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ABSTRACT

As part of the long-term waste management program at the Savannah River Laboratory, several ^{137}Cs sorbents were evaluated for incorporation into concrete. The sorbents studied were: *Linde* AW-300, AW-500, 13-X, and SK-40; Norton *Zeolon* 200, 500, and 900; clinoptilolite; and vermiculite. The parameters studied were sorption kinetics, leachability, and compressive strength of the concrete. The best sorbents identified were *Linde* AW-500 and Norton *Zeolon* 900. In all tests, these two sorbents performed almost identically: sorption kinetics were acceptable, both strengthened the concrete, and both gave relatively leach-resistant concrete.

Vermiculite that had been heated to collapse its lattice around ^{137}Cs gave the most leach-resistant concrete. However, it sorbed cesium slowly, and the resulting concrete was very weak.

When silica gel was added to concrete to react with free calcium, the addition had no effect on cesium leachability.

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INTRODUCTION

The Savannah River Laboratory (SRL) is evaluating methods for solidification and storage of Savannah River Plant (SRP) high-level liquid radioactive waste.[1-5] In one method under consideration, solidified waste would be stored in an onsite, retrievable surface storage facility until the waste could be shipped to a Federal repository.

An earlier report[1] detailed the origins and characteristics of SRP waste, the criteria for acceptable solid forms, and the potential solid forms for SRP waste. That study was used to formulate the conceptual process shown in Figure 1.

SRP waste consists of an alkaline salt solution; a solid salt cake; and an insoluble sludge containing large amounts of iron, aluminum, manganese, uranium, and other elements. In the conceptual process, waste would be removed from its underground tank by dissolving the salt cake with water and sluicing the slurry of sludge and solution from the tank. Sludge and solution would be separated by centrifugation and filtration. ^{137}Cs, the principal biological hazard in the solution, would be removed by ion exchange and then sorbed on zeolite. Sludge would be washed to remove soluble salts, dried, and blended with the cesium-zeolite for solidification. The two best matrices identified for solidification are concrete and glass.

If glass is used as a solidification matrix, ^{137}Cs eluted from the ion exchange resin can be mixed directly with the glass-making components. If concrete is the final matrix, ^{137}Cs in the concentrated eluate will be loaded onto a sorbent[6] and mixed with cement and sludge.

Previous tests[3] showed that high alumina cement (HAC) gave concrete with the lowest cesium leachabilities. Pozzolanic cement (I-P) gave concrete with about twice the cesium leachability of HAC, and other cements were still more leachable.

Other conclusions were:

- The thermal stabilities of the concretes were acceptable.

- The compressive strengths of the concretes were acceptable (>2000 psig), but they vary with sludge type and loading.

- ^{90}Sr and gross alpha leachabilities were both low [10^{-3} to 10^{-5} g/(cm^2)(day)].

- ^{137}Cs leachabilities for concrete containing both sludge and ^{137}Cs were rather high [1 to 10^{-2} g/(cm^2)(day)].

Figure 2 shows the amount of ^{137}Cs, ^{90}Sr, and alpha activity leached as a function of time from HAC concrete containing simulated sludge and cesium-loaded zeolite (*Linde** AW-500). The amount of ^{137}Cs leached from the concrete was 10^2 to 10^3 times higher than the amount of ^{90}Sr or alpha activity leached.

Figure 3 compares the cumulative fractions of ^{137}Cs leached from concrete castings made with I-P or HAC, sludge, and zeolite over a period of about 6 weeks. During this period, the leaching from the glass waste form was about 10^{-5}%. The concrete leachabilities exceed that of glass by factors or 10^4 to 10^5.

The purpose of this study was to determine if the cesium leachabilities of HAC and I-P concrete could be significantly reduced. Alternative cesium sorbents and processing methods were studied. The important parameters studied for each sorbent were cesium sorption kinetics, compressive strength of concrete containing the sorbent, and leachability.

TESTS OF ALTERNATIVE SORBENTS

Sorption Tests

Table 1 lists the sorbents tested. The sorbents were washed with at least one liter of 2M $NaNO_3$ per 5 g of sorbent to ensure that each was in the sodium form. Each was then washed with at least one liter of distilled water per 5 g of sorbent. The wet sorbents were dried at 110°C to constant weight.

The sorptive power of each sorbent for cesium was tested by equilibrating 100 ml of a 0.02M $CsNO_3$ solution containing ^{137}Cs with 2.00 g of the sorbent. The liquid was periodically sampled and analyzed for ^{137}Cs by gamma ray spectroscopy. These static tests measured the relative sorption kinetics for each sorbent;

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* Union Carbide Corp. trademark.

