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Binding mechanisms of radionuclides to cement

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Abstract

Radionuclide solubility is one of the factors that can determine the 'source term' for potential migration to the far field. Hence, the mechanisms of immobilisation of radionuclides in cements need close study in order to quantify the nature of the binding. The nature of the binding forces in a cement matrix is very species sensitive, so it is difficult to produce a general description. This review summarises the main sorption mechanisms and then details immobilisation mechanisms for many elements.

Keywords: Radioactive waste; Waste management

Contents

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1. Introduction

Radionuclide solubility is one of the factors, along with sorption and inventory, that can determine the ‘source term’ for potential migration to the far field of a nuclear waste repository. Several processes can affect the concentration of a radionuclide in cement porewater, e.g.:

a) precipitation as a simple salt;
b) coprecipitation with other phases;
c) lattice incorporation in the major cement hydration products (solid solution);
d) sorption at hydrous surfaces (chemisorption, adsorption);
e) complex and colloid formation in the aqueous phase [1].

The best case for retardation of radionuclide mobility is to have a low aqueous solubility, with a robust solubility controlling phase. An understanding of interaction mechanisms is important where data are required for performance assessment, that are outside the range of experimental systems studied (e.g. pH range, timescales). If the wrong mechanism is assumed, this could lead to inappropriate values being selected on estimation. It should be noted that mechanisms found to occur on laboratory timescales are not necessarily those that will operate on much longer (repository-related) timescales.

One aspect that is not covered in this review is the effect of carbonation of cements on radionuclide immobilisation. This is due to insufficient data being available in the literature used to compile this review.

Sorption is a generic term, which covers the processes of absorption, physical adsorption and chemical adsorption. Sorption mechanisms depend on the chemical speciation of the sorbate, and the chemical and physical properties of the sorbent.

Absorption is the incorporation of a sorbate within the physical or molecular structure of a sorbent, i.e. the sorbate has access to the bulk, not just the surface, of the sorbent. Physical adsorption can be divided into three types:

(a) Surface complexation, which is mixture of chemical and electrostatic interactions;
(b) Ion exchange, which is an example of electrostatic adsorption due to coulombic forces of attraction between charged sorbate species and the sorbent;
(c) Other mechanisms, e.g. solid-solution formation, coprecipitation.

The most important reactions of cement with waste are those which lead to binding [2], i.e. a chemical reaction. The nature of the binding forces in a cement matrix is species specific, so it is difficult to produce a general description. Many species also form one or more solubility-limiting phases by reaction with cement components. “Solubility-limiting” implies the formation of a phase which would not ordinarily exist in cement, because it contains one or more radioactive species.

2. Review of reported immobilisation mechanisms by element

2.1. Group I elements

The sorption of Li, Na, K and Cs on calcium silicate hydrate (CSH) studied by Iwaida et al. [3], was found to increase inversely in proportion to the Stokes radius of the hydrated ions for cements with various Ca:Si ratios. The authors concluded that sorption was electrostatic on a negatively charged CSH site. Hong et al. have suggested [4] that this is at silanol (Si–OH) sites, arising from the density of silanol bonds and the sites’ mean acidity, both of which increased as the Ca:Si ratio decreased [4].

2.1.1. Caesium

The binding capacity of cement for Cs is dependent on chemical composition, as the different phases have different binding capacities [5]. Cs retention has been found to increase 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 in the same ratio [5]. However, Cs retention was found to decrease with increasing $SiO_2:CaO$ ratio [5], the opposite effect was found by Noshita and Aggarwal et al. [6], but not commented upon by the authors. Sorption decreased further with increasing alumina content, at constant $SiO_2:CaO$ ratio. Similarly, for compositions with constant $Al_2O_3:SiO_2$ content, an increase in the Ca:Si ratio resulted in a decrease in R_d values, although increasing the CaO content with a constant $Al_2O_3:SiO_2$ ratio increased Cs retention [5].

Solid-state NMR was used to investigate Cs speciation in cements by Hanna et al. [7]. Cs in Ordinary Portland Cement (OPC) appeared to remain in solution, whether or not blast furnace slag (BFS) or Condensed Silica Fume (CSF) were present. Differences due to Cs partly inhabiting semi-crystalline or amorphous solid sites were observed after 1 year in the slag-containing cement, but the majority of the Cs was apparently restricted to partially or fully solvated states in the aqueous phase. However, Atkinson and Nickerson [8] concluded that the diffusivity of Cs^+ ions in OPC was significantly lower than that of Cl^- and Na^+ ions. The use of zeolite as a blending material in cement has been found to cause an 80-fold reduction in Cs leaching [9,10], and in other studies, the use of slag also had an influence by a factor of 4–5 on leaching [11,12].

Sorption experiments with ^{137}Cs on four types of concrete (normal density, normal density with fuel ash, high density and high density with silica fume) were carried out by Jakubick et al. [13] in 3 groundwaters. Cs showed no significant sorption on normal-density concrete and sorption on carbonate aggregates was also very low. Greater sorption occurred along the cleavage planes of gneiss aggregates containing mafic minerals (biotite and pyroxene). The high-density sample showed preferential sorption of Cs on the magnetite aggregates and on the fine grains of specularite, a variety of haematite characterised by aggregates of silvery, metallic, specular haematite flakes or tabular, anhedral crystals, also known as grey haematite.

