeolite was placed in the Erlenmeyer flask, to which 10 ml. of Potassium ferrocyanide was added. Select optimum conditions for concentration of potassium ferrocyanide, reaction time, temperature and pH. Wash off the unreacted potassium ferrocyanide by distilled water and dried at 60°C. It was found that the highest exchange capacity may be achieved by using 0.25 M of potassium ferrocyanide to react with Zn-form zeolite for 30 min. at room temperature and pH 9. The compositions of Zn and Fe in the various form of zeolite were determined by neutron activation analysis using the research nuclear reactor of the National Tsing Hua University (THOR) using pure Zinc Sulfate and iron powder as standards. The radioactivities of Zn-65 and Fe-59 in the zeolite samples and the standards were measured by using 50 c.c. Ge(Li) detector and MCA system. The contents of Zn and Fe were obtained by comparing the radioactivities induced in various forms of zeolite with those of in the pure chemical standards and used for characterization of the various forms of zeolite.

Procedure for removal of cesium using various forms of zeolite as exchangers

Weigh exactly 0.2 g. of various forms of zeolite and placed in 50 ml. Erlenmeyer flask to which 10 ml. of simulated HLLW solution was added. The mixture was shaken for 6 hrs. before centrifugation. 1 ml. of supernatant was taken and the radioactivity was measured by ordinary gamma counting system using NAI(Tl) detector(C). Another 1 ml. sample was taken from the initial HLLW solution and its radio- activity was measured (Co). Then the distribution coefficient, Kd was defined as follows :

$$K_d = \frac{[C_s^+]_s}{[C_s^+]_l} = \frac{(C_0 - C)}{C} \frac{V}{m} \quad (1)$$

where

V : the volume of HLLW Solution

m : the weight of zeolite.

Solidification, Ignition and Leaching Rate Measurement

On completion of exchange reaction, all forms of zeolite were dried in the air. About 1 g. of those zeolite was pressed with 150 Kg/cm² into pellet shape, and ignited for 4 hrs. at 800, 1000 and 1200°C, respectively. The surface area (SA) of all forms of the ignited zeolite were measured, and suspended in the 100 ml. PE container. Add NaCl solution corresponding 100 times that of the surface area of the zeolite (8). Place in the thermostat adjusted at 40°C and keep for 7, 14, 21 and 28 days, respectively. The radioac-

tivities of the ignited zeolite before and after leaching test were measured. The leaching rate is estimated according to the definition shown below (8)

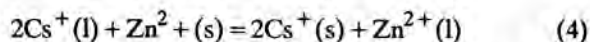
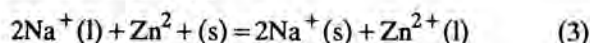
$$NL_i = \frac{m_i}{f_i \times SA} \quad (2)$$

where NL_i is the amount (g/m²) lost from unit surface area for element i, m_i, the amount (g) of i in the leachate, and f_i weight fraction of i in solid phase.

RESULTS AND DISCUSSIONS

Distribution coefficients were determined for various metal forms of zeolite and the results were summarized in Table I. As can be seen in the Table, the distribution coefficient for Na-form or other metals with positive one oxidation state is rather poor. Divalent metals such as Mg, Sr, Ba, Pb, Co and Cu forms of zeolite also showed low Kd values. When Na ion in the Na-form zeolite is replaced by divalent cations such as Ni(II) Ca(II) and Zn(II), the Kd values were increased. Especially, Zn-form zeolite was found to increase about 6 times that of Na-form zeolite. The content of zinc in the Zn-form zeolite was determined by using neutron activation analysis. It was found that 89% of Na ion in the Na-form zeolite was replaced by Zn ion.

The HLLW solutions usually contains high sodium ion which will compete with Cs ion in the exchange reaction. Thus, it is of interest to examine the changes of exchange capacities of various metal forms zeolite under different Na ion concentrations (10⁻⁴~ M ~ 2M). The Kd values are summarized in Table II. It is clearly indicated that Kd decreases as the concentrations of Na ion in the HLLW solution increase. This trend is prevailing among the three kinds of zeolite. The competition reactions between Na ion and Cs ion in HLLW solution may be expressed as follows, e.g. for the Zn-form zeolite (9):



Let K₁ and K₂ be the equilibrium constants of Eq.(3) and (4), then

$$K_1 = \frac{[Zn^{2+}](l) [Na^+]^2(s)}{[Zn^{2+}](s) [Na^+]^2(l)} \quad (5)$$

TABLE I

Exchange Capacities of Various Metal-Forms Zeolite.

