

EFFECTS OF PHASE COMPOSITION ON THE CESIUM LEACHABILITY OF CEMENT-BASED WASTE FORMS

Susan Hoyle and Michael W. Grutzeck
Materials Research Laboratory
The Pennsylvania State University

ABSTRACT

Although portland cement has long been used as an encapsulant/host phase for a variety of radioactive waste streams, the phase chemistry/stability relations which exist are still poorly defined. It was our objective to investigate low temperature phase relations, predominantly in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$, in order to better understand the underlying physical/crystal chemical principles which ultimately govern the leachability of a given ion. The present paper, dealing with cesium leachability, is the first in a series of such papers.

A series of mixtures in the vicinity of Stratling's compound ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot 8\text{H}_2\text{O}$) were prepared from Type I portland cement, calcium aluminate cement and condensed silica fume. Samples were formulated using either deionized water or deionized water containing added cesium hydroxide. After curing at 38°C in sealed glass jars, the samples were characterized via compressive strength, x-ray diffraction and scanning electron microscopy. Cesium leachability of 28-day cured samples was determined using a modified MCC-1 leach test. Solutions were analyzed for Ca, Al, Si, Na, K and Cs.

All samples were found to be as strong if not stronger than their non-cesium containing counterparts. Leaching results indicated that the enrichment of the bulk composition of a mixture in silica and/or alumina enhanced cesium retention. Phase and composition data were used to construct a highly schematic, phase equilibrium diagram for the lime-rich section of the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. Leach data are evaluated in terms of proposed phase assemblages. Phases responsible for cesium retention may include Stratling's compound, Al-substituted calcium-silicate-hydrate, Si-substituted hydrogarnet and a yet unidentified cesium-containing hydrate.

INTRODUCTION

Due to its availability, low cost and ease of use, portland cement has long been used as an encapsulant for radioactive waste. However, portland cement is a relatively poor host for cesium which, because of size and charge considerations, is one of the most difficult ions to isolate. Cesium retention has been improved by adding colloidal silica to the cement paste¹, but the underlying reason for the improvement is not yet clear. Is the cesium adsorbed onto the surface of the colloidal silica¹ or is the cesium incorporated in an existing or new cesium-containing phase²? This uncertainty arises in part due to the poor definition of the low temperatures (less than the critical point of water) phase relations in the quaternary system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$; the lime-rich corner of this system is directly applicable to the hydration of portland cement. In the past, the majority of research has focused on the compositional areas in the immediate vicinity of portland cement. Most studies have reported an improvement in cesium retention as fly ash³, silica fume, clay or zeolites⁴ have been added to modify the bulk composition of portland cement. We feel that these improvements are a direct relationship of the phases present. It was our objective to determine phase relations for adjusted bulk compositions in the vicinity of Stratling's compound ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot 8\text{H}_2\text{O}$) and to determine the suitability of less lime-rich, aluminosilicate hydrates in general for the fixation of cesium. Would they be better hosts than portland cement itself?

Five mixtures, having varying compositions, were formulated from portland cement, calcium aluminate cement and condensed silica fume. After mixing with deionized (DI) water or DI water containing cesium hydroxide, the mixtures were allowed to cure at 38°C . Samples were characterized as a function of time starting at 3 and ending at 90 days. Cesium leachability for 38-day, 38°C cured samples was determined using a modified MCC-1 leach test⁵. Triplicate

solution samples obtained at 3, 7, 14, 28, 56 and 90 days were analyzed for Ca, Al, Si, Na, K and Cs. On occasion, pH was also measured.

All samples were cementitious, the cesium hydroxide apparently enhancing the strength of the samples. Leaching data indicated that the enrichment of a mixture in silica and/or alumina enhanced cesium retention. Relatively speaking, high calcium content is apparently correlated to high cesium leachability. Phase and composition data were used to construct a schematic, phase equilibrium diagram for the lime-rich part of the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. Phases responsible for cesium retention may include Stratling's compound, Al-substituted calcium-silicate-hydrate (C-S-H), silica-substituted hydrogarnet ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$) and a yet unidentified cesium-containing hydrate.