The identification of the hydrated phases responsible for Cs incorporation in concrete was investigated by Hoyle and Grutzeck [14]. Calcium aluminosilicate glasses were mixed with CsOH or CsCl solutions and allowed to hydrate. Glasses exposed to CsOH (aq) were more reactive than their counterparts exposed to CsCl (aq). At least two Cs-containing zeolites were identified in the 90 °C CsOH solution; a Cs-containing wairakite ($CaAl_2Si_4O_{12}\cdot 2H_2O$) analogue, and another unidentified Cs-containing zeolite. However, strätlingite did not appear to take up Cs.

Noshita et al. [15] found that Cs was highly sorbed by calcium silicate compounds (in agreement with [6]). It was sorbed onto those with lower Ca:Si molar ratios, such as CSH. This suggests that sorption was mainly determined by Ca:Si ratios, regardless of crystal structure. Iwaida et al. [3] observed a shortening of the silicate chains in CSH which had sorbed Cs, indicating that breakage of the silicate chains had occurred. The authors suggested that hydroxide played an important role in this process. Energy dispersive analysis of silica fume clusters in cement by BarNes et al. [16] suggested that Cs tends to concentrate inside agglomerated silica particles.

2.1.2. Sodium

Sodium substitutions in CSH phases have been reported [17]. CSH gel dissolution experiments in NaCl(aq) showed an increase in Ca concentration at higher Na concentrations. This was interpreted in terms of an ion exchange process between Ca and Na [18], although an alternative explanation could lie in the formation of chlorocomplexes.

2.2. Actinides

2.2.1. Americium

Experiments [13] using ^{241}Am have indicated preferential sorption in cementitious paste. Normal-density specimens containing fuel ash sorbed more than standard compositions, with voids showing rims of enhanced sorption. Considerable sorption was observed on carbonate aggregates and mafic components of the granitic and gneiss aggregates. A slightly higher sorption on magnetite than on specularite or hematite was observed [13]. Baston et al. [19] quantified Am sorption data using a surface complexation model, in which the main surface sites were $>SiO^-$ and $>SiOCaOH$, with Am hydroxide species assumed to be the sorbing species. Noshita et al. [20], have found that Am is highly sorbed onto CSH gel, and they concluded that Am is anionic in cement.

2.2.2. Curium

Stumpf et al. using time-resolved laser fluorescence spectroscopy (TRLFS) [21] identified 4 different Cm(III) species. A non-fluorescing species which corresponds to curium hydroxide real colloids, a fluorescing Cm(III)-portlandite sorption species, and two fluorescing Cm(III)-CSH species. From fluorescence emission lifetimes it was predicted that the two fluorescing Cm(III)-CSH species had 1 to 2, and zero water molecules respectively, in their 1st coordination sphere, suggesting that these species were incorporated in the CSH structure. Measurements on HCP systems in artificial cement porewater showed that initially Cm(III) is sorbed on the portlandite fraction. With time, two forms of Cm(III) incorporated in the CSH fraction, where it occupies 2 different positions in the CSH structure [22], became dominant.

2.2.3. Neptunium

Sylwester et al. [23] observed a reduction from Np(V) to Np (IV) as it interacted with OPC; the amount of reduction increasing with equilibration time. The absence of Np–Np interactions in the extended X-ray absorption fine structure (EXAFS) spectra provided evidence that Np partitioning was controlled by sorption of Np(V), followed by reduction, and not by reduction followed by formation of Np(IV) surface precipitates. Matzen et al. [24] identified immobilised Np at, or near, the fracture surface when soluble and colloid-associated Np were eluted into a fractured, hydrothermally altered, concrete core.

2.2.4. Plutonium

Jakubick et al. [13] have shown that the surface distribution pattern of Pu follows the concrete structure selectively. Preferential sorption in the cement paste over that on aggregates was characteristic of both normal and high-density concrete. Sorption on carbonate aggregates was slightly higher than, or comparable with, that on gneiss fragments. Sorption patches of Pu were also observed on the mafic components of the granitic aggregates. However, the quartz components remained inactive. In the high-density concrete, the magnetite aggregates proved to be more sorptive than hematite and specularite. Aggarwal et al. [6] found that sorption increased with increasing fraction of OPC in PFA/OPC blends. There was a downward trend in R_d with decreasing Ca:Si ratio for C_3S hydrates. Comparison of the sorption on cements with that on CSH, indicated that most sorption occurred on the CSH, but in BFS/OPC blends, other phases may have contributed.

2.2.5. Thorium

Tits et al. [25] have shown that the sorption process controlling the retention of Th(IV) on CSH is fast. Sorption distribution ratios in the range of 10^5 to 10^6 dm^3 kg^{-1} were found.