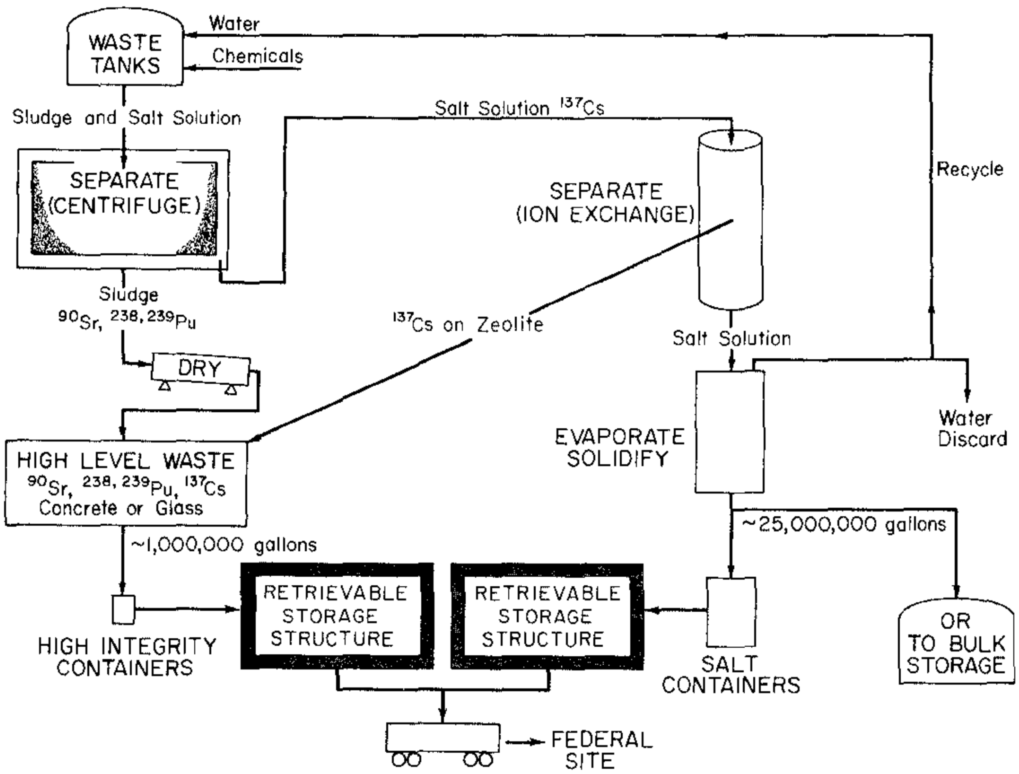

FIGURE 1. Conceptual Waste Solidification Process

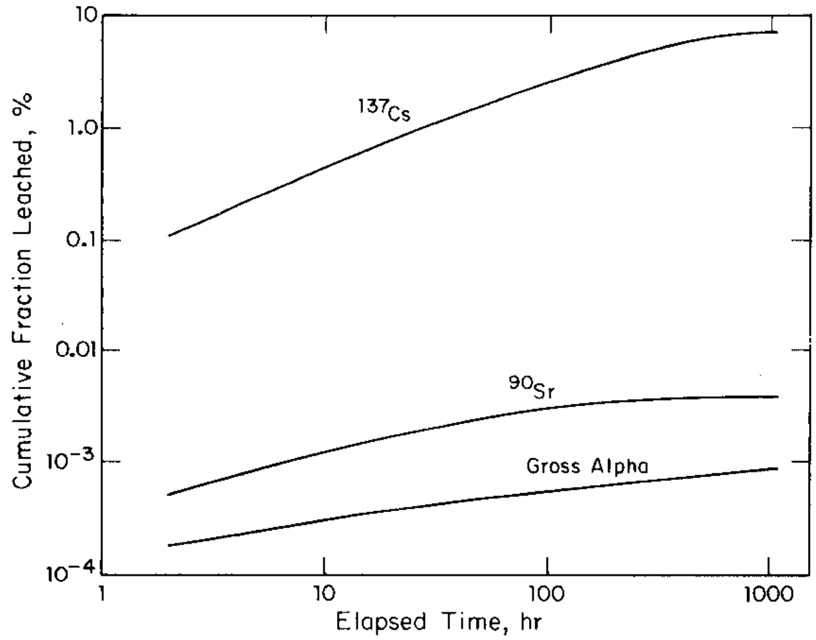

FIGURE 2. Leaching of Various Radionuclides from HAC/Sludge Concrete

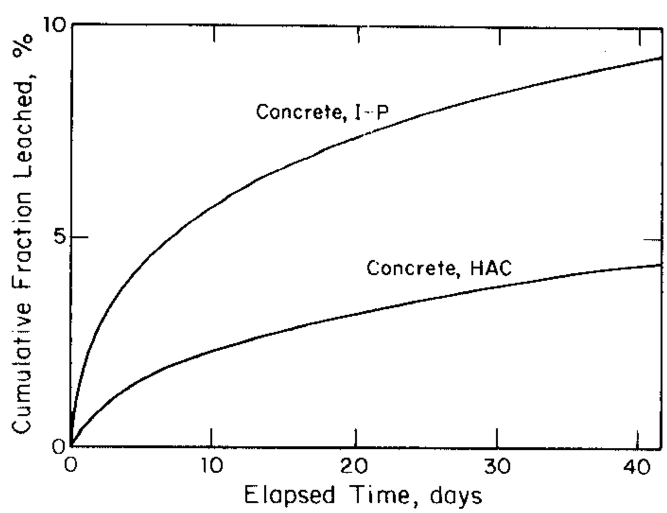

FIGURE 3. Leaching of Cesium from Concrete

TABLE 1

Sorbents Tested

Sorbent	*Mineral Structure*	*Pore Size, Å*	*Vendor*
Zeolon 200* (Z-200)	Mordenite	7-10	Norton Company
Zeolon 500 (Z-500)	80% Chabazite- 20% Erionite	4-5	
Zeolon 900 (Z-900)	Mordenite	4-5	
Linde 13-X**	Faujasite	10-12	Union Carbide Corp.
Linde AW-300	Mordenite	7-8	
Linde SK-40	Zeolite Y	7-8	
Linde AW-500	Chabazite	4-5	
Clinoptilolite	-	4-6 10-15	National Lead Corp.
Vermiculite	-	13-20	Zonolite Corp.

