



#### ACKNOWLEDGMENTS

The author expresses her appreciation to E. J. Nowak (5843) for informative discussions and help in obtaining experimental data pertaining to this study. Thanks also to R. Z. Lawson (5843) and M. K. Gordon (formerly of Sandia National Laboratories) for help with the measurements reported here.

## CONTENTS

	<u>Page</u>
Abstract	1
Acknowledgments	2
Table of Contents	3
Introduction	5
Experimental	
Materials	8
Procedures	10
Results	
Distribution Coefficient Calculations	12
Batch Sorption Results for $^{85}\text{Sr}(\text{II})$	15
Effect of a Support Material on the Sorption of $^{85}\text{Sr}(\text{II})$ on Sodium Titanate	18
Batch Sorption Results for $^{85}\text{Sr}(\text{II})$ on Sodium Titanate at Different Total Strontium Concentrations	20
Effect of Contact Time on the Batch Sorption of $^{85}\text{Sr}(\text{II})$	20
Batch Sorption of $^{85}\text{Sr}(\text{II})$ at Different Competing Ion Concentrations	21
Batch Sorption Results for $^{137}\text{Cs}(\text{I})$	23
A Comparison of the Sorption of $^{137}\text{Cs}(\text{I})$ on Synthetic Zeolites	27
Batch Sorption Results for $^{137}\text{Cs}(\text{I})$ at Different Total Cesium Concentrations	29
Effect of Contact Time on the Batch Sorption of $^{137}\text{Cs}(\text{I})$	31
Batch Sorption of $^{137}\text{Cs}(\text{I})$ at Different Competing Ion Concentrations	32
Evaluation of Sorption Results	32
Thermal Stability	36
Conclusions	36
References	38
Appendix A: Sources, Analytical Results, and References for Solid Sorbents	42
Appendix B: Detailed Compositions of Brines A and B	49

TABLES

<u>Table</u>		<u>Page</u>
1	Representative Brine Compositions Major Constituents, Molarity	10
2	Batch Sorption Results for $^{85}\text{Sr}$ in Brine A at Room Temperature	16
3	Batch Sorption Results for $^{85}\text{Sr}$ in Brine B at Room Temperature	17
4	Effect of a Support Material on the Sorption of $^{85}\text{Sr}$ on Sodium Titanate at Room Temperature	19
5	Batch Sorption Results for $^{85}\text{Sr}$ on Sodium Titanate at Different Total Strontium Concentrations	20
6	Effect of Contact Time on the Batch Sorption of $^{85}\text{Sr}$ at Room Temperature	21
7	Batch Sorption of $^{85}\text{Sr}$ at Different Competing Ion Concentrations	22
8	Batch Sorption Results for $^{137}\text{Cs}$ in Brine A at Room Temperature	24
9	Batch Sorption Results for $^{137}\text{Cs}$ in Brine B at Room Temperature	26
10	Batch Sorption Results for $^{137}\text{Cs}$ on Synthetic Zeolites in Brine B at Room Temperature	28
11	Batch Sorption Results for $^{137}\text{Cs}$ at Different Total Cesium Concentrations	30
12	Effect of Contact Time on the Batch Sorption of $^{137}\text{Cs}$ at Room Temperature	31
13	Batch Sorption of $^{137}\text{Cs}$ at Different Competing Ion Concentrations	33

THE SORPTION OF CESIUM AND STRONTIUM FROM  
CONCENTRATED BRINES BY BACKFILL BARRIER MATERIALS

Introduction

Backfill barrier materials are being examined as possible components in a multi-barrier system for radioactive waste isolation (Combs et al, 1980; KBS, 1980; Nowak, 1980c; ONWI, 1980). A backfill can serve as a potential hydrologic and physicochemical barrier to intruding groundwater or brine, inhibiting fluid movement and, through its buffering capacity, minimizing the corrosiveness and leaching effectiveness of the fluid. A short history and description of the backfill barrier and its functions has been previously presented (Nowak, 1980a).

Should any radioactive species be released from the wasteform and its containers (e.g., canister and overpack), either by intruding groundwater or liquid originating in the waste, the backfill can serve as a barrier that retards the migration of radionuclides. Through the use of getters which sorb radionuclides, the backfill can delay the transport of radioactive species into the surrounding geologic medium.

The smectite swelling clays bentonite (containing montmorillonite) and hectorite are firmly established as primary backfill barrier material candidates by virtue of their desirable physical properties (Pusch, 1977;

Nowak, 1980b; Nowak, 1980c). Further, it has been demonstrated that these clays are effective getters for transuranics in the concentrated brine solutions which might intrude in a bedded salt repository (Nowak, 1980c). However, neither bentonite nor hectorite is an effective getter for the fission products, cesium and strontium, in concentrated brines (Nowak, 1980c). In order for a backfill primarily composed of bentonite or hectorite to be effective in retarding the migration of Cs or Sr, it will be necessary to also incorporate getter materials which can effectively sorb these radionuclides.

The literature contains many references to work concerning the retention of Cs and Sr on geologic media in groundwater (e.g., Robinson, 1962; Erdal et al, 1977; Hinkebein and Hlava, 1977; Barney and Anderson, 1978; Erdal et al, 1978; Gillham, 1978). The effect of liquid phase composition on the sorption of Cs and Sr on geologic media has also been examined (Dosch and Lynch, 1978; Meyer et al, 1978; Allard et al, 1979; Beall et al, 1979; Relyea and Serne, 1979; Shiao et al, 1979; Erdal et al, 1980). In all cases, sorption decreased as the total salt concentration of the liquid phase increased. Erdal et al (1980) state that this reduction in sorption is "undoubtedly due to the effect of the increased amount of competing ions," thus lending support to an ion exchange mechanism. Based on his own work and a review of the earlier literature pertinent to radioactive waste management, Tamura (1972) suggests the use of illite for selectively sorbing radiocesium from high-sodium, aluminum or calcium solutions. His research also indicates that alumina and related hydrous oxides selectively sorb radiostrontium in alkaline sodium systems. These latter materials, however,

are of little practical importance as backfill materials due to possible structural instability.

Various inorganic ion exchangers have been studied for the sorption of alkali and alkaline earth metals (Akatsu et al, 1965; Vol'Khin et al, 1975; Dosch, 1978; Krylov and Larina, 1978a; Krylov and Larina, 1978b; Abe, 1979; Abe and Uno, 1979; Clearfield and Garces, 1979). Sodium titanate has already been shown to be extremely effective in sorbing strontium from a dissolved salt cake simulant (Dosch, 1978). While zirconium phosphate has been demonstrated to have a strong affinity for cesium (Akatsu et al, 1965), no reports of studies on the sorption of cesium from concentrated brines were found.

The ability of zeolitic minerals to sorb Cs and Sr has also been examined (Ames, 1961; Mercer and Ames, 1963; Neretnieks, 1977; Gradev et al, 1978). As before, sorption of Cs and Sr was lower for the groundwaters with a greater total salt concentration (Neretnieks, 1977). Neretnieks recommends further study of clinoptilolite if zeolites are chosen to be used as backfill materials. Gradev et al (1978) found that a "good selectivity of calcium clinoptilolite in relation to cesium and strontium is displayed in the presence of sodium," however, "at low concentrations of cesium the calcium clinoptilolite is selective for potassium."

The literature cited above was used to guide the selection of materials to be further examined as suitable getters for Cs and Sr in a backfill barrier. Due to the variation of sorbent effectiveness with liquid phase

composition it was necessary that studies using site-specific brines be done as part of this examination.

The purpose of this report is to present the sorption properties of potential sorbents for use in the Waste Isolation Pilot Plant (WIPP), a proposed geologic radioactive waste repository in bedded salt. WIPP brines A and B, brine simulants specific to the WIPP site, were used as solution phases in this work. Sorption properties are quantified through the use of empirical distribution coefficients,  $K_d$ 's. This report contains the results of screening sorption studies and initial mechanistic and kinetic studies. Using a linear sorption model for migration and low backfill permeability, calculated estimates of breakthrough times for a 3 foot backfill barrier containing getters for cesium and strontium are used to evaluate the sorption results.

## Experimental

### Materials

A variety of solid sorbents was examined, including clays, zeolites, and sodium titanate. Attapulgite and illite were obtained from the Source Clay Minerals Repository (van Olphen and Fripiat, 1975). The attapulgite was used as received. The illite was ground with ceramic surfaces and the -60 sieve fraction (material passing through U.S.A. Standard Testing Sieve No. 60) was selected for sorption measurements. Anhydrite was obtained from a geologic formation in southeastern New Mexico. It was prepared for use in



the same manner as the illite, Eleana shale was obtained from a geologic formation in the Calico Hills region of the Nevada Test Site. It was pulverized until 95 percent was -170 mesh and the remaining 5 percent was -66 mesh. Samples of commercially available bentonite, clinoptilolite, a mordenite-type zeolite, chabazite/erionite, vermiculite, and synthetic zeolites (4A, 5A, 13X) were obtained from commercial suppliers. They were used as received. Synthetic zeolites AW300 and AW500 were obtained from commercial suppliers. They were also ground with ceramic surfaces and the -100 sieve fractions were selected for the sorption measurements. The sodium titanate and titanate-loaded zeolite were prepared by R. G. Bosch, Sandia National Laboratories, Albuquerque, NM. Sources, analytical results, and references for these solid materials are given in Appendix A.

