

PHASE CHARACTERIZATION OF CEMENTITIOUS COMPONENTS OF A WASTE REPOSITORY AND THE POTENTIAL OF INDIVIDUAL PHASES FOR SORPTION OF RADIOISOTOPES

S. Aggarwal, M. J. Angus and A. Tyson
AEA Technology, Windscale
Seascale, Cumbria
CA20 1PF

ABSTRACT

Various cement blends have been cured over a range of temperatures to accelerate aging, and have been characterized qualitatively and quantitatively to determine the phases present. Sorption measurements have been made with Cs and Pu to study the effect of phase changes caused by accelerated curing on sorption. A series of calcium silicate hydrates (C-S-H) representing the full range of C-S-H expected to be formed in aged cements has also been prepared. Sorption measurements on these materials have been compared with sorption on cement. Sorption of Cs and Pu on C-S-H accounts for most of the sorptive properties of the cements studied.

INTRODUCTION

Cement grouts based on ordinary Portland cement are to be used in the formulation of matrices for the encapsulation of intermediate-level wastes, in repository structural components and in backfill materials. Many of these grouts will include the following basic constituents: Ordinary Portland cement (OPC), blast furnace slag (BFS) and pulverized fuel ash (PFA). In turn, each of these consists of a number of components the relative proportions of which may vary depending on source of supply, as well as production process parameters.

Hydrated cement blends consist of several individual hydrated phases, any one (or more) of which may be responsible for sorption of isotopes of a particular element. Furthermore, cements continue to age over very long time-scales so the phases present after one year's hydration may be different from those present after one thousand years. The number of variables in the compositions of cements to be used in repository is therefore large. Indeed, it is not known whether sorption measurements made on freshly prepared cement samples are relevant to the long-term repository situation. A full appreciation of the phases responsible for sorption of particular isotopes and the mechanism of sorption by these phases is therefore desirable. Figure 1 demonstrates for the lime-silica-water system how mix proportioning, curing time and temperature can affect the products. Clearly, a cement-based system is potentially far more complex, as it contains a number of other minor elements which can either form additional phases or solid solutions with calcium silicate phases.

A series of 5 typical cement blends (3:1 and 9:1 BFS/OPC, 3:1 and 10:1 PFA/OPC and 6:1 lime-stone/OPC) hydrated at three temperatures (25, 60 and 110°C) have been characterized to determine qualitatively and, where possible, quantitatively the degree of hydration and the hydration products. The first three of these formulations will be used as encapsulating matrices for

UK intermediate-level waste, while the last two have been considered as backfill formulations for a deep underground repository, although they have since been rejected.

Calcium silicate hydrate (C-S-H) is the major hydration product formed in all these cement blends. In ordinary Portland cement, it is formed from hydration of the tricalcium silicate and dicalcium silicate components. In cements containing BFS and PFA, the additive contributes lime and/or silica to the C-S-H. C-S-H is a material of variable composition. The lime/silica (Ca/Si) ratio of the C-S-H formed will depend on the amount and reactivity of the additive used. In a hydrated OPC the Ca/Si ratio is likely to be around 1.5. The minimum Ca/Si ratio of C-S-H is 0.83 and this may be achieved by adding to the OPC a sufficient quantity of siliceous additive such as PFA. When C-S-H is first formed (i.e., within a few days of start of hydration), it is a gel-like material with no crystalline structure. After several months or years of aging, it

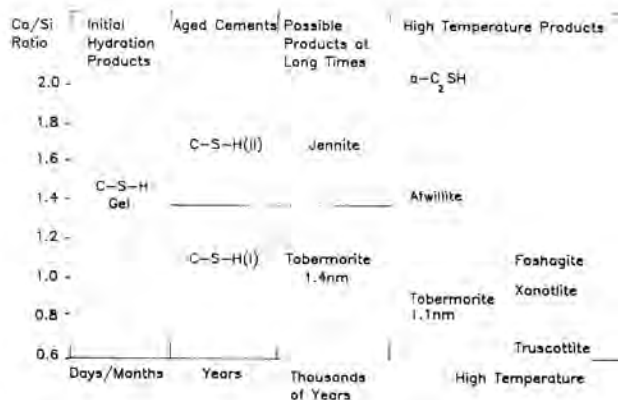


Fig. 1. Possible Phase Changes During Ageing/High Temperature Curing of Lime-Silica Slurries.

