Cements in radioactive waste disposal: some mineralogical considerations

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ABSTRACT. Cementitious matrices are being assessed for immobilization of radioactive wastes. This paper discusses some mineralogical aspects of cement chemistry and the uses of siliceous minerals as selective sorbants to enhance immobilization potential.

Studies of sorption and leaching of caesium from pulverized fuel ash (PFA), blast furnace slag, tobermorite, xonotlite, and clinoptilolite are reported. The role of incorporation of these additives in cement and the effect on the nature of the composite matrix on caesium behaviour has been investigated. Specific mechanisms of the interaction of additives with highly alkaline cement environment are described. While slags, PFA, and clinoptilolite undergo reaction at different rates, tobermorite and xonotlite appear to be stable in cement.

KEYWORDS: radioactive waste, cement, caesium, ash, slag, tobermorite, xonotlite, clinoptilolite.

SPENT fuel elements may undergo a lengthy and complex reprocessing cycle before disposal of the resulting waste streams can be accomplished; moreover, storage, transportation, and reprocessing operations give rise to other waste streams. The bulk of these are non-heat generating. The estimated United Kingdom arisings from all sources have been estimated to the year 2000 and classified according to volume and radioactivity (Duncan and Brown, 1982).

It is apparent that cement and concrete will find much application in waste disposal, mainly of non-heat generating wastes. We exclude from consideration its structural applications, e.g. in silos, tanks, bunkers, tunnel linings, and concentrate instead on non-structural applications, e.g. as a primary matrix for immobilization of wastes or in secondary barriers such as grouts or sealants. Cements are tolerant of water, resistant to the action of certain salts, have a long history of use and lend themselves to remote handling. Moreover, they are cheap. However, they may constitute a chemically reactive, microporous matrix and the interactions between cements and waste form, or cements and their environment, or both, have many features which are of interest to mineralogists and geochemists.

This paper concentrates on the behaviour of caesium and caesium-containing materials in a cement matrix. Caesium was chosen as the first target for two reasons. First, it occurs as an important component of many waste streams, where it constitutes a significant radiological hazard. Secondly, being monovalent and soluble, even under the strongly alkaline conditions obtaining in the cement environment, its chemical behaviour is comparatively simple. Cs is difficult to immobilize in a cement matrix because of its solubility. Although the components of the matrix, especially the amorphous (or nearly so) calcium silicate hydrogel phase has a very high specific surface area, $c.\ 10^4$–10^6 cm^2 g^{-1} (N$_2$ sorption), it affords virtually no sorptive potential for monovalent ions; studies by Anderson et al. (1981), Glasser et al. (1982a), Komarneni and Roy (1981), and Matsuzuru et al. (1977) reach essentially identical conclusions in this respect. Thus, the cement matrix affords only physical encapsulation for Cs.

However, the mineralogy of cements is susceptible to considerable variation, mainly through the use of inorganic additives. These may be classified into two types; those normally permitted in civil engineering codes of practice and those either not permitted or specifically excluded. Additives in the latter class include, for example, naturally occurring clay minerals. However, certain glassy slags, PFA (pulverized fly ash, obtained from coal-burning power stations) natural pozzolan and silica fume are permitted additives. When incorporated in cement, these permitted additives are known to react chemically with cement, thereby altering the aqueous phase composition, as well as the nature of the crystalline and amorphous hydration products and the microstructure.

The objective of the present paper is to call attention to the wider aspects of the immobilization of radwastes in cement, especially those which are relevant to mineralogy, and describe experiments

bearing on the conditioning of cement matrices to accept and immobilize Cs-bearing wastes. The conditioning has been performed using additives acceptable to civil engineers.

Environmental reaction of cement-immobilized wastes

The chemical and mineralogical composition of waste streams may impose unusual requirements on the cement matrix. Experience of the matrix in ordinary civil engineering may offer some guidance for example, to the tolerance of cements to sulphate-rich solutions, but offers little guidance to the behaviour of borate-rich solutions and is of no help in predicting the behaviour in cements of elements not normally occurring in nature, e.g. Tc, Pu, Np. Moreover, the waste form will have to perform well over very long periods of time. Table I summarizes some of the environments which cement-based systems will encounter in the course of storage, transportation and disposal. While much research is in progress on virtually all factors listed in Table I, there is general agreement amongst various groups that the time factor is the most difficult to compress into a shorter scale. Moreover, no clear-cut choice of repository conditions has yet been made; the chemical and mineralogical factors obtaining in the different environments are as yet incompletely defined.

TABLE I. Applications of cement and concrete to radioactive waste disposal

ENVIRONMENT AND TIME SCALE FOR REACTION	NATURE OF MINERALOGICAL REACTION AND ENVIRONMENTAL CONDITIONS
Above Ground *(Mainly short term, 0-25 yrs)*	Normal mineralogical changes arising during the setting of cements or modified cement mixtures. Abnormal changes arising from short-term chemical and mineralogical reactions with active and inactive waste-form constituents, e.g., salts metals, flocs.
Transitional *(Mainly short to medium term, up to 100 yrs.)*	Mineralogical consequences of accidents e.g., fire. Stability and durability of temporary storage facilities, e.g., tanks, sheds, floor pads.
Below Grade Shallow to Deep structures *(Mainly long term, up to 10^3-10^4 yrs.)*	Reaction of cement system with ground waters, constructional aggregates, adjacent strata and other repository materials, e.g., glass or ceramic waste forms, sealants, backfills. Pressure and temperature effects. Marine environments. Reactions with micro organisms.
All Environments *(All ages)*	Radiolysis and radiation damage, possibly leading to enhanced reactivity of waste form with its environment. Slow reaction with waste burden.