EXPERIMENTAL PROCEDURE

Compositions of the five mixtures were chosen in such a way that the ratio of two major components were held constant while the third was varied (see Fig. 1). For example, compositions 3, 4 and 5 have the same CaO/SiO_2 ratio, but a varying Al_2O_3 content. Mixtures 1 and 3 have the same $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio, but a varying CaO content, etc. Starting materials were Type I portland cement, calcium aluminate cement and condensed silica fume (see Table I for their chemical analyses). The mixtures (see Table II for their formulations) were dry blended and mixed with either DI water or with DI water containing 5 g $\text{CsOH}/100$ g H_2O using a modified ASTM C 305 mixing procedure.

Compressive Strength, X-ray Diffraction and Scanning Electron Microscopy

For the compressive strength tests, the water to solid (w/s) ratio was maintained at 0.3 except for Mixture 5 which was too thick to work despite the addition of a superplasticizer/retarder. Therefore the water/solid ratio for Mixture 5 was increased to 0.5.

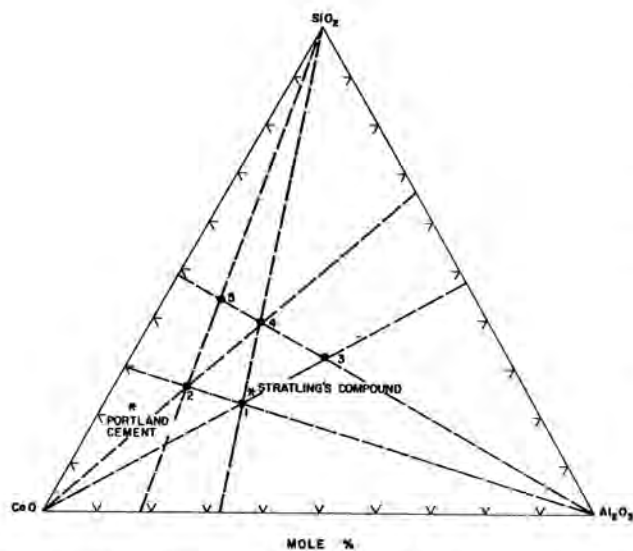


Fig. 1. Compositions of mixtures 1-5 in terms of major oxides.

In this study, two sets of samples were prepared: one doped with cesium hydroxide, the other undoped. Once mixed the pastes were cast into cylindrical molds 25mm in diameter by 50mm in length and cured at 38°C in sealed glass jars. Compressive strength was measured using a Tinius Olsen hydraulic press at 7, 28 and 56 days. After testing, some of the shards were freeze dried for later examination by x-ray diffraction (Rigaku DMAX) and scanning electron microscopy (SEM) [ISI DS 130 microscope equipped with electron dispersive x-ray (EDX) analytical capabilities]. In addition to compressive strength samples, leached samples were also subjected to x-ray and SEM analysis, both prior to and after leaching in order to monitor phase stability/degree of hydration.

TABLE I
Chemical analyses of starting materials.

wt.% oxide	portland cement type I	calcium aluminate cement	condensed silica fume
SiO ₂	20.84%	0.68%	95.32%
Al ₂ O ₃	4.10	71.3	0.02
TiO ₂	0.27	0.01	<0.01
Fe ₂ O ₃	2.90	0.09	0.08
MgO	4.05	0.46	0.19
CaO	63.84	26.80	0.38
MnO	0.21	<0.01	<0.01
SrO	0.05	0.02	<0.01
BaO	0.02	0.01	<0.01
Na ₂ O	0.07	0.37	0.08
K ₂ O	0.74	0.02	0.55
P ₂ O ₅	0.21	0.05	0.06
SO ₃	2.67	0.04	0.24
LOI	1.32	0.70	3.05
RbO	<0.01	<0.01	<0.01
Cs ₂ O	<0.01	<0.01	<0.01
Totals	101.27%	100.50%	99.91%

Leach Testing

The cesium-retaining capacity of the five formulations were evaluated using a modified MCC-1 leach test⁵. The cement pastes were mixed in the same manner as the compressive strength samples, but with a w/s of 0.6. The pastes were cast in cylindrical molds

