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CAESIUM IMMOBILISATION IN HYDRATED CALCIUM-SILICATE-ALUMINATE SYSTEMS

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ABSTRACT

A special field of application of cementitious materials is using cements for immobilisation of low and medium level radioactive wastes. Clarification of mechanisms of binding is complicated by the multicomponent nature of the solidifying matrix. In the present work, interest is turned to one of the most difficult to confine, long half-life isotopes, the caesium isotope. The cement matrix for solidification of the radioactive waste can be considered, with simplification, as a $CaO-SiO_2-Al_2O_3-H_2O$ system. The various compositions of hydrated cementitious assemblages were investigated with respect to their Cs sorption by measuring the Cs distribution ratios (R_d) therein. Trends in sorption properties were detected, and the section of the ternary phase diagram with the best performance was identified. *© 1998 Elsevier Science Ltd*

Introduction

Among radioactive wastes arising during operation of nuclear power plants, the ^{137}Cs isotope deserves attention from the point of view of immobilisation due to its amount, half-life, and high solubility. The conventional cementation technique is widespread for solidification of low and intermediate activity wastes (1). But although some metals are either precipitated in the high pH environment of cements [e.g., ^{60}Co (2,3)] or built into the matrix due to similarities of chemistry of the waste and a cement constituent [e.g., ^{90}Sr (3)], Cs mainly remains dissolved in the pore fluid of the cement matrix, from which it can readily migrate into the biosphere.

Caesium binding capacity of a cement matrix is significantly dependent on the chemical composition of the cement used, as the various phases formed during hydration have different binding capacities (4). Before recommending the optimum composition matrix, admixtures exhibiting high sorption capacities should be studied.

In the present work, hydrated systems composed of the three main cement constituents (CaO, SiO_2, Al_2O_3) in their suitably reactive form were investigated for Cs immobilisation using a static sorption method. Composition of the samples in the C-S-A system were chosen in such a way that one could systematically assess their binding capacities

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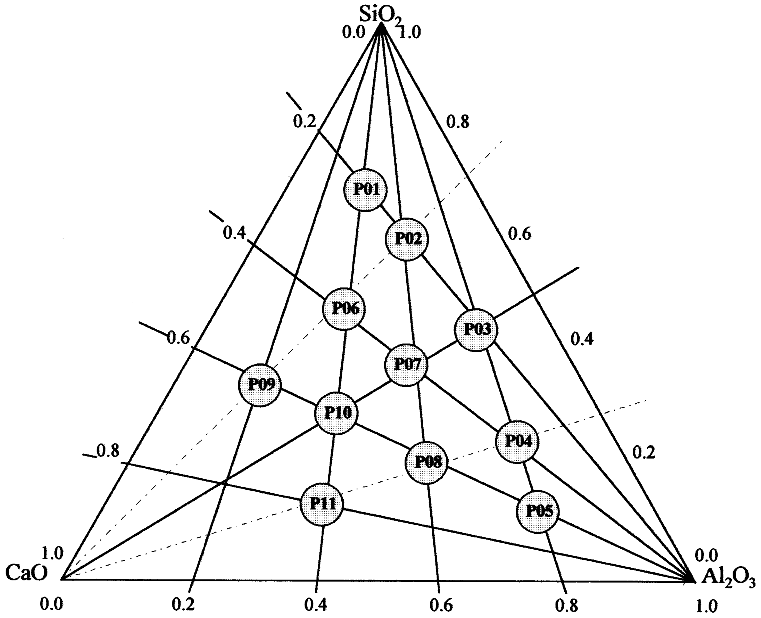

FIG. 1.
Starting compositions of the solid samples prepared.

as a function of composition in several relations. Trends in sorption properties were detected, and the section of the ternary phase diagram with the best performance was identified.

Experimental Methods

Preparation of samples in the CaO-SiO_2-Al_2O_3-H_2O system

There were 11 different compositions prepared during the experiments. The composition of the samples were selected so that the corresponding points lie on the intersections of the weigh lines in the C-S-A[2] ternary diagram (Fig. 1). By doing so it was possible to consider a sample in two or three relations and reduce the number of samples accordingly. The effect of increase or decrease of the amount of a component could be assessed by keeping the ratio of the other two components constant [S/C = constant, C/A = constant, A/S ≈ constant (Table 1)].

The samples were composed of freshly calcined CaO, highly disperse SiO_2, and $AlOOH{\cdot}xH_2O$ (as alumina source). The constituents were weighed, homogenised, and mixed

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[2] According to the conventional cement nomenclature C: CaO, S: SiO_2, A: Al_2O_3, H:H_2O.