2.2.6. Uranium

The reactions between CaO, SiO_2 and schoepite ($UO_3{\cdot}2H_2O$) were studied by Moroni and Glasser [26] in aqueous suspensions at 85 °C. Several solubility-limiting, but hitherto uncharacterised, $CaO–UO_3–SiO_2–H_2O$ phases were described. It was concluded that weeksite-like and becquerelite-like structures were probably developed. With the formation of crystalline phases, U solubilities declined to the region of 10^{-8}–10^{-9} mol dm^{-3}. Some slight U sorption into the gel may have occurred. Sylwester et al. [23] have shown that U remains in the form of UO_2^{2+}. Evidence of inner-sphere interactions on both treated and untreated cements at all pH values was found, with UO_2^{2+} complexing with the mineral surface via sharing of equatorial oxygens. On hydrothermally treated cement near-neighbour U–U interactions were also observed, indicating the formation of oligomeric surface complexes, or surface precipitates.

Wet chemistry and EXAFS studies on U(VI) uptake by HCP by Wieland et al. [27] showed that sorption was linear up to about 6×10^{-6} mol dm^{-3}. Above this, the immobilisation was due to the formation of a calcium uranate precipitate. A study by Pointeau et al. [28] showed that the uptake of U(VI) increased when comparing the least and most degraded cement pastes, whereas the initial composition of the cement had relatively little effect. Sorption isotherms were linear with a slope of 1, indicating the predominance of sorption processes. As sorption and desorption values were close, the uptake mechanism seemed to be reversible.

Harfouche et al. [29] either sorbed U(VI) onto previously precipitated CSH phases (sorption samples) or added during C–S–H synthesis (coprecipitation samples). The coordination environment of U(VI) in the sorption samples was independent of CSH synthesis procedure. The coordination environment of U(VI) in the coprecipitated samples depended on the synthesis method, and the spectra differed from those for the sorption samples.

2.3. 'P' block elements

2.3.1. Arsenic

Kumarathasan et al. [30] observed that the replacement of SO_4^{2-} by arsenate in ettringite, and quasi-instantaneous equilibrium (<1 min) was observed by Myneni et al. [31] for this process. A study by Phenrat et al. [32] found As–Fe hydroxide sludge to be immobilised by 3 mechanisms, sorption onto the CSH surface, replacing SO_4^{2-} in ettringite and, predominantly, the formation of solubility-limiting Ca–As compounds.

Stronach et al. [33] report that hydrated Portland cement limits the solubility of As(III) to 7.0 mmol kg^{-1}. The authors also observed that this is due to the substantial buffering reserve of $Ca(OH)_2$, which is in theory able to immobilise 1 As atom per Ca atom by the formation of the sparingly soluble $CaAsO_2OH$.

2.3.2. Organic carbon

Batch sorption experiments using acetic acid, formaldehyde, acetaldehyde and arginine were carried out by Matsumoto et al. on various types of cementitious mortars [34] at different pHs. The sorption experiments showed that aqueous organic ^{14}C was not sorbed to any great extent on mortar at high pH. In the mortar–acetaldehyde system sorption was not affected by pH. In the mortar–arginine system, it was found that sorption behaviour changed on either side of the isoelectric point of arginine, i.e. sorption of negatively charged arginine above pH 12.5 was low, whereas that of the positively charged species below pH 12.5 was high. Therefore, it was concluded that organic carbon is mainly adsorbed onto the surface of mortar via silanol groups electrostatically, and so sorption will depend on the ionic speciation of the organic carbon species in aqueous solution.

2.3.3. Inorganic carbon

Inorganic ^{14}C sorption by cementitious materials can be roughly divided into two reactions; (i) adsorption onto a positive site and (ii) precipitation. Noshita et al. [35] have suggested that $^{14}CO_3^{2-}$ was sorbed onto the cement surface electrostatically, due to the reaction between SiO_2 and CaO contained in the cement. That is, SiO_2 was originally anionic (SiO^-), but became cationic through interaction with Ca^{2+}. The ^{14}C K_d was increased from 2000 to 7000 ml g^{-1} by adding SiO_2 to OPC. Banba et al. [36] also suggested that this immobilisation was also by adsorption onto colloidal compounds in cement.

Noshita et al. [15] found that CO_3^{2-} is sorbed onto calcium silicate compounds with lower Ca:Si ratios if the bulk solution was in NaOH(aq), but that sorption was less in bulk $Ca(OH)_2$ solution This indicated that formation of $CaCO_3$ may affect R_d values, although the initial carbonate concentration was adjusted to below its maximum solubility. In $Ca(OH)_2$ solution, the order of sorption was gibbsite>brucite>portlandite, which may reflect the tendency of $CaCO_3$ to flocculate and precipitate as colloids.

2.3.4. Chlorine

Several authors, e.g. Brown and Bothe [37] and Damidot et al. [38] have characterised the formation of basic chlorides, (hydr)oxychlorides, in cement systems. The interaction of Cl^- ions with a cement matrix depends on several parameters.

Chloride can react with unhydrated aluminate phases to form new compounds such as Friedel's salt [37–39]. Sorption, or secondary phase formation, depends on the type of binder and the nature of the cations in the pore solution [40–43] as well as on the pore solution concentration and composition. For example, the amount of bound Cl^- added as $CaCl_2$ has been found to be significantly higher than for Cl^- added as NaCl [44,45], but the reason for this is not clear. It has been suggested that $CaCl_2$ interacts with $Ca(OH)_2$ at low temperatures, and high Cl^- concentrations, to give $CaO–CaCl_2–H_2O$ complex salts with varying compositions [44]. Tang et al. [40] observed that the Cl^- binding capacity of HCP strongly depends on the content of CSH gel.