* Zeolon is a Norton Co. trademark.

** Linde is a Union Carbide Corp. trademark.

Figure 4 shows the results. The sorption curves for SK-40 and 13-X zeolites are not shown but would lie slightly above that of vermiculite. Both resins sorbed cesium very poorly, and SK-40 was nearly impossible to separate from the aqueous phase. Therefore, these two resins were rejected for further work.

*Zeolon** 900(Z-900), Z-500, AW-500, and vermiculite were tested further. Concentrated eluate from *Duolite*** ARC-359 ion exchange resin columns was sorbed on each.[7] The concentrated eluate solution, 0.019M $^{137}Cs_2CO_3$ in 1.75M Na_2CO_3, was passed through a 100-ml column of each sorbent at 1 column volume/hour (1 CV/hr). AW-500 and Z-900 were equivalent, each showing 100% retention of ^{137}Cs after 70 CV of eluate and 60% retention after 80 CV. Z-500 had 100% retention of ^{137}Cs for only 1 CV, and none at all after 8 CV. Vermiculate had no retention of ^{137}Cs after 2 CV. These results showed that AW-500 and Z-900 were the best cesium sorbents, in terms of sorption kinetics.

Strength Tests

Simulated sludge, sorbent, and mixtures of the two, were incorporated into concretes, and the compressive strengths of the resulting materials were tested. The simulated sludge used for these tests contained 50 mole % $Fe(OH)_3$, 25 mole % $Al(OH)_3$, and 25 mole % MnO_2. The concretes were made by slowly adding water to the mixtures until good workability was achieved. The wet mixtures were poured into plastic tubes (1-in. diameter and 5-in. long), capped, and allowed to harden.

Water-to-cement ratios ranged from 0.25 to 0.30 with no sludge or sorbent to 0.50 to 0.60 with 40 wt % sludge. For samples containing various sorbents, the water-to-cement ratio depended on the sorbent; vermiculite required the highest water content, and AW-500 and Z-900 the lowest. These ratios were similar to those previously reported.[3]

After the concrete castings cured in a humid atmosphere, the plastic tubes were removed. The top and bottom 1/4 to 1/2 in. of the casting were sawed off and discarded. Pieces $\sim$2 in. long were cut from the castings, and the ends of each piece were sanded until they were flat and parallel. The diameter and length of the pieces were measured, and the pieces weighed. They were then placed in a press, and the force needed to break them was determined. The compressive strengths were calculated from the force measurements and cross-sectional areas.

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* Norton Co. trademark.

** Diamond Shamrock Chemical Co. trademark.

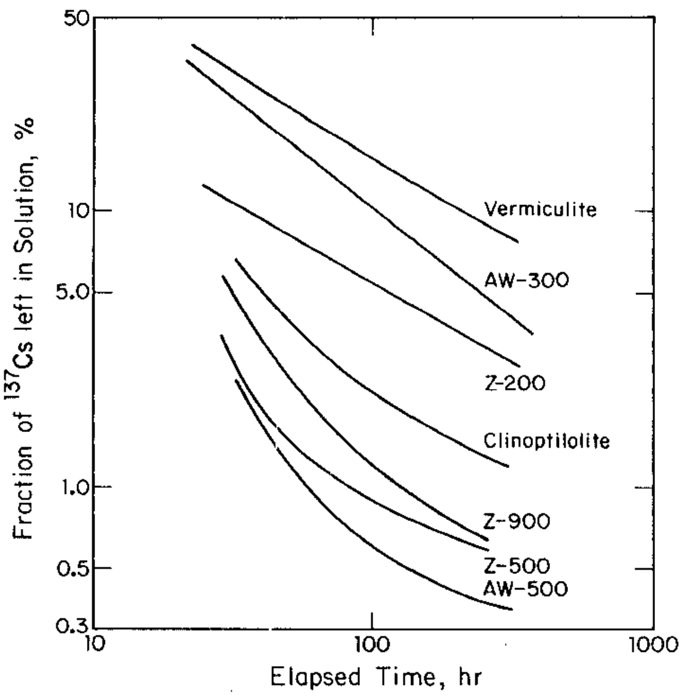

FIGURE 4. Cesium Sorption Under Static Conditions

Most of the compressive strength measurements were made on HAC concrete castings, because these reach at least 75% of their final strength within 48 hours.[8] Values for I-P concrete castings were measured after 28 days, when the casting had at least 90% of its final strength.[8]

Previous work[3] showed that the proportion of sludge in the concrete is the most important factor affecting the compressive strength. For HAC concrete, Table 2 shows that as the amount of sludge increases to 40 wt % of the dry mixture the compressive strength drops by a factor of four.