TABLE II
Formulation of Mixtures 1-5 (grams)

Component	Mixture				
	1	2	3	4	5
portland cement	164	269	36	141	216
calcium aluminate cement	194	92	269	157	72
condensed silica fume	42	39	94	110	122
superplasticizer with retarder	5.2	5.2	7.8	7.8	7.8
water ^a	120	120	120	120	205

^aWater/solid (w/s) ratios were varied depending upon anticipated testing. Compositions of compressive strength samples are given in the table. Since these were rather viscous samples, each samples were prepared using a w/s ratio of 0.6.

with a diameter of 16.7mm. After curing for 28 days at 38°C in sealed jars, the samples were removed from the molds and cut to appropriate size using a low-speed diamond saw. The surface area of the resultant specimens were approximately 660mm² (±2.5%). The samples were ultrasonically cleaned in alcohol, weighed, then placed in individual Teflon containers along with 55ml of deionized water maintained at 38°C. A total of 18 samples, three for each time period (3, 7, 14, 28, 56 and 90 days), were used. The containers were weighed and placed in 38°C chamber. For each time period, three samples were removed from solution and allowed to air dry for 12 hours before reweighing and freeze drying. The freeze-dried samples that were unleached, leached for 3 days and 90 days were analyzed using x-ray and SEM techniques. The pH of the leachates was measured, the leachates were acidified with HCl and sealed for analysis. Leachates were analyzed for Ca, Al, Si, Na and K content using a DC-plasma emission spectrophotometer (Beckman/SKIIIB). The cesium content of the solutions was determined by atomic absorption analysis (Perkin Elmer 703).

RESULTS

Compressive Strength and X-ray Diffraction Data

The compressive strength of the undoped and doped samples was measured to determine if the cement pastes were cementitious and to determine the effect of cesium hydroxide on the compressive strength. The results of these tests are given in Table III. All samples were cementitious and had more than sufficient strength to form a free-standing monolith. These data are consistent with earlier studies^{6,7}. The addition of CsOH to the cement mixtures had a varied effect on the compressive strength. For Mixture 1 the CsOH reduced the compressive strength substantially at 7 days, however, it also prevented the retrograde strength development at 28 days displayed by the undoped mixture. For the other mixtures the CsOH samples had compressive strengths comparable to or larger than the undoped samples and often reduced retrograde strength loss seen in the undoped samples.

Examination of shards from the undoped samples by x-ray diffraction techniques revealed that the primary phases present were Stratling's compound, Si-substituted hydrogarnet, calcium-silicate-hydrate (C-S-H), gibbsite and anhydrous portland cement (Table IV). As was expected the relative amounts of the phases varied with bulk composition of the paste so that Mixtures 2 and 5 were the only ones containing significant amounts of C-S-H gel, Mixture 5 having a larger amount. Likewise

TABLE III
Compressive strength (MPa) of Mixtures 1-5
as a function of time.^a

Time (days)	Mixture				
	1	2	3	4	5
	Undoped				
7	45	24	28	38	10
28	12	29	24	44	41
56	53	45	41	13	19
	Cesium Doped				
7	18	41	35	32	23
28	15	57	27	32	40
56	22	73	23	40	32

^aValues given are an average of two determinations. Water/solid ratios were fixed at 0.3 except for Mixture 5 which was increased to 0.5 in order to mitigate rapid thickening.

TABLE IV
56-Day x-ray diffraction data for undoped
compressive strength samples.

Phases	Mixture				
	1	2	3	4	5
hydrogarnet	X	X	X	X	Tr
Stratling's compound	X	X	X	X	Tr
C-S-H		Tr			X
gibbsite			X		
anhydrous cement	X	X	Tr	X	X
unknown	Tr		Tr		

X = significant Tr = trace

Mixture 3 had the smallest amount of anhydrous cement and the most gibbsite present. The higher silica content mixtures were generally less crystalline signifying the presence of more C-S-H gel. All mixtures contained Stratling's compound. When present, the diffraction peaks for hydrogarnet were shifted toward higher angles, towards those of grossular, as a function of time and increasing silica content of the mixture. The formation of a Si-substituted hydrogarnet at low temperatures has recently been reported by Midgley and Rao⁵, and Abo-El-Enein et al.⁸ in their studies of Stratlingite-related mixtures.