Several possible states of Cl^- in the hydration of tricalcium silicate in the presence of $CaCl_2$ have been suggested [46] These include a chemisorbed [46] Cl^- layer on the surface of CSH, in the interlayer space and incorporated in the CSH lattice. Beaudoin et al. have suggested that most of the chloride ions are chemisorbed on the surface of hydrated C_3S [47].

^{35}Cl NMR relaxation methods [48] indicated that the majority of the sorbed Cl^- near the surfaces of solid phases such as portlandite and jennite was in a solution-like environment, and was in rapid exchange with free Cl^- in the bulk solution. The total amount of sorbed Cl^- on jennite was substantially greater than could be accommodated by coordination directly to the solid surfaces and the amount predicted to exist in the Stern and diffuse layers based on Gouy–Chapman calculations. The authors postulated that this excess was probably due primarily to formation of metal complexes or ion pairs.

2.3.5. Iodine

The mechanism of I^- uptake in cement hydrate phases is sorption and/or incorporation according to Glasser [49]. Precipitation as a simple iodide salt is most unlikely, because its salts are either too soluble, or else sufficient insolubilising cations are not normally present in cements (e.g., Ag^+, Pb^{2+}) [49].

Long-term experiments have shown that I^- sorption increases with increasing Ca:Si ratio in CSH gels (in agreement with [6]), despite increased competition from OH^- for sorption sites at higher Ca:Si ratios [15,49], suggesting that I^- was sorbed electrostatically. AF_t behaved similarly to high Ca:Si ratio CSH. AF_m however, has been shown to be a much more efficient scavenger with 70–80% removal from 10^{-3} mol dm^{-3} solutions.

Iodide sorption on three commercial alumina cements mixed with $CaSO_4$ and/or $Ca(OH)_2$ was investigated by Toyohara et al. [50,51]. The highest sorption was obtained with $CaSO_4$ added to alumina cement to a SO_4:Ca mole ratio of 0.16. The I^- replaced the OH^- in $4CaO·Al_2O_3·13H_2O$ to form the new hydrate $3CaO·Al_2O_3·CaI_2·12H_2O$. The results of sorption and desorption experiments showed that I^- sorption was reversible and independent of concentration up to 1×10^{-2} mol dm^{-3}.

CSH has a much stronger affinity for iodate than iodide. This is probably due to the more complex structure of the iodate anion with the surrounding oxygens acting as bridges with the complex CSH substrate. Slight desorption occurs with time, which is thought to be due to occlusion of aqueous iodate in CSH followed by diffusion of the excess back to solution. A similar phenomenon has been found for sulphate in CSH [44].

2.3.6. Lead

Glasser [52] suggests that Pb will generally replace Ca in cement hydrate phases. Moulin et al. [53] found that whereas Pb shows a poor affinity to calcium aluminate phases (due to precipitation of PbO), it was strongly retained by hydrated phases coming from C_4AF hydration, and that the Pb was linked to silica tetrahedra. The authors attributed this strong retention of lead to the hydrated "ferrite" phase.

Sorption isotherms of Pb(II) carried out on C_3S and CSH showed that Pb has differing affinities for calcium silicate in a concentration range lower than the saturation concentration value of PbO [54]. Structural retention mechanisms have been attributed to Q_{1Mc} sites involving Si–O–Pb bonds by Rose et al. [55].

Johnson et al. [56] have shown that a relatively high proportion of Pb precipitated out on the cement matrix, rather than in the precipitated layer as was the case for Cr, Cu and Zn. It is possible that isomorphic substitution of Ca^{2+} by Pb^{2+} (ionic radii 1.00 and 1.17 A, respectively) had taken place in the cement matrix.

An investigation by Coleman et al. [57] into the interactions of aqueous Pb^{2+} ions with crushed concrete fines (CCF), showed that the surface of Pb–CCF was generally composed of a reticular, lead-bearing, calcium silicate network and, occasionally, lead-bearing, calcium-rich, distorted polygons. Removal of Pb^{2+} from solution took place by diffusion into the cement matrix. The authors postulated that the underlying mechanism was isomorphic substitution by Pb^{2+} for Ca^{2+} in the CSH. The rare, calcium-rich, heavy metal-bearing polygons observed on the surfaces of each of the recovered CCF specimens were suggested to be re-precipitated portlandite crystals, distorted from their normal hexagons by the inclusion of Pb^{2+} ions.

Many authors have examined the influence of Pb on the hydration properties of cement. Thomas et al. [58] observed retardation of hydration, due to a rapid precipitation of basic lead compounds. The precipitate that coated the surface of the cement grains was essentially formed of a colloidal gelatinous material. According to Cartledge et al. [59], coatings, which hinder cement hydration, can be formed by lead hydroxide, sulphate, and nitrate mixed salts. Cocke et al. [60–62] have argued that the coatings act as diffusional barriers to water. A charge dispersal model in which the calcium ions induce a charge reversal of the silicate surface allowing $Pb(OH)_3^-$ ions to be adsorbed has been proposed for retardation by Yousuf et al. [63] and Asavapisit et al. [64]. On the other hand, Ortego et al. [65] have suggested that the presence of lead could result in a slight enhancement of silicate polymerisation.

