

NATURAL ZEOLITES AND CLAYS - THE PROMISING MEDIA FOR
SELECTIVE RADIOISOTOPE PARTITION/IMMOBILIZATION

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ABSTRACT

Natural zeolites, a naturally occurring crystalline aluminosilicate material have immense potential for selective radioisotope partition/immobilization. Unlike activated carbons and silica gel, these zeolites have uniform pore sizes (3Å to 10Å) which are uniquely determined by the unit structure of the crystal. These zeolites are available as mined material in various regions of the United States at extremely attractive prices. Clays are another promising material for isotope decontamination/immobilization. Several varieties are available in the different regions of the United States at extremely low prices.

This paper will discuss the application of a few promising natural zeolites (e.g., erionite, chabazite, clinoptilolite, phillipsite, and large port mordenite) for effective partition/immobilization of Cs-137 and Sr-90 isotopes. It will also discuss the application of a few clay materials (e.g., conasauga shale, cattaraugus shale, and nontronite) for the same isotope immobilization.

The paper will also discuss that the adsorption of the isotopes like Cs-137 and Sr-90 on the zeolite/clay surface is generally governed by Freundlich adsorption isotherms $C_R = \alpha C_W^\beta$ where

- C_R = Concentration of the isotope on the adsorbed phase (g/g)
- C_W = Concentration of the isotope in the aqueous phase (g/ml)
- α, β = constants for a particular isotope and adsorption media and generally obtained by the linear regression fit of the log-log plot.

The overall partitioning/immobilization process is a complex physico chemical phenomenon depending upon the equilibrium contact time, zeolite/clay type, sorbent ratio, reversibility/irreversibility of the reaction, concentration of the radionuclides, presence of other competing ions in the transport phase and some physical parameters (e.g., temperature, pressure, etc.).

INTRODUCTION

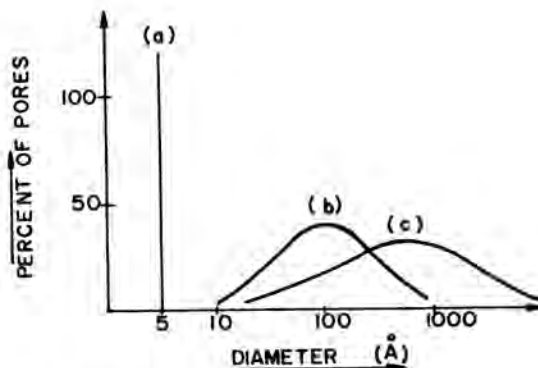
Natural zeolites are naturally occurring crystalline aluminosilicate materials having fairly uniform pore sizes between 3Å and 10Å. The pore sizes are uniquely determined by the unit structure of the crystal. These pore will completely exclude molecules which are large than their diameter. Figure 1 illustrates the distribution of pore sizes between natural zeolites, activated charcoals, and silica gels.

As shown in Fig. 1, the dehydrated zeolite has fairly uniform average pore size of 5Å, whereas a typical silica gel pore size varies from 10Å to 700Å and for activated charcoal the range is even wider (from 20Å to 3000Å).

STRUCTURE AND PROPERTIES OF ZEOLITES

The crystal structure of natural zeolites vary widely from one another. The Secondary Building Unit (SBU), associated with the characteristics of the tetrahedra also varies widely. Erionite has a hexagonal crystal structure and a Single 6 Ring (S6R) SBU. Clinoptilolite has a monoclinic crystal structure and a complex 4-4-1, $T_{10}O_{20}$ SBU. Chabazite has a rhombohedral crystal structure and a Double 6 Ring (D6R) SBU, whereas mordenite has an orthorhombic crystal structure and a complex 5-1, T_8O_{16} SBU. Figure 2 shows the various SBUs in zeolite structures. The positions of the Tetrahedral (T) silicons and aluminiums are shown. The oxygen

atom lie near the connecting solid lines. The 5-1 unit is based on the configuration of five rings found in T_8O_{16} SBU. The 4-4-1 unit is based on the configuration of the tetrahedra found in $T_{10}O_{20}$ SBU.