develops a quasi-crystalline structure. X-ray diffraction patterns identify two such structures, C-S-H(I) and C-S-H(II), depending on the Ca/Si ratio. Various theories have been suggested for the crystalline structure of C-S-H. Taylor (1) has concluded that in OPC, the C-S-H is a mixture of jennite-like ($C_9S_6H_{11}$) and tobermorite-like ($C_5S_6H_5$) layers. If this is the case, it seems likely that a C-S-H of high Ca/Si ratio would have a predominance of jennite-like layers, while a C-S-H of low Ca/Si ratio would be more similar to tobermorite. Figure 1 is intended to highlight this concept without necessarily implying that the final product of cement aging is either of these pure minerals. High temperature ($> 100^\circ\text{C}$) products are also included in this figure, based on Ref. 2. There is however no evidence that these would be produced in a deep underground repository. The hydrated calcium silicate phase in an aged cement is likely to lie somewhere between the two extremes of amorphous gel and a pure-crystalline phase. An understanding of sorption properties of this range of materials is therefore likely to contribute to the understanding of sorption on cement itself. It is recognized that there are many other possible phases in a cement cured over long periods and that C-S-H will contain other impurity elements in solid solution. The cement characterization work emphasizes this point, but also confirms that C-S-H is the main phase. For this reason, C-S-H was chosen for detailed study.

Samples of individual calcium silicate hydrates (C-S-H) have therefore been prepared. These synthetic materials form the full range of possible C-S-Hs likely to be found in cements cured at temperatures up to 100°C in terms of composition and crystallinity, as shown in Fig. 1.

Batch sorption experiments using plutonium-238 and cesium-137 have been carried out on the cements and the C-S-Hs. These radionuclides were chosen from the many radionuclides of concern to represent one actinide and one fission product. The results for the characterized cements are compared with those of the synthetic C-S-Hs to determine the importance of C-S-H in the overall sorption of cements.

PREPARATION OF C-S-H

Two methods of C-S-H preparation have been used:

1. Tricalcium Silicate Hydration. Tricalcium silicate (C_3S), the main anhydrous cement phase was prepared by firing a mixture of calcium oxide and quartz at 1500°C in a Pt crucible after first grinding with ethanol in an agate mortar to mix the particles of starting material intimately. The products were checked for purity by X-ray powder diffraction. A paste was then prepared by mixing C_3S with various amounts of silica fume along with sufficient water to give a smooth paste. The mixtures were then cured at either room

temperature or at 60°C to give a C-S-H product of the required Ca/Si ratio.

Although this method is likely to produce a paste containing some unreacted starting material as well as $\text{Ca}(\text{OH})_2$, its main benefit is that it is expected to produce C-S-H with morphological and surface characteristics as close as possible to that of real cements.

2. Lime-silica Slurry. In this method, calcium oxide and silica fume were mixed with an excess of water under a carbon dioxide atmosphere to give slurries of various Ca/Si ratios which were then cured at 60°C or 80°C . This method was used to produce tobermorite. The method was also chosen as a backup method for producing partially crystallized C-S-H (C-S-H[I] and C-S-H[II]).

CHARACTERIZATION OF CEMENTS AND C-S-Hs

The cements were characterized using X-ray diffractometry, differential thermogravimetry and gravimetric determination of degree of hydration. Electron microscopy has also been used to some extent. The results are summarized in Table I.

X-ray diffractometry was used to establish which phases were present in the hydrated pastes under study. Differential thermogravimetry was used to determine the amount of bound water (mainly in C-S-H), $\text{Ca}(\text{OH})_2$, CaCO_3 and any other peaks. Two gravimetric methods were used for determining degree of hydration of cement additives. For PFA/OPC blends, a salicylic acid-methanol solution was used. With BFS/OPC blends, an aqueous solution of EDTA, sodium carbonate and triethanolamine at pH 11.6 was used (3). The results are shown as degree of hydration, i.e., the percentage of additive (BFS or PFA) which has reacted to produce a soluble hydration product, mainly C-S-H but including other minor phases.

BFS/OPC BLENDS

X-ray diffractometry of the BFS/OPC identified calcium hydroxide in all mixes. A broad reflection at around $29^\circ 2\theta$ was attributed to C-S-H in the 25° and 60°C cured cements. With 110°C , curing this peak was very sharp and several other unidentified peaks appeared. Hydrotalcite ($\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$) was present at all temperatures. Monosulphate ($\text{C}_4\text{A}\cdot\text{SH}_{12}$) was also present except in the samples cured at 110°C .