TABLE 1
Relations for the C-S-A ternary diagram.

	I			II			III	
	CaO/Al_2O_3 = constant			SiO_2/CaO = constant			Al_2O_3/SiO_2 ~ constant	
	SiO_2 —increases→			Al_2O_3 —increases→			CaO —increases→	
v	P11, P10, P06, P01	3 : 2	v	P01, P02, P03	4 : 1	v	P04, P08, P11	7 : 3
v	P08, P07, P02	2 : 3	v	P06, P07, P04	3 : 2	v	P03, P07, P10	1 : 1
v	P05, P04, P03	1 : 4	v	P09, P10, P08, P05	2 : 3	v	P02, P06, P09	3 : 7
	R_d ←almost constant→			R_d ←increases—			R_d —increases→	

with a large quantity of deionised water (W/S ratio ≈ 10:1). The samples were stored for 10 days at 25°C, during which period the sample containers were shaken once daily. The samples then were filtered, dried (at 105°C for 24 h), and ground to particle sizes smaller thanb 200 μm.

Determination of distribution ratios

Powder samples of 0.5 g were transferred into three air-tight polythene vessels for each of the 11 compositions (thus resulting in 33 vessels). These were filled with 25 mL of solution of either 1, 10, or 100 ppm Cs concentration. The solutions were prepared using CsCl spiked with ^{134}Cs ($t_{1/2}$ = 2.04 year) isotope. Activities of 1-mL samples taken from the 33 compositions and from the standard Cs solutions were measured after 1 day, 3 weeks, and 1 year (Fig. 2). The measurements were performed by a radiochemical method using an NaI(Tl) scintillation detector.

The aqueous caesium concentrations after the specified reaction times were calculated from the concentrations and activities of the standard solutions as well as from the activities of the 1-mL samples taken. Distribution ratios R_d (mL/g) to describe caesium confinement were calculated using Eq. 1. Other elements of the equation were the quantities of solids and solutions.

$$R_d = \frac{C_{solid}}{C_{eq.solution}} = \frac{C_{initial} - C_{eq.solution}}{C_{eq.solution}} \cdot \frac{V_{solution}}{m_{solid}} \qquad (1)$$

where $C_{initial}$ (mg/L) = initial concentration of Cs in the solution, $C_{eq.solution}$ (mg/mL) = equivalent concentration, V (mL) = volume of the various solutions used, m (g) = relevant mass of the solid phase, and C_{solid} (mg/g) = equivalent concentration on the solid phase.

Reliability of the measurement assembly by virtue of its unique shape and the applied analytic method by far supercedes that of the flame emission method (generally used for Cs detection). Our measurement set-up also enabled refilling the solution retained after activity measurements. Therefore, the same mixtures could be used at subsequent measurements (to assess the evolution of sorption over time), eliminating errors in composition if parallel mixtures would have been used.