Radiotracers were obtained in aqueous stock solution as  $^{137}\text{Cs}(\text{I})$  in 1 M HCl and  $^{85}\text{Sr}(\text{II})$  in 0.5 M  $\text{HNO}_3$  or 0.5 M HCl. Aliquots of the diluted stock solutions were evaporated to dryness and the remaining solid residue dissolved in brine at a pH value approximately equal to the desired sample pH. These radiotracer-containing brine solutions were used for spiking the batch sorption samples.

Synthesized WIPP brines A and B were used as solution phases in the initial screening sorption studies. Brine A is representative of ground-water in contact with the potash-containing layers overlying the vicinity of the proposed WIPP site, while brine B represents water in contact with the halite of the proposed waste horizon. The major constituents of these brines are denoted in Table 1. Detailed compositions are given in Appendix B.

TABLE 1  
 Representative Brine Compositions  
 Major Constituents, Molarity

	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>++</sup>	Ca <sup>++</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>--</sup>	HCO <sub>3</sub> <sup>-</sup>	BO <sub>3</sub> <sup>---</sup>
Brine A	1.8	0.8	1.4	0.02	5.4	0.04	0.01	0.02
Brine B	5.0	---	---	0.03	5.0	0.04	----	----

Two other solution phases were incorporated into this work for purposes of mechanistic studies. In order to determine the effect of the competing ion concentration on  $K_d$ , a 1:99 dilution of brine A (i.e., a 1% brine A solution) was prepared with deionized water and was used as the liquid phase in several sorption measurements. A second, variant brine A was prepared in which Cs(I), Sr(II) and several other minor constituents were omitted (see Appendix B). This brine was used in sorption measurements in an effort to determine what effect, if any, a change in Cs(I) or Sr(II) concentration would have on  $K_d$ .

#### Procedures

The following procedure was used for all batch sorption measurements. Initially, 10 ml of brine were agitated with the solid sorbent for at least 24 hours. In most cases the quantity of solid material in each sample was

0.5 g. Exceptions to this amount have been noted in the data tables. Following this initial contacting step, the pH of the solid-brine slurry was adjusted to a prechosen pH value by additions of aqueous HCl or NaOH. The pH values of 6.5 (for samples containing brine A or 1% brine A) and 7.5 (for those solids in brine B) were chosen on the basis of work which determined these to be the approximate resulting pHs when these brines are contacted with bentonite or hectorite (memo to M. A. Molecke, 4512, by C. D. Winslow, 5812, dated February 19, 1980). Ten ml of brine containing radiotracer, also adjusted to the prechosen pH value, were then added to the slurry for a final, total liquid volume of 20 ml.

Batch contacting was done at room temperature (22-24°C) and with agitation. For most samples, contact times were 1 week. Several duplicate samples were contacted for a 2 week period to determine if the batch composition had reached constant values during the first week.

The pH of the slurry was measured, but not adjusted, following the contacting period. A portion of the slurry was centrifuged at 12,000 G for 10 minutes. The supernatant brine was then filtered through 0.8  $\mu$  pore size Micropore filters. A 5 ml aliquot of filtered supernatant was analyzed with a gamma spectrometric counter containing a sodium iodide well-type detector. Reference counting standards of known concentration were counted with the samples.

Blanks (solids-free samples) and, when necessary, control samples (containing bentonite) were prepared and carried through all steps, with the exception of centrifugation for the blanks. The controls and blanks were included in order to correct the results for losses of radionuclide from solution not attributable to the presence of the sorber under study. All samples were prepared and run in duplicate.

## Results

### Distribution Coefficient Calculations

The distribution coefficient,  $K_d$ , is defined as the ratio of the quantity of sorbed species per unit mass of solid-phase sorbent,  $C_s$ , to the concentration per unit volume of that species in the liquid phase,  $C_l$ .

A  $K_d$  is not a basic chemical property of the system. It is an empirical ratio of solid phase to liquid phase concentrations under the conditions of measurement. It can be a function of the concentrations of all species in solution, including solution pH and Eh. The sorption isotherm is linear when the ratio of the equilibrium concentrations in the two phases is independent of concentration. Algebraically, this linear sorption isotherm relationship can be expressed as follows:

$$K_d = \frac{C_s}{C_l} \quad (1)$$

The linear sorption isotherm has been chosen as the model for the results in this report. This may not necessarily be the case and one must be careful about generalizing batch sorption  $K_d$  results to conditions other than those under which the results were obtained. However, such results are useful in roughly evaluating potential getters for use in a backfill barrier.

For most samples in this study,  $K_d$  values (in units of ml/g) were calculated by using the following equation:

$$K_d = \frac{V}{W} \frac{(R_f - R_s)}{(R_s - R_b)} \quad (2)$$

where:

$V$  = total liquid volume (ml) in contact with solid sorbent

$W$  = mass (g) of solid sorbent in sample

$R_f$  = average count rate per unit volume of feed brine

$R_s$  = average count rate per unit volume of filtered sample  
supernatant brine

$R_b$  = average background count rate normalized to a unit volume of  
counted brine

In all instances,  $R_f$  was taken to be equal to the average count rate for the blank samples of tracer-containing brine which contained no solids but had the same history as corresponding solids-containing samples.

For those samples which contained bentonite as well as the solid whose sorption properties were to be examined, the  $K_d$  (corrected for the sorption contribution of bentonite) for the solid sorbent of interest was calculated using the following expression:

$$K_d = \frac{V}{W} \left[ \frac{(R_f - R_s)}{(R_s - R_b)} - \frac{(R_f - R_{sb})}{(R_{sb} - R_b)} \right] \quad (3)$$

where:

$V, R_f, R_s, R_b$  = as in previous expression

$W$  = mass (g) of the solid sorbent of interest (i.e.,  
mass of mixture minus mass of bentonite)

$R_{sb}$  = average count rate per unit volume of filtered  
supernatant brine for samples containing only  
bentonite

Repeatability of results was within a factor of 2 for duplicate samples and, therefore, precision within a factor of 2 was judged to be acceptable.

### Batch Sorption Results for $^{85}\text{Sr(II)}$

Batch sorption results for  $^{85}\text{Sr(II)}$  in brine A and brine B are given in Tables 2 and 3, respectively. For the majority of sorbents examined, the values of  $K_d$  range from 0-100 ml/g. These results are consistent with the high total salt concentration of these brines.

Of the materials examined, sodium titanate is the sorbent with the highest  $K_d$  in both brine A ( $K_d = \sim 125$  ml/g) and brine B ( $K_d = 500-600$  ml/g). These  $K_d$  values are still considerably lower than  $\sim 10^4$  ml/g which was reported by Dosch (1978) for the sorption of strontium by sodium titanate in a salt cake simulant doped with cation impurities. While the salt cake simulant is high in sodium concentration ( $> 6 \text{ M Na (I)}$ ), other cations which could effectively compete with Sr(II) and reduce Sr(II)

TABLE 2

Batch Sorption Results for  $^{85}\text{Sr}$  in Brine A  
at Room Temperature

---

Initial Tracer Concentration,  $C_0 = \sim 5 \times 10^{-11} \text{ M}$   
 Total Strontium Concentration =  $\sim 6 \times 10^{-5} \text{ M}$   
 Batch Contact Time = 1 Week

---

Sorbent	Sample Number	pH	$K_d$ , ml/g	Final Liquid Molar Concentration of Tracer
Anhydrite	1	6.4	0	$4.7 \times 10^{-11}$
	2	6.6	0.8	$4.6 \times 10^{-11}$
Chabazite/Erionite	1	6.6	0.6	$4.6 \times 10^{-11}$
	2	6.6	0.5	$4.7 \times 10^{-11}$
Clinoptilolite	1	6.5	2.5	$4.4 \times 10^{-11}$
	2	6.6	2.1	$4.5 \times 10^{-11}$
Eleana Shale	1	6.7	0.5	$4.6 \times 10^{-11}$
	2	6.7	0	$4.7 \times 10^{-11}$
Illite	1	6.7	0.2	$4.7 \times 10^{-11}$
	2	6.7	0.3	$4.7 \times 10^{-11}$
*Sodium Titanate	1	6.7	130	$1.4 \times 10^{-11}$
	2	6.7	120	$1.5 \times 10^{-11}$
Sodium Titanate-loaded Zeolite	1	6.6	3.4	$4.3 \times 10^{-11}$
	2	6.7	3.2	$4.4 \times 10^{-11}$
Zeolite (4A)	1	6.6	8.4	$3.9 \times 10^{-11}$
	2	6.6	6.5	$4.0 \times 10^{-11}$
Zeolite (13x)	1	6.6	19	$3.2 \times 10^{-11}$
	2	6.6	20	$3.1 \times 10^{-11}$

