Pergamon

Cement and Concrete Research 30 (2000) 1619–1623

CEMENT AND CONCRETE RESEARCH

Cerium(III, IV) in cement
Implications for actinide (III, IV) immobilisation

C.L. Dickson, F.P. Glasser*

Department of Chemistry, University of Aberdeen, Meston Walk, Room 033, Meston Building, Old Aberdeen, Scotland AB24 3UE, UK

Received 24 January 2000; accepted 10 July 2000

Abstract

Cementitious materials show potential for the immobilisation of radionuclides, including actinides. The mechanism by which such elements interact with the immobilisation matrix is of fundamental importance to an assessment of future performance. Ce(III, IV) were used as actinide (III, IV) simulants to study the reactions of aqueous solutions of cerium with cement components and characterise the likely solubility-limiting phases in cement–actinide systems. Two newly identified phases are reported, namely $CeSiO_4$ and $Ca_2Ce_8(SiO_4)_6O_2$. The many examples of naturally occurring minerals with these structure types suggest the potential for long-term immobilisation of actinide (III, IV) elements in cement. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Actinide simulants; Radioactive waste; Cement; Crystal structure; TEM

1. Introduction

A significant disadvantage of using nuclear fuel is the problem of radioactive-waste disposal. Actinides are generated as by-products of the nuclear fission process. Such elements pose a considerable biological hazard and thus demand a safe and effective means of disposal, perhaps requiring additional man-made barriers. In this context, considerable research effort has been made to investigate the capacity of cements to immobilise radionuclides [1–5].

Since actinides are difficult and costly to study directly, a chemical analogue approach was adopted, whereby the behaviour of actinides may be simulated by inactive or less active elements. A critical review of the literature concerning the oxidation state, ionic radius, hydrolysis and redox behaviour of relevant species suggested the use of Ce(III, IV) as analogue species for An(III, IV) (where An represents an actinide element), its oxidation state depending on the prevailing conditions. Cerium has been used as a chemical analogue for plutonium in other radwaste immobilisation studies [6,7].

Reaction of Ce(III) and Ce(IV) with C–S–H of two different C/S target ratios was carried out to determine the solubility-limiting phases in these systems and assess the benefits of cement conditioning. Two phases that have not previously been described in cement systems were identified from these reactions, namely $Ce(IV)SiO_4$ and $Ca_2Ce(III)_8(SiO_4)_6O_2$.

2. Experimental

2.1. Synthesis

Target C/S ratios towards the low (C/S = 1.0) and high (C/S = 1.8) ends of the compositional range of C–S–H were investigated. The source of cerium was cerium(III) nitrate hexahydrate, $Ce(NO_3)_3 \cdot 6H_2O$ (Aldrich). The nitrate salt was chosen because it is readily soluble, does not form strong complexes with the reactants, and does not significantly interfere with cement hydration. Ce(IV) was apparently generated spontaneously (i) during hydrothermal reactions, especially at ≥120°C and (ii) at lower temperatures, if solutions remained acidic.

CaO, prepared by decomposition of $CaCO_3$ (BDH) at 1000°C, SiO_2 (Aerosil 300, Degussa) and an appropriate amount of crystalline cerium nitrate hydrate were thoroughly mixed and then hydrated under a nitrogen atmo-

---

* Corresponding author. Tel.: +44-1224-272906; fax: +44-1224-272908.

E-mail address: f.p.glasser@abdn.ac.uk (F.P. Glasser).

