



Analysis of barium retention mechanisms on calcium silicate hydrate phases



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ABSTRACT

Calcium silicate hydrate (C-S-H) phases mostly contribute to contaminant retention in cement. The adsorption mechanisms of Ba on C-S-H phases with four different Ca/Si ratios were investigated by batch sorption experiments. The sorption kinetics, the effects of the solid to liquid ratio and the presence of alkalis in solution were analysed. Sorption isotherms in a wide range of Ba concentrations (from 10^{-10} to $1 \cdot 10^{-1}$ M) were performed. To understand the underlying retention mechanisms, the effects of Ba adsorption on surface potentials were additionally examined. The main objective of this study was to develop a sorption model able reproducing not only the Ba sorption behaviour, but also the C-S-H surface potential before and after Ba uptake. The reactions and model parameters selected for satisfying these conditions are discussed in the paper. A three-site model, with *weak* and *strong* silanol sites and one exchange site, which satisfactorily fulfils the initial aims, is proposed.

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1. Introduction

Cement-based materials are widely used in radioactive waste repositories [1–5]. In fact, they have high sorption capacity for many contaminants, presenting different highly sorbing minerals; additionally, under the alkaline conditions generated by cement systems, many contaminants become much less soluble and mobile [6].

Calcium silicate hydrate (C-S-H) phases are the most relevant amongst the cement sorbing components: they represent between the 50 and 70% of the hardened cement paste (HCP), and due to their microstructure and high surface area ($BET > 100 \text{ m}^2/\text{g}$), they control radionuclide retention in cements [7–9]. Other important hydration products of HCP are portlandite ($\text{Ca}(\text{OH})_2$); Ettringite (AFt) or AFm phases [10].

The C-S-H phases (also called cement gels) are nano-sized materials usually amorphous or poorly crystallized and may have a variable chemical composition $x\text{CaO} \cdot \text{SiO}_2 \cdot y\text{H}_2\text{O}$, with $0.6 < x < 1.8$ approximately; the Ca/Si ratio is responsible of the different physical-chemical characteristics of the phases [11] during different stages of cement aging. The C-S-H structure is comparable to other more crystalline minerals like tobermorite or jennite, consisting on Ca-O central layers sandwiched by tetrahedral silicate layers [11–14]. The silicate chains are arranged following a pattern repeated every three tetrahedral (*dreierkette* structure): two of the three tetrahedra (paired) are linked together and

share O-O edges with the central Ca-O; the third one (bridging) shares an oxygen atom at the pyramidal apex of Ca and connects paired tetrahedra. Increasing the Ca/Si ratio, the number of bridging tetrahedra decreases (being replaced by Ca ions), thus the C-S-H structure can be defined as a ‘defect tobermorite structure’ [15,13]. The region between layers (interlayer) hosts water molecules, calcium and other ions.

Ochs et al. [5] recently reviewed sorption data on cementitious material of several elements relevant for radioactive and industrial wastes, and provided a sorption coefficients database. Sorption values were linked to various stages of cement degradation, and possible underlying retention mechanisms were discussed. They considered strontium and radium as the most relevant divalent elements (M^{2+}) in the contest of radioactive waste disposals, and summarised the main studies existing on their sorption behaviour in cementitious materials [7,16–21]. The scarceness of data on radium retention was especially evidenced: indeed, for its long life (approximately 1600 years), ^{226}Ra is a critical radionuclide from an environmental point of view.

The mechanisms suggested by different authors for the retention of cations on cement, are different: from the complexation on deprotonated silanol groups [22], to its binding via cation exchange by stoichiometric replacement of Ca^{2+} by M^{2+} at the surface sites of C-S-H phases [19–20]. Wieland et al. [21] observed by XAFS studies in cement that Sr was sorbed mainly on C-S-H phases as partly hydrated species via two bridging oxygen atoms; however, they interpreted wet chemistry data using the classical ion exchange theory and neglecting specific uptake mechanisms.

It is generally agreed that sorption of earth alkaline ions in cementitious materials is strongly influenced by the aqueous Ca (the highest the

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Ca content the lower sorption) and that other ions may also compete for sorbing sites. Alkalis, as sodium and potassium are of special importance, because their presence is often significant in cement pore-water and furthermore they were observed to decrease M^{2+} sorption on C-S-H phases [15,19–20]. Other studies suggested different interactions of Cs (specific) or Na (indifferent) towards the C-S-H surface [23–24].

In this study, the sorption behaviour of Ba on C-S-H phases will be deeply analysed. Four phases with different Ca/Si ratio (from 0.8 to 1.6) will be used and characterized previous to retention tests. The main objective is to analyze the mechanisms of Ba sorption on these phases and to develop a sorption model being able simulating: a) Ba retention behaviour within the widest as possible range of tracer concentration; b) the possible competition effects on Ba sorption of alkali ions (Na, K and Cs) and c) to sketch the surface potential behaviour (trend and magnitude) of the materials before and after Ba adsorption. This last point is especially relevant to identify specific retention mechanisms.

To the best of our knowledge, previous studies on retention of Ba on C-S-H with modelling do not exist. The main advantage of using Ba, to improve the knowledge of retention mechanisms of alkaline earth elements in cementitious material (and especially Ra), are multiple. First of all, Ba and Ra have a very similar ion radius (1.34 Å and 1.43 Å) [25] and thus similar chemical behaviour. Barium can be used in a very wide range of concentrations, whereas the use of Ra must be limited to trace concentrations, for its very high radiotoxicity.