The effect of various sorbents on the compressive strength of concretes was measured in both the presence and absence of simulated sludge. Table 3 shows that in the absence of simulated sludge, AW-500 and Z-900 have relatively little effect on the strength of the concrete. Z-200, AW-300, and vermiculite severely weakened the concrete.

In the presence of sludge, Z-900 and AW-500 actually strengthened the concrete, while vermiculite weakened it badly, as shown in Table 4. The other sorbents had less effect.

Although there are no standards for compressive strengths of concrete waste forms, this and earlier work at SRL showed that 1000 psig may be a reasonable lower limit. Concrete castings with lower compressive strengths often crumbled easily during handling. Strong waste forms are desirable for greater safety during transportation and storage.

The results of the strength tests showed that acceptably strong concrete waste forms containing up to 40 wt % simulated sludge can be made. Also, in the presence of sludge, AW-500 and Z-900 (the best cesium sorbents) strengthen the concrete.

Leaching Tests

Concretes containing various cesium sorbents were tested for leachability. The sorbents were each loaded with 0.5 meq cesium/g sorbent, spiked with ^{137}Cs as tracer. 2.00 g of washed, cesium-loaded sorbent, 66.0 g of HAC cement, and 32.0 g of simulated sludge were mixed. Water was added slowly to the mixture to achieve good workability, with water-to-cement ratios ranging from 0.5 to 0.6. The wet mixtures were poured into plastic tubes, capped, and cured as before. After at least one month, they were removed from the tubes. Two pieces (1-in. diameter and 1-in. long) were cut from each casting. Each piece was weighed, its surface area was determined, and it was then leached in 268 ml of distilled water.[3] The leach water was changed after 2 hours, 6 hours,

TABLE 2

Effect of Sludge on Compressive Strength of HAC Concrete

% Simulated Sludge[a]	*Compressive Strength, psig*
0	6900
10	3400
20	2800
30	2300
40	1500

a. 50 mole % $Fe(OH)_3$, 25% $Al(OH)_3$, and 25% MnO_2.

TABLE 3

Effect of Sorbents on Compressive Strength of HAC Concrete

Sorbent[a]	*Compressive Strength, psig*
None	6900
AW-500	5400
Z-900	5400
Clinoptilolite	3200
Z-500	3100
Z-200	1400
AW-300	1000
Vermiculite	1000

a. 10 wt % in concrete.

and 1, 3, 7, 14, and 28 days. The water removed was analyzed for cesium by gamma ray spectroscopy. Each reported value is the average of the results from the two pieces.

Test pieces made with I-P cement were also tested. The original scope of the study included determining ^{137}Cs leachabilities as a function of sludge loadings to gain additional information on the relative leachabilities of HAC and I-P concretes. The I-P concrete castings were made with 80 g of cement, 18.0 g of sludge, and 2.00 g of cesium-loaded sorbent, and tested in the same manner as the HAC concretes. The scope of the study was subsequently reduced, and other sludge loadings were not studied. Therefore, results from leaching I-P (18% sludge) waste forms are not directly comparable to HAC (32% sludge) results.

Table 5 shows the fraction of cesium leached after 28 days from HAC concrete containing various sorbents. In the order of increasing leachability (Table 5), which is the inverse of effectiveness as sorbents, vermiculite was more effective as a sorbent than would be predicted.

Figures 5 and 6 show the cumulative fraction of cesium leached and the leachabilities of HAC concretes. Figures 7 and 8 show the same data for I-P waste forms. The fraction leached was calculated as VC/C_o, where V is the volume of leach water (268 ml), C is the cesium concentration in the leach water, and C_o is the total amount of cesium originally in the concrete section. The cumulative fraction is the sum of the individual fractions.

Leachability (L) was calculated by the equation:

$$L = \frac{mVC}{AC_o \, \Delta t} \, , \; g/(cm^2)(day)$$

where m is the mass of the concrete piece; A its surface area in cm^2; Δt the leach time in days; and V, C, and C_o are as stated above.

As shown in Figures 5 through 8, the leachabilities of the concretes containing AW-500 and Z-900 differ slightly in their reaction with leach time. AW-500 concretes had lower initial leachabilities, while the leachabilities of Z-900 concretes decreased more quickly. However, the cumulative fractions of cesium leached after 28 days were about the same.

TABLE 4

Effect of Sorbents on Compressive Strengths of Concrete Containing Simulated Sludges

Sorbent[a]	*Compressive Strengths, psig*	
	HAC	*I-P*
None	1200	2300
Z-900	2100	3200
AW-500	2000	3200
Z-200	1900	2300
Clinoptilolite	1700	3100
Vermiculite	400	1100

a. 10 wt % sorbent, 30 wt % simulated sludge.