Mineralogical constitution of cement and hydration products

Ordinary Portland cement is made by thermal treatment of the appropriate raw materials, normally in the range 1350–1500 °C. During thermal treatment, partial fusion occurs but the final product, known as clinker, crystallizes almost completely, so that its phase content conforms closely to predictions made from phase equilibrium diagrams of the CaO–Al_2O_3–Fe_2O_3–SiO_2 system. The resulting clinker is finely ground in order to enhance its reactivity towards water and set-retarding additives—normally gypsum, or so-called hemi-hydrate or 'soluble anhydrite' are added.

Within seconds of mixing Portland cement with water, the aqueous phase reaches a pH of about 13. The alkalinity remains roughly constant with time, although the chemical balance of the aqueous phase changes. During the initial set, the alkalinity is maintained principally by the $Ca(OH)_2$ component, but after the first few days the steadily increasing content of alkali hydroxides depresses the $Ca(OH)_2$ solubility. The initial water: cement ratio is an important parameter of the system; it strongly influences the microstructure as well as the aqueous-phase composition. The ultimate products of hydration include both crystalline phases, e.g. portlandite, $Ca(OH)_2$, ettringite, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$, as well as amorphous phases, e.g. a calcium silicate hydrogel, usually designated C–S–H because its composition is variable.

The micropore structure of cement is much influenced by the water: cement ratio, hydration conditions (humidity, temperature) and the duration of cure. The micropore structure can be mapped by a number of techniques. In general, the finer micropores—those approaching atomic dimensions—are an intrinsic feature of the C–S–H gel phase while the larger micropores are controlled by the factors listed above. Diffusion measurements made on dense cement pastes, those from which larger micropores have been eliminated, give diffusivity values of the same order of magnitude as those reported for crystalline igneous and metamorphic rocks (Glasser *et al.*, 1983; Anderson *et al.*, 1982). It is thus apparent that Cs leach rates will depend rather critically on the amount and interconnectivity of micropores.

Zeolites have been widely used to immobilize radioactive waste species because of their high ion-exchange capacity for specific ions. Therefore clinoptilolite, which is frequently used to remove Cs, was an obvious choice for the study of what happens when zeolites are subsequently incorporated in cement.

This paper also includes studies on tobermorite

and xonotlite, which are mineral phases resulting from hydrothermal treatment of calcium silicates. Although tobermorite and xonotlite are normally encountered as hydration products only when cements are cured at elevated temperatures, they were studied because they possess sorption potential for Cs but, unlike zeolites, are probably thermodynamically stable in cement matrices. Tobermorite and xonotlite are commercially available and can be blended with cement.

Materials

Slags and PFA. Siliceous materials, such as slag and PFA, have traditionally been added to cement formulations for a variety of reasons: to increase workability of the wet mix, to reduce heat evolution during set and to improve the durability and resistance to chemical attack, particularly by sea water, of the set product. Slags mainly arise as by-products of the iron blast furnace: in order to be reactive with cement, the slag must have a high glass content. Thus, slags are relatively homogeneous; moreover, metallurgical requirements generally fix the slag composition within well-defined limits. PFAs, on the other hand, are notably inhomogeneous both within grains as well as from grain to grain. PFA normally contains unmelted relict minerals (e.g. quartz), as well as thermally generated minerals (e.g. mullite, graphite, spinel) contained within a glassy matrix. Most European PFAs contain these minerals in a siliceous glass, but coal seams are known which yield high-lime PFAs.

Tobermorite and xonotlite. These calcium silicate hydrates occur rarely in nature, but are readily synthesized. They are not employed in normal constructional concretes but have been used for decades in high-temperature cement-based insulations.

The synthesis was accomplished following the method given by Kalousek and Roy (1957): lime and quartz were reacted at saturated steam pressures at 180 °C. Al- and Na-doped preparations were made by adding γ-Al_2O_3 or sodium silicate solutions. The target ratios of Ca/(Si + Al) were 0.8 and 1.0 for tobermorite and xonotlite respectively. Reaction times ranged from 7 to 14 days, and the product phases were characterized using a Hägg Guinier camera with monochromatized Cu-$K\alpha$ radiation.

Zeolites—clinoptilolite. The considerable ion-exchange capacities of zeolites have led to their being used for removal of radioactive ions from low- and intermediate-level waste streams and clinoptilolite in particular, with its high selectivity for Cs and Sr, has been used for this purpose since 1959 (Sand and Mumpton, 1978). The Cs- and Sr-exchanged forms may then be incorporated in a cement matrix for subsequent disposal.