\* $C_0 = \sim 6 \times 10^{-11} \text{ M}$



TABLE 3

Batch Sorption Results for  $^{85}\text{Sr}$  in Brine B  
at Room Temperature

---

Initial Tracer Concentration,  $C_0 = \sim 5 \times 10^{-11} \text{ M}$   
 Total Strontium Concentration =  $\sim 2 \times 10^{-4} \text{ M}$   
 Batch Contact Time = 1 Week

---

Sorbent	Sample Number	pH	$K_d$ , ml/g	Final Liquid Molar Concentration of Tracer
Chabazite/Erionite	1	7.3	1.6	$4.7 \times 10^{-11}$
	2	7.3	0.9	$4.7 \times 10^{-11}$
*Sodium Titanate	1	7.2	490	$4.6 \times 10^{-11}$
	2	7.5	590	$3.9 \times 10^{-11}$
Sodium Titanate-loaded Zeolite	1	7.6	14	$3.6 \times 10^{-11}$
	2	7.7	15	$3.5 \times 10^{-11}$
Zeolite (4A)	1	8.5	79	$1.6 \times 10^{-11}$
	2	8.2	73	$1.7 \times 10^{-11}$
Zeolite (13x)	1	7.6	23	$3.1 \times 10^{-11}$
	2	7.5	25	$3.0 \times 10^{-11}$

\* $C_0 = \sim 6 \times 10^{-11} \text{ M}$

sorption (such as Ca(II) and Mg(II)), are present only as trace impurities (<10 ppm). In WIPP brine A, however, the concentrations of Mg(II) and Ca(II) are 1.4 M and 0.02 M, respectively. In brine B, the concentration of Ca(II) is 0.03 M. The difference, then, in composition between the salt cake simulant doped with cation impurities and the WIPP brines is the likely explanation for the discrepancy in  $K_d$ 's. No systematic study to identify the most significant competing cations was done.

While Gradev et al (1978) found clinoptilolite to be selective for strontium in the presence of sodium, their work did not examine the sorption of Sr(II) in the presence of other competing ions. The results reported here show clinoptilolite to be a poor sorbent for strontium in brine A ( $K_d = \sim 2.5$  ml/g).

Since sodium titanate is the most effective getter, of the materials examined for  $^{85}\text{Sr(II)}$  in WIPP brines, any further study on strontium sorption should include other inorganic ion exchangers (such as zirconium phosphate).

#### Effect of a Support Material on the Sorption of $^{85}\text{Sr(II)}$ on Sodium Titanate

The sorption of  $^{85}\text{Sr(II)}$  on two different forms of sodium titanate was studied. The sodium titanate was utilized both as a pure powder and loaded onto a zeolite support material. The  $K_d$  values obtained are reported in Table 4.

The titanate content of the zeolite was found by Dosch (private communication) to be 11.1 percent. In Table 4, the  $K_d$  values for the

TABLE 4

Effect of a Support Material on the Sorption  
of  $^{85}\text{Sr}$  on Sodium Titanate at Room Temperature

Sodium Titanate			Sodium Titanate-loaded zeolite	
Brine	pH	$K_d$ , ml/g	pH	* $K_d$ , ml/g
A	6.7	130	6.6	31
A	6.7	120	6.7	29
B	7.2	490	7.6	130
B	7.5	590	7.7	140

\* $K_d$  based on weight of the sodium titanate only (~0.056 g/sample)

titanate-loaded zeolite are based on the weight of the sodium titanate only (~0.056 g per sample). In both brines A and B, the  $K_d$  for  $^{85}\text{Sr}(\text{II})$  on the titanate-loaded zeolite is approximately 4 times smaller than that for the powder. Apparently, the presence of the zeolite support material hinders the sorption of  $^{85}\text{Sr}(\text{II})$  on sodium titanate. One possible explanation for this might be the physical blocking of sorption sites by competing cations within the pores of the zeolite.

For purposes of incorporation in a backfill barrier, a support material would not be necessary and the sodium titanate would best be utilized as a powder.

Batch Sorption Results for  $^{85}\text{Sr}(\text{II})$  on Sodium Titanate at Different Total Strontium Concentrations

Table 5 contains  $K_d$  values representing the sorption of  $^{85}\text{Sr}(\text{II})$  on sodium titanate powder at total strontium concentrations of  $6 \times 10^{-11} \text{ M}$  (variant brine A) and  $6 \times 10^{-5} \text{ M}$  (brine A). The  $K_d$  is virtually the same at these different concentrations, being equal to  $\sim 130 \text{ ml/g}$  in both cases. A constant  $K_d$  is consistent with a linear sorption isotherm model for this concentration range; however, data at intermediate concentrations would be needed to confirm linearity.

Effect of Contact Time on the Batch Sorption of  $^{85}\text{Sr}(\text{II})$

Duplicate sets of chabazite/erionite and zeolite (4A) samples were contacted with radiostrontium-containing brines for one and two-week periods of time. The  $K_d$  results are presented in Table 6. There is no

TABLE 5  
Batch Sorption Results for  $^{85}\text{Sr}$  on Sodium Titanate  
at Different Total Strontium Concentrations

---

Initial Tracer Concentration,  $C_0 = \sim 6 \times 10^{-11} \text{ M}$   
Batch Contact Time = 1 Week  
Room Temperature  
pH = 6.7

---

		$K_d$ , ml/g	
Sorbent	Sample Number	Total Strontium Concentration = $6 \times 10^{-11} \text{ M}$ (variant brine A)	Total Strontium Concentration = $6 \times 10^{-5} \text{ M}$ (brine A)
Sodium Titanate	1	130	130
	2	120	130

---

TABLE 6

Effect of Contact Time on the Batch Sorption of  $^{85}\text{Sr}$   
at Room Temperature

Initial Tracer Concentration, $C_0 = \sim 5 \times 10^{-11} \text{ M}$ Total Strontium Concentration = $\sim 6 \times 10^{-5} \text{ M}$ in Brine A = $\sim 2 \times 10^{-4} \text{ M}$ in Brine B						
			One Week Contact Time		Two Week Contact Time	
Sorbent	Brine	Sample Number	$K_d$ , ml/g	pH	$K_d$ , ml/g	pH
Chabazite/ Erionite	A	1	0.6	6.6	0.2	6.7
		2	0.5	6.6	0.8	6.9
Zeolite (4A)	A	1	8.4	6.6	8.2	6.8
		2	6.5	6.6	7.0	6.9
Chabazite/ Erionite	B	1	1.6	7.3	1.4	7.4
		2	0.9	7.3	1.2	7.4
Zeolite (4A)	B	1	79	8.5	81	8.0
		2	73	8.2	86	8.4

significant difference in  $K_d$  between one and two weeks of contact time.

These data show that the batch composition reached constant values during the first week.

#### Batch Sorption of $^{85}\text{Sr}$ (II) at Different Competing Ion Concentrations

In Table 7,  $K_d$ 's for the sorption of  $^{85}\text{Sr}$ (II) on different sorbents in brine A, brine B, and 1% brine A are presented. In agreement with the literature (Gradev et al, 1980; Neretnieks, 1977), sorption of  $^{85}\text{Sr}$ (II) was greater in those solutions of lower total ionic strength.

TABLE 7

Batch Sorption of  $^{85}\text{Sr}$  at Different Competing Ion Concentrations

Initial Tracer Concentration,  $C_0 = \sim 5 \times 10^{-11} \text{ M}$  (except as noted)  
 Total Strontium Concentration =  $\sim 6 \times 10^{-5} \text{ M}$  in Brine A  
                                       =  $\sim 2 \times 10^{-4} \text{ M}$  in Brine B  
                                       =  $\sim 6 \times 10^{-7} \text{ M}$  in 1% Brine A  
 Batch Contact Time = 1 Week at Room Temperature

Sorbent	Sample Number	1% Brine A		Brine A		Brine B	
		$K_d$ , ml/g	pH	$K_d$ , ml/g	pH	$K_d$ , ml/g	pH
Chabazite/ Erionite	1	-----		0.6	6.6	1.6	7.3
	2	-----		0.5	6.6	0.9	7.3
Sodium Titanate	1	*65,000	7.3	*130	6.7	*490	7.2
	2	*120,000	7.2	*120	6.7	*590	7.5
Sodium Titanate- loaded zeolite	1	*3,400	7.7	3.4	6.6	14	7.6
	2	*3,500	7.8	3.2	6.7	15	7.7
Zeolite (4A)	1	*25,000	7.0	8.4	6.6	79	8.5
	2	*23,000	7.0	6.5	6.6	73	8.2
Zeolite (13X)	1	*14,000	6.6	19	6.6	23	7.4
	2	*13,000	6.6	20	6.6	25	7.5

$$^*C_0 = \sim 6 \times 10^{-11} \text{ M}$$

Comparing sorption in brine A with that in 1% brine A (a two-orders-of-magnitude change in the competing ion concentration),  $K_d$ 's are approximately three-orders-of-magnitude greater in 1% brine A. These results are consistent with a competing ion effect and, thus, an ion exchange mechanism. However, it is impossible with these data alone to determine if ion exchange is the only sorption mechanism operative.