Mattus et al. [66] have suggested that retardation is due to precipitation of sparingly soluble compounds onto the surface of silicate phases, thus preventing their access to water. However, the retardation effect is concentration-dependent, so that Pb has been shown to be a set accelerator in some cases [67].

2.3.7. Selenium

Selenate sorbs via weakly bonded outer-sphere complexes [68]. Kumarathasan et al. [30] and Baur and Johnson [68] have reported the replacement of SO_4^{2-} by selenate in ettringite, and this has also been observed in ‘monosulphate’ which has a crystalline layer structure derived from that of $Ca(OH)_2$ by the ordered replacement of one Ca^{2+} ion in three with Al^{3+} or Fe^{3+}. These layers alternate with ones containing anions, which balance the charge (e.g. SO_4^{2-}, OH^-, etc.) and H_2O. The composition is $[Ca_2(Al,Fe)(OH)_6]\cdot Z\cdot xH_2O$, where Z represents the interlayer anion [31,69,70,71].

Solem-Tishmack et al. [72] have interpreted the more efficient retention of selenite over selenate by the formation of selenite ettringite in cementitious material. However, $CaSeO_3$ precipitation seems the more likely reason for the retention [65].

Bonhoure et al. [73] have shown that Se redox reactions do not influence uptake processes in cementitious systems. EXAFS spectra of Se(IV) and Se(VI) bound to CH, AFt, AFm and CSH were similar to those of SeO_4^{2-} and SeO_3^{2-} in solution, indicating a “solution-like” coordination environment on uptake by cement minerals. The results suggested that the coordination spheres of selenate and selenite are maintained on immobilisation.

2.3.8. Sulphate

Kalousek [1] proposed that SO_4^{2-} ions present in cement eventually enter CSH and experimental studies [74,75] have demonstrated that sulphate can bind to CSH. Nachbaur [76] showed that the mechanism of sulphate binding was a surface phenomenon. The main quantitative results were obtained by Divet and Randriambololona [77], who found that sulphate sorption on CSH fitted a Langmuir isotherm, and that sorption increased with pH and temperature, and that sulphate binding increases with the Ca:Si ratio of CSH.

2.3.9. Tin

A study by Seby et al. [78] showed a strong uptake of Sn(IV) by HCP at pH 13.3 at Sn concentrations well below the solubility limit of Ca-stannate. Bonhoure et al. [79] have suggested that CSH phases may not be the uptake-controlling phase in the cement matrix. An alternative model was proposed [79] on the assumption that ettringite is the uptake-controlling phase. A study of Sn immobilisation by cement and CSH by Wieland et al. [27] showed that, on HCP, sorption was linear up to a maximum equilibrium concentration of about 8×10^{-7} mol dm^{-3}. Above this immobilisation was due to the formation of a Ca-stannate precipitate, often described in the literature as $CaSn(OH)_6$.

2.4. Transition elements

2.4.1. Cadmium

Bonen and Sarkar [80] have reported ettringite accommodating Cd^{2+} at the M^{2+} site in the crystal structure. Polettini et al. [81] found chemical immobilisation of Cd within CSH at pH > 10. Furthermore, the low aqueous Cd concentrations found at high pH may account for its immobilisation within portlandite, as Cd is known to provide nucleation sites both for CSH and portlandite [66].

2.4.2. Chromium

Chromium’s oxidation state and its immobilisation by cements are closely related. Kumarathasan et al. [30] have reported the replacement of SO_4^{2-} by chromate in ettringite. Moulin et al. [53] have observed interactions between Cr and hydrated cement phases. It was found that Cr showed a strong affinity for hydrated C_4AF “ferrite” phases. Cr(III) is structurally incorporated by hydrogarnet phases, but Cr(VI) only showed an affinity for hydrated calcium aluminate phases. For Cr(III), whatever the cement phases studied, a hydrogarnet phase of variable composition was formed. Cr(VI) was weakly retained by calcium silicate, but more by calcium aluminate and aluminoferrite. According to other results [82–84], ion exchange between CrO_4^{2-} and OH^- in the AF_m phase is responsible for immobilisation.

According to Polettini et al. [81] Cr(III) is known to be able to increase the amount of heat liberated during early hydration, promoting the formation of ettringite crystals, probably by reducing the degree of supersaturation [85]. There is evidence for the ability of CSH to incorporate Cr^{3+} ions through Si substitution in poorly crystalline structures [81]. Calcium aluminate hydrate phases can also be formed where octahedrally coordinated aluminium is partly replaced by Cr (III) [81].

2.4.3. Cobalt

Bonen and Sarkar [80] have reported ettringite accommodating Co^{2+} at the M^{2+} site in the crystal structure, while Noshita et al. showed that it was strongly sorbed onto CSH gel [20].

Vespa et al. [86] found that, for samples prepared in air, Co (II) is oxidized to Co(III) after 1 h of hydration time and that the relative amount of Co(III) increased with hydration time. Co(II) was predominately present as a Co-hydroxide-like phase and/or Co-phyllosilicates, whereas Co(III) tended to be incorporated into a CoOOH-like phase and/or Co-phyllomanganates. Samples prepared in the absence of oxygen revealed solely the presence of Co(II), indicating that oxygen plays an important role in Co oxidation in cement.