Clinoptilolite (typical formula, $Na_{2.3}K_{1.7}Ca_{0.5}Mg_{0.2}Al_{0.2}(Si_{30}Al_6)O_{72} \cdot 24H_2O$) has a Si/Al ratio c. 5.3, with 10-ring and 8-ring channels of dimensions $7.9\,\text{Å} \times 3.5\,\text{Å}$ and $4.4\,\text{Å} \times 3.0\,\text{Å}$ respectively (Sand and Mumpton, 1978). The natural zeolite is largely in the Na- and K-exchanged form, with Ca and Mg also present in smaller quantities.

The supplier of the sample used in this study (Norton Chemical Process Products, Ltd., UK) states it is 80-90% crystalline and that any contamination is in the form of mordenite. Some of the oxides of Ti and Fe may also be present. The sample is in the form of a very fine powder with particle diameters 5-20 μm.

Samples used in non-radioactive experiments were in the natural form, while samples used in radioactive leaching experiments were loaded with Cs, including [134]Cs to c. 50% capacity (80 mg Cs/g zeolite).

Experimental

Sorption Studies. The methods used for determining Cs uptake from solution involves the monitoring of radio-caesium in the aqueous phase as it is placed in contact with the material of interest. An accurately weighed quantity of powdered sample (2–2.5 g) is added to 500 ml of distilled water containing CsCl along with a known amount of Cs-134 tracer activity. These are then placed in a box shaker and agitated continuously; after suitable periods of time, aliquots of the solution are taken and centrifuged to remove any solid particulates remaining in solution. Plastic tubes and bottles were used throughout this study in order to minimize the effect of Cs adsorption on to container walls (McKinley and West, 1981, 1983). An Eppendorf pipette was then used to extract exactly 5 ml of the supernatant liquid for determination of the Cs-134 activity, via gamma spectroscopy. The number of disintegrations per minute from the solution were used to follow on a relative basis, the sorption of Cs.

Leach Tests. These experiments were performed using cylinders of 45 mm diameter and 80 mm height. Each cylinder was made using cement or cement plus additive and water, with a solid to water ratio of 0.5 or 0.6, containing a sufficient level of Cs-134.

These were mixed rapidly in a laboratory blender to avoid exessive CO_2 contamination, cast into 'Perspex' moulds and aged at approximately 18 °C and 100% humidity for 28 days prior to commencing leach tests. The cylinders were then immersed in 350 ml of distilled water at 25 °C which was completely renewed at each sampling date. The method followed was that recommended by Hespe (1971) and Rees (1983). Sampling occurred daily for the first week, weekly for the following 8 weeks and at monthly intervals thereafter. An aliquot was taken from the leachant at each sample change and the Cs content determined by gamma counting. Thus, the total amount of Cs leached from the cylinders with time is determined.

TABLE II.   The sorptive behaviour of PFA and slag in solutions containing
Cs on a weight and surface area basis

| Material | Surface Area* m^2/g | Sorption of Caesium | | | |
| | | 1d | | 20d** | |
		µgCs/g	µgCs/m^2	µgCs/g	µgCs/m^2
PFA;					
Barony	4.16	13.61	1.13	14.51	1.39
Eggbrough	0.82	3.83	4.98	11.30	14.35
Fiddlers Ferry	1.77	10.46	6.31	13.11	7.91
Ironbridge	1.48	9.06	6.14	11.75	7.93
Longannet	1.82	9.86	5.42	14.68	8.07
West Burton	1.17	6.64	5.68	11.14	9.52
Slag	1.40	2.96	2.11	3.43	2.45

* Surface area was determined by N_2 adsorption (BET method)

** 20d represents time to achieve steady state sorption

Results and discussion

PFA and slag. Table II records data obtained under comparable conditions on the sorption of Cs from solution. The uptake characteristics are defined in terms of sorption per unit weight and per unit area. The uptake of PFA is rather variable, ranging up to 14 µg Cs per g sorbate, whereas slag falls close to the lower range of values recorded for PFA. Sorption is achieved rather slowly, PFAs requiring up to 20 days to achieve steady-state values. Figs. 1 and 2 compare these steady-state values, from which the differences between comparisons on a weight and surface area basis can be appreciated; for example, Barony PFA has a high efficiency on a weight basis, but this is due to its

high specific surface area. Ranked on surface area, it is one of the least efficient sorbers tested, having an efficiency similar to that of slag.