- (a) DEHYDRATED ZEOLITE.
- (b) TYPICAL SILICA GEL.
- (c) ACTIVATED CHARCOAL.

Fig. 1. Distribution of pore sizes between natural zeolites, activated charcoals, and silica gels.

The location of the hydrated cations (effective exchange sites) of the zeolites also vary widely. For example, the chabazite hydrated cations are located in the cavity, coordinated with $4H_2O$; whereas for erionite, they are located in the ϵ cages (ϵ cages are polyhedra zeolite framework having 11-hedron), and for mordenite, the Na^+ ions are restricted in the channels perpendicular to the axis. The typical oxide formula, the Si/Al ratio and the active sites for the zeolites are as follows:

- i) Chabazite + oxide formula:
 $CaO \cdot Al_2O_3 \cdot 4SiO_2 \cdot 6.5H_2O$
 $Si/Al = 1.6$ to 3
 Active sites $\rightarrow Na^+, K^+$ (little Ca^{++})
- ii) Clinoptilolite + oxide formula:
 $(Na_2, K_2)O \cdot Al_2O_3 \cdot 10 SiO_2 \cdot 8H_2O$
 $Si/Al = 4.25$ to 5.25
 Active sites $\rightarrow Na^+, K^+$ (little Ca^{++} and Mg^{++})
- iii) Erionite + oxide formula:
 $(Ca, Na_2, Mg, K_2)O \cdot Al_2O_3 \cdot 6SiO_2 \cdot 6H_2O$
 $Si/Al = 3$ to 3.5
 Active sites $\rightarrow Na^+, K^+$ (little Ca^{++} and Mg^{++})
- iv) Mordenite + oxide formula:
 $Na_2O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 6H_2O$
 $Si/Al = 4.17$ to 5.10
 Active sites $\rightarrow Na^+$ (little K^+ and Ca^{++})

In general, zeolites with higher Si/Al ratio shows greater resistivity against degradation when exchanged with acidic waste solution.

SELECTIVE APPLICATION FOR SPECIFIC ISOTOPE PARTITION

The zeolites in general show good selective adsorption for Cs and Sr isotopes. Beside Cs and Sr, it is also shown effective for Co and Zr isotopes. Erionite and phillipsite (untreated), in particular, show extremely high selectivity for Cs isotopes. Clinoptilolite (untreated) shows very high affinity for both Cs and Sr isotopes. Chabazite and mordenite (untreated) prefer Cs lot better over Sr isotopes. Vermiculite clay is more effective for Cs but also partitions Sr at the same time. While nontronite clay is equally effective for Cs and Sr isotopes, conasauga shale shows more affinity for Cs over strontium. Table I shows some distribution coefficients (K_d) for the various zeolites and clays. K_d is the ratio of the grams of radionuclide adsorbed per gm of adsorbent to the gms of radionuclide unadsorbed per cc of solution, when equilibrium is reached.

All the above K_d values are functions of pH of the solution, influent radionuclide concentration, temperature, presence of competing ions like Ca^{++} or Mg^{++} or Fe^{++} , etc, sorbent ratio, system pressure, etc.

Table II gives an example of how the partition/distribution coefficient is affected by the presence of competing ions like Ca^{++} . The exchange media used is clinoptilolite and the Ca^{++} concentration is 0.013 mole/lit.

Among all the zeolites mentioned, only phillipsite shows a significant reduction of K_d values (from 11,700 to 240 for Cs and from 460 to 25 for Sr) upon heating to 200°C at 30 MPa pressure.¹ This could be attributed to its open structure which altered to the nonporous analcime which does not easily exchange its cations.

ION EXCHANGER DESIGN

The zeolite ion exchange columns are normally designed with a lower flux rate as compared to organic ion exchange column. The flux rate normally used is 0.5 gpm/ft. This results in a much higher diameter for the exchange bed. Testing is being conducted at Westinghouse R & D Center in Pittsburgh to evaluate the effect of the exchange kinetics and partition factors that will result from using a conventional flux rate, say 4 gpm/ft². The bed length (packing height) for a natural zeolite ion exchange column is around three feet. This is close to the number what is conventionally used for organic ion exchange column.