0008-8846/00/$ – see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0008-8846(00)00362-8

Table 1
Results of experiments with C/S = 1.0

Weight CaO (g)	Weight SiO_2 (g)	Weight $Ce(NO_3)_3 \cdot 6H_2O$ (g)	Mol% Ca	Mol% Si	Mol% Ce	Temperature (°C)	Ageing time (days)	pH[a]	Products[b]	Comments[c]
0.1300	0.1393	0.9991	33.4	33.4	33.2	55	700	4.1	$CeSiO_4$ (colloidal)	All Ca removed as $Ca(NO_3)_2$
0.5181	0.5555	2.0091	40.0	40.0	20.0	85	700	4.4	$CeSiO_4$	Amorphous phase containing Ca, Ce and Si seen by TEM
0.1282	0.1383	0.9884	33.3	33.5	33.2	85	700	3.5	$CeSiO_4$	All Ca removed as $Ca(NO_3)_2$
0.0695	0.0690	1.0003	26.4	24.5	49.1	130	21	3.7	$CeSiO_4 + CeO_2$	All Ca removed as $Ca(NO_3)_2$; excess Ce as CeO_2
0.2190	0.2110	3.0040	27.0	25.0	48.0	180	14	3.1	$CeSiO_4 + CeO_2$	All Ca removed as $Ca(NO_3)_2$; excess Ce as CeO_2
0.2190	0.2110	3.0040	27.0	25.0	48.0	180	21	3.3	$CeSiO_4 + CeO_2$	All Ca removed as $Ca(NO_3)_2$; excess Ce as CeO_2

[a] pH at the end of the ageing period.
[b] Products identified by X-ray diffraction.
[c] See Discussion.

sphere (AtmosBag™, Aldrich) at room temperature using double-distilled decarbonated water before being transferred to sealed containers for ageing at the desired temperature. Oversaturation experiments were performed using relatively high concentrations of cerium (10–50 mol%) in order that a cerium-containing solid phase could be precipitated from solution and subsequently analysed by X-ray diffraction. The water/solid ratio varied from ~7 to 100, dependant on reactor vessel capacity.

For experiments at temperatures above 100°C, the samples were aged in tightly sealed reactors (Parr Instrument), ranging in capacity from 10 to 250 ml and filled approximately two-thirds full. The smaller vessels were placed in ovens regulated at 130 ± 2°C and 180 ± 2°C. The larger pressure vessels were heated on magnetic stirrer hotplates (Bibby Sterilin). The temperature was monitored by means of an iron–constantan thermocouple attached to a high-resistance millivolt meter (Cambridge Instrument). The temperature was maintained to within ± 0.5°C of the required temperature by insulating the vessel with an aluminium foil–glass wool cover. Pressures within the reaction vessel did not exceed 20 bar.

After ageing for the predetermined period of time required to synthesise the phase of interest, the pH of the sample solution was measured (Whatman "pH Checker") before the contents of the vessel were filtered under nitrogen. Due to the design of the pressure vessels, it was not possible to take samples for pH analysis during the course of experiments: pH values given are those taken after the vessels had cooled to room temperature. The solid was retained for X-ray analysis. Initial product characterisation was by X-ray powder diffraction.

2.2. Crystal structure determination

Rietveld refinement of the crystal structures of both $CeSiO_4$ and $Ca_2Ce_8(SiO_4)_6O_2$ was carried out and has been described in detail elsewhere [8]. $CeSiO_4$ was confirmed to be a zircon structure type, with space group $I4_1/amd$ and unit cell parameters $a = 6.9564(3)$, $c = 6.1953(4)$ Å.

Table 2
Results of experiments with C/S = 1.8

Weight CaO (g)	Weight SiO_2 (g)	Weight $Ce(NO_3)_3 \cdot 6H_2O$ (g)	Mol% Ca	Mol% Si	Mol% Ce	Temperature (°C)	Ageing time (days)	pH[a]	Products[b]	Comments[c]
0.8419	0.4997	1.8072	54.6	30.3	15.1	85	530	11.8	$Ca_2Ce_8(SiO_4)_6O_2$	In all cases: not enough NO_3^- to remove Ca; C–S–H phase seen by TEM
0.1683	0.1006	0.3579	54.3	30.8	14.9	130	21	11.7	$Ca_2Ce_8(SiO_4)_6O_2$	
1.4140	0.8410	3.0000	55.0	30.0	15.0	180	21	11.3	$Ca_2Ce_8(SiO_4)_6O_2$	
1.4140	0.8410	3.0000	55.0	30.0	15.0	180	28	11.3	$Ca_2Ce_8(SiO_4)_6O_2$	
0.1682	0.0998	0.4696	52.3	28.9	18.8	180	14	11.2	$Ca_2Ce_8(SiO_4)_6O_2$	
0.1682	0.0998	0.4696	52.3	28.9	18.8	180	28	11.4	$Ca_2Ce_8(SiO_4)_6O_2$	

[a] pH at the end of the ageing period.
[b] Products identified by X-ray diffraction.
[c] See Discussion.