At least two mechanisms are believed to account for the observed uptake of Cs and its dependence on surface area, time, and pH. An initial rapid uptake is followed by a slower uptake, which is more significant for PFA than slag. The sorption is attributed to the conditioning of the surface of the glass, which is rapid in the case of the less-durable slag glasses than for the glassy phase of PFA. Conditioning occurs by a hydroxylation of the surface which creates 'acidic' sites suitable for retention of monovalent ions. The extent and rate of hydroxylation are a function of pH, with the result that uptake is characteristically increased in
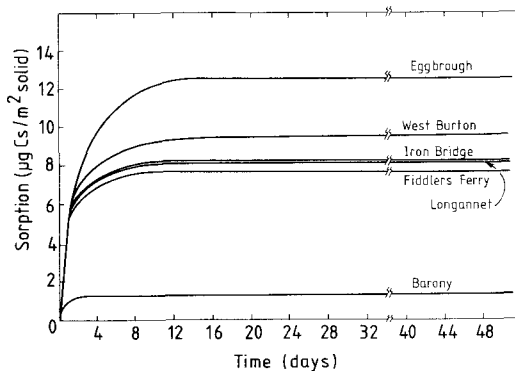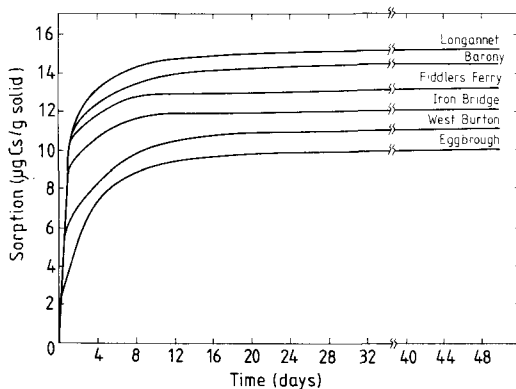
FIGS. 1 and 2. FIG. 1 (*left*). Cs sorption per unit weight on various fly ashes. FIG. 2 (*right*). Cs sorption per unit area on various fly ashes.

alkaline solution. The crystalline mineral content of PFAs makes an insignificant contribution to Cs uptake. When the surface area of a PFA is increased artifically by grinding, crystalline material is increasingly exposed by fracture. Hence the sorption per unit weight increases only slightly, relative to unground PFA, while the sorption per unit area decreases.

The sorption characteristics have not been studied as a function of Cs concentration, but by analogy with flame-hydrolysis silica, for which experimental data are available (McCulloch et al., 1983), the behaviour of slag and PFA will probably follow a Freundlich-type isotherm. When these non-crystalline aluminosilicates (slag, glassy PFA fraction, etc.) are incorporated in cement, they react chemically. Moreover, competition for the 'active' sites responsible for uptake may occur between Na^+ and K^+ arising from the cement, and Cs^+ in the radwaste. A start has been made on assessing the longer term potential of cement-slag-PFA systems for Cs retention; this includes a sampling programme in which direct analyses of the pore fluid compositions of aged cements are determined (Glasser et al., 1983; Marr and Glasser, 1983).

Tobermorite and xonotlite. It has long been known that autoclaving cements results in leaching much of the Cs content into the aqueous phase. However, the Cs which is retained is not readily leached in further testing at ambient temperatures.

While many reasons could be suggested for this behaviour, Komarneni and Roy (1982) showed that tobermorite, synthesized by reaction of lime, quartz, and water in an autoclave in saturated steam at 180 °C, was a strong sorber for Cs at ambient temperature. In the title study, tobermorite and xonotlite were synthesized using the method of Kalousek and Roy (1957). If it was desired to incorporate Al or Na in the stuctures, these were added to the other reactants as γ-Al_2O_3 and sodium silicate solution, respectively. Batches intended for tobermorite synthesis were adjusted to give $Ca/(Si + Al) = 0.8$ and for xonotlite, this ratio was kept at 1.0. Reaction times ranging from 7 to 14 days gave phase pure solids, judged by XRD using a Hägg Guinier camera.

Data on the uptake of Cs by tobermorite and xonotlite are shown in Tables III and IV. The tobermorite did not contain more than traces of Al, and experiments made on Al-containing tobermorites gave essentially identical results. The data may be treated in terms of a distribution coefficient, K_d, defined as the ratio of concentrations of Cs on the solid/Cs in solution (units $\mu g/g$ and $\mu g/ml$ respectively). The K_d values are useful in comparing the sorption efficiencies of different materials. McKinley, 1980; IAEA, 1982). There are, however, indications that K_d is concentration-dependent and in assessing data obtained across a wide range of Cs concentrations it may be desirable to employ a

TABLE III. Relation between solution Cs concentrations and Cs uptake onto 11Å tobermorite

Experiment numbers	I	II	III	IV	V	VI
Initial Cs conc. (M) in aqueous phase	1.4×10^{-6}	1×10^{-5}	2×10^{-5}	1×10^{-4}	1×10^{-3}	1×10^{-2}
Final Cs conc. (M) in aqueous phase	1.6×10^{-7}	2.1×10^{-6}	7.2×10^{-6}	4.4×10^{-5}	7.9×10^{-4}	8.9×10^{-3}

TABLE IV. Relation between solution Cs concentration and Cs uptake onto Xonotlite [*]

Experiment numbers	I	II	III	IV	V	VI
Initial Cs conc. (M) in aqueous phase	1.4×10^{-6}	1×10^{-5}	5×10^{-5}	1×10^{-4}	3.2×10^{-4}	1×10^{-3}
Final Cs conc. (M) in aqueous phase	2.1×10^{-7}	3.1×10^{-6}	2.7×10^{-5}	6.7×10^{-5}	2.4×10^{-4}	8.1×10^{-4}