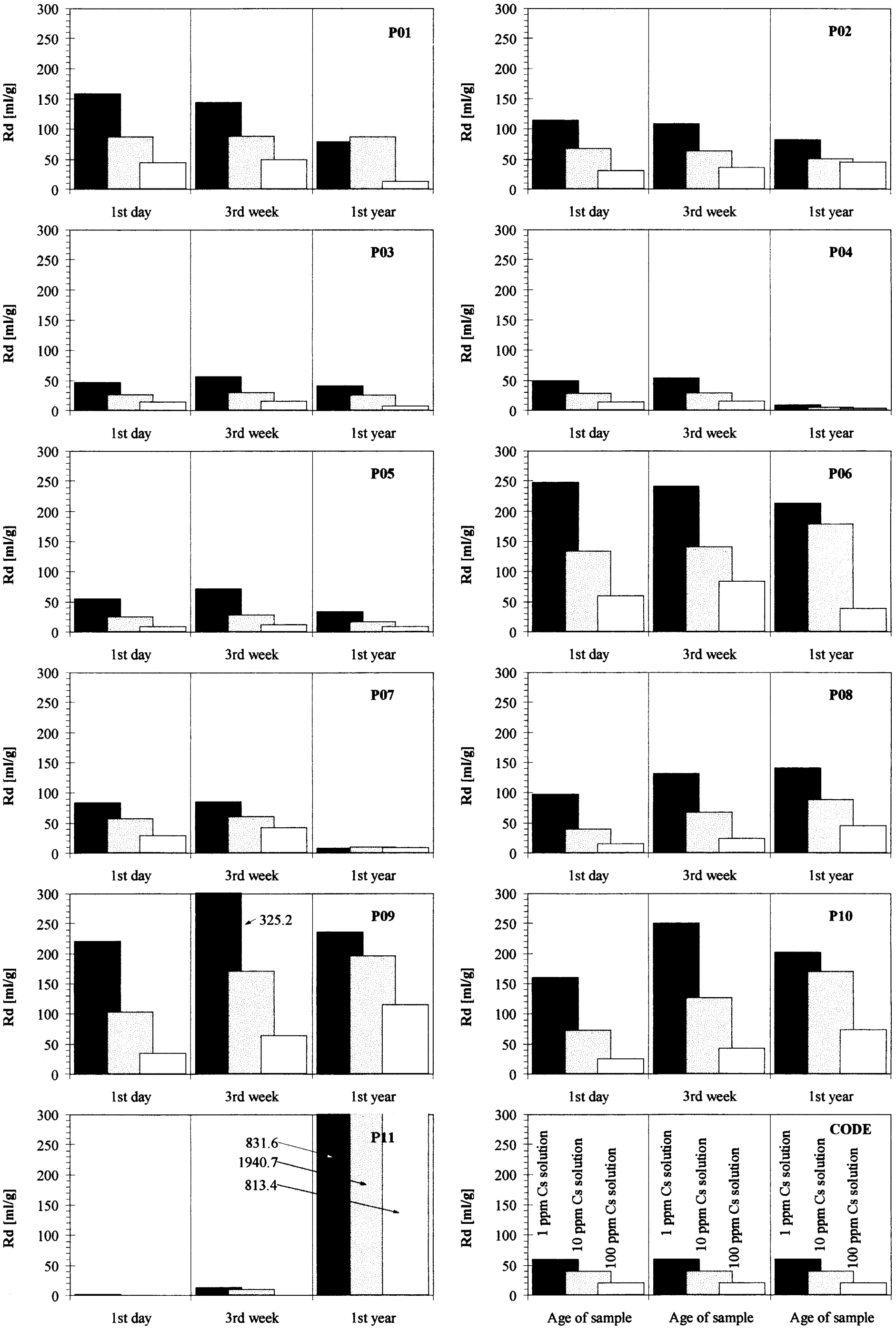

FIG. 2.

Distribution ratios of solids (P01... P11) contacted with 1, 10, and 100 ppm Cs solutions after 1 day, 3 weeks, and 1 year. Inset *(bottom right)* shows a key to the data (temperature 25°C).

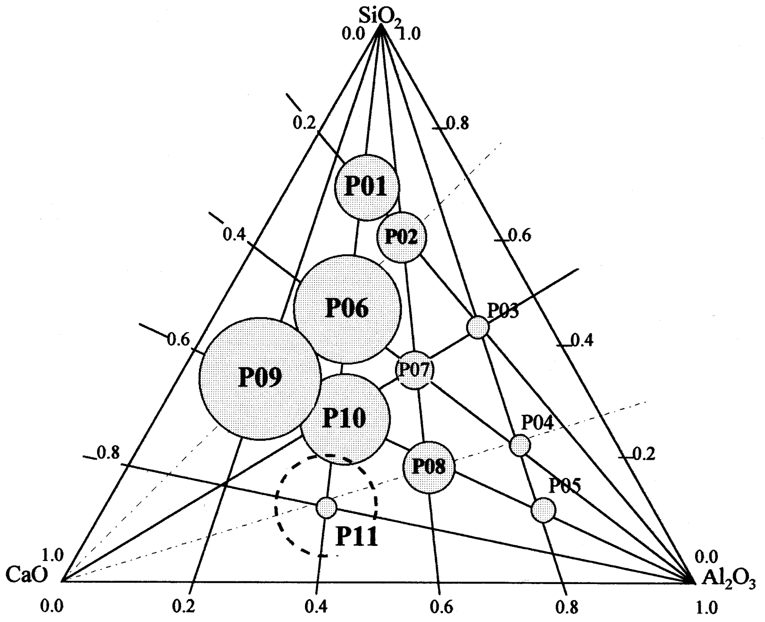

FIG. 3.
Schematic representation of distribution ratios (R_d) for caesium in the C-S-A system.