Fig. 1. TEM micrograph of $CeSiO_4$.

$Ca_2Ce_8(SiO_4)_6O_2$ was shown to have the apatite structure, with space group $P6_3/m$ and unit cell parameters $a = 9.4343(3)$, $c = 6.8885(4)$ Å.

3. Results

Table 1 summarises the experimental conditions under which $CeSiO_4$ was obtained. It is a pale yellow solid, which was produced rapidly at higher temperatures or over very long ageing times at lower temperatures. Structure determination and Rietveld refinement confirmed that the compound was $CeSiO_4$ [8], isostructural with zircon, $ZrSiO_4$.

Table 2 summarises the experimental conditions under which $Ca_2Ce_8(SiO_4)_6O_2$ was obtained. This phase is a pale yellow solid, which was produced typically at higher temperatures or over very long ageing times at lower temperatures. Structure determination and Rietveld refinement confirmed that the compound was $Ca_2Ce_8(SiO_4)_6O_2$ [8], isostructural with apatite, $Ca_{10}(PO_4)_6(F, Cl, OH)_2$.

No evidence was obtained for solid solution of Ce(III, IV) in C–S–H, although the experiments were not designed to test whether low level substitution (parts per million range) could occur. We are not aware of any large trivalent or tetravalent ions that substitute into C–S–H, although an amorphous phase containing Ca, Ce and Si was found (Table 1). This phase is as yet incompletely characterised.

4. Discussion

Cerium nitrate is strongly acidic and therefore has a high capacity to neutralise cement components. Table 1 shows that the amount of nitrate present in solution was generally sufficient to solubilise much of the calcium in the samples as calcium nitrate. In the case of the experiment with $C/S = 1.0 + 20$ mol% cerium at 85°C, the remaining calcium was bound in a Ca–Ce–Si amorphous phase (see below), distinct from the normal C–S–H phase of cements. The Ca–Ce–Si phase would not be expected to significantly raise the pH of the solution.

$CeSiO_4$ was found to form over the temperature range 55–180°C by reaction of cerium nitrate with C–S–H at a low C/S ratio such that the initial precipitation occurred at $pH < 7$. It was produced more readily at higher temperatures,