[*] Xonotlite used contains 0.7 wt% Na.
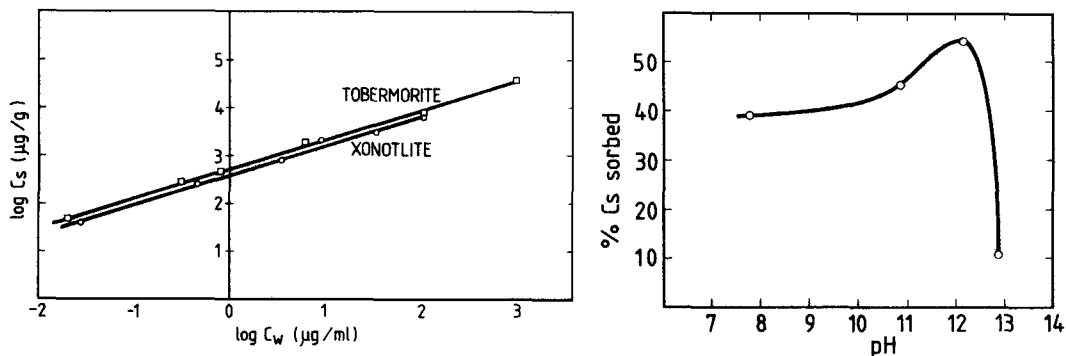
FIGS. 3 and 4. FIG. 3 (*left*). Freundlich isotherms for sorption of Cs on tobermorite and xonotlite. FIG. 4 (*right*). Effect of pH on the uptake of Cs by tobermorite. (pH was adjusted by addition of LiOH, the rapid release of Cs above pH *c*. 12 is probably not a pH effect but is due to competitive interaction with the large quantity of Li^+ present at this stage.)

Freundlich isotherm of the type $C_s = K[C_w]^n$ where C_s and C_w represent the concentrations of caesium on the solid and in the aqueous phase respectively: K and n are constants which can give information on the mechanism of the uptake (Langmuir, 1981). Fig. 3 shows the isotherms which have essentially constant slopes over the concentration range 10^{-2} to 10^{-6} M. The resulting equations are:

$$\text{(tobermorite) } C_s = 436[C_w]^{0.607}$$
$$\text{(xonotlite) } C_s = 356[C_w]^{0.613}$$

Although both tobermorite and xonotlite show good uptake of Cs from water, it is also important to determine release rates. For this purpose, tobermorite and xonotlite solids (2 g) were placed in Cs solution and loaded to approximate caesium concentrations of 1.8 mg Cs/g and 0.8 Cs/g respectively. The solid was recovered by filtration, washed and air-dried. The loaded materials were placed in (i) distilled water, (ii) 0.1 M KOH, (iii) 0.1 M KCl, (iv) 0.1 M NaCl, and (v) 0.1 M $CaCl_2$ solutions. These were intended to simulate fresh leachant (i); pore fluids in set cements (ii); and various naturally

occurring environments (iii–v). The resulting K_d values are given in Tables V and VI. Large exchanges of Cs occurred, indicating that the initial uptakes are partially reversible. The presence of chloride, in particular, led to considerable exchange.

In mixtures with Portland cement, tobermorite and xonotlite will be in an alkaline environment. The extent of the uptake was determined for 11 Å tobermorite, with the results shown in fig. 4 and Table VII. In order to vary pH independently, without complications arising from exchange reactions with other alkali ions, LiOH was used to vary the pH. The initial Cs concentration was kept at 6.0×10^{-5} M. The relative amount of sorption increases gradually over the pH range up to *c*. 12.2, after which it decreases markedly.

The leachant analyses are given in Table VIII and the cumulative percentage leached shown in fig. 5. The cylinders of OPC and OPC+tobermorite initially contained *c*. 3–6 mg Cs. Supplementary mercury intrusion porosimetry studies were made at 28 days to characterize the micropore structure. Table IX shows that the total intruded

TABLE V.   Distribution of Cs between Tobermorite *
and aqueous solution

Content of aqueous phase	% Cs lost to aqueous phase	mg Cs/g solid	mg Cs/mℓ aqueous phase	K_d (mℓ/mg)
H_2O (distilled)	16.5	1.503	1.06×10^{-3}	1418
KOH (0.1N)	52.1	0.862	3.33×10^{-3}	259
KCℓ (0.1N)	73.1	0.484	4.68×10^{-3}	103
$CaCℓ_2$ (0.1N)	53.2	0.842	3.40×10^{-3}	248

* initial loading: 1.8mg Cs/g tobermorite

TABLE VI. Distribution of Cs between Xonotlite[*]
and aqueous solution

Content of aqueous phase	% Cs lost to aqueous phase	mg Cs/g solid	mg/Cs/mℓ aqueous phase	K_d (mℓ/mg)
H_2O (distilled)	44.7	0.442	1.43×10^{-3}	309
KOH (0.1N)	65.9	0.273	2.11×10^{-3}	130
NaCℓ (0.1N)	72.2	0.222	2.31×10^{-3}	96
$CaCℓ_2$(0.1N)	46.0	0.432	1.47×10^{-3}	?94

[*] Initial loading: 0.8 mg Cs/g xonotlite

volume up to a maximum pressure of 220 MPa is not significantly affected by 6% tobermorite, but increased somewhat at 10% tobermorite. The cumulative leach data show (i) the presence of 6% tobermorite drastically lowers leaching, relative to OPC (ii) the slope of the leach curve is significantly less in the presence of tobermorite and (iii) tobermorite contents greater than 6% are ineffective in producing more leach resistance, probably because the addition of more Cs uptake capacity occurs at the expense of increased porosity.