The conventional organic ion exchangers in industry are normally designed for a fixed bed trickle flow type arrangement. This normally requires a higher bed length and lowers the capacity. A flooded bed zeolite column should be able to increase the capacity and cut down the bed length. It is envisaged that the final loading of Cs and Sr for normal radwaste application will be approximately 10^{-2} mole/litre of zeolite.³ Although this number is based on clinoptilolite, it is also applicable for other natural zeolites. A properly designed selective natural zeolite column should produce a decontamination/partition factor of 10^3 or better for Cs and Sr.

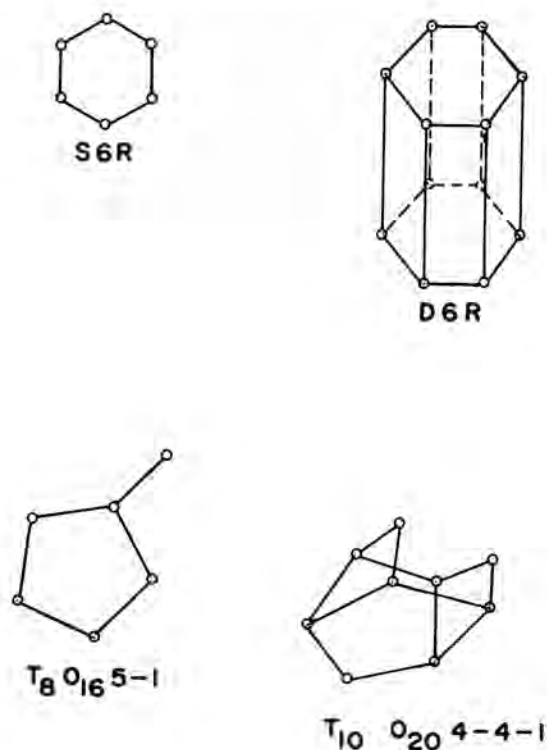


Fig. 2. SBU's in zeolite structures.

TABLE I^{1,2}Distribution coefficients (K_d) for the Various Zeolites and Clays

Zeolite/Clay	K_d for Cs Isotopes (cc/gm)	K_d for Sr Isotopes (cc/gm)
Erionite, CA	9,500	490
Phillipsite, NV	11,700	460
Clinoptilolite, ID	3,900	3,000
Clinoptilolite, CA	5,600	4,700
Chabazite, AZ	6,600	310
Mordenite, NV	6,400	170
Mordenite, AZ	8,300	310
Vermiculite, SC	8,900	2,000
Nontronite	80-225,000	4-225,000
Conasuga Shale	100	57

TABLE II

Partition/distribution coefficient is Affected by the Presence of Competing Ions like Ca^{++}

Liquid	pH	K_d (Cs)	k_d (Sr)
Distilled Water	7.3	$2.6(+0.9) \times 10^5$	$2(+1) \times 10^5$
Saturated $Ca(OH)_2$	12.4	$2.1(+0.6) \times 10^4$	$5(+3) \times 10^4$

MATERIAL AVAILABILITY AND PRICE

The natural zeolites are available in Western and Southwestern United States as mined material. Several mesh sizes are available to suit a particular application. Clays are available all over the country ranging from South Carolina to Tennessee and Southwestern New York to Northwestern Pennsylvania. The price of the natural zeolites range from 3 cents to 25 cents per pound depending on mesh or micron size. For clays, the price should be less than 3 cents per pound.

MECHANISM OF PARTITION/IMMOBILIZATION

The adsorption of radionuclides to the zeolite/clay surface are generally governed by the fundamental adsorption principles. The partitioning of isotopes (e.g., Cs, Sr, and Co) between the solid and carrier phases is shown to be a complex function of equilibrium time, zeolite/clay/argillaceous material type, reaction direction, and radionuclide concentration. For a particular media, the dependence of the media/water partition coefficient on elemental concentration of spike is generally well described for both Cs and Sr by Freundlich adsorption isotherms which, to a lesser extent, also provide a convenient empirical description for the Co isotopes.⁴

In standard nomenclature, the Freundlich isotherm is described by:

$$C_R = \alpha C_W^\beta \quad (1)$$

where

C_R = the concentration of the spike in the adsorbed phase (gm/gm)

C_W = the concentration of the spike in the carrier (aqueous) phase (gm/cc)

α, β = the constants obtained by a linear regression fit of the log-log plot of C_R vs C_W .