To extend the range of tracer concentration in sorption isotherms is fundamental to gather information on C-S-H phases sorption sites, which density is expected to be very large; furthermore the possible effects on the surface charge or potential, due to the incorporation of the element, can be detected only at relatively high sorbing element concentration ($>1 \cdot 10^{-3}$ M).

The whole experimental data will be interpreted by modelling and the advantages or limitation of possible different approaches will be discussed.

2. Materials and methods

2.1. C-S-H gels preparation and characterisation

Four C-S-H phases with different CaO/SiO₂ (Ca/Si) molar ratios were synthesized. The target Ca/Si ratios were: 0.8, 1, 1.2 and 1.6. The method used for producing the phases was the “direct method”, as described in several papers [7,9,20].

The preparation was carried out in an anoxic glove box, under N₂ atmosphere (O₂ < 1 ppm). For their synthesis CaO (Alfa Aesar 99.95% purity) and SiO₂ (Aldrich 99.8% purity, surface area 175–225 m²/g, as indicated by the supplier) were used. Both solids were weighted to obtain the requested molar Ca/Si ratios and a solid to liquid ratio of 10 or 20 g/L; afterwards they were mixed to 1 L deionised water previously boiled and bubbled with N₂ to minimize the CO₂ contamination.

The suspensions were prepared in HDPE dark bottles and maintained under stirring to obtain a homogeneous product [26]. Conductivity and pH were periodically measured until the steady-state was

reached (10–15 days approximately), indicating the completion of the synthesis process.

Measurements of pH (± 0.10) were made using a Mettler Toledo (S220) pH-meter with a solid polymeric electrode (Xerolyt) or a Crison pH-ion meter (GLP225) with a combined glass pH electrode (Metrohm). Electrodes calibration was made with buffer solutions at pH 2.00, 4.00, 7.00, and 10.00. Conductivity measurements were carried out with a Crison EC Meter Basic 30⁺.

The final pH and conductivity of gel suspensions are specific for each Ca/Si ratio and summarised in Table 1. Sorption experiments and ζ -potential measurements were carried out directly with these suspensions.

Upon the formation of the C-S-H phases, an aliquot of 250 mL of each suspension was filtered by 0.1 μ m. Part of the supernatant (50 mL) was used for Ca and Si quantification, and the other fraction stored for its use for dilutions. Ca and Si in the supernatant were measured by ICP-OES with a VARIAN 735ES spectrometer. The filtered solid was used for further analyses. In some cases, the solid was previously “washed” with ethanol and deionised water before the measurement.

The C-S-H surface area was measured by N₂-BET, their composition and homogeneity by (micro)proton induced X-ray emission (μ PIXE). μ PIXE measurements were carried out at the nuclear microprobe facility at the Laboratori Nazionali di Legnaro (INFN-LNL) in sample area of 2×2 mm².

Atomic force microscopy (AFM), in tapping mode, was used to analyze their microstructure with a Nanoscope IIIa apparatus (Digital Instruments). AFM samples were prepared depositing a drop of the suspensions onto a freshly cleaved mica substrate (after Poly-L-Lysine coating) and left drying in the anoxic chamber under N₂ atmosphere overnight. AFM image analysis was carried out with the WSXM 4.0 software [27].

2.2. C-S-H gels surface charge measurement

The ζ -potential of the C-S-H phases (initial and upon Ba addition) was measured by means of the laser Doppler electrophoresis technique using a Malvern Zetamaster apparatus equipped with a 5-mW He-Ne laser ($\lambda = 633$ nm, scattering angle 90°). The samples in which radioactive tracer was adsorbed, were analysed with a ZetaSizer Nano ZS (Malvern) (He-Ne laser, $\lambda = 633$ nm, scattering angle 173°) available in the radioactive laboratory. This apparatus allows the measurement of both particle size and ζ -potential. In all the C-S-H phases, the suspended particles were observed to form large aggregates with size >1 μ m. In fact, the water in equilibrium with the gels has relatively high salinity and calcium content, these factors favouring particle aggregation.

To measure the variation of the surface potential upon Ba addition, the C-S-H phases were contacted with the tracer during three days and maintained under stirring. Measurements of ζ -potential were carried out using the original suspensions at 10 g/L, to mimic the conditions of sorption isotherms, or diluted to 1 g/L, to facilitate ζ -potential measurements. The aggregated particles sediment very fast, making the measurement difficult.

The ζ -potential was calculated from the measured electrophoretic mobility using the Smoluchowski equation [28].

Table 1

Chemical analyses of the solid or supernatant of the C-S-H phases.

Sample	pH	Conductivity (μ S/cm)	Ca (mg/L)	Si ppm (mg/L)	Ca/Si (μ PIXE)	N ₂ -BET (m ² /g)
C-S-H (0.8) 10 g/L	10.38	201	44	75	0.89 \pm 0.04	200 \pm 3
C-S-H (0.8) 20 g/L	10.36	202	45	84	n.d.	n.d.
C-S-H (1.0) 10 g/L	11.41	926	82	4	1.03 \pm 0.04	124 \pm 2
C-S-H (1.2) 10 g/L	12.19	2140	204	1.5	1.26 \pm 0.15	109 \pm 2
C-S-H (1.6) 10 g/L	12.37	6240	600	0.2	1.60 \pm 0.11 ^a	73 \pm 1

^a After washing.

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