The uptake of Cs by crystalline tobermorite is greater than that of xonotlite, but both have uptakes more than an order of magnitude better than silica's, measured at equivalent Cs concentrations and pH. Furthermore, the uptake by tobermorite (and probably xonotlite) is independent of surface area. Hence, these materials are believed to exhibit *structural* uptake. Tobermorite has a layer structure, with a characteristic repeat of *c.* 11.3 Å; its layer unit consists of a central sheet comprising Ca–O ions with the empirical composition CaO_2^{2-}. Both sides of this sheet share oxygen with SiO_4 tetrahedra which are linked into metasilicate chains as represented in fig. 6. The stacking of these layers leaves channels which accommodate water and additional Ca ions to complete the charge balance (Megaw and Kelsey, 1956; Mamedov and Belov, 1958). However, most real crystals have been found to exhibit stacking disorder which has been investigated by Hamid (1981) and Wieker (1982). The uptake of Cs is believed to arise from the presence of local charge imbalance, created by the presence of defects and omission of interchannel cations. Thus, tobermorites are believed to act zeolitically. This explanation is contrary to that advanced by Komarneni *et al.* (1982) who reported that the presence of Al in the structure was essential for Cs uptake. They suggested that during synthesis $H_3O^+ + Al^{3+}$ substitute for Si^{4+}, subsequent Cs uptake occurring by Cs^+ for H_3O^+ exchange. We suggest that since tobermorite synthesis takes place in an alkaline medium, in which the H_3O^+ concentration is low, H_3O^+ is an unlikely substituent in the structure. Moreover, we find that the presence of Al in the structure has no significant effect on the sorption.

Xonotlite has a structure similar in many respects to that of tobermorite (Mamedov and Belov, 1955; Dent and Taylor, 1956). The limits of

TABLE VII. Cs sorption onto tobermorite as[*] a function of pH

pH of aqueous phase	% Cs sorbed
7.8	39.7
10.9	45.3
12.2	54.4
12.8	10.1

[*] Initial Cs concentration: 1.6×10^{-5}M.

TABLE VIII. Cumulative amount of Cs leached (%) from cement cylinders as a function of time

Time (days)	Cumulative percentage of Cs leached		
	(a) 100% OPC	(b) 94% OPC 6% tobermorite	(c) 90% OPC 10% tobermorite
1	9.12	5.68	5.78
2	9.54	6.02	6.12
3	10.40	6.90	6.40
4	11.25	7.12	6.66
5	11.88	7.32	7.32
6	12.19	7.60	7.58
7	12.70	8.00	7.80
14	18.61	11.20	10.48
21	22.57	13.30	12.86
28	27.80	15.42	15.06
35	31.07	16.68	16.20
42	36.30	18.32	17.64
49	40.33	19.48	18.54
56	44.04	20.56	19.38
63	47.37	21.56	19.98

FIG. 5. Leach profiles of Cs-134 from cylinders containing selected quantities of tobermorite (W/S = 0.5).

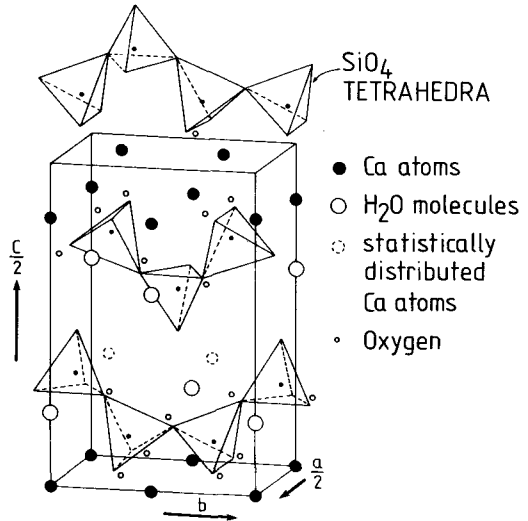FIG. 6. A three-dimensional view of the tobermorite structure using the orthorhombic axis, $a/2 = 5.58$ Å, $b = 7.39$ Å and $c/2 = 11.39$ Å (Hamid, 1981).

Al substitution were found by Kalousek *et al.* (1977) to be about 2%; it is also known that some (Na, K) can substitute in the structure, presumably for Ca (Kudoh and Takéuchi, 1979). In this study, we have synthesized alkali-containing xonotlites, as well as those containing alkali and aluminium. Studies on these materials are in progress.

Clinoptilolite. When clinoptilolite is put into ordinary Portland cement, a series of reactions, occurring in three overlapping stages, leads to release of its Cs content. The first stage is an initially rapid ion-exchange between the Na^+, K^+, and Ca^{2+} present in cement pore fluid and Cs^+ in the clinoptilolite (Glasser *et al.*, 1982*b*). The second stage is a 'pozzolanic'-type reaction between portlandite, arising from the hydrated cement paste, and clinoptilolite; the latter acts as a source of reactive silica.