Results and Discussion

Leaching behaviour of cemented waste streams is influenced greatly by the several solid phases present and by the porosity of the matrix itself. The main solid phase is poorly (if at all) crystalline calcium-silicate-hydrate coexisting with the pore fluid and minor solid phases whose X-ray diffraction peak intensities were too small for unambiguous identification. Good retention of a certain waste in cement is indicated by its high solid–liquid distribution ratio as a consequence of certain immobilising phase(s) promoting confinement by chemical fixation. On increase of distribution ratios (R_d), Cs confinement on the solid improves. Table 1 summarises the tendencies found for R_d values of solids as a function of composition. There are three relations to observe. Within each, the molar ratio of two of the main constituents is kept constant and the third is increased (from left to right) in the lines starting with the "v" sign.

It is noted that Cs retention (expressed by the increase of R_d values) increases with increasing CaO/Al_2O_3 ratio, yet R_d values remain almost constant if the quantity of SiO_2 in the matrix composition increases along these constant CaO/Al_2O_3 ratio lines (Relation I in Table 1). However, Cs retention decreases with increasing SiO_2/CaO ratio and drops further with increasing Al_2O_3 content along constant SiO_2/CaO ratio lines (Relation II). Likewise, for compositions with constant Al_2O_3/SiO_2 content (Relation III), increase of the ratio results in decrease of R_d values, although increasing the CaO amount along constant Al_2O_3/SiO_2 ratio lines improves Cs retention.

Sorption of caesium on the solid phase is, therefore, promoted by the decrease of

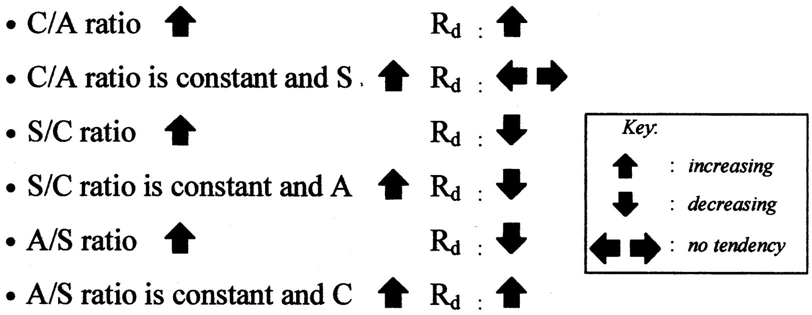

FIG. 4.
Summary of changes of distribution ratios (R_d) as a function of composition of the C-S-A-H system.

Al_2O_3/SiO_2 molar ratios and the increase of CaO/Al_2O_3 molar ratios. Soundness of matrix compositions, assessed by the R_d value, is demonstrated via circles whose area is proportional to R_d in Figure 3. Favourable blend compositions are thus allocated in the ternary phase diagram of a higher calcium oxide, higher silica, as well as smaller alumina content. This region can be found in the C-S-A ternary diagram around the P06, P09, and P10 points.

By considering these tendencies one may allocate a field in the $CaO-Al_2O_3-SiO_2$ phase diagram bordered by points P06, P09, and P10 with excellent Cs retention. This field is characterised by a relatively low Al_2O_3 content and nearly equimolar SiO_2 and CaO composition. It is also noteworthy that this field is liable to form zeolitic phases whose presence needs verification in the future.

It is assumed that by selecting a cement matrix of an overall composition lying in the determined field, one may ensure optimum Cs retention. Similar behaviour of actual cements to that of the model system assembled using basic chemicals (reactive CaO, SiO_2, and $AlO(OH)\cdot xH_2O$) is to be verified and, if proved to be applicable, composition of the matrix with the best Cs retention would be determined in subsequent work.

The P11 coded sample composition showed very low retention for Cs at the first two measurement periods. Unexpectedly, however, after 1 year its binding capacity increased almost by an order of magnitude. This phenomenon can be explained by probable formation of gismondine, a mineral known for excellent Cs binding potential in a cementitious environment (5), but the complexity and low peak intensity of the X-ray defraction spectrum did not allow unambiguous identification.

Conclusions

- Cs retention in cementitious matrices may be improved by proper selection of composition.
- The immobilisation may involve chemical fixation by formation of crystalline or non-crystalline compounds and sorption.
- A matrix composition low in Al_2O_3 and nearly equimolar in SiO_2 and CaO content proved to be the best for Cs retention.

- Verification of similar behaviour of actual cement systems to that of the best model compositions should be done as the next step toward finding an optimum immobilisation medium for Cs in repositories. Tendencies found on changing the matrix composition are illustrated in Figure 4.

Acknowledgment

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