The DTG results showed that the $\text{Ca}(\text{OH})_2$ contents for each of the BFS/OPC blends was not affected by curing temperature. In both blends, the main C-S-H water loss peak, which is normally below 200°C , increased to 250°C with curing at 110°C . This observation coincides with the increased crystallinity of the C-S-H phase in

TABLE I
Summary of Cement Blends Characterization

Cement	Curing Temp. °C	Degree of Hydration (% additive reacted)	Ca(OH) ₂ (%)	CaCO ₃ (%)	Other DTG peaks (°C)	XRD Phases Identified
3:1 BFS/OPC	25	28	3.1	0.6	200,400	C-S-H, Ca(OH) ₂ , hydrotalcite, monosulphate.
	60	29	3.5	0	180,390	C-S-H, Ca(OH) ₂ , hydrotalcite, monosulphate.
	110	25	2.5	0	250	Ca(OH) ₂ , hydrotalcite, unidentified phase.
9:1 BFS/OPC	25	18	0.67	0.05	180,390	C-S-H, Ca(OH) ₂ , hydrotalcite.
	60	16	0.66	0.02	180,390	C-S-H, Ca(OH) ₂ , hydrotalcite, monosulphate.
	110	31	0.66	0.04	250	C-S-H, Ca(OH) ₂ .
3:1 PFA/OPC	25	19	0	0	190,700	Ca(OH) ₂ , C-S-H, stratligite, monosulphate.
	60	24	0	0	170	Ca(OH) ₂ , C-S-H, stratligite, monosulphate.
	110	32	0	0	170	C-S-H, stratligite, mullite.
10:1 PFA/OPC	25	8.7	0	0	180,550,730	Stratlingite, mullite.
	60	12	0	0	180,520,720	Monosulphate, stratligite, mullite.
	100	9.5	0	0	180,520,720	Mullite.
6:1 Limestone /OPC	25	-	1.4	-	150,370	Ca(OH) ₂ , CaCO ₃ , ettringite.
	60	-	1.8	-	180,340	Ca(OH) ₂ , CaCO ₃ , ettringite.
	110	-	1.1	-	not done	Ca(OH) ₂ , CaCO ₃ .

these samples and suggests that the structural water is more strongly bound at higher curing temperatures.

The degree of hydration of the BFS/opc samples was low in all cases, regardless of the curing temperature. This is surprising because BFS is considered to be an inherently hydraulic material, which when in contact with alkaline solution will hydrate without consuming much of the alkali produced by the OPC activator. These results suggest that after an initial rapid reaction, the rate of hydration of BFS is very slow even at elevated temperatures.

Transmission electron microscopy with energy dispersive X-ray analysis has been used to study the structure and composition of some of the cements. The results indicate that the 9:1 BFS/OPC (25°C cure) has a C-S-H product with a Ca/Si ratio of approximately 1.2. Some areas of C-S-H had a high Mg and Al content, but this appeared not to affect the Ca-Si ratio.

PFA/OPC Blends

The XRD patterns of PFA/OPC (both 3:1 and 10:1) consisted mainly of mullite ($Al_6 Si_2 O_{13}$) reflections at all temperatures. This phase is not involved in pozzolanic reaction so was not affected by curing temperature. Stratigite ($C_2 A SH_8$) was also present as a hydration product at all curing temperatures. Monosulphate was present in the 3:1 PFA/OPC sample cured at 25°C but not at higher temperatures. There was little evidence for monosulphate in the 10:1 sample. There was no calcium hydroxide except in the 3:1 mix at 25°C.

Differential thermogravimetry of the PFA/OPC showed that the position of the main C-S-H dehydration peak was not affected by curing temperature in the PFA/OPC samples as it was with BFS/OPC. However, the peak areas increased with the curing temperature in the 3:1 PFA/OPC, indicating a larger quantity of C-S-H was present.

The degree of hydration of PFA was low especially in the 10:1 PFA/OPC mix. This is not surprising as the reactivity of the PFA is limited by the availability of calcium hydroxide produced by the cement. In 10:1 PFA/OPC, this is a very small quantity and, consequently, the amount of PFA which can react is also small.