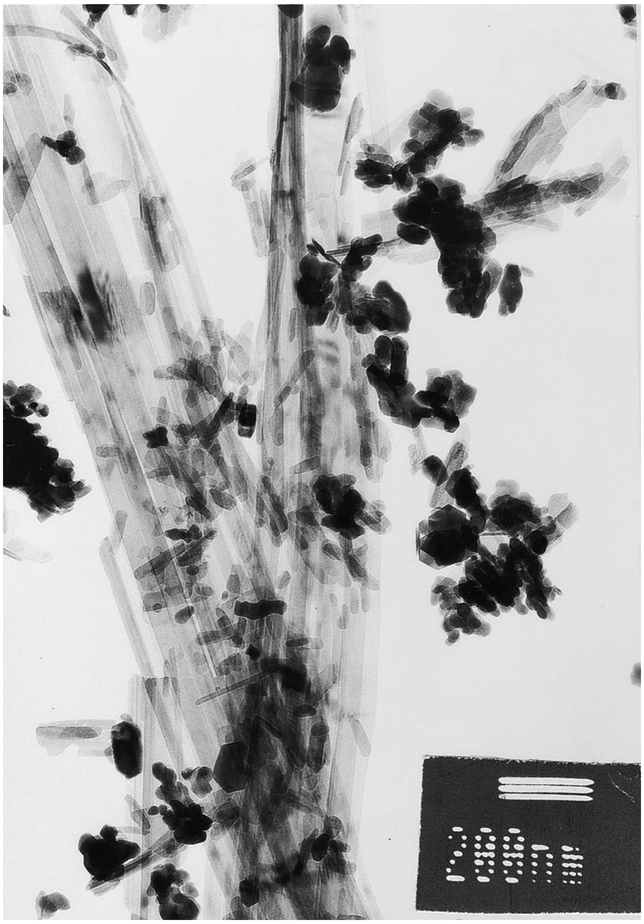

Fig. 2. TEM micrograph of $Ca_2Ce_8(SiO_4)_6O_2$ (platelets and prisms) and C–S–H impurity (laths and needles).

i.e., > 100°C, than at lower temperatures: very long ageing times (1–2 years) were required to induce crystallinity at $T < 100°C$. In preparations with low pH (~ 4), colloidal suspensions of $CeSiO_4$ (see below) could be formed easily at 55°C and remained persistent at this temperature for up to 2 years. However, once the solutions became alkaline, the colloid flocculated and precipitated rapidly.

In some samples, the powder pattern for $CeSiO_4$ showed CeO_2 to be present as an impurity. It was not possible to remove this secondary phase. Analytical electron microscopy revealed that the $CeSiO_4$ was microcrystalline; the typical particle size was in the range 50–200 nm. An amorphous phase containing Ce, Si and a small amount of Ca was also identified in some samples. Fig. 1 shows one of the larger crystals of $CeSiO_4$, probably with tetragonal bipyramidal morphology. The amorphous impurity phase is visible in the top left-hand corner of the micrograph.

Thermogravimetry up to 1000°C was carried out to investigate inclusion of water in the zircon-structured phase. Two regions of water loss were observed. The first occurred over the temperature range 630–680°C, corresponding to 0.5 wt.% H_2O while the second occurred over the temperature range 840–900°C, corresponding to 1 wt.% H_2O. Since the sample contained impurity phases, the weight losses may not be attributed exclusively to $CeSiO_4$. XRD after TG analysis did not show any structural change or decomposition of the sample and the reflections were as sharp as they had been initially. It is therefore unlikely that the loss results from reduction of Ce(IV) to Ce(III) (with associated loss of oxygen) and is also unlikely to be due to the relatively poorly crystalline C–S–H phase. Owing to the stepwise nature of the loss and the relatively high temperatures at which loss occurs, the water may be structural. If so, the formula of the zircon-structured phase would be approximately $CeSi[O_{3.8}(OH)_{0.4}]$. Whether or not the thorium and zirconium analogues of $CeSiO_4$ contain structural water has been the subject of much debate [9–12].

$CeSiO_4$ could only be produced in acidic solution, thus stability studies of $CeSiO_4$ in alkaline solution were carried out by addition of CaO until the solution pH was ~ 12.5. Samples of the solid were taken periodically, filtered and analysed by X-ray powder diffractometry. After 3 months, the pH had remained high in all solutions and the $CeSiO_4$ remained unchanged. After 18 months, the solution pH had dropped slightly to ~ 11 but sharp X-ray reflections corresponding to $CeSiO_4$ were still obtained for the experiments run at room temperature and 55°C. These results indicate that $CeSiO_4$ remains stable at high pH, at least in the short term, despite its initial formation under acidic conditions.

$Ca_2Ce_8(SiO_4)_6O_2$ was found to form by reaction of cerium nitrate with high C/S ratio C–S–H at $T > 100°C$ (or after ~ 18 months at 85°C) in alkaline solution. Although apparently phase pure by XRD, transmission electron microscopy showed that the sample of $Ca_2Ce_8(SiO_4)_6O_2$ was in fact a mixture of two solid phases (see Table 2 and Fig. 2). Hexagonal platelets of the cerium-containing apatite phase could be clearly distinguished from the needle-like morphology of a calcium silicate hydrate phase.