Metal in zeolite	Kd (ml./g.) *	Metal in zeolite	Kd (ml./g.) *
Na	10.8	Ba	10.2
K	8.7	Pb	8.9
NH ₄	9.6	Co	10.7
Ag ⁺	6.6	Ni	16.7
Mg	10.3	Cu	2.9
Ca	24.1	Zn	57.4
Sr	8.2		
* Average of two runs.			

TABLE II

Exchange Capacities of Various Kinds of Zeolite for Cs-137 in Different Sodium Ion Concentrations.

[Na ⁺] (M)	Kd (ml./g.) *		
	Na-form	Zn-form	Zn-ferr. form
1E-04	708	3348	27217
1E-03	707	3067	13429
5E-03	705	3234	9850
0.01	510	2609	8566
0.05	202	1230	4026
0.1	103	534	2531
0.5	25.0	157	2257
1.0	22.4	142	1939
1.2	14.1	75.0	1742
2.0	10.8	57.4	1395
* Average of two runs.			

$$K_2 = \frac{[Zn^{2+}](l) [Cs^+]^2(s)}{[Zn^{2+}](s) [Cs^+]^2(l)} \quad (6)$$

By combining Eq.(1) and Eq.(6), one obtains Eq.(7)

$$K_2 = K_d^2 \frac{[Zn^{2+}](l)}{[Zn^{2+}](s)} \quad (7)$$

Similarly Eq.(5) and (6) give Eq.(8).

$$K_d^2 = \left(\frac{K_2}{K_1} \right) \frac{[Na^+]^2(s)}{[Na^+]^2(l)} \quad (8)$$

From Eq.(8) one gets

$$\log K_d = \text{const} + \log[Na^+](s) - \log[Na^+](l) \quad (9)$$

When the zeolite exchangers are saturated with sodium ion, then the term $\log[Na^+](s)$ will become a constant, and Eq. (10) is obtained.

$$\log K_d = \text{constant} - \log[Na^+](l) \quad (10)$$

In Fig. 1 K_d and $\log[Na^+](l)$ values in Table II are plotted according to Eq.(10). It is found that for Na-form and Zn-form zeolite, plateaus appear in the plots within the region where $[Na^+](l) < 10^{-2}$ M. This means that within this range sodium ion in the exchanger zeolite does not reach the saturation, i.e. $[Na^+](s)$ is not a constant. Thus, in the presence of sodium ion these two forms of zeolite do not show high selectivity toward cesium ion during the exchange reaction. For Zn ferrocyanide-form zeolite, on the other hand the selectivity toward cesium is rather high, and no plateau is observed in the region where sodium ion concentration is below 10^{-2} M.

A series of mixtures of Zn-form zeolite and Zn ferrocyanide-form zeolite were formulated with the following compositions (in terms of weight fraction of Zn-form zeolite): 1.0, 0.8, 0.6, 0.6, 0.5, 0.4, 0.2 and 0. The exchange capacities were measured for each composition. The results are summarized in Fig.2. It was observed that no synergistic effect was found in the exchange capacities for cesium ions. Instead, the additivity exists between the exchange capacities of various mixtures and those of individual com-

ponents, which fact indicates that the effects of competitions toward cesium ion for those two forms of zeolite are independent.

All forms of zeolite saturated with cesium were dried, pelletized and ignited to high temperatures (800°-1000°C). Leaching rates were measured with standard procedures (8) by suspending ignited pellets in NaCl solutions for 7, 14, 21 and 28 days at 40°C. The results are summarized in Table III. It was concluded that zeolite ignited at 1000°C showed slower leaching rate than those zeolite ignited at 800°C. Among different forms of zeolite, the leaching rates were found Na-form > Zn ferrocyanide-form > Na-form. It is noteworthy to point out that cesium leached out from Zn-form zeolite and Zn ferrocyanide-form zeolite are much less than cesium leached out from borosilicate glass, concrete or synrock. Thus, it may be concluded that modified forms of zeolite can be used as prosperous exchanger to remove cesium from the HLLW solution for minimization of its radioactivity hazard during the solidification process and final disposal.

TABLE III

Leaching Rates of Various Kinds of Zeolite.