TABLE 5

Leaching of Concretes

Sorbent[a]	*% Cesium Leached After 28 Days*	
	HAC	*I-P*
AW-500	5.7	4.6
Z-900	6.0	3.9
Vermiculite	6.3	3.8
Z-500	6.5	4.5
Z-200	9.1	6.5
Clinoptilolite	13.1	9.2
AW-300	17.9	9.3

a. 2 wt % in concrete.

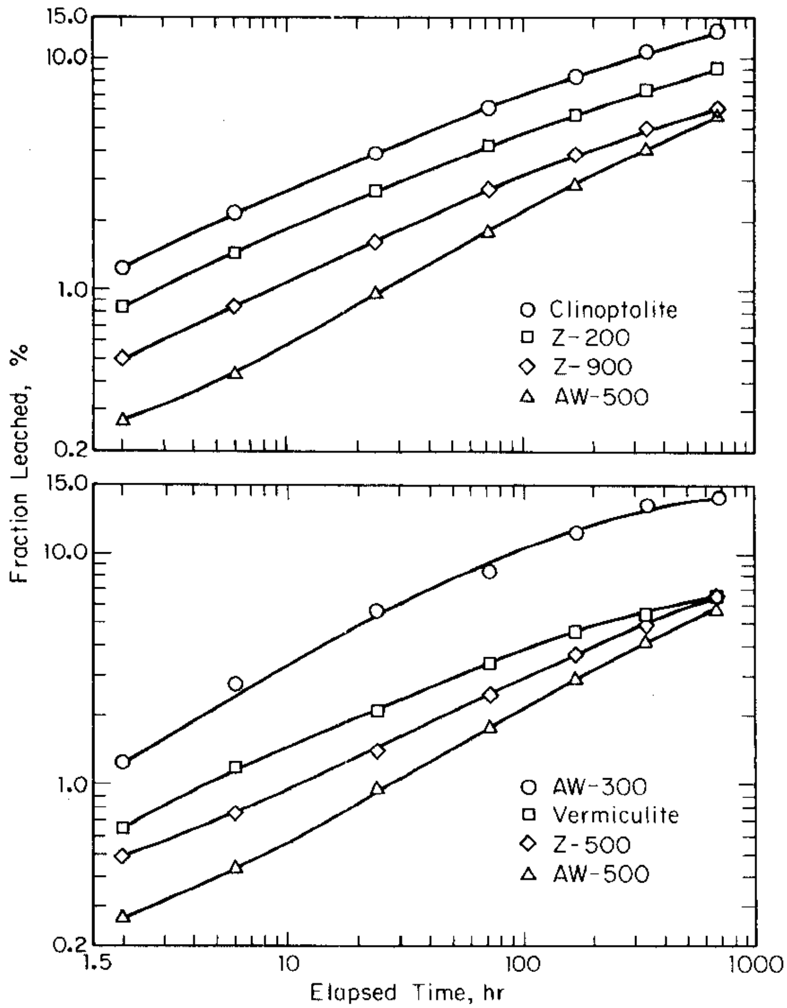

FIGURE 5. Fraction of Cesium Leached from HAC Concrete Containing Various Sorbents