Sodium titanate has a  $K_d$  on the order of  $10^5$  ml/g in the 1 $\mu$  brine A, a result which is in close agreement with the value of  $1.2 \times 10^5$  ml/g (weight of sodium titanate = 0.5 g, volume = 25 ml; contact time = 144 hours) reported by Dosch (1978) for the sorption of strontium by sodium titanate in cation-doped salt cake simulant.

Comparisons of  $K_d$ 's obtained in brine A and brine B are more complicated. While the concentration of Na(I) and Ca(II) is greater in brine B, the K(I) and Mg(II) present in brine A is absent in brine B. Changes in  $K_d$  in going from brine A to B vary from virtually no change at all (chabazite/erionite and zeolite (13X)) to an increase of nearly 10 (zeolite (4A)). These variances may arise from differences in cation selectivity among the sorbents examined.

#### Batch Sorption Results for $^{137}\text{Cs(I)}$

Batch sorption results for  $^{137}\text{Cs(I)}$  in brine A and brine B are given in Tables 8 and 9, respectively. As was the case with  $^{85}\text{Sr(II)}$ ,  $K_d$ 's are low to moderate (1-100 ml/g) for the majority of sorbents examined, as might be anticipated by the high salt concentrations of the brines.

Of the materials examined, the mordenite-type zeolite is the sorbent with the highest  $K_d$  in brine A ( $K_d = 27$  ml/g), while illite has the highest  $K_d$  in brine B ( $K_d = \sim 115$  ml/g). The use of illite for sorbing radiocesium from solutions of high sodium concentration (concentration of sodium in brine B is 5 M) agrees with the previously mentioned findings of Tamura (1972).

TABLE 8

Batch Sorption Results for  $^{137}\text{Cs}$  in Brine A  
at Room Temperature

Initial Tracer Concentration,  $C_0 = \sim 9 \times 10^{-9} \text{ M}$   
 Total Cesium Concentration =  $\sim 1 \times 10^{-5} \text{ M}$   
 Batch Contact Time = 1 Week

Sorbent	Sample Number	pH	* $K_d$ , ml/g, Based on Mass of Bentonite-free Sorbent for All Mixtures	Final Liquid Molar Concentration of Tracer
Attapulgit	1	6.6	3.2	$7.9 \times 10^{-9}$
	2	6.7	3.0	$8.0 \times 10^{-9}$
Bentonite	1	6.6	7.1	$4.8 \times 10^{-9}$
	2	6.7	7.2	$4.0 \times 10^{-9}$
Chabazite/ Erionite	1	6.6	18	$5.9 \times 10^{-9}$
	2	6.6	19	$5.9 \times 10^{-9}$
20 wt. % Clinoptilolite 80 wt. % Bent- onite	1	6.5	9.9	$4.2 \times 10^{-9}$
	2	6.5	11	$4.1 \times 10^{-9}$
20 wt. % Eleana Shale 80 wt. % Bent- onite	1	6.6	2.7	$4.6 \times 10^{-9}$
	2	6.6	4.1	$4.5 \times 10^{-9}$
Illite	1	6.6	6.1	$7.5 \times 10^{-9}$
	2	6.7	7.0	$7.4 \times 10^{-9}$
Mordenite (zeolite)	1	6.7	27	$5.1 \times 10^{-9}$
	2	6.7	27	$5.1 \times 10^{-9}$
Sodium Titanate	1	6.7	2.5	$8.1 \times 10^{-9}$
	2	6.7	2.6	$8.1 \times 10^{-9}$
Sodium Titanate loaded zeolite	1	6.6	26	$5.2 \times 10^{-9}$
	2	6.7	26	$5.2 \times 10^{-9}$
Vermiculite	1	6.4	13	$6.3 \times 10^{-9}$
	2	6.4	15	$5.9 \times 10^{-9}$
Zeolite (AN500)	1	6.7	23	$5.4 \times 10^{-9}$
	2	6.7	23	$5.4 \times 10^{-9}$



TABLE 8--Continued

Sorbent	Sample Number	pH	*K <sub>d</sub> , ml/g, Based on Mass of Bentonite-free Sorbent for All Mixtures	Final Liquid Molar Concentration of Tracer
Zeolite (4A)	1	6.7	3.9	7.9 x 10 <sup>-9</sup>
	2	6.7	4.2	7.8 x 10 <sup>-9</sup>
Zeolite (13X)	1	6.6	1.3	8.4 x 10 <sup>-9</sup>
	2	6.6	1.2	8.4 x 10 <sup>-9</sup>

<sup>1</sup>Mass of Bentonite = 2.0 g

<sup>2</sup>Total Mass of Solids = 2.5 g

\*For all mixtures, the K<sub>d</sub> is corrected for the contribution to cesium sorption by the bentonite, using a K<sub>d</sub> for bentonite of 7.1 ml/g.

The low K<sub>d</sub> of approximately 2.5 ml/g for sodium titanate is in agreement with the findings of Dasch (1978), who concluded that a high sodium concentration precluded the use of sodium titanate for cesium removal. While Nowak (1980c) reports a K<sub>d</sub> of approximately 3.0-5.0 ml/g for the sorption of <sup>137</sup>Cs(I) on bentonite in WIPP brines, a slightly higher K<sub>d</sub> of 7.1 ml/g was observed in this work.

The final pH values for those sorbents in brine A are close to the prechosen pH of 6.5. However for samples consisting of sorbents in brine B, the final pH values range from 5.6 to 8.4 (prechosen pH was 7.5). This variability in pH for sorbents in brine B as opposed to the relative pH stability in brine A probably arises from a difference in buffering capacity of the two solutions. This buffering action in brine A can be attributed to that brine's higher bicarbonate concentration.

TABLE 9

Batch Sorption Results for  $^{137}\text{Cs}$  in Brine B  
at Room Temperature

Initial Tracer Concentration,  $C_0 = \sim 9 \times 10^{-9} \text{ M}$   
 Total Cesium Concentration  $= \sim 1 \times 10^{-5} \text{ M}$   
 Batch Contact Time = 1 Week

Sorbent	Sample Number	pH	$K_d$ , ml/g	Final Liquid Molar Concentration of Tracer
Attapulgitite	1	6.4	8.7	$6.9 \times 10^{-9}$
	2	6.5	12	$6.6 \times 10^{-9}$
Chabazite/ Ericomite	1	6.0	57	$3.5 \times 10^{-9}$
	2	6.1	56	$3.5 \times 10^{-9}$
Illite	1	5.6	112	$2.2 \times 10^{-9}$
	2	5.7	118	$2.1 \times 10^{-9}$
Mordenite (Zeolite)	1	6.6	74	$3.0 \times 10^{-9}$
	2	6.6	74	$3.0 \times 10^{-9}$
Sodium Titanate	1	6.9	2.0	$8.1 \times 10^{-9}$
	2	6.9	4.0	$7.7 \times 10^{-9}$
Sodium Titanate- loaded Zeolite	1	5.9	62	$3.3 \times 10^{-9}$
	2	6.1	72	$3.0 \times 10^{-9}$
Vermiculite	1	7.5	9.3	$7.1 \times 10^{-9}$
	2	7.4	9.5	$7.1 \times 10^{-9}$
Zeolite (AW300)	1	7.4	61	$3.5 \times 10^{-9}$
	2	7.5	58	$3.6 \times 10^{-9}$
Zeolite (AW500)	1	6.7	89	$2.6 \times 10^{-9}$
	2	6.7	98	$2.5 \times 10^{-9}$
Zeolite (4A)	1	8.4	2.3	$7.9 \times 10^{-9}$
	2	8.4	1.7	$8.1 \times 10^{-9}$
Zeolite (5A)	1	7.7	4.8	$7.8 \times 10^{-9}$
	2	7.6	5.2	$7.9 \times 10^{-9}$
Zeolite (13X)	1	6.3	2.7	$7.9 \times 10^{-9}$
	2	6.4	3.4	$7.7 \times 10^{-9}$

### A Comparison of the Sorption of $^{137}\text{Cs(I)}$ on Synthetic Zeolites

Table 10 presents the  $K_d$  values obtained for the sorption of  $^{137}\text{Cs(I)}$  on several synthetic zeolites in brine B, along with some of the published zeolitic properties. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and the nominal pore diameter are only two of several possible contributing factors to the sorption behavior of a zeolite. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio determines the anionic field strength of the exchanger (i.e., the smaller the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, the greater the number of  $\text{AlO}_4^-$  tetrahedra per unit volume and the greater the anionic field strength). Nominal pore diameter size influences the accessibility of ions to the exchange sites within the pores of the zeolites.

The relationships between getter sorption behavior and the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and pore diameter are not simple. These two factors are, themselves, interrelated. The nominal pore diameter is determined by the zeolite structure which, in turn, is determined by the number and type of tetrahedra and the way in which the tetrahedra link in space. The effects of the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio or pore diameter size cannot be isolated from one another, nor can they be isolated from other, unknown contributing factors. However, any trends that can be discerned may be useful in selecting additional zeolites to examine for the sorption of  $^{137}\text{Cs(I)}$ . For example, it would be expected that cesium, with a cation diameter of 3.38 Å, would not readily diffuse into a zeolite with a nominal pore diameter  $\sim 3$  Å. Also, data in Table 10 indicate that zeolites with a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio less than 3 are not effective for sorption of cesium ( $K_d$ 's are less than 6 ml/g).