2.4.4. Copper

Johnson et al. [56] have shown that precipitation, in addition to lowering solubility at elevated pH, is responsible for the immobilisation of Cu. Analysis of Cu-containing crystals showed a Ca to Cu molar ratio of 1:11. Coleman et al.’s [57] study of sorption onto crushed concrete fines (CCF) showed 2 distinct Cu-bearing phases on the surface of Cu–CCF, a Cu-rich foliaceous mass and rare, Cu-bearing, Ca-rich, distorted polygons. The principal mechanism of Cu uptake was precipitation of the foliated crystals onto the surface. No appreciable diffusion of Cu^{2+} into the cement matrix was observed.

2.4.5. Iron

In 1952, Kalousek proposed that all Fe^{3+} ions present in cement eventually enter CSH [1]. Copeland et al. [87] provided some support to this theory by suggesting that two Fe^{3+} atoms replace one calcium and one silicon.

2.4.6. Mercury

Poon et al. [88] have produced evidence of Hg immobilisation by ettringite.

2.4.7. Molybdenum

Mo(VI) can be immobilised in HCP as both $CaMoO_4$, and as a Mo-substituted AF_m phase [2].

2.4.8. Nickel

Bonen and Sarkar [80] report ettringite accommodating Ni^{2+} at the M^{2+} site in the crystal structure. Ni sorbed onto calcium silicates was reported by Noshita et al. [15] that showed no dependence on Ca:Si ratios, eliminating electrostatic adsorption as a mechanism. Coprecipitation or surface complexation via the hydroxyl group have been suggested [89,90]. Ni has also been found highly sorbed onto hydroxides, probably due to coprecipitation or surface complexation [89–91]. This finding contradicts the suggestion of an adsorption-type uptake process. Several authors have noted that there is evidence for a solubility-controlled uptake process [92–94].

Johnson et al. [56] found that precipitation mechanisms in addition to the reduction in solubility at elevated pH, are responsible for Ni immobilisation. Analysis showed a Ca:Ni molecular ratio of 1.10 in the botryoidal Ni-containing precipitate. Scheidegger et al. [92] showed that mixed Ni–Al layered double hydroxides (LDH) may form in cement systems, and thus, Ni–Al LDHs are regarded as solid phases being potentially present in the waste matrix and governing nickel uptake, this has been confirmed by Vespa et al. [95]. The work of Johnson and Glasser [93], however, indicates that $Ni_4Al_2(OH)_{12}CO_3{\cdot}2H_2O$, which has a LDH-type structure, is unlikely to account for the limited solubility of Ni in cement systems.

2.4.9. Vanadium

Kumarathasan et al. [30] has reported the replacement of SO_4^{2-} by vanadate in ettringite.

2.4.10. Zinc

Bonen and Sarkar [80] report ettringite incorporating Zn^{2+} at the M^{2+} site. Moulin et al. [53] found interactions between hydrated cement phases and Zn, and concluded that Zn showed a strong affinity for hydrated ferrite phases and that it was linked to the silica tetrahedra of CSH. From sorption experiments by Ludwig et al. [94], it appears that Zn is strongly retained by CSH. This retention has been attributed to the linkage of tetrahedral Zn to CSH tetrahedral silicate chains [54,82].

Ziegler et al. [96,97] found that at high Zn(II) concentrations (>1 mmol dm^{-3}), the precipitation of β_2-$Zn(OH)_2$ ($<$pH 12) and calcium zincate $Zn_2Ca(OH)_6{\cdot}2H_2O$ ($>$pH 12) occurred, but do not indicate the concentration at which precipitation begins. Surface precipitation was not found. Zn was observed to incorporate into the CSH(I) particles, but it did not appear to substitute for calcium or silicon.

XAFS spectra of the Zn(II) equilibrated with CSH(I) suggested tetrahedral coordination of Zn(II) by 4 oxygen atoms in the atomic shell. This coordination environment was related by the author to the structure of hemimorphite, a naturally occurring zinc silicate, and/or the presence of γ-$Zn(OH)_2$.

Johnson et al. [56] found that cubic crystals observed on concrete particles following contact with Zn^{2+} solution were found to be calcium-rich, whereas the underlying precipitate was Zn-rich. Coleman et al's study [57] of CCF sorption showed a Zn-rich porous ‘cancellated’ network and occasional, zinc-bearing, calcium-rich, distorted polygons over which a further diffuse deposit had formed. The authors concluded that the mechanism of uptake of Zn by CCF was characterised by 3 stages. Firstly, deposition of a Zn-rich precipitate on the surface of CCF, a few microns in depth. Secondly, the formation of a second deposit of around 10 μm and, thirdly, a final superficial precipitate. The authors postulated that the different precipitation processes were mediated by pH and the concentration and speciation of Zn^{2+} ions in solution. Zn^{2+} ions did not appear to have penetrated the cement matrix to any appreciable extent.