Taking logarithm of the both sides of the equation (1), we can write

$$\text{Log } C_R = \text{Log } \alpha + \beta \text{ Log } C_W \quad (2)$$

Equation (2) resembles to $y = mx + c$ form and a plot of $\text{Log } C_R$ vs $\text{Log } C_W$ will give a y axis intercept equal to $\text{Log } \alpha$ at $\text{Log } C_W = 0$ and the gradient of the straight line will equal to β .

McKinley & West⁴ reported that the above isotherm plot for the Cs isotope has an error of <1%. For Sr isotope, the error is -1-2% and for Co isotope it could go as high as -10%. Figures 3, 4, and 5 show the isotherms for Sr, Cs, and Co respectively. The experiment is based on adsorbing the isotopes on a argillaceous material.

Among the above isotherms, Co isotope shows poor linearity. It also shows partial irreversibility of adsorption and especially at concentration for $C_w < 10^{-5}$ gm/cc it indicates an increase in adsorption with increased temperature.

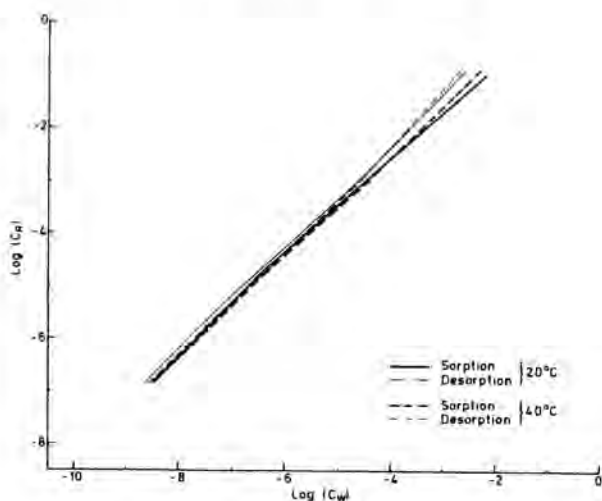


Fig. 3. Freundlich isotherms for Sr.

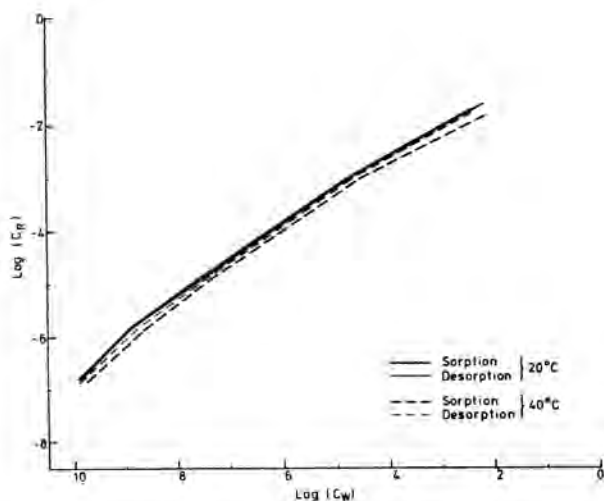


Fig. 4. Freundlich isotherms for Cs.

Several trends have been noted from the above three Figures:

- i) Isotherm linearity shows the general trend of $Sr > Cs > Co$;
- ii) There is a slight trend in the general increase in linearity of desorption isotherms to their adsorption equivalents, for all radionuclides;

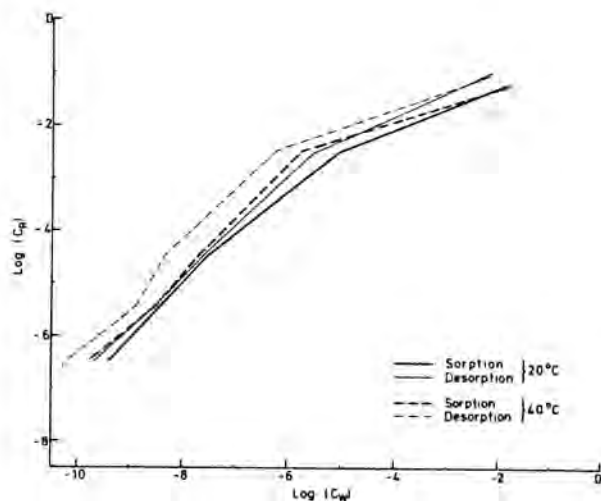


Fig. 5. Freundlich isotherms for Co.