TABLE 10

Batch Sorption Results for  $^{137}\text{Cs}$  on Synthetic  
Zeolites in Brine B at Room Temperature

Sorbent	Sample Number	$K_d$ , ml/g	Published Zeolitic Properties	
			$\text{Si}_2\text{O}/\text{Al}_2\text{O}_3$	Nominal Pore Diameter (Å)
Mordenite (Zeolite)	1	74	10	7
	2	74		
Zeolite (AW300)	1	61	10	4
	2	58		
Zeolite (AW500)	1	89	4-5	5
	2	98		
Zeolite (4A)	1	2.3	2	4
	2	1.7		
Zeolite (5A)	1	4.8	2	5
	2	5.2		
Zeolite (13X)	1	2.7	2.8	10
	2	3.4		

A variation in getter effectiveness with  $\text{Si}_2\text{O}/\text{Al}_2\text{O}_3$  ratio (and, hence, the anionic field strength) is consistent with Eisenman's selectivity model (Sherry, 1969). In this model, selectivity series are predicted for sorption of univalent ions by sorbers having different anionic field strengths. According to selectivity patterns predicted by Eisenman's treatment, a zeolite such as mordenite (high  $\text{Si}_2\text{O}/\text{Al}_2\text{O}_3$  ratio) should exhibit the selectivity pattern  $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$  (or  $\text{Cs} > \text{K} > \text{Rb} > \text{Na} > \text{Li}$ ), while the zeolite (4A) (low  $\text{Si}_2\text{O}/\text{Al}_2\text{O}_3$  ratio) should exhibit the selectivity

pattern  $\text{Na} > \text{K} > \text{Rb} > \text{Li} > \text{Cs}$ . On the basis of selectivity patterns alone, it might be anticipated that mordenite would be more effective in sorbing Cs(I) from brine solutions than would zeolite (4A). Results presented in Table 10 are consistent with this prediction.

On the basis of the pore size and selectivity patterns predicted by the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, candidates for further cesium sorption studies include zeolite Y (pore size  $\sim 7\text{\AA}$ ,  $\text{SiO}_2/\text{Al}_2\text{O}_3 \approx 5$ ) and zeolite ZK-4 (pore size  $\sim 5\text{\AA}$ ,  $\text{SiO}_2/\text{Al}_2\text{O}_3 \approx 4$ ).

Batch Sorption Results for  $^{137}\text{Cs(I)}$  at Different Total Cesium Concentrations

Table 11 contains  $K_d$  values representing the sorption of  $^{137}\text{Cs(I)}$  on several sorbents at total cesium concentrations of  $9 \times 10^{-9} \text{ M}$  (variant brine A) and  $1 \times 10^{-5} \text{ M}$  (brine A). With the exception of illite,  $K_d$ 's are virtually unchanged at the two concentrations and it would appear that the sorption isotherm for these solids is linear in this concentration range. The  $K_d$  for illite decreases from approximately 7.4 ml/g to 3.9 ml/g in going from a total cesium concentration of  $9 \times 10^{-9} \text{ M}$  to  $1 \times 10^{-5} \text{ M}$ . While this decrease in  $K_d$  is less than a factor of 2 over a three-orders-of-magnitude increase in cesium concentration, it does exhibit the trend reported by Tamra (1960), who observed that the percentage of cesium sorbed on illite decreased continuously over the cesium concentration range of 0.1-10,000 mg/l.

TABLE 11

Batch Sorption Results for  $^{137}\text{Cs}$  at Different  
Total Cesium Concentrations

Initial Tracer Concentration, $C_0 = \sim 9 \times 10^{-9} \text{ M}$ Batch Contact Time = 1 Week Room Temperature Mass of Bentonite in Samples = 2.0 g pH = $\sim 6.6$				
* $K_d$ , ml/g, Based on Mass of Bentonite-free Sorbent for All Mixtures				
Sorbent	Total Mass of Solids, g	Sample Number	Total Cesium Concentration $= \sim 9 \times 10^{-9} \text{ M}$ (variant Brine A)	Total Cesium Concentration $= 1 \times 10^{-5} \text{ M}$ (Brine A)
Bentonite	2.0	1	7.6	7.1
		2	8.0	7.2
20 wt. % Clinoptilolite	2.5	1	9.7	9.9
80 wt. % Bentonite		2	11	11
20 wt. % Eleana Shale	2.5	1	2.6	2.7
80 wt. % Bentonite		2	3.6	4.1
5 wt. % Illite	2.1	1	7.4	3.9
95 wt. % Bentonite				
9 wt. % Illite	2.2	1	7.3	3.8
91 wt. % Bentonite				
20 wt. % Sodium Titanate-loaded Zeolite	2.5	1	27	23
80 wt. % Bentonite		2	27	27

\*For all mixtures, the  $K_d$  is corrected for the contribution to cesium sorption by the bentonite, using a  $K_d$  for bentonite of 7.1 ml/g (where the total cesium concentration =  $\sim 1 \times 10^{-5} \text{ M}$ ) or 7.8 ml/g (where the total cesium concentration =  $\sim 9 \times 10^{-9} \text{ M}$ ).

Effect of Contact Time on the Batch Sorption of  $^{137}\text{Cs(I)}$

Duplicate sets of illite and zeolite (4A) samples were contacted with radiocesium-containing brines for one- and two-week periods of time. The  $K_d$  results are presented in Table 12. There is no significant difference in  $K_d$  between one and two weeks of contact time, showing that constant batch composition has been attained in samples contacted for one week. Sawhney (1966) found that "the Cs sorbed by Ca-illite . . . quickly reached approximate equilibrium" and the sorption decreased "only slightly with time." However, Tamura (1960) reported that illite required a long time to come to equilibrium with cesium and that even after six months the sorption of cesium increased. The  $K_d$  for illite in brine B increases only slightly

TABLE 12  
Effect of Contact Time on the Batch Sorption of  $^{137}\text{Cs}$   
at Room Temperature

Initial Tracer Concentration, $C_0 = \sim 9 \times 10^{-9} \text{ M}$ Total Cesium Concentration $\approx \sim 1 \times 10^{-5} \text{ M}$							
Sorbent	Brine	Sample Number	One Week Contact Time		Two Week Contact Time		
			$K_d$ , ml/g	pH	$K_d$ , ml/g	pH	
Illite	A	1	6.1	6.6	6.6	6.8	
		2	7.0	6.7	6.6	6.8	
Zeolite (4A)	A	1	3.9	6.7	4.6	6.8	
		2	4.2	6.7	4.5	6.8	
Illite	B	1	112	5.6	126	7.4	
		2	118	5.7	128	7.4	
Zeolite (4A)	B	1	2.3	8.4	0.5	8.3	
		2	1.7	8.4	3.1	8.6	

between one and two weeks of contact time, and this small increase (approximately 1.1 times) is within the acceptable precision factor of 2 (discussed previously).

#### Batch Sorption of $^{137}\text{Cs(I)}$ at Different Competing Ion Concentrations

In Table 13,  $K_d$ 's for the sorption of  $^{137}\text{Cs(I)}$  on sorbents in 1% brine A, brine A, and brine B are presented. As was the case with  $^{85}\text{Sr(II)}$ , sorption was greater in those solutions of lower total salt concentration. Comparing sorption in brine A versus that in 1% brine A,  $K_d$ 's are approximately two to three-orders-of-magnitude greater in 1% brine A.  $K_d$ 's are 2-18 times greater in brine B as compared with brine A. These results are indicative of a competing ion effect and, hence, an ion exchange sorption mechanism. Again, it is impossible to determine from these studies alone if sorption mechanisms other than ion exchange are involved. Tamura (1972) reports that a nearly constant  $K_d$  for the sorption of cesium by illite in distilled water and 0.1 N NaCl solution can "only be explained by a special mechanism operative in this mineral." He states that "by comparing adsorption of cesium by minerals of known lattice parameters and minerals whose lattice parameters were altered by selected treatments, (it was) concluded that the ion-exchange selectivity was due to limited access of ions (molecular sieve) into interlayer positions near the edges of crystallites."

#### Evaluation of Sorption Results

The relative merit of the  $K_d$  values presented in this report can be evaluated in terms of calculated estimates of breakthrough times for a 3-ft-thick backfill-getter barrier. For these calculations, breakthrough



TABLE 13

Batch Sorption of  $^{137}\text{Cs}$  at Different Competing Ion Concentrations

Initial Tracer Concentration, $C_0 = 9 \times 10^{-9} \text{ M}$							
Total Cesium Concentration = $1 \times 10^{-5} \text{ M}$ in Brines A and B							
= $1 \times 10^{-7} \text{ M}$ in 1% Brine A							
Batch Contact Time = 1 Week							
Room Temperature							
Sorbent	Sample Number	1% Brine A		Brine A		Brine B	
		$K_d$ , ml/g	pH	$K_d$ , ml/g	pH	$K_d$ , ml/g	pH
Chabazite/ Erionite	1	3,900	7.2	18	6.6	57	6.0
	2	4,100	7.3	19	6.6	56	6.1
Illite	1	990	7.6	6.1	6.6	112	5.6
	2	1,000	7.7	7.0	6.7	118	5.7
Mordenite (Zeolite)	1	12,000	7.4	27	6.7	74	6.6
	2	12,000	7.3	27	6.7	74	6.6
Zeolite (AW500)	1	5,900	7.0	23	6.7	89	6.7
	2	5,800	7.0	23	6.7	98	6.7

is defined as the appearance of a migrating species at 1 percent of its initial concentration. A fixed bed model with sorption by linear equilibrium ion exchange is used as a first empirical approximation. Details of this model and appropriate mathematical expressions are given by Nowak (1980a).