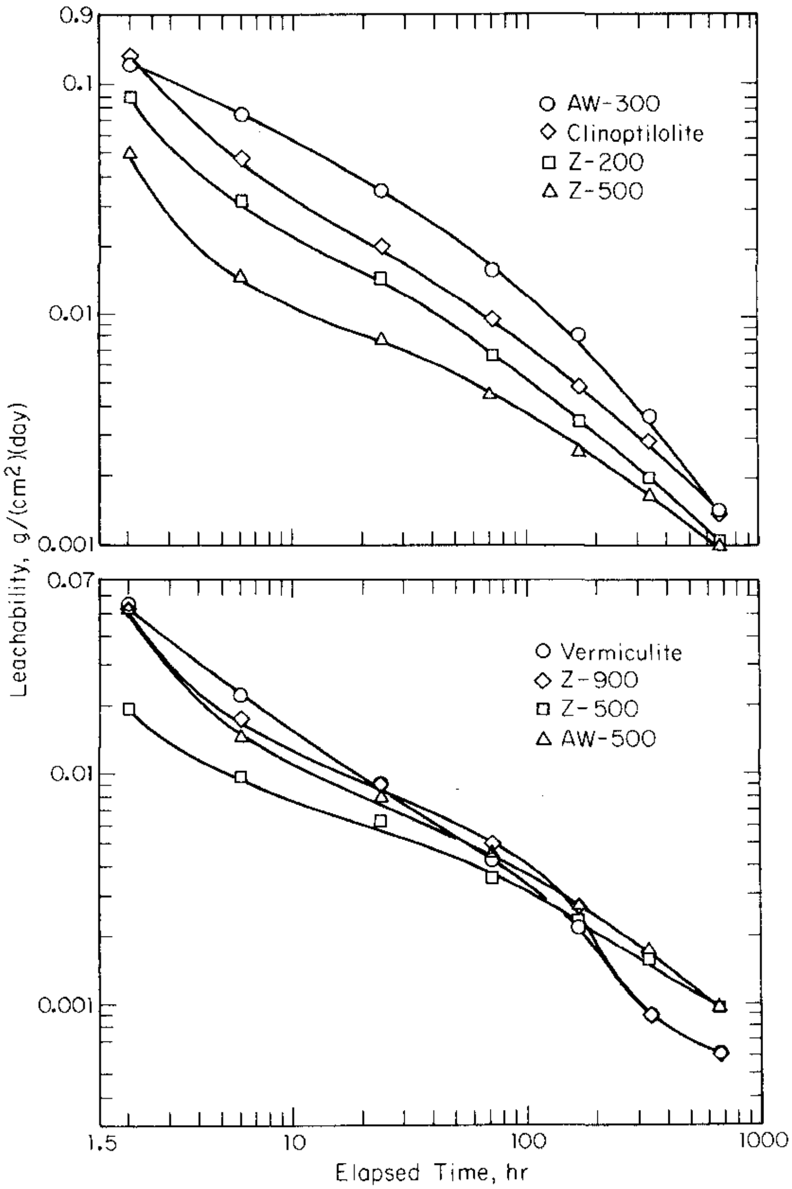

FIGURE 6. Cesium Leachability of HAC Concrete Containing Various Sorbents

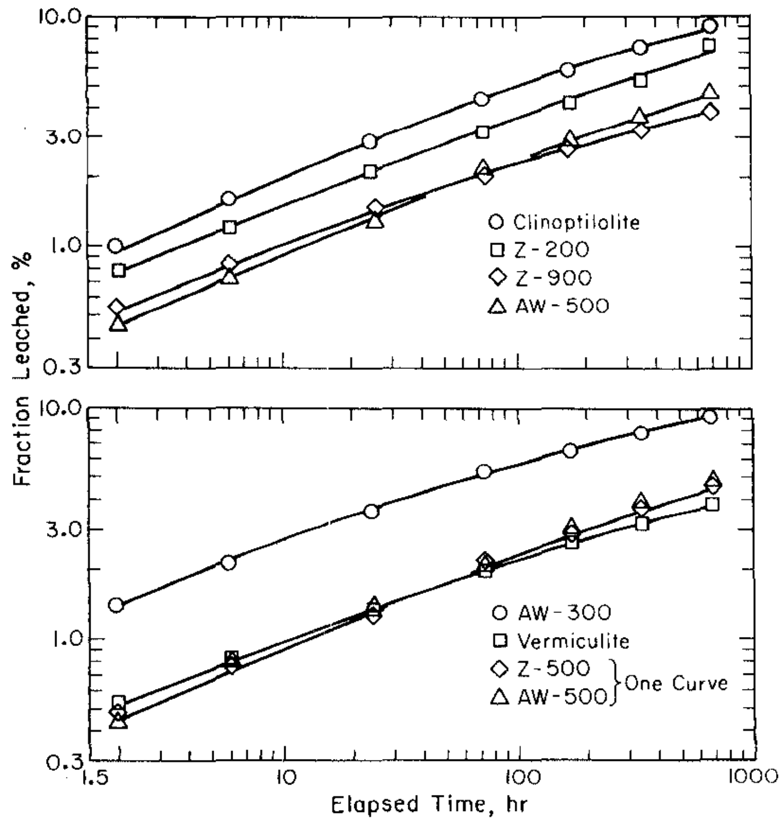

FIGURE 7. Fraction of Cesium Leached from I-P Concrete Containing Various Sorbents