The product of this second reaction is an amorphous calcium-silicate-hydrate gel at temperatures less than 100 °C (Držaj *et al.*, 1978) and a well-crystallized tobermorite at temperatures greater than 100 °C (Komarneni *et al.*, 1982). The third reaction, occurring over longer times is a reaction with C–S–H, leading to the formation of low-lime C–S–H.

The ion exchange is essentially complete within the first few hours or days of mixing, but the two

TABLE IX. Mercury intrusion results for cement cylinders

Sample	Mercury intrusion volume (cm³/g)
100% OPC	0.165
94% OPC +6% tobermorite	0.176
90% OPC + 10% tobermorite	0.228

slower reactions continue to longer ages, well after the cement is set. As the zeolite is physically consumed, its Cs content is discharged into the pore fluid.

Clinoptilolite-cement samples were prepared using a clinoptilolite in powder form. This was mixed in 1:1 weight ratio with OPC, to a water/solid ratio of 0.5. The ability to determine unreacted clinoptilolite rests on the observation that it is insoluble in methanolic-salicylic acid solutions while cement hydration products are soluble. Thus, a chemical extraction method, essentially as described by Mohan and Taylor (1981), has been used to determine the amount of unreacted zeolite. In this way, four isothermal plots were obtained at 50, 70, 100, and 150 °C. A characteristic feature of these plots is that the fraction of clinoptilolite consumed is a linear function of $\log_{10}t$(time). The variation of slope and intercept of these isotherms with temperature are plotted in figs. 7 and 8 respectively.

Cement–zeolite composites have been subjected to a standard leaching method proposed by Hespe (1971). The rate of leaching has been presented as percentage of [134]Cs (initially in zeolite) leached versus time. From figs. 7 and 8, an equation can be derived to predict the quantity of clinoptilolite which has reacted with OPC phases at any time or temperature, subject to the restrictions that: (i) the clinoptilolite is in powder form, particle size 5–20 μm diameter; (ii) the mixture is 1:1 weight ratio, zeolite:cement, with w/s ratio 0.5; (iii) tem-
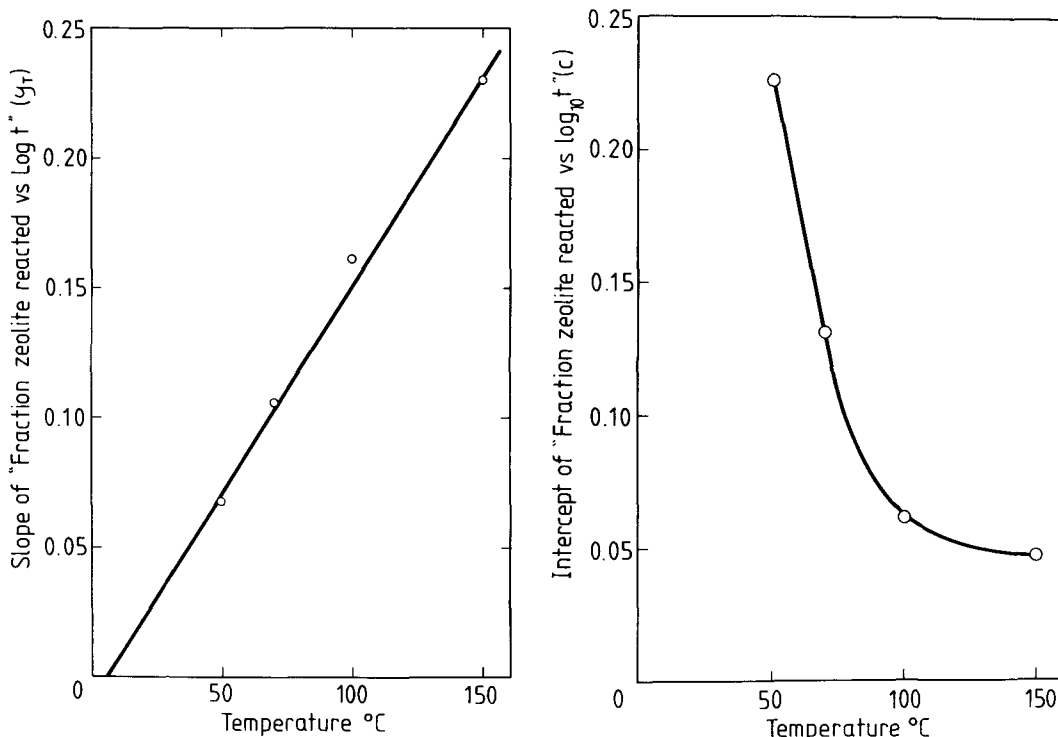
FIGS. 7 and 8. FIG. 7 (*left*). Effect of reaction temperature on slope (y_T) of several isothermal clinoptilolite–cement reactions. FIG. 8 (*right*). Effect of reaction temperature on intercept (*c*) of several isothermal clinoptilolite–cement reactions.

perature is between 273 and 423 K; and (iv) the reaction time is greater than 1 day.