Zinc has been reported as causing a substantial retardation in the setting of cement by formation of a protective layer over the cement grains. In the case of C_3S, Ortego et al. [65] demonstrated that polymerisation was retarded by its presence. Arliguie and Grandet [98] and Gawlicki and Czamarska [99] have suggested that this retardation results from precipitation of an amorphous layer of $Zn(OH)_2$ onto the anhydrous grains, but that the hydration process could be restarted once the Ca concentration in solution was sufficient to induce crystallisation of calcium zinc hydroxide. Yousuf et al. [63,100] suggest that surface formation of $CaZn_2(OH)_6{\cdot}2H_2O$ prevented the necessary material transport for the hydration of C_3S. A similar process was proposed by Asavapisit et al. [64] for clinker particles. Others studies [94,101] seem to indicate that Zn might be incorporated into the CSH framework.

2.5. Lanthanides

2.5.1. Europium

Tits et al. [25] described the adsorption of Eu(III) on CSH. The results showed that the sorption process controlling the retention of Eu is fast indicating that uptake is probably controlled by an adsorption process. Very high sorption distribution ratios in the range of 105 to 106 dm^3 kg^{-1} were found.

The sorption mechanisms of Eu on CSH phases of hydrated cement were investigated by Pointeau et al. [102]. The CSH phases, to simulate long-term behaviour, were chosen to have a Ca:Si ratio corresponding to aged cements and, at the same time, equal to the ratio of 0.83 in tobermorite. Eu was not precipitated in solution despite its low solubility limit. It was strongly retained on the CSH (more than 99.8% sorbed). Two main sorption sites were characterised. One site, with a long lifetime (>1 ms), was interpreted as Eu substituting for Ca in the framework of the CSH. Another, with a shorter lifetime (>0.4 ms), was interpreted as a site with a high hydroxylated environment, but one that is less than that of $Eu(OH)_3$, which corresponded to surface complexation or precipitation at around 10^{-10} mol dm^{-3}. The authors thought it reasonable that Eu might be withdrawn from the liquid phase by a simple precipitation process, due to its low solubility limit, but results

Table 1

Element	Solid studied	Mechanism	Reference
Group 1	CSH	Electrostatic sorption[a]	[3]
Group 1	CSH	Electrostatic sorption to silanol[a]	[4]
Al	CSH	Substitution for Si	[87]
Am	Concrete	Mineralogical control	[13]
Am	Concrete	Surface area control	[13]
Am	OPC	Via hydroxide species	[19]
As	OPC	Sorption onto CSH	[32]
As	OPC	SO_4^{2-} substitution in ettringite	[32,30]
As	OPC	Ca–As compound formation	[32,33]
Ba	CSH	Substitution for Ca	[52]
C (Org)	Mortar	Electrostatic sorption[a]	[34]
Cd	CSH	Immobilisation within CSH structure	[81]
Cl^-	HCP	Formation of $CaO–CaCl_2–H_2O$	[44]
Cl^-	Concrete	Chemisorbed layer on the surface of CSH	[46]
Cl^-	CSH	Chemisorbed on hydrated C_3S surface	[47]
Cl^-	(Synthetic) CSH	Freidel's salt formation	[37–39]
Cm^{3+}	CSH	Incorporation in CSH	[21,22]
CO_3^{2-}	HCP	Precipitation[b]	[15]
CO_3^{2-}	Cement	Adsorption on colloids	[36]
CO_3^{2-}	HCP	Electrostatic adsorption onto a positive site[a]	[37]
Cr(III)	Hydrogarnet	Incorporation by hydrogarnet	[53]
Cr(III)	CSH	Si substitution in CSH	[81]
Cr(III)	CSH	Al substitution in Ca aluminate hydrate	[81]
Cr(VI)	Aluminate	Ion-exchange with OH^-	[82–84]
Cr(VI)	OPC	SO_4^{2-} substitution in ettringite	[30]
Cs	CSH Aluminate		[5]
Cs	CSH	Electrostatic sorption[a]	[15]
Cs	CSH		[6]
Cs	CSH	Breakage of silicate chain	[3]
Cs	Cement	Inside agglomerated silica particles	[16]
Cu	CCF	Precipitation[c]	[56,57]
Eu	CSH	Adsorption	[25]
Eu	CSH	Surface complexation or precipitation[d]	[102,22]
Hg	Ettringite		[88]
I^-	Alumina cement	Replacement of OH^-	[50]
I^-	CSH	Electrostatic sorption[a]	[15]
I^-	OPC	Electrostatic sorption[a]	[49]
I^-	OPC	Incorporation	[49]
Mo(VI)	HCP	$CaMoO_4$ and Mo-substituted AF_m phase	[2]
Na	CSH	Substitution	[17]
Na	CSH	Ion exchange	[18]
Ni	CSH		[15]
Ni	CSH	Coprecipitation or surface complexation	[90]
Ni	HCP	Coprecipitation or surface complexation	[56,91]
Ni	HCP	Formation of LDH	[92]
Np	OPC	Sorption followed by reduction	[23]
Pb	CSH	Linked to silica tetrahedra in ferrite	[53]
Pb	CSH	Formation of Si–O–Pb bonds	[54,55]
Pb	CCF	Precipitation[e]	[56]
Pb	OPC	Precipitation[b]	[58,59]
Pb	CSH	Sorption of $Pb(OH)_3^-$	[63,64]
Pb	CCF	Substitution for Ca	[57]
Pu	Concrete	Preferential on cement paste over aggregates	[13]
SeO_3^{2-}	Ettringite	Formation of $CaSeO_3$	[68]
SeO_3^{2-}	Ettringite	Electrostatic sorption[a]	[68]
SeO_4^{2-}	Ettringite	Substitution for SO_4^{2-} in ettringite and monosulphate	[69,71]
Sn	CSH	Ca-stannate formation[b] sorption at lower concentrations	[27]
SO_4^{2-}	CSH	Surface sorption	[76]
Sr	C_3AH_6	Substitution for Ca	[104]
U(VI)		Formation of solubility-limiting phases with Ca and Si[f]	[26]
U(VI)	OPC	Inner sphere interactions	[23]
U(VI)	OPC	Formation of oligomeric surface complexes or precipitates[b]	[23]
U(VI)	HCP/CSH	Calcium uranate precipitate[b]	[27]
U(VI)	CSH	Sorption	[28]
VO_3^-	OPC	SO_4^{2-} substitution in ettringite	[30]
Zn	CSH	Linked to Si tetrahedra in CSH	[53,54,82]
Zn	CCF	Precipitation[g]	[56]
Zn	Ferrite	Formation of Fe–O–Zn bonds in ferrite	[94]
Zn	CSH	Precipitation of zincate phases[b]	[96]