The possibility that the apatite phase was a hydroxyapatite ($Ca_2Ce_8(SiO_4)_6(OH)_4$) rather than an oxyapatite ($Ca_2Ce_8(SiO_4)_6O_2$) was considered, since the samples had been prepared hydrothermally. XRD alone would not be able to distinguish between an oxy- and hydroxyapatite phase, thus a thermal analysis of the sample was carried out. Thermogravimetry showed a weight loss of $\sim 1\%$ occurring over the temperature range 530–600°C and a small, gradual weight loss towards the end of the run at 1000°C but these weight losses are considerably smaller than would be expected if the phase had a significant hydroxyl content. Brown and Chow [13] state that the OH^- in hydroxyapatite is driven off at temperatures of around 1200°C, somewhat higher than the temperatures of weight loss reported here. Moreover, the loss cannot be unequivocally attributed to the apatite because of the presence of a calcium silicate hydrate impurity phase. For charge balance, the hydroxyapatite model would represent the composition $A_{10}(XO_4)_6Y_4$ (Y = OH), no examples of which are known. It seems likely, therefore, that the sample is an oxyapatite but the inclusion of a small amount of hydroxyl cannot be discounted.

$Ca_2Ce_8(SiO_4)_6O_2$ was found to be stable under alkaline conditions and remained unchanged in contact with saturated $Ca(OH)_2$ solution for 10 months at room temperature. An equimolar mixture of the apatite and calcium hydroxide was prepared and left to stand in air for carbonation to occur. After about 1 month, the solution pH had dropped from its initial value of ~ 12.5 to ~ 8.5. X-ray analysis showed the solids to comprise a mixture of $Ca_2Ce_8(SiO_4)_6O_2$ and $CaCO_3$, illustrating the persistence of the apatite-structured phase in near-neutral pH environments.

5. Conclusions

In the reaction of cerium with C–S–H, zircon and apatite-structured phases were identified. There are many examples of naturally occurring minerals having these structure types [14,15]. This is of considerable significance, as the occurrence of actinide orthosilicates and lanthanide/actinide-containing apatites in nature suggests a high potential for the immobilisation of radioelements in such minerals and the long-term persistence and low solubility of such minerals is easier to assess. Much research has been devoted to developing tailor-made ceramics with lanthanide/actinide ions fixed in leach-resistant crystalline phases and to using geologically stable minerals as hosts for crystallochemical immobilisation of radioactive species. Apatite is one such mineral [16–18].

The apatite structure is of particular interest due to its high capacity for isomorphous substitution [19–21]. It is likely that a wide range of radioelements could be incorporated into its structure, making it a highly effective host for radionuclide containment. However, in most cases described in the literature, chemical adjustment to the waste composition and much processing are required to produce an apatite-structured phase. The experiments reported here suggest that in cement systems it is comparatively easy to adjust compositions such that an apatite-structured phase will form spontaneously, especially in warm conditions.

The characterisation of two new phases illustrates the importance of the experimental approach to actinide immobilisation. The formation and persistence of these phases would not have been predicted by modelling studies and therefore could not have been taken into account in performance assessment studies. Although formed under acidic conditions, $CeSiO_4$ was demonstrated to persist under alkaline conditions, at least in the short term.

The likelihood of $CeSiO_4$ being formed in mixtures of cerium with OPC is reduced by the fact that the SiO_2 activity will be low in such a system. Nevertheless, blended cements containing a significant quantity of supplementary materials such as fly ash have much higher SiO_2 activities and may be more suitable for stabilising orthosilicate phases. These cements also have slightly lower pH than OPC. Further investigations should recognise the importance of pH and SiO_2 activity in the immobilisation of actinides.

It may be concluded that cement has the potential to be a very effective immobilisation matrix for actinide (III, IV) elements. C–S–H is demonstrated to have an insolubilising effect on cerium, leading to precipitation and compound formation. These reactions are relatively slow at $T < 120°C$. and at lower temperatures metastable phase assemblages may be persistent. However, reaction directions are believed to have been defined. The resultant solubility-limiting phases have naturally occurring analogues that are known to be environmentally stable and have low solubilities. The simulant studies also indicate what experiments should be done with real actinides to verify these conclusions and provide supporting data on the solubility-limiting source term for performance assessments.