Leach Data

The cesium content of the leachates as a function of time is given in Figure 2. Based on our original experimental design (Figure 1) groups of these data should reflect changes directly attributable to the composition of a single oxide. In all cases, improvement in cesium leachability is achieved by increasing silica content (cesium in leachate for Mixture 5 < 2, 4 < 1), and/or increasing alumina content (cesium in leachate for Mixture 1 < 2, 3 < 4 < 5). Relatively speaking, a high calcium content is apparently correlated with a high cesium leachability (cesium in leachate for mixture 4 < 2, 3 < 1).

Looking at the shapes of the curves, one is struck with their similarity. For example, curves for Mixtures 1 and 3 and also the curves for Mixtures 4 and 5 look very much alike. The curve for Mixture 2 looks

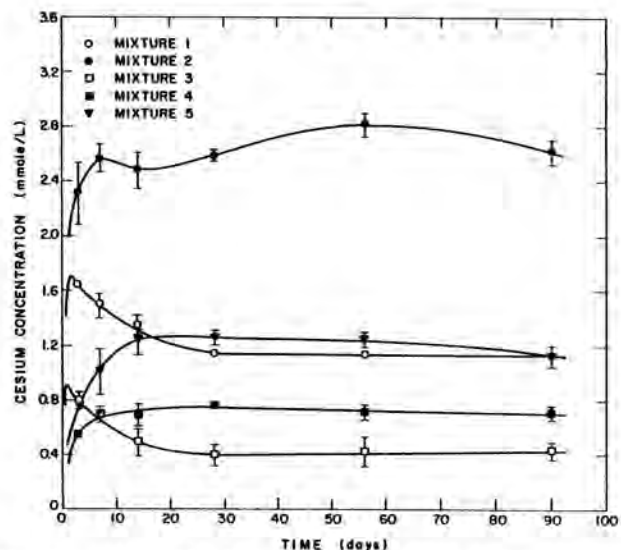


Fig. 2. Leach data for all cesium-doped compositions.

somewhat intermediate in behavior. The high initial concentration of cesium in solution prior to 3 days for Mixtures 1 and 3, suggest a washout of cesium, cesium concentrated in the pore solution of the cement rather than a hydrated phase. The low initial leachability of cesium from Mixtures 4 and 5 suggests the formation of a cesium host phase which gives up cesium more slowly. No "wash out" is observed.

Interestingly, once the cesium is in solution, for example, Mixtures 1 and 3, the solutions experience negative leach rates, suggesting the continued formation of a cesium-containing hydrate as the sample is leaching. We attribute the improvement in leachability, as one moves away from the lime corner (essentially ordinary portland cement), to the formation of phases such as Stratling's compound ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot 8\text{H}_2\text{O}$), Si-substituted hydrogarnet ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$), and C-S-H. In addition, it is also conceivable that yet unidentified cesium-containing zeolite-like or clay-like phases could be forming.

SEM Data

Representative scanning electron photomicrographs of an unleached and companion 90-day leached pellet for each mixture are presented in Figure 3. The photomicrograph of the unleached pellet of Mixture 1 (Fig. 3A) shows a pocket in the surface in which hydrogarnet crystals have grown with a cubic morphology similar to those described by Abo-El-Enein et al.⁸ and Sersale⁹. The identity of these crystals was verified by x-ray diffraction of some of the crystals from a similar pocket. Similar crystals, only slightly larger, are also present in the photomicrograph of the 90-day leached sample (Fig. 3B) along with toothlike calcite crystals. The calcite crystals might have formed from the reaction of calcium hydroxide and carbon dioxide in the deionized water used as leachant. The other photomicrograph for Mixture 1 (Fig. 3C) is another image of the calcite crystals at a higher magnification. The unleached pellet of Mixture 2 (Fig. 3D) had no hydrogarnet crystals on the surface, but after 90 days of leaching (Fig. 3E,F), the surface is covered with crystals similar to those in Mixture 1. In Mixture 2 the hydrogarnet crystals are surrounded by a gel-like phase which shrank away from the hydrogarnet upon drying (Fig. 3E). Mixture 2 appears to have the greatest amount of hydrogarnet on its surface. The photomicrographs of Mixtures 3, 4 and 5 (Figs. 4G,J,M) show the presence of little or no hydrogarnet for the