Zeolite (Ign. Temp)	7 days	14 days	21 days	28 days
	Leach Amt. $\frac{g}{m \cdot d}$	Leach Amt. $\frac{g}{m \cdot d}$	Leach Amt. $\frac{g}{m \cdot d}$	Leach Amt. $\frac{g}{m \cdot d}$
Zn-ferro form (1000°C)	0.050±0.014	0.042±0.012	0.029±0.009	0.023±0.003
Zn-form (1000°C)	D.L.*	D.L.	D.L.	D.L.
Na-form (1000°C)	0.149±0.426	0.091±0.015	0.064±0.003	0.050±0.002
Zn-ferro. form (800°C)	0.71±0.061	0.405±0.049	0.322±0.032	0.262±0.029
Zn-form (800°C)	0.180±0.017	0.093±0.004	0.090±0.010	0.007±0.005

* D.L. Detection Limit

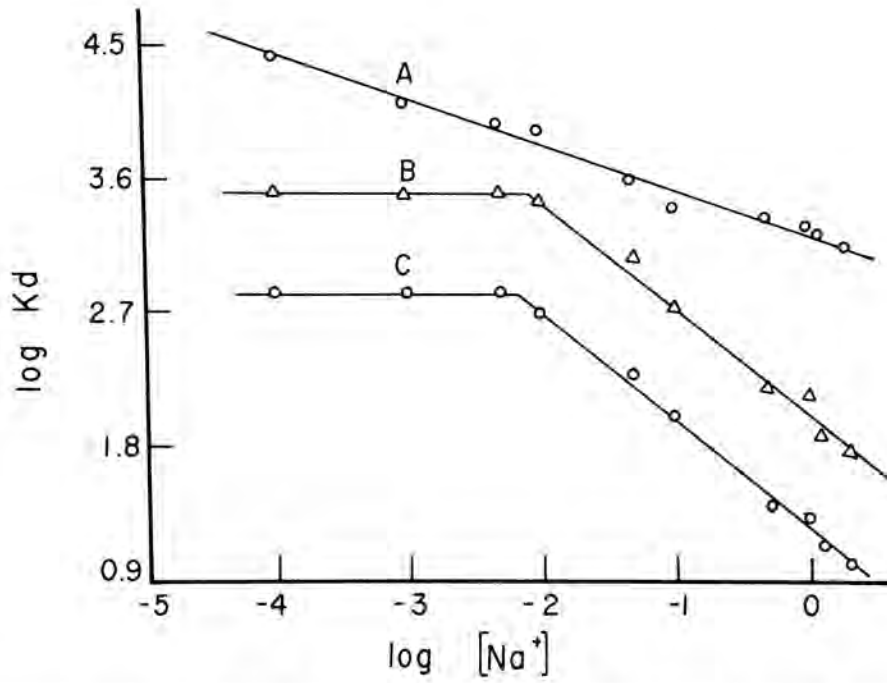


Fig. 1. Exchange Capacities for Various Forms of Zeolite in Different Sodium Ion Concentrations. (A) Zinc Ferrocyanide-Form, (B) Zn-Form (c) Na-Form.

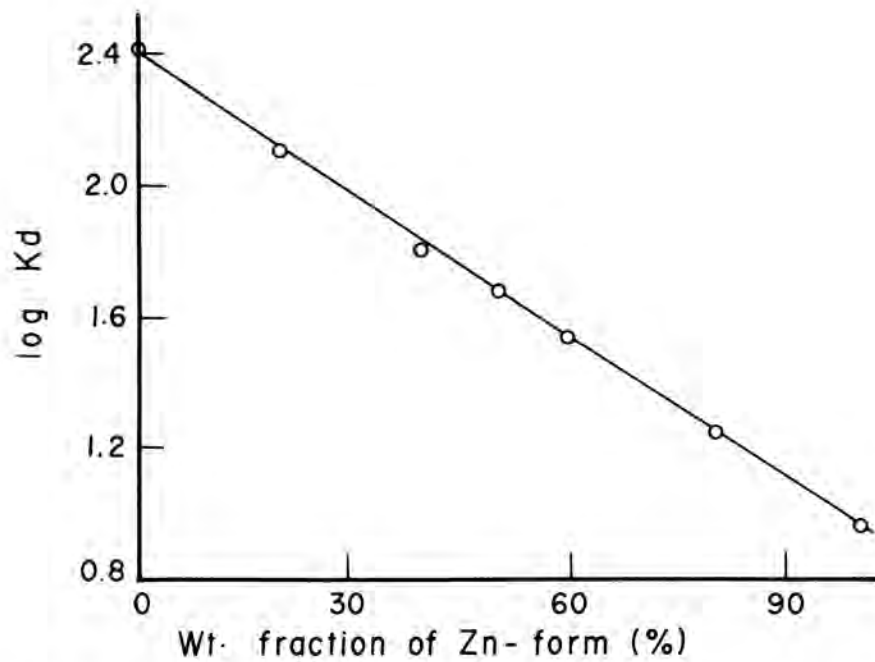


Fig. 2. Exchange Capacities of Mixtures of Zn-Form and Zn Ferrocyanide Form-Zeolite.

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