The C-S-H phase of hydrated 10:1 PFA/OPC (25°C) can be identified under the electron microscope as either "inner product" of "outer product" depending on whether the material is inside or outside a visible boundary which marks the outline of the original unreacted PFA particle. Figure 2 compares transmission electron micrographs of PFA/OPC with a sample of C-S-H produced by the lime-silica slurry method. However, in 10:1 PFA/OPC, the composition of the two types of C-S-H appears not to vary significantly. The Ca-Si ratio of the inner product

was slightly lower than that of the outer product (inner product = 0.92, outer product = 1.14).

Limestone/OPC

The XRD patterns of 6:1 limestone/OPC consisted mainly of calcite and calcium hydroxide at all temperatures. The major feature of the DTG traces was the loss of carbon dioxide from the limestone at about 900°C, although it should also be noted that very little weight loss is associated with the C-S-H in the samples cured at 60°C and 110°C.

Calcium Silicate Hydrates

The same methods of characterization were used on the C-S-Hs as the cements except that no suitable gravimetric method was found. The characterization results are in Table II. Briefly, these confirmed that C-S-H samples of varying crystallinity had been produced using both preparation methods, ranging from poorly crystalline C-S-H to well-crystallized 14Å tobermite.

BATCH SORPTION EXPERIMENTS

Batch sorption tests have been carried out on all the cement and C-S-H formulations to determine:

- The extent to which phase changes in the real cements, brought about by varying the curing temperature affect sorption,
- How variations in composition and crystallinity of synthetic C-S-H affect sorption of Pu and Cs.

The batch sorption method is intended to produce a distribution ratio, R_d , representing the separation of the sorbing species between the solid and liquid phases. The abbreviation R_d is used rather than K to avoid the implication that equilibrium has necessarily been reached.

The distribution ratio is calculated as follows:

$$R_d = \frac{\text{concentration on solid}}{\text{concentration in solution}} = \left(\frac{C_o - C_t}{C_t} \right) \cdot R \quad (\text{M/G}) \quad (\text{Eq. 1})$$

where;

R_d = distribution ratio

C_o = initial radionuclide concentration in solution

C_t = radionuclide concentration in solution at time t

R = liquid/solid ratio (ml/g)

Method

A quantity of cement equilibrated water was prepared by contacting crushed cement (< 1.4mm) of the appropriate blend with distilled water at a water-solid ratio

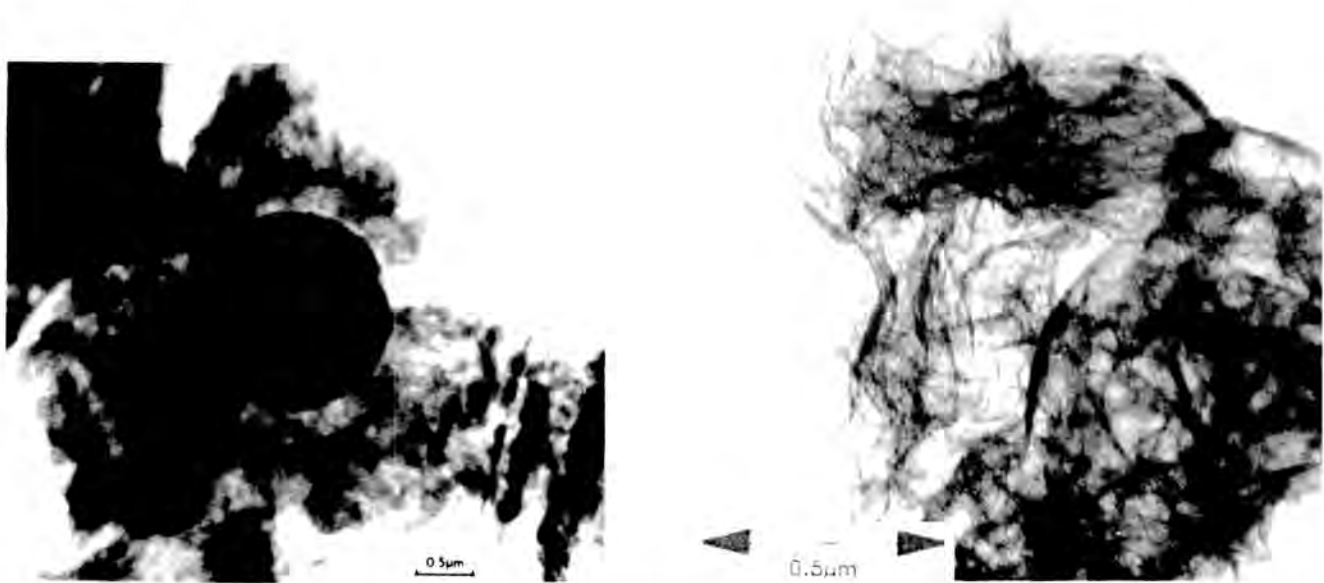


Fig. 2. Transmission Electron Micrograph of 10:1 PFA/OPC (left) and C-S-H Prepared from Lime-Silica Slurry (right).