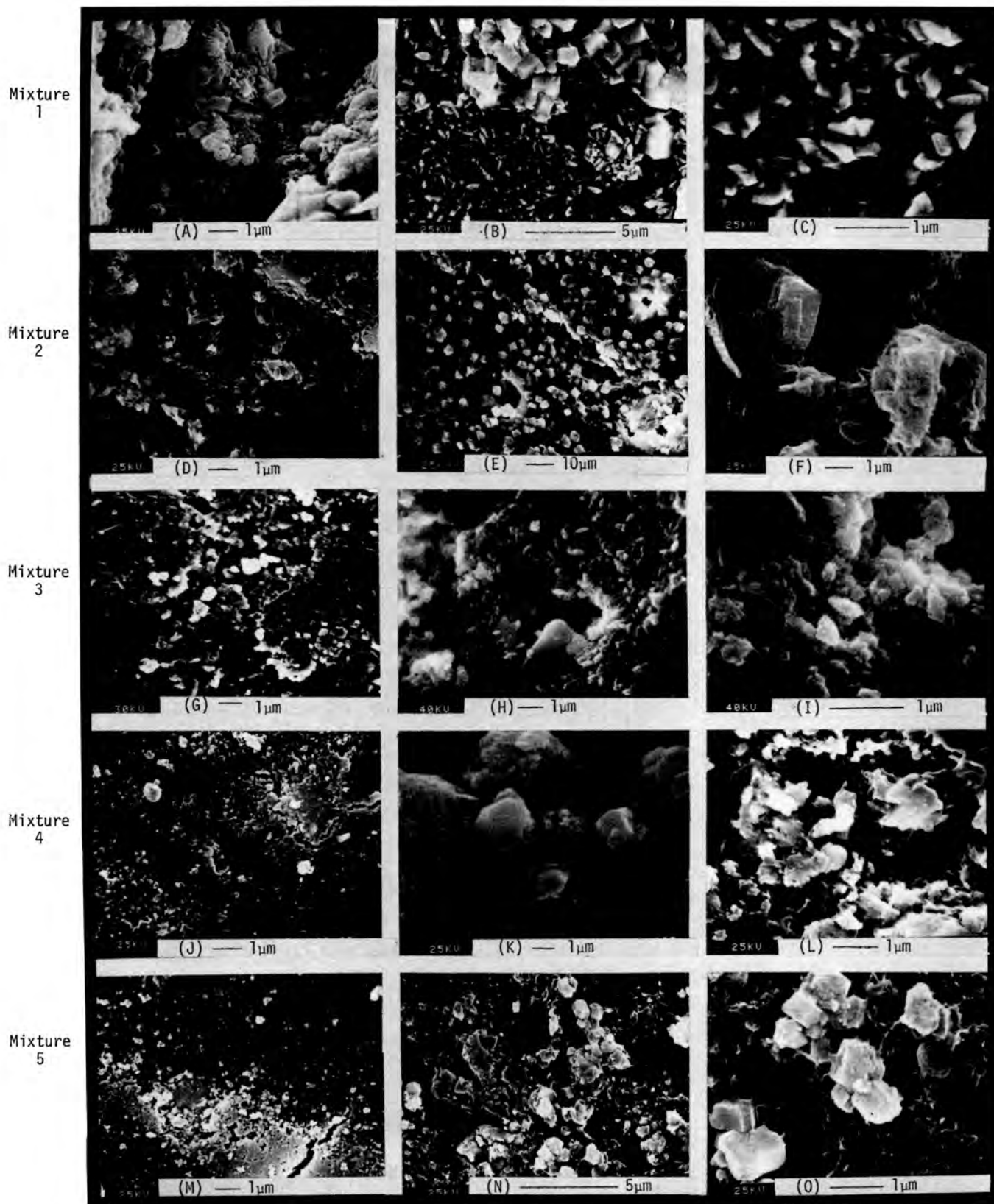


Figure 3. Scanning electron photomicrographs of unleached (left) and companion 90-day leached pellets (center and right) for Mixtures 1-5.