Acknowledgments

This work was supported by the Commission of the European Communities, Contract FI4W-CT96-0030.

References

[1] F.P. Glasser, M. Atkins, Cements in radioactive waste disposal, Mater Res Soc Bull (1994) 33–38 (Dec).

[2] M. Atkins, F.P. Glasser, Application of portland cement-based materials to radioactive waste immobilisation, Waste Management 12 (1992) 105–131.

[3] D.E. Macphee, F.P. Glasser, Immobilisation science of cement systems, Mater Res Soc Bull (1993) 66–71 (Mar).

[4] S. Komarneni, D.M. Roy, Mechanisms of immobilisation of nuclear waste elements by cement minerals, cement and mortar, Cem Concr Res 11 (1981) 789–794.

[5] P. Barret, D. Bertrandie, J.M. Casabonne-Masonnave, D. Damidot, Short term processes of radionuclide immobilisation in cement: a chemical approach, Appl Geochem (Suppl. Pt. 1) 1992, pp. 109–124.

[6] B.D. Begg, E.R. Vance, G.R. Lumpkin, Charge compensation and the incorporation of cerium in zirconolite and perovskite, Mat Res Soc Symp Proc 506 (1998) 79–86.

[7] S.S. Shoup, C.E. Bamberger, Synthesis of titanate-based hosts for the immobilisation of Pu(III) and Am(III), Mat Res Soc Symp Proc 465 (1998) 379–386.

[8] J.M.S. Skakle, C.L. Dickson, F.P. Glasser, The crystal structures of $CeSiO_4$ and $Ca_2Ce_8(SiO_4)_6O_2$, Powder Diffr (in press).

[9] C. Frondel, Hydroxyl substitution in thorite and zircon, Am Min 38 (1953) 1007–1018.

[10] M. Taylor, R.C. Ewing, The crystal structures of the $ThSiO_4$ polymorphs: huttonite and thorite, Acta Cryst Sect B 34 (1978) 1074–1079.

[11] L.H. Fuchs, E. Gebert, X-ray studies of synthetic coffinite, thorite and uranothorites, Am Min 43 (1958) 243–248.

[12] F.A. Mumpton, R. Roy, Hydrothermal stability studies of the zircon–thorite group, Geochim Cosmochim Acta 21 (1961) 217–238.

[13] W.E. Brown, L.C. Chow, Chemical properties of bone mineral, Annu Rev Mater Sci 6 (1976) 213–236.

[14] J.A. Speer, Orthosilicates, Reviews in Mineralogy, Vol. 5, Mineralogical Society of America, Washington, 1980.

[15] D. McConnell, Apatite, Springer-Verlag, Berlin 1973.

[16] G.J. McCarthy, High-level waste ceramics: materials considerations, process simulation and product characterisation, Nucl Technol 32 (1) 1977, pp. 92–105.

[17] J.M. Rusin, M.F. Browning, G.J. McCarthy, Development of multibarrier nuclear waste forms, Scientific Basis Nucl Waste Manage 1 (1978) 169–180.

[18] J. Carpena, F. Audubert, D. Bernache, L. Boyer, B. Donazzon, J.L. Lacout, N. Senamaud, Apatitic waste forms: process overview, Scientific Basis Nucl Waste Manage XXI (Mater Res Soc Symp Proc) 506 1997, pp. 543–549.

[19] L. Boyer, J. Carpena, J.L. Lacout, Synthesis of phosphate–silicate apatites at atmospheric pressure, Solid State Ionics 95 (1997) 121–129.

[20] M.E. Fleet, Y. Pan, Rare earth elements in apatite: uptake from H_2O-bearing phosphate–fluoride melts and the role of volatile components, Geochim Cosmochim Acta 61 (22) (1997) 4745–4760.

[21] W.J. Weber, Radiation damage in a rare earth silicate with the apatite structure, J Am Ceram Soc 65 (11) (1982) 544–548.