[a] Electrostatic mechanism implies opposite charge on the sorbate.

[b] No indication of concentration at which precipitation began.

[c] [Cu(aq)] after precipitation = 1 ppm.

[d] Solubility limit ~10^{-10} mol dm^{-3} [99].

[e] [Pb(aq)] after precipitation = 9.4 ppm.

[f] [U(VI)(aq)] after precipitation = 10^{-8}–10^{-9} mol dm^{-3}.

[g] [Zn(aq)] after precipitation = 27.5 ppm.

showed that this was not the case. It was suggested that the presence of CSH causes a dragging force, which prevents normal precipitation. Tits et al. [22] have corroborated this.

Eu LIII-edge EXAFS spectra collected by Schlegel et al. [103] on samples of Eu sorbed on, or coprecipitated in, CSH differed from that of $Eu(OH)_3(s)$ expected to precipitate under the pH conditions of CSH waters, ruling out precipitation of pure hydroxide phases, despite total Eu concentrations well above supersaturating conditions. These results indicated that the sorbed or coprecipitated Eu was located at Ca structural sites in a CSH-like environment. Kinetics and spectroscopic results were consistent with either Eu diffusion within CSH particles, or precipitation of Eu with Ca and Si, creating a CSH-like solid phase.

2.6. Group II elements

2.6.1. Strontium

The behaviour of Sr in cements might be expected to mirror that of Ca. However, it is more soluble in NaOH or KOH, to the extent that $Sr(OH)_2$ precipitation in cements is unlikely [104]. OPC is a very efficient scavenger for Sr: Atkins et al. found that 95% of ^{89}Sr was associated with the solid phase. The hydration products of C_4AF and C_3A can also completely accommodate low Sr levels. At 25 °C, and in the absence of sulphate, the authors suggested that the major product was probably C_4AH_{13} [104]. CSH gels of Ca:Si ratio 1.7 and $Ca(OH)_2$, appear to be less efficient sorbers, but higher sorption might be expected at lower Ca:Si ratios. This might be expected for βC_2S, since it hydrates slowly relative to the other clinker phases, but C_3S hydrates at a similar rate and yet only 34% of the strontium was solid-associated.

Possible substitution of Sr in C_3AH_6 has been studied [104]. Analytical electron microscopy (AEM) showed that the mean $SrO:Al_2O_3$ mole ratio was 0.052, equivalent to ca. 1.6% substitution of Sr for Ca. All the Sr in the system had been taken up in the solid phase. Higher levels of substitution are probably achievable in more Sr-rich starting materials, e.g. the phase Sr_4AH_6 has been shown to exist.

The major sink for Sr was probably the calcium aluminium (sulphate) hydrates. Appreciable substitution of strontium in AF_t and C_3AH_6 has been demonstrated, and was thought to be likely by the authors in AF_m-type phases [104]. Therefore, cements high in Ca and Al, such as high alumina cement (HAC), will have the best 'sorption' characteristics for Sr. Leach experiments on Sr loaded pastes, in conjunction with consideration of the effect of carbonation, have indicated coprecipitation of $SrCO_3$ to be a solubility-limiting process for release. An ettringite analogue with Sr replacing Ca has been reported [105].

2.6.2. Barium

Glasser [52] has suggested that Ba will generally replace Ca in cement hydrate phases.

2.7. Group III elements

2.7.1. Aluminium

Kalousek has proposed that all Al^{3+} ions present in cement eventually enter CSH [1]. Copeland et al. [87] concluded that Al^{3+} enters the CSH by joining with a proton to replace an Si atom or by joining with another Al^{3+} ion to replace 3 Ca^{2+} ions.

3. Summary

The various immobilisation mechanisms identified have been summarised in Table 1.

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