The following relationship from Crank (1956), appropriate to migration by molecular diffusion, was used to calculate estimates of breakthrough times:

$$C/C_o = 1 - \operatorname{erf} \left\{ \frac{X}{2 \left[ \frac{D_f t}{\rho_b R_f} \right]^{1/2}} \right\} \quad (4)$$

where:

$$R_f = \text{retardation factor} = 1 + \left( \frac{\rho_b K_d}{\epsilon} \right)$$

$$\rho_b = \text{bulk density} = 2 \text{ g/cm}^3$$

$$K_d = \text{distribution coefficient, ml/g}$$

$$\epsilon = \text{effective porosity of bed} = 0.1$$

$$D_f = \text{liquid phase molecular diffusivity} = 10^{-5} \text{ cm}^2/\text{s}$$

$$t = \text{time, sec}$$

$$X = \text{backfill thickness} = 90 \text{ cm (3 ft)}$$

$$C_o = 0.01 \text{ (definition of breakthrough)}$$

Detailed justification of the chosen parameter values for Equation (4) are given elsewhere (Nowak, 1980a).

If effective getters for cesium and strontium are components of a backfill mixture (i.e., the getters are diluted by other backfill constituents),

$K_d$ 's for these getters must be expressed per unit mass of that total mixture for use in Equation (4). This procedure accounts for the dilution of the getter in the backfill. A  $K_d \approx 100$  ml/g was found for the sorption of Sr(II) on sodium titanate in brine A and for the sorption of Cs(I) on illite in brine B. If each of these getters comprised 20 percent, by weight, of the backfill barrier, the appropriate  $K_d$  value would be 20 ml/g. For a 90-cm-thick (3-ft-thick) backfill, this  $K_d$  value results in a breakthrough time of  $\sim 1 \times 10^3$  years, sufficient time for most of the fission products to decay to very low concentrations. In brine B, sodium titanate, with a  $K_d = 500 - 600$  ml/g, would delay the breakthrough of the strontium for even longer periods of time. The gettering ability of the mordenite-type zeolite for Cs(I) in brine A ( $K_d \approx 27$  ml/g) is not sufficient to prevent breakthrough for  $10^3$  years, although it would reduce the migration of cesium through the backfill and delay breakthrough for  $\sim 300$  years (assuming the mordenite to comprise 20 percent, by weight, of the backfill mixture).

The larger the  $K_d$  for a fission product getter, the smaller the required quantity of that getter in the basic backfill matrix. It would, therefore, be advantageous to identify sorbents with higher  $K_d$ 's for Cs(I) and Sr(II) in concentrated brines. Additional work to identify a more effective getter for the sorption of Cs(I) in brine A would be especially useful. As mentioned previously, attention might be directed to the examination of additional zeolitic materials (for cesium sorption) and inorganic ion exchangers (for strontium sorption).

## Thermal Stability

Research, by others, indicates that the gettering ability of the sorbents identified in this report (sodium titanate, illite, and a mordenite-type zeolite) should not be affected by exposure to the high temperatures which could possibly be encountered in the waste repository. The Sr sorption capacity of sodium titanate decreases as the temperature used to heat the sodium titanate prior to contact with the Sr solution increases (Dosch, 1978); however, its selectivity for strontium is unaffected up to temperatures between 500 and 600°C (Dosch, 1980). Tamura and Jacobs (1960) found that the sorption of cesium by illite was not affected by oven-drying the illite at 100°C. No information concerning the hydrothermal stability of mordenite was found; however Breck (1964) states that mordenite is remarkably stable to heat and that "a temperature of about 700°C is required in order to decompose the crystal structure."

## Conclusions

Significant progress has been made in identifying effective getters for the sorption of  $^{85}\text{Sr(II)}$  and  $^{137}\text{Cs(I)}$  in concentrated brines. Sodium titanate powder can be used as a getter for  $^{85}\text{Sr(I)}$ . A mordenite-type zeolite and illite act as getters for  $^{137}\text{Cs(I)}$ . A backfill mixture containing these getters would potentially be an effective barrier to the migration of strontium and cesium into the surrounding geologic medium.

Sorption of the  $^{85}\text{Sr}(\text{II})$  and  $^{137}\text{Cs}(\text{I})$  by these getters exhibits behavior which is consistent with an ion exchange mechanism and constant batch compositions are attained within one week of contact time.

Screening of potential getters for fission products should continue in an effort to identify sorbents with higher  $K_d$ 's. Higher  $K_d$ 's could decrease the amount of getter needed in the backfill mixture. Attention should especially be focused on the sorption of cesium in WIPP brine A. Results presented in this report may serve as guidelines in selecting materials for future study. One important area for future study is the effect of irradiation on the sorption properties of the selected getter materials.

#### References

- Abe, M., 1979, Synthetic inorganic ion-exchange materials 18. Ion-exchange equilibria of crystalline antimonic (V) acid with alkali metal ions, J. Inorganic Nuclear Chemistry, 41:1:85.
- Abe, M., and Uno, K., 1979, Synthetic inorganic ion-exchange materials XIX. Ion-exchange behavior and separation of alkaline earth metals on crystalline antimonic (V) acid as a cation exchanger, Separation Science Technology, 14:4:355.
- Akatsu, E., Ono, R., Tsukuechi, K., and Uchiyama, H., 1965, Radiochemical study of adsorption behavior of inorganic ions on zirconium phosphate, silica gel, and charcoal, J. Nuclear Science and Technology, 2:141.
- Allard, B., Rydberg, J., Kipatsi, H., and Torstenfelt, B., 1979, Disposal of radioactive waste in granitic rock in "Radioactive Waste in Geologic Storage," Sherman Fried, ed., ACS Symposium Series 100, American Chemical Society, Washington, D.C.
- Ames, L. L., Jr., 1961, Cation sieve properties of the open zeolites chabazite, mordenite, erionite, and clinoptilolite, The American Mineralogist, 46:1120.
- Barney, G. S., and Anderson, P. D., 1978, The kinetics and reversibility of radionuclide sorption with rocks--Progress report for fiscal year 1978, in: "Proceedings of the Task 4 Waste Isolation Safety Assessment Program Second Contractor Information Meeting," Vol 2, Battelle Pacific Northwest Laboratories, report PNL-SA-7352, October 1978.
- Beall, G. W., Kettle, B. H., Harie, R. G., and O'Kelley, G. D., 1979, Sorption behavior of trivalent actinides and rare earths on clay minerals, in "Radioactive Waste in Geologic Storage," Sherman Fried, ed., ACS Symposium Series 100, American Chemical Society, Washington, D.C.
- Breck, D. W., 1964, Crystalline Molecular Sieves, J. of Chemical Education, 48:678.
- Breck, D. W., 1974, "Zeolite Molecular Sieves Structure, Chemistry, and Use," John Wiley & Sons, New York.
- Clearfield, A., and Garces, J. M., 1979, Mechanism of ion exchange in zirconium phosphates 24. Exchange of alkali metal ions on  $\gamma$ -zirconium phosphate, J. Inorganic Nuclear Chemistry, 41:6:879.
- Coons, W. E., Moore, E. L., Smith, M. J., and Kaser, J. D., 1980, "The Functions of an Engineered Barrier System for a Nuclear Waste Repository in Basalt," Rockwell Hanford Operations, report RHO-BWI-LD-23, January 1980.
- Crank, J., 1956, "The Mathematics of Diffusion," Oxford Press, London.