unleached pellets. At 90 days a few are present (Figs. 3I,K,O) but not as ubiquitous as in Mixture 2. The hydrogarnet in Mixture 5 (Fig. 3O) is surrounded by a gel phase that may be C-S-H gel.

Discussion

X-ray diffraction data for compressive strength, leached and unleached samples, indicate that the primary phases present are Stratling's compound, C-S-H gel, Si-substituted hydrogarnet and gibbsite. Previous studies on Stratlingite-related compositions⁶⁻⁸, have shown the presence of a Si-substituted hydrogarnet¹⁰ approaching that of katoite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot 4\text{H}_2\text{O}$) recently described by Sacerdoti and Passaglia¹¹. Our experience showed that the silica content of the hydrogarnet increased with time, but never quite reached the 1:4 $\text{SiO}_2/\text{H}_2\text{O}$ ratio present in katoite.

The leach data indicate that the cesium retention of portland cement-based waste forms can be increased by modifying the bulk composition of the formulation with additions of silica and/or alumina (fly ash, silica fume, slag, etc.). We feel that the leach data reflect the degree of hydration of the host formulation and its progress towards an equilibrium situation. It is suggested that hydrogarnet forms first and later converts to a Si-substituted hydrogarnet, additional Stratling's compound and/or some Si-rich phase such as a zeolite or clay precursor. The kinetics of this transformation are certainly related to the relatively low solubilities of silica and alumina in solution. Perhaps this argument can be used to explain the observed leach behavior of cesium. The slow formation of Stratling's compound containing Cs+Al rather than Si and a Si-substituted hydrogarnet, which is a potential host for cesium via a Cs+Si for a Ca+Al substitution, could explain the observed negative leach data for Mixtures 1 and 3. These are also the mixtures which contain gibbsite rather than C-S-H.

These data have been used to construct the highly schematic, phase equilibrium diagram given in Figure 4. We have included the before-mentioned shift in the hydrogarnet peaks as indicating a limited solid solution. The differences between Mixtures 1 and 3 (gibbsite) and 2, 4 and 5 (C-S-H), suggests a boundary of some sort between these mixtures. Since the nature of the unknown phases in Mixtures 3 and 4 are different, we have included a 3-phase area between the mixtures, rather than a single boundary. The data are internally consistent except for the ubiquitous presence of hydrogarnet, much of which, in light of the diagram and data, we feel is metastable.

The diagram implies that the C-S-H which forms in lime-poor formulations, is richer in silica and alumina than the C-S-H normally found in hydrated portland cement. Since a Cs+Al substitution in tobermorite has been recognized², such a substitution could also apply to our C-S-H. This may explain the improvement in cesium leach data which occurs relatively early in Mixtures 2 and 5, rather than the aluminosilicate hydrate conversion seen later in Mixtures 1, 3 and 4.

Unfortunately, at these temperatures, the phase relations in the silica-rich corner of the diagram (Fig. 4) are unknown. However, we are able to speculate that groups of clays, zeolites and silica gel itself are potential host phases for cesium which may in fact be in equilibrium with C-S-H or Stratling's compound. If this is true, the improvement in cesium retention of the less lime-rich phases might be explained in terms of the formation of one of these phases. Experimental work in this area is continuing.