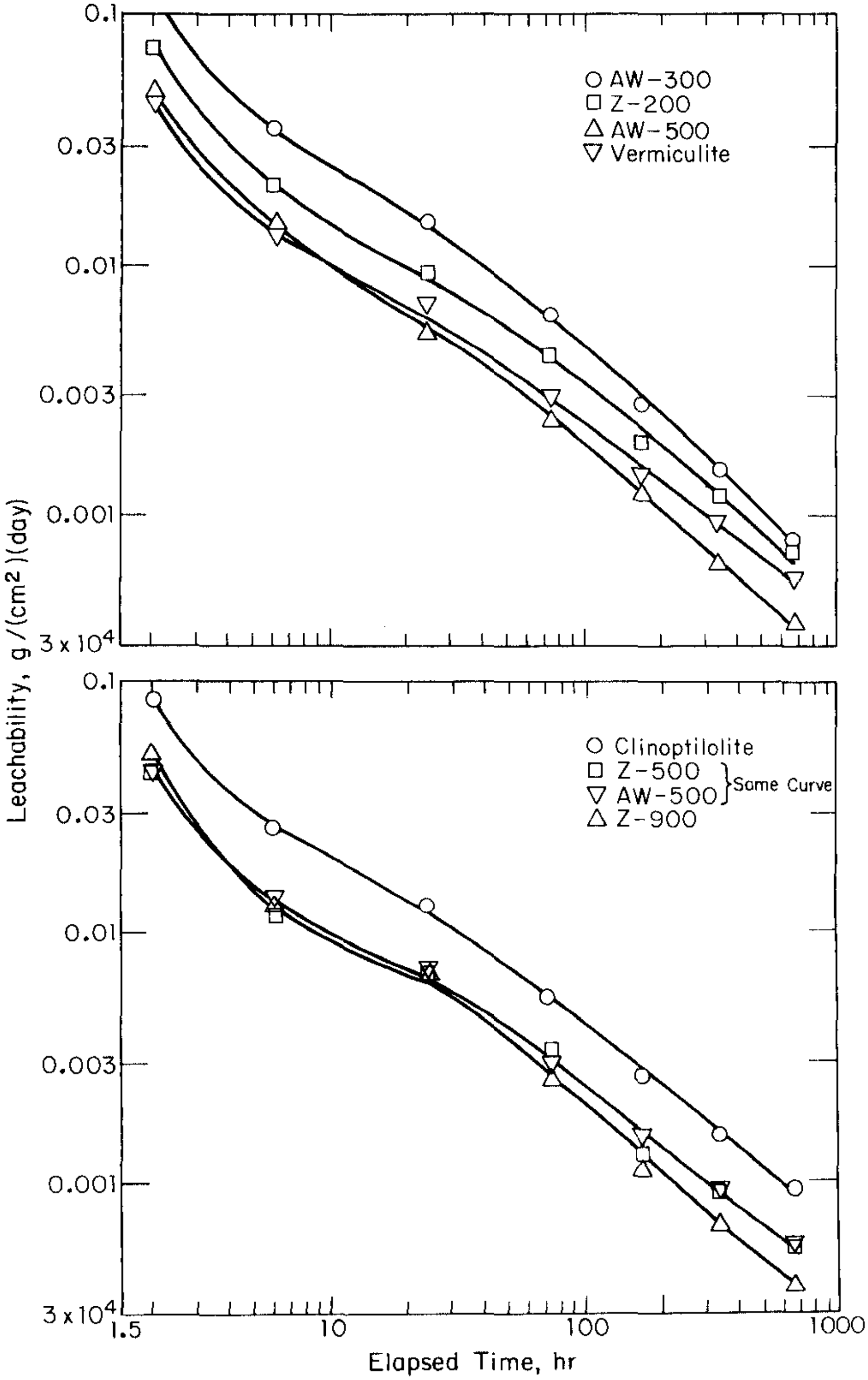

FIGURE 8. Cesium Leachability of I-P Concrete Containing Various Sorbents

HEAT TREATMENT OF VERMICULITE

Although the sorption rate of cesium onto vermiculite was slow, additional tests were made to determine whether heat-treated vermiculite would produce a less-leachable concrete. These tests showed that the fraction of cesium leached from vermiculite-containing concrete in 28 days could be reduced by ∿50% by heat treatment of the vermiculite (Figures 9 and 10), but that concretes containing vermiculite are weak (Figure 11).

Untreated vermiculite is lamellar, with layers spaced about 14 Å apart, which sorb cesium in between and at the edges. Possibly, cesium is also sorbed at localized binding sites within layers, but this type of sorption is much less important.[9,10]

Other workers[9,10] showed that sorption of potassium and subsequent heating caused collapse of the vermiculite (lattice) to illite, more closely confining the potassium ions. The heated vermiculite was much more resistant to exchange of sodium for potassium.

Two 2.00-g samples of vermiculite were loaded with cesium (as in Sorption Tests). Both samples were heated at 215 ±5°C; one for 48 hours, the other for 115 hours. Each was then incorporated in concretes containing 80 g of I-P cement and 18 g of simulated sludge. Leaching tests were performed as with unheated vermiculite.

Figures 9 and 10 compare the cesium leachabilities of and the cumulative fraction leached from I-P concretes containing heated or unheated vermiculite. As shown in Figure 9, the fraction of the cesium leached was almost halved by heating the vermiculite. However, the difference between heating 48 hours and heating 115 hours was small.

To test the effect of heating vermiculite on compressive strengths of concretes, four 4.00-g samples of cesium-loaded vermiculite were heated at 215 ±15°C, for 18 to 120 hours. Each sample was then incorporated into an HAC concrete of the same composition as above. Figure 11 shows the strength dependence of these materials on heating time. Heating the vermiculite increased the compressive strength of the resulting concrete linearly up to ∿60 hours. Longer heating had no additional effect. All concretes containing vermiculite were weak.

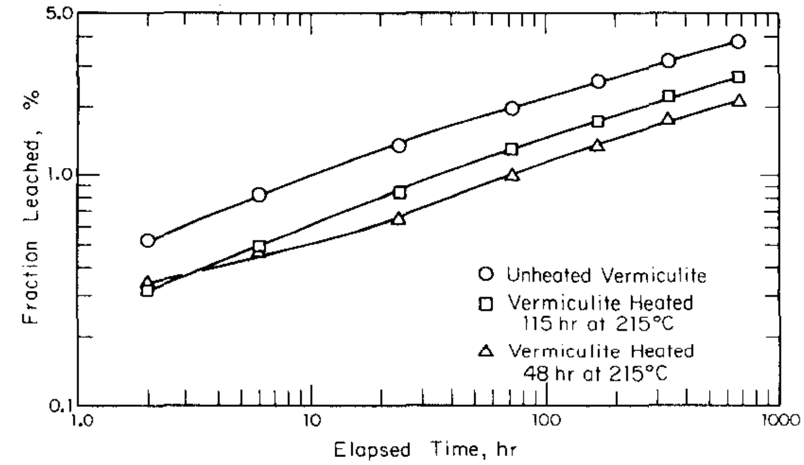

FIGURE 9. Fraction of Cesium Leached from I-P Concrete Containing Heated and Unheated Vermiculite