Isothermal reaction of OPC–clinoptilolite composites gives a reaction rate linear with $\log_{10}$ time such that:

$$\alpha = y_T \log_{10} t + c$$

where α = fraction of clinoptilolite consumed, y_T = a temperature dependent constant, t = time in hours and c = a complex function of temperature, established empirically. The temperature-dependent constants y_T and c can be obtained from figs. 7 and 8, so that at any time and temperature, the fraction of clinoptilolite reacted can be predicted.

From these results it is obvious that the rate of zeolite consumption is sharply temperature dependent. If this is the case, we should observe a higher rate of leaching of [134]Cs in samples cured at higher temperatures provided the product of reaction is still C–S–H. Fig. 9 shows this to be the case. Reaction of cement–clinoptilolite at 98 °C is also known to cause microstructural stress leading to microcracking and hence a more open pore net-

work (Glasser et al., 1982a) is created; this, as well as release of [134]Cs from the clinoptilolite as it reacts, contributes to the higher leach rates obtained after curing at higher temperatures. While higher temperature curing may not be used deliberately, it should be recalled that the setting of cement is strongly exothermic and, on that account, the centre temperatures of monoliths may be quite high.

After long curing times at 25 °C (10–100 years) a considerable fraction of clinoptilolite is likely to be consumed (i.e. about 50 %) and a composite could be expected to give similar leach rates to one cured for one month at 100 °C. Cement-immobilized clinoptilolite composites exhibit rather high leach rates, and these are likely to worsen with time as zeolite is physically consumed. Various methods of improving the leach resistance are being considered. Since the main causes of high leach rates reported here are ion-exchange and chemical reaction with alkaline species in cement pore fluids and $Ca(OH)_2$, several chemical methods may be employed to minimize reaction between the two. One solution uses high-alumina cement (HAC).
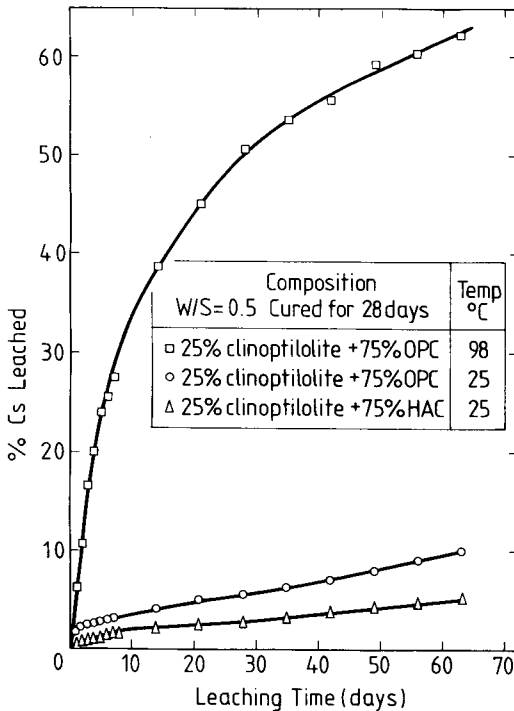
FIG. 9. Cumulative Cs leaching from cement-zeolite
composites.

HAC is extremely low in alkali and, moreover, does
not develop free portlandite during its setting. For
these reasons, it is much less alkaline than OPC.
Fig. 9 shows some test data in which the per-
formance of HAC can be compared with that of
OPC and modified OPC composites. These trials
are encouraging and suggest that while it may not
be possible to tailor cement compositions to
eliminate reaction, it may be possible to reduce
greatly the rate of reaction with concomitant
improvement in the leach resistance.

Conclusions

The materials examined in this study, PFA, slag,
clinoptilolite, tobermorite, and xonotlite, all show
to a greater or lesser degree a potential for im-
mobilizing Cs when incorporated into cement.
However, the mechanism of Cs uptake, the be-
haviour of each material in the strongly alkaline
cement environment and the nature of reactions
with liberated $Ca(OH)_2$ varies from one additive to
the next and hence special individual considera-
tions have to be given to each material in order to
optimize its immobilization potential for Cs. PFA
and slag do not sorb Cs to the same extent as

clinoptilolite but their reaction with $Ca(OH)_2$
appears to be slower and hence by studying com-
posites with PFA or slag at different levels of
incorporation this property may be brought out to
advantage, especially in HAC. HAC may also have
a part to play in reducing the consumption of
zeolites by cement for, if the quantity of $Ca(OH)_2$,
Na^+, and K^+ can be suppressed in the cement pore
system, then the various mechanisms that lead to
the release of Cs may be suppressed. Tobermorite
and xonotlite unlike the other substances examined
are stable in the cement environment and appear
to uptake Cs by structural incorporation into the
lattice, where it substitutes for Ca and fills vacant
sites. Despite the incorporation of Cs into the
lattice of tobermorite and xonotlite it is subject to
partial exchange in various leachants and studies
are underway to try and reduce this reversible
reaction. Nevertheless, tobermorite and xonotlite
show considerable promise as additives to improve
Cs immobilization in cement systems.

What must be borne in mind, however, is that
tailored systems that may optimise conditions for
Cs immobilization might not represent the best
case for other radioactive waste species; these and
other factors are currently being investigated.

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