- Dosch, R. G., 1978, "The Use of Titanates in Decontamination of Defense Waste," Sandia National Laboratories, report SAND78-0710, June 1978.
- Dosch, R. G., 1980, "Final Report on the Application of Titanates, Niobates, and Tantalates to Neutralized Defense Waste Decontamination-Materials Properties, Physical Forms, and Regeneration Techniques," Sandia National Laboratories, report SAND80-1212, 1980.
- Dosch, R. G. and Lynch, A. W., 1978, "Interaction of Radionuclides with Geomedia Associated with the Waste Isolation Pilot Plant (WIPP) Site in New Mexico," Sandia National Laboratories, report SAND78-0297, June 1978.
- Erdal, B. R., Wolfsberg, K., Vidale, R., Duffy, C., and Hoffman, D.C., 1977, Laboratory measurements of radionuclide distribution between selected groundwater and geologic media. I.  $K_d$  values for alluvium and bentonite, in "Waste Isolation Safety Assessment Program. Task 4: Contractor Information Meeting Proceedings," Battelle Pacific Northwest Laboratories, report PNL-SA-6957, 1977.
- Erdal, B. R., Aguilar, R. D., Bayhurst, B. P., Daniels, W. R., Duffy, C. J., Lawrence, F. O., Maestas, S., Oliver, P. Q., and Wolfsberg, K., 1978, Sorption-desorption studies on granite I. Initial studies of strontium, technetium, cesium, barium, cerium, europium, uranium, plutonium, and americium, in: "Proceedings of the Task 4 Waste Isolation Safety Assessment Program Second Contractor Information Meeting," Vol 2, Battelle Pacific Northwest Laboratories, report PNL-SA-7352, October 1978.
- Erdal, B. R. compiler, 1980, "Laboratory Studies of Radionuclide Distributions Between Selected Groundwaters and Geologic Media. Annual Report," October 1, 1978-September 30, 1979, Los Alamos Scientific Laboratory, report LA-8088-PR, February 1980.
- Gillham, R. W., 1978, Cesium and strontium migration in unconsolidated geologic materials, in: "Proceedings of the Task 4 Waste Isolation Safety Assessment Program Second Contractor Information Meeting," Vol 2, Battelle Pacific Northwest Laboratories, report PNL-SA-7352, October 1978.
- Gradev, G. D. Milanov, M. V., Prodanov, Y. D., and Stephanov, G. I., 1978, A study of the sorption properties of natural calcium clinoptilolite by using radioactive indicators, J. of Radioanalytical Chemistry, 45:103.
- Hinkebein, T. E., and Blava, P. F., 1977, Micro-structural interactions of geologic media with waste radionuclides, in: "Waste Isolation Safety Assessment Program Task 4: Contractor Information Meeting Proceedings," Battelle Pacific Northwest Laboratories, report PNL-SA-6957, 1977.
- Hower, J., and Mowatt, T. C., 1966, The mineralogy of illites and mixed-layer illite/montmorillonites, The American Mineralogist, 51:825.

- KBS, 1980, "KBS Annual Report, 1979, Including Summaries of Technical Reports Issued During 1979," KBS, report KBS79-28, Stockholm, Sweden, March 1980.
- Krylov, V. N., and Larina, K. P., 1978a, Exchange of alkali metal cations on amorphous hafnium phosphate, Zh. Fiz. Khim., 52:8:2040.
- Krylov, V. N., and Larina, K. P., 1978b, Exchange of alkali metal cations on titanium (4) phosphate, Zh. Fiz. Khim., 52:8:2035.
- Mercer, B. W., Jr., and Ames, L. L., Jr., 1963, "The Adsorption of Cesium, Strontium, and Cerium on Zeolites from Multication Systems," General Electric Co., Hanford Atomic Products Operation, report HW-78461, August 1963.
- Meyer, R. E., Shiao, S. Y., Rafferty, P., Johnson, J. S., Jr., Thomas, I. L., and Kraus, K. A., 1978, Systematic study of metal ion sorption on selected geologic media, in: "Proceedings of the Task 4 Waste Isolation Safety Assessment Program Second Contractor Information Meeting," Vol 2, Battelle Pacific Northwest Laboratories, report PNL-SA-7352, October 1978.
- Neretnieks, I., 1977, "Retardation of Escaping Nuclides from a Final Repository," KBS Teknisk Rapport 30, Stockholm, Sweden.
- Nowak, E. J., 1980a, "The Backfill Barrier as a Component in a Multiple Barrier Nuclear Waste Isolation System," Sandia National Laboratories, report SAND79-1109, March 1980.
- Nowak, E. J., 1980b, The backfill as an engineered barrier for nuclear waste management, in: "Scientific Basis for Nuclear Waste Management," Vol 2, C. J. Northrup, ed., Plenum Press, New York.
- Nowak, E. J., 1980c, "Radionuclide Sorption and Migration Studies of Getters for Backfill Barriers," Sandia National Laboratories, report SAND79-1110, July 1980.
- ONWI, 1980, "Draft NWS Waste Package Program Plan," Vol 1, Office of Nuclear Waste Isolation, report ONWI-96, May 1980.
- Pusch, R., 1977, "Required Physical and Mechanical Properties of Buffer Masses," KBS Teknisk Rapport 33, Stockholm, Sweden.
- Relyea, J. F., and Serne, R. J., 1979, "Waste Isolation Safety Assessment Program Publication Number 2: Interlaboratory Comparison of Batch  $K_d$  Values," Pacific Northwest Laboratory, report PNL-2872, June 1979.
- Robinson, B. P., 1962, "Ion-Exchange Minerals and Disposal of Radioactive Wastes--A Survey of Literature," Geological Survey Water Supply Paper 1616, United States Government Printing Office, Washington, D.C.
- Sawhney, B. L., 1966, Kinetics of cesium sorption by clay minerals, Soil Science Society of America Proceedings, 30:565.



- Sherry, H. S., 1969, The ion-exchange properties of zeolites, in: "Ion-Exchange," J. A. Marinsky, ed., Vol 2, Marcel Dekker, New York.
- Shiao, S. -Y., Rafferty, P., Meyer, R. E., and Rogers, W. J., 1979, Ion exchange equilibria between montmorillonite and solutions of moderate-to-high ionic strength, in "Radioactive Waste in Geologic Storage," Sherman Fried, ed., ACS Symposium Series 100, American Chemical Society, Washington, D.C.
- Tamura, T., 1960, Selective sorption reactions of cesium with soil minerals, Nuclear Safety, 5:262.
- Tamura, T., 1972, Sorption phenomena significant in radioactive waste disposal, in: "Underground Waste Management and Environmental Implications," T. D. Cook, ed., American Association of Petroleum Geologists, Tulsa, Oklahoma.
- Tamura, T., and Jacobs, D. G., 1960, Structural implications in cesium sorption, Health Physics, 2:391.
- van Olphen, H., and Fripiat, J. J., eds., 1979, "Data Handbook for Clay Materials and other Non-Metallic Minerals," Pergamon Press, Oxford.
- Vol'Khin, V. V., Leont'eva, G. V., and Tatlieva, T. N. 1975, Cesium extraction from solutions by magnesium phosphates sorption, Izu. Vyssh. Uchebn. Zaved. Tsvet. Metall., 5:86.

## APPENDIX A

### Reference Clay Materials

The following reference clay materials were obtained from the curator of the "Source Clays" sample collection for the Clay Minerals Society "Source Clays Program": Professor William D. Johns, Department of Geology, University of Missouri, Columbia, MO 65201. Source of the attapulgite and data which characterizes this clay material has been given by van Olphen and Fripiat (1979). Source of the illite and data which characterizes this clay material has been given by Hower and Mowatt (1966). Some of these data are summarized below:

#### PFL-1, Attapulgite, Florida

Cation exchange capacity: 19.5 meq/100 g.

Exchangeable cations: Mg (principal)

Ca, K, and Na (minor and may be present as soluble salts).

Surface area:  $136 \text{ m}^2/\text{g}$  by  $\text{N}_2$  BET (method of Brunauer, Emmett and Teller).

#### I-Mont-1, Illite, Silver Hills, Montana

Cation exchange capacity: 15 meq/100 g.

Exchangeable cations: K (principal).

Surface area: Not determined.

Characterization by x-ray diffraction: Strong illite and quartz patterns and no weak patterns.

## Commercial Samples

Samples of commercial bentonite, chabazite/erionite, clinoptilolite, a mordenite-type zeolite, zeolites 4A, 5A, 13X, AW300, and zeolite AW500 were obtained from commercial sources. Some of the characterizing information follows:

### Bentonite

Source: Georgia Kaolin Company.

Product specification: Bentonite, Brock, Pulverized, 200 mesh, no chemical added.

Location of origin: Kaycee, Wyoming, Mowry formation.

Approximate composition:

85% to 90% montmorillonite.

10% to 15% quartz and mica shale.

(depending on location in formation).

Cation exchange capacity: 75 meq/100 g obtained for Na- or Li-saturated clay fractions with particle size  $< 1 \mu\text{m}$  to remove mineral impurities. Thompson and Moll (Thompson, T. D. & Moll, W. F., Oxidative Power of Smectites Measured by Hydroquinone, Clays and Clay Minerals, 21, 337-350, 1973) gave these and other characterization data for this clay which they designated as "K-2 Brock."

Exchangeable cations: Na (major), Ca (minor).

Characterization by x-ray diffraction: Strong montmorillonite and quartz patterns; weak calcite and cristobalite patterns.

### Chabazite/Erionite

Source: Norton Company Chemical Process Products Division, New York,  
New York.

Product specifications: Zeolon 500, 20/50 mesh.

Composition:  $\text{Ca}_2 \left[ (\text{AlO}_2)_4 (\text{SiO}_2)_8 \right] \cdot 13\text{H}_2\text{O}$  (chabazite).

$(\text{Ca}, \text{Mg}, \text{K}_2, \text{Na}_2)_{4.5} \left[ (\text{AlO}_2)_9 (\text{SiO}_2)_{27} \right] \cdot 27\text{H}_2\text{O}$  (erionite).

Effective pore diameter: 4-5 Å.

Exchangeable cation: Mixed.