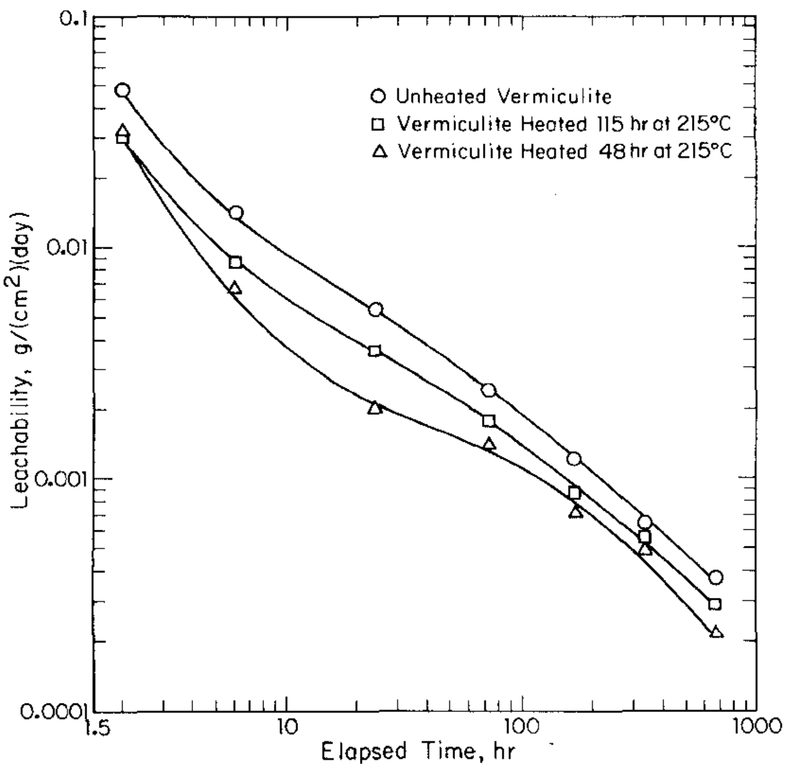

FIGURE 10. Cesium Leachability of I-P Concrete Containing Heated and Unheated Vermiculite

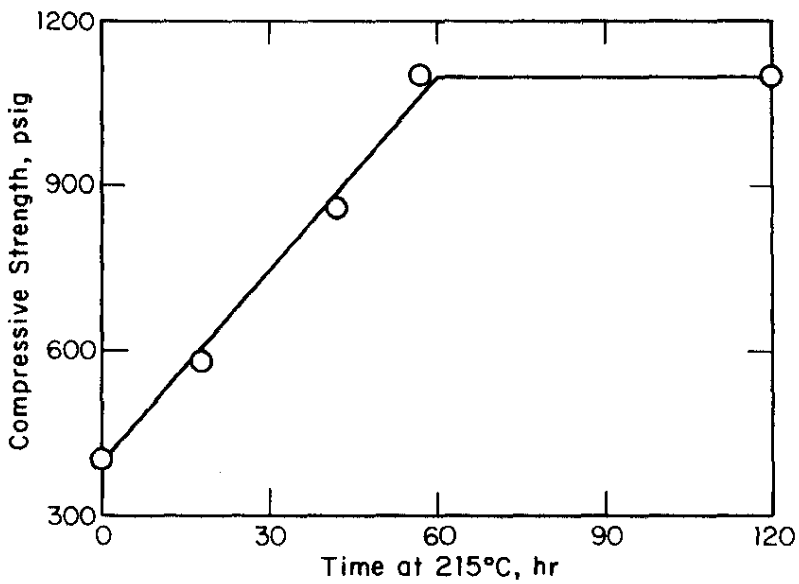

FIGURE 11. Compressive Strengths of HAC Concrete Containing Heated Vermiculite

ADDITION OF SILICA GEL

Other workers[11,12] have shown that addition of silicates to cements reduces free calcium in the final product. It was postulated that free calcium in concrete might displace cesium from the zeolite or other ion exchange sites in the concrete-sludge mixture. Therefore, by reacting the calcium with silica gel, cesium might be more tightly held in concrete. This postulate was tested by adding silica gel to concretes containing sludge and sorbents.

HAC waste forms containing simulated sludge, cesium sorbents (AW-500, Z-900, Z-500, and clinoptilolite), and 6 wt % silica gel were made and leached (as in Leaching Tests). As Table 6 shows, addition of silica gel does not make the concretes more leach-resistant.

TABLE 6

Effect of Silica Gel on Leaching of HAC Concretes

Sorbent	*Fraction Leached, %*[a]
AW-500	5.6
AW-500 plus silica gel	9.6
Z-900	6.0
Z-900 plus silica gel	6.8
Z-500	6.5
Z-500 plus silica gel	10.7
Clinoptilolite	13.1
Clinoptilolite plus silica gel	9.4

a. After 28 days leaching.

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