- iii) The gradients for all adsorption-desorption isotherms are less than one, implying a general decrease in adsorption with increased solid phase loading;
- iv) Sr gradients are generally greater than those for Cs and Co, which tend to be similar to each other in both trends and absolute values;
- v) Average Cs isotherm shows a very little change, indicating complete reversibility;
- vi) In general, increase in temperature results in decreasing α, β values for Cs and slightly increasing the α, β values for Co and Sr.

CONCLUSION

The following illustration using a Low-Level Waste Treatment Facility operation at West Valley indicates the cost effectiveness and functional superiority of the natural zeolites over the organic cation exchange resins. The facility uses Duolite CS-100 (Cs^+ specific) organic cation exchange resin and processes -9 million gallons of mildly contaminated water annually (gross beta $< 5 \times 10^{-3} \mu Ci/cc$). The organic ion exchanger has a bed volume of 65 ft³ and requires elution and regeneration after each 800 Bed Volumes (BV). Each elution and regeneration cycle requires approximately \$1,444 worth of nitric acid and caustic soda. The cost of Duolite resin is -\$170/cu ft. Therefore, one BV Duolite resin cost = $65 \times 170 = \$11,050$ and elution/regeneration cost per year is

$$= \frac{9 \times 10^6}{65 \times 800 \times 7.48} \times \$1,444$$

(no. of regeneration cycle) x (cost per cycle)

$$= \$33,412.$$

The 65 ft³ Duolite resin lasts about 45 to 50 elution/regeneration cycle, before it is replaced. Forty-five to fifty regeneration cycle corresponds to approximately two years of operation.

Therefore, overall Duolite resin processing cost for two years.

$$\begin{aligned}
 &= \text{Actual resin cost} + \text{cost of} \\
 &\quad \text{elution/regeneration} \\
 &= \$11,050 + 2 \times 33,412 \\
 &= \underline{\$77,874.00}
 \end{aligned}$$

Now we shall compare this number with the cost figure generated below, if selective natural zeolites are used instead of Duolite resin. Very conservatively, we assume that the zeolite bed (65 ft capacity) has to be replaced (without regeneration) after processing 2,400 BV. This 2,400 BV number is quite conservative, since selective natural zeolites have much higher capacity for specific isotopes and should result in accepting much higher BV thruput before breakthrough. Needless to mention the higher DF of the isotopes across the column. The cost of natural zeolites, including shipping from Western United States, is approximately 8 cents per pound.

Therefore, amount of zeolite required in two years:

$$\begin{aligned}
 &= \frac{9 \times 10^6 \times 2}{2,400 \times 65 \times 7.48} \times 65 \text{ cu ft} \\
 &\quad \text{(no. of changeouts)} \quad \text{(vol. of each changeout)} \\
 &= 1,003 \text{ cu ft}
 \end{aligned}$$

Bulk density of hydrated zeolite is 46 lbs/cu ft.

$$\begin{aligned}
 \therefore \text{Mass of zeolite required in two years} \\
 &= 46 \times 1,003 \text{ lbs.} \\
 &= 46,138 \text{ lbs.}
 \end{aligned}$$

$$\begin{aligned}
 \therefore \text{Cost of zeolite for two years} \\
 &= 46,138 \times \$0.08 \\
 &= \underline{\$3,691.00}
 \end{aligned}$$

Comparing the above cost figure with the overall processing cost of Duolite resin, we see a savings of \$74,183.

This cost calculation does not include the additional waste stream generated during the Duolite elution/regeneration cycle (e.g., ~50,000 gallons of waste is generated for each regeneration cycle). It also does not include the additional drumming cost required for the zeolites, since they will produce more solidified drum than the Duolite resin. It is expected these two costs will balance each other.

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