Characterization by x-ray diffraction: Strong chabazite and erionite  
patterns; large unidentified line.

### Clinoptilolite

Source: Leonard Resources, Albuquerque, NM.

Location of origin: Near Silver City, NM.

Product specifications: 9036-5, 200 mesh.

Chemical analysis (from source supplier):

$\text{SiO}_2$	62.73%	oxide
$\text{Al}_2\text{O}_3$	11.78	
$\text{Fe}_2\text{O}_3$	1.34	
$\text{FeO}$	0.0	
$\text{MgO}$	1.38	
$\text{CaO}$	3.86	
$\text{Na}_2\text{O}$	0.45	
$\text{K}_2\text{O}$	0.88	
$\text{H}_2\text{O}$	16.10	
$\text{TiO}_2$	0.12	
$\text{P}_2\text{O}_5$	0.01	
$\text{MnO}$	0.02	
$\text{SrO}$	0.09	
	<u>98.76</u>	

Cation exchange capacity: ~130 meq/100 g (from Ames, L. L., The Cation

Sieve Properties of Clinoptilolite, The American Mineralogist, 45,  
689-699, 1960).

Exchangeable cations: Ca, Na, K.

Characterization by x-ray diffraction: Strong clinoptilolite pattern,  
and no weak patterns.

#### Mordenite-type Zeolite

Source: Norton Company, Chemical Process Products Division, New York,  
New York.

Product specifications: Zeolon 900, Lot 40366, 20/50 mesh, Na-form.

Composition:  $\text{Na}_8 \cdot \text{Al}_8 \cdot \text{Si}_{40} \cdot \text{O}_{96} \cdot 24 \text{H}_2\text{O}$

Effective pore diameter: 7 Å.

Surface area: 400 to 450 m<sup>2</sup>/g N<sub>2</sub> BET.

Exchangeable cation: Na.

Characterization by x-ray diffraction: Strong mordenite pattern and no  
weak patterns.

#### Vermiculite

Source: Solico Southwest Vermiculite Company, Inc., Albuquerque, NM.

Product specifications: Coarse.

Characterization by x-ray diffraction: No noticeable impurities.

The following synthetic zeolites were obtained from Union Carbide Corporation--Linde Division, Houston, Texas. Data characterizing these zeolites have been given by Breck (1974). Some of these data are summarized below:

#### Zeolite (4A)

Product specifications: Type 4A, Lot 49410770065, Powder.

Composition:  $\text{Na}_{12} \left[ (\text{AlO}_2)_{12} (\text{SiO}_2)_{12} \right] \cdot 27\text{H}_2\text{O}$

Nominal pore diameter: 4Å.

Exchangeable cation: Na.

Characterization by x-ray diffraction: Strong A-type zeolite structure pattern and no weak patterns.

#### Zeolite (5A)

Product specifications: Type 5A, Lot 9430790047, Powder.

Composition:  $\text{Ca}_6 \left[ (\text{AlO}_2)_{12} (\text{SiO}_2)_{12} \right] \cdot x \text{H}_2\text{O}$

Nominal pore diameter: 5Å.

Exchangeable cation: Ca.

Characterization by x-ray diffraction: Strong A-type zeolite structure pattern and no weak patterns.

#### Zeolite (13X)

Product specifications: Type 13X, Lot 13945040064, Powder.

Composition:  $\text{Na}_{86} \left[ (\text{AlO}_2)_{86} (\text{SiO}_2)_{106} \right] \cdot 264 \text{H}_2\text{O}$

Nominal pore diameter: 10Å.

Exchangeable cation: Na.

Characterization by x-ray diffraction: Strong faujasite pattern and no weak patterns.

#### Zeolite (AW300)

Product specifications: Type AW300, Lot 3940560026, 1/16 inch pellets.

Composition:  $\text{Na}_8 \left[ (\text{AlO}_2)_8 (\text{SiO}_2)_{40} \right] \cdot 24 \text{H}_2\text{O}$

Nominal pore diameter: 4Å.

Exchangeable cation: Na.

Particle size: Through No. 100 U.S.A. Standard Testing Sieve.

Characterization by x-ray diffraction: Strong pattern similar to that of clinoptilolite and no weak patterns.

Zeolite (AW500)

Product specifications: Type AW500, Lot 59429770013, 1/16 inch pellets.

Composition:  $\text{Ca}_2 \left[ (\text{AlO}_2)_4 (\text{SiO}_2)_8 \right] \cdot 13 \text{H}_2\text{O}$

Nominal pore diameter:  $5\text{\AA}$ .

Exchangeable cation: Na, Ca.

Particle size: Through No. 100 U.S.A. Standard Testing Sieve.

Characterization by x-ray diffraction: Strong chabazite and erionite patterns and no weak patterns.

Miscellaneous Solids

Anhydrite

Source: Southeastern New Mexico.

Qualitative Composition: Mainly anhydrite with some salt.

Particle Size: Through No. 60 U.S.A. Standard Testing Sieve.

Characterization by x-ray diffraction: Strong anhydrite and NaCl patterns; a few very weak lines not identified.

Eleana Shale

Source: Calico Hills, Nevada Test Site.

Particle Size: 95% through No. 170 and 5% through NO. 66 U.S.A. Standard Testing Sieve.

Characterization by x-ray diffraction: Strong quartz and kaolinite patterns; weak illite and other weak clay patterns not identified.

Sodium Titanate

Source: prepared by R. G. Dosch, Sandia National Laboratories,  
Albuquerque, NM.

Particle Size: Through No. 40, on No. 140 U.S.A. Standard Testing Sieve.

Surface Area:  $200 \text{ m}^2/\text{g}$  (Dosch, 1980).

Characterization by x-ray diffraction: Amorphous.

Sodium Titanate--Loaded Zeolite

Source: Prepared by R. G. Dosch, Sandia National Laboratories,  
Albuquerque, NM.

Composition: Sodium titanate included in Zeolon 900 (Norton Co.).

Titanate content of sieve = 11.1% by weight.

Characterization by x-ray diffraction: Strong mordenite pattern; very weak lines not identified; large unidentified line.



APPENDIX B

Detailed Compositions of Brines A and B

The following two tables have been taken from a memo to distribution from M. A. Molecke, "Revised Representative Brines/Solutions for WIPP Experimentation" dated October 8, 1976. They give brine compositions and the compounds used to prepare brines A & B for this work. Brine A represents water in contact with potash-containing horizons in the vicinity of the proposed Waste Isolation Pilot Plant (WIPP) site. Brine B represents water in contact with the halite of the proposed WIPP horizon.

TABLE B1  
Representative Brines for WIPP Experimentation

<u>Ion</u>	<u>Solution "A"</u> (mg/liter) (+ 3%)	<u>Solution "B"</u> (mg/liter) (+ 3%)
Na <sup>+</sup>	42,000	115,000
K <sup>+</sup>	30,000	15
Mg <sup>++</sup>	35,000	10
Ca <sup>++</sup>	600	900
Fe <sup>+++</sup>	2	2
Str <sup>++</sup>	5	15
Li <sup>+</sup>	20	---
Rb <sup>+</sup>	20	1
Cs <sup>+</sup>	1	1
Cl <sup>-</sup>	190,000	175,000
SO <sub>4</sub> <sup>--</sup>	3,500	3,500
B (BO <sub>3</sub> <sup>----</sup> )	1,200	10
HCO <sub>3</sub> <sup>-</sup>	700	10
NO <sub>3</sub> <sup>-</sup>	---	---
Br <sup>-</sup>	400	400
I <sup>-</sup>	10	10
pH (adjusted with NaOH)	6.5	6.5
specific gravity	1.2	1.2

TABLE B?

Recommended Chemical Compounds for Preparing Representative  
Brines/Solutions For WIPP Experimentation

<u>Compound</u>	<u>Solution "A"</u> (mg/liter)	<u>Solution "B"</u> (mg/liter)	<u>Variant</u> <u>Solution "A"</u> (noCs <sup>+</sup> , noSr <sup>++</sup> ) (mg/liter)
NaCl	100.10 g	287.00 g	110.10 g
Na <sub>2</sub> SO <sub>4</sub>	6.20 g	6.20 g	6.20 g
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> · 10H <sub>2</sub> O	1.95 g	16	1.95 g
NaHCO <sub>3</sub>	960	14	960
NaBr	520	520	520
NaNO <sub>3</sub>	--	--	--
KCl	57.20 g	29	57.20 g
KI	13	13	--
MgCl <sub>2</sub>	137.00 g	40	137.00 g
MgSO <sub>4</sub>	--	--	--
CaCl <sub>2</sub> · 2H <sub>2</sub> O	2.20 g	3.30 g	2.20 g
CaSO <sub>4</sub> · 2H <sub>2</sub> O	--	--	--
FeCl <sub>3</sub>	6	6	6
SrCl <sub>2</sub> · 2H <sub>2</sub> O	11	33	--
LiCl	125	--	--
Rb <sub>2</sub> SO <sub>4</sub>	30	1.6	--
CsCl	1.3	1.3	--
pH (adjusted with NaOH)	6.5	6.5	6.5
Total Dissolved Solids	306.3 g/l	297.2 g/l	306.1 g/l