TABLE II
Summary of C-S-H Characterization

Lime-Silica Slurries

Ca/Si	Ca(OH) ₂ (%)	CaCO ₃ (%)	Other DTG peaks (°C)	XRD Phases Identified
0.83	0	0.9	160	14Å tobermorite
0.9	0	1.0	160	Very crystalline C-S-H(I)
1.4	0	0.1	160,400	Poorly crystalline C-S-H
1.5	0	0.6	160,300	C-S-H(II)

Hydrated C₃S Pastes

Ca/Si	Ca(OH) ₂ (%)	CaCO ₃ (%)	Other DTG peaks (°C)	XRD Phases Identified
0.83	0	0.7	No peaks	Well-formed C-S-H(I)
0.9	0	0.1	150	
1.5	-	-	150	C-S-H(I)
1.8	0.15	-	-	
Pure C ₃ S	13.7	0.1	150,350	Amorphous C-S-H, Ca(OH) ₂

of 5:1. After seven days, the solution was filtered through a Whatman 540 filter to remove particulate and the pH was measured. For sorption on C-S-H, saturated calcium hydroxide solution was used as the aqueous phase. To set up the sorption test, cement equilibrated water was added to a quantity of cement or C-S-H crushed to $< 850 \mu\text{m}$ in a polythene container to give a liquid/solid ratio of 50:1. A spike of plutonium-238 (to give a starting concentration of $2\text{E}-10\text{M}$) or cesium-137 (to give a starting concentration of $825\text{E}-5\text{M}$) was added and an equivalent volume of sodium hydroxide solution (2M) was then added to compensate for the acid present in the spike (nitric acid 2M). The solutions were sampled at various times using a 30,000 MWCO (molecular weight cut-off) filter.

For Pu-238, the solution was acidified and electrodeposited onto a stainless steel planchet with Pu-236 internal standard, then counted up to 48 hours on an alpha spectrometer (passivated implemented planar silicon detector) (4). Cs-137 was counted on a scintillation counter using the Cerenkov radiation.

The results of the sorption experiments are given in Tables III and IV.

DISCUSSION

The characterization of the cements highlighted clear changes in the hydration products due to varying curing temperatures in the range $25-110^\circ\text{C}$, with the largest differences being between $60-110^\circ\text{C}$. The main differences were the increased crystallinity of the C-S-H phase and possible formation of a new phase at high curing temperatures especially with BFS/OPC. It was difficult to identify changes in the PFA/OPC with increased curing temperatures due to the high background effects of the unreacted PFA. However, it is very likely that pozzolanic reaction at elevated temperatures would produce tobermorite-like phases, especially at 110°C (1). In the context of waste disposal in a repository, two questions arise from this study. Firstly, can such phase changes be expected in a repository, and secondly, if they do occur, how will they affect sorption? There is no doubt that a deep underground repository will be at a somewhat higher temperature than the surface ambient temperature due to a combination of geothermal gradient and waste heat generation. However, it is not suggested that this temperature will be as high as 110°C . The reason for using the increased temperature was to accelerate hydration and possibly produce different hydration products than at 25°C . The 110°C curing temperature was therefore selected as an extreme in which curing over six months may produce similar products to many years of curing at a slightly lower temperature. Although it is not certain that any one of the three temperatures covered will be a realistic simulation of a

deep underground repository, the real situation should fall within this range.

Since these phases represent the extremes of a repository system, how do they affect sorption? In most cases, the sorption of cesium was low. The phase changes in the BFS/OPC formulations did not affect this low figure. However, sorption of cesium on PFA/OPC increased with curing temperature. This may be due to increased crystallinity of the C-S-H producing a structure similar to that of tobermorite which is known to sorb cesium (5).