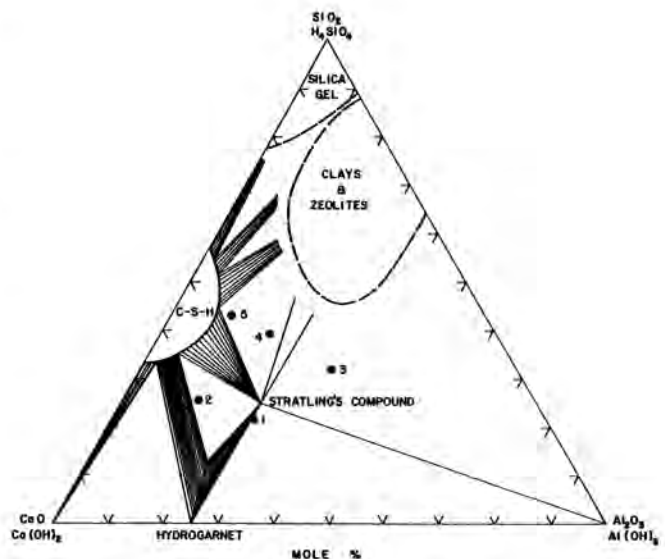


Fig. 4. Schematic representation of possible low temperature phase relations in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. Hydrates in equilibrium with excess water have been projected onto the anhydrous base. Numbered, solid circles, represent compositions of mixtures studied.

ACKNOWLEDGMENTS

We would like to acknowledge the Department of Energy for their continuing support. The senior author (SH) was a recipient of a stipend under the Nuclear Waste Technology Traineeship Program (DOE Grant No. DE-FG01-83NE44503) and later funded under Contract No. DE-AC02-83ER45013 and Grant No. DE-FG02-84ER45145 both to MWG.

REFERENCES

1. C.E. McCULLOCH, A.A. RAHMAN, M.J. ANGUS, F.P. GLASSER and R.W. CRAWFORD, "Immobilization of Cesium in Cement Containing Reactive Silica and Pozzolans," *Advances in Ceramics: Nuclear Waste Management*, Vol. 8, p. 413, Am. Ceram. Soc. (1984).
2. S. KOMARNENI and D.M. ROY, "New Tobermorite Cation Exchangers," *J. Mat. Sci.* 20, p. 2930 (1985).
3. C.E. McCULLOCH, M.J. ANGUS, R.W. CRAWFORD, A.A. RAHMAN, and F.P. GLASSER, "Cements in Radioactive Waste Disposal: Some Mineralogical Considerations," *Miner. Mag.* 49, p. 211 (1985).
4. H. MATSUZURA and A. ITO, "Immobilization of Cesium-137 in Cement-Waste Composites by Addition of Mineral Zeolites," *Health Phys.* 34, p. 643 (1977).
5. Materials Characterization Center. *Nuclear Waste Materials Handbook*, DOE/TIC-11400, Pacific Northwest Laboratory, Richland, WA (1981).
6. H.G. MIDGLEY and P. BHASKARA RAO, "Formation of Stratlingite, $2\text{CaO}\cdot\text{SiO}_2\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$, in Relation to the Hydration of High Alumina Cement," *Cement Concrete Res.* 8, p. 169 (1978).

7. P. BHASKARA RAO and V.N. VISWANATHAN, "Chemistry of Arresting Strength Retrogression in Structural High Alumina Cements," 7th intl. Congress on the Chemistry of Cement, Paris, 1980, Vol. III, p. V51, Editions, Septima, Paris (1980).
8. S.A. ABO-EL-ENEIN, N.A. GABR and S. Sh. MIKHAIL, "Morphology and Microstructure of Autoclaved Slag-Clinkered Pastes in Presence and Absence of Silica Sand," Cement Concrete Res. 7, p. 363 (1977).
9. RICCARDO SERSALE, "Habitus Cristallino Degli Alluminati di Calcio Idrati," La Ricerca Scientifica 27, p. 777 (1957).
10. R. BASSO, "Crystal Chemistry and Crystallographic Properties of Compounds with Garnet or Hydrogarnet Structure," N. Jb. Mineral. Mh. 1985, p. 108 (1985).
11. M. SACERDOTI and E. PASSAGLIA, "The Crystal Structure of Katoite and Implications within the Hydrogrossular Group of Minerals," Bulletin Minéral. 108, p. 1 (1985).