Sorption of plutonium was in all cases very high. Any differences in Rd between cements are therefore not of major concern in terms of disposal. The changes in the hydration products of the BFS/OPC and decreased further with increased curing temperature, although the lowest results recorded still represented good sorption properties. The lowest results were obtained with the highest PFA content, which indicates that the unreacted PFA has no significant sorption properties. The relatively low Rd values were partly due to the smaller amount of hydration product in these cements.

Comparison of the sorption properties of C-S-H with real cement provides some understanding of the sorption behavior of the cement. For the cesium results it is useful to compare pure tricalcium silicate with limestone/OPC. Bulk lime-silica ratios of 1.8 and 1.5 will produce a C-S-H of lower Ca/Si ratio than OPC, probably in the same region as BFS/opc mixes. The C-S-Hs with low Ca/Si ratio (0.9 and 0.83) are most similar to the PFA/OPC mixes. Using this comparison there is a remarkable similarity between cesium sorption on C-S-H and on the comparable cement formulation. These results imply that what little sorption capacity for cesium exists in cements is due to the C-S-H component.

The sorption results for plutonium on C-S-H are difficult to interpret. In all cases sorption was high, Rd values being comparable with the PFA/OPC blends in particular. While there is a downward trend in Rd with the C₃S mixes the opposite is true for the lime-silica slurries, so no conclusions can be drawn on these variations. However, it can be concluded that the high sorption of Pu on cements can also be explained by the C-S-H component. It is possible that another mechanism may be operating in the BFS/OPC systems in which Pu sorption is higher than on C-S-H.

CONCLUSIONS

A series of cement formulations of the types likely to be used in a deep underground repository has been cured at a range of temperatures for six months. Characterization of these cements using a variety of techniques has identified the degree of hydration and the phases present.

TABLE III
Sorption of Plutonium on Cements and C-S-Hs - Rd in ml/g

Cement Formulation	Curing Temperature °C		
	25	60	110
6:1 Limestone/OPC	268 000	170 000	72 000
3:1 BFS/OPC	289 000	262 000	125 000
9:1 BFS/OPC	153 000	166 000	272 000
3:1 PFA/OPC	126 000	78 000	34 000
10:1 PFA/OPC	33 000	16 000	5 000
Ca/Si Ratio	CS3 Mixes	Lime-Silica Slurries	
Pure CS3	32 000	-	
1.8	9 100	-	
1.5	7 400	9 000	
1.4	-	4 600	
0.9	10 800	22 000	
0.83	5 400	35 300	

TABLE IV
Sorption of Caesium on Cements and C-S-Hs - Rd in ml/g

Cement Formulation	Curing Temperature °C		
	25	60	100
6:1 Limestone/OPC	4.4	6.6	7.2
3:1 BFS/OPC	3.8	2.6	4.3
9:1 BFS/OPC	-	2.3	8.2
3:1 PFA/OPC	17.7	21.1	53.8
10:1 PFA/OPC	4.5	7.3	24.7
Ca/Si Ratio	C ₃ S Mixes		
Pure C ₃ S	0.27		
1.8	3.1		
1.5	2.5		
0.9	27.1		
0.83	52.3		

Sorption of cesium on these cements was low but increased with curing temperature in PFA/OPC mixes. Sorption of plutonium was high. The highest values were obtained with BFS/OPC mixes and the lowest with 10:1 PFA/OPC which consists largely of inert unhydrated material.

Sorption measurements on synthetic C-S-H suggests that the C-S-H component of these cement formulations is responsible for most of the Pu sorption and all of the Cs sorption.

REFERENCES

1. TAYLOR, H. F. W., "The Chemistry of Cements," Academic Press (1964).
2. LEA, F. M., "The Chemistry of Cement and Concrete," 3rd ed. Edward Arnold (1976).
3. LUKE, K. and GLASSER, F. P., "Selective Dissolution of Hydrated Blast Furnace Slag Cements, Cem. Concr. Res. 17, 273-282 (1987).
4. Talvitie NA Electrodeposition of Actinides for Alpha Spectrometric Determination, Anal. Chem. 44, 280-283 (1972).
5. GLASSER, F. P., RAHMAN, A. A., CRAWFORD, R. W., McCULLOCH, C. E. and ANGUS, M. J., "Conditioning of Cement Matrices to Immobilize Cs" in Testing, Evaluation and Shallow Land Burial of Low and Medium Radioactive Waste Forms, Ed. W. Krischer and R. Simon, Harwood Academic Pub. EEC Conference Proc., 195 (1983).