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Measurement and modeling of the surface potential evolution of hydrated cement pastes as a function of degradation

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Abstract

Hydrated cement pastes (HCP) have a high affinity with a lot of (radio)toxic products and can be used as waste confining materials. In cementitious media, elements are removed from solution via (co)precipitation reactions or via sorption/diffusion mechanisms as surface complexation equilibria. In this study, to improve the knowledge of the surface charge evolution vs the degradation of the HCP particles, two cements have been studied: CEM-I (ordinary Portland cement, OPC) and CEM-V (blast furnace slag and fly ash added to OPC). Zeta potential measurements showed that two isoelectric points exist vs HCP leaching, i.e., pH. Zeta potential increases from −17 to +20 mV for pH 13.3 to pH 12.65 (fresh HCP states) and decreases from 20 to −8 mV for pH 12.65 to 11 (degraded HCP states). The use of a simple surface complexation model of C-S-H, limited in comparison with the structural modeling of C-S-H in literature, allows a good prediction of the surface potential evolution of both HCP. Using this operational modeling, the surface charge is controlled by the deprotonation of surface sites ($>\mathrm{SO}^-$) and by the sorption of calcium ($>\mathrm{SOCa}^+$), which brings in addition a positive charge. The calcium concentration is controlled by portlandite or calcium silicate hydrate (C-S-H) solubilities.

Keywords: Cement; C-S-H; Leaching; Degradation; Zeta potential; Surface complexation; Solubility

1. Introduction

Cement materials are often used as a waste-confining barriers for heavy metals or in design of deep radioactive waste repositories as container or buffer and backfill materials in the engineered barrier system. Different modeling approaches have been developed in the literature to predict the behavior of radiocontaminants in cementitious media, such as solid solutions modeling [1,2] or surface complexation modeling (SCM) [3–5]. The choice of the model often depends on the most relevant cementitious phase for the considered radiocontaminant.

In the case of SCM, the surface charge of the solid phase could have a strong effect on the description of the radiocontaminant species interaction with the solid surface if an electrostatic term were considered in the modeling [6]. An experimental estimate of the surface electrical potential can be made via zeta potential (ζ) measurement, which consists in electrophoretic measurements of cement suspensions. Indeed, small particles in suspension can move in solution when they are placed in an electric field and the determination of the electrophoretic mobility can be related to their surface charge and to ζ, with a strong dependence on the surface/solution interface modeling used.

The ζ of calcium silicate hydrates (C-S-H) has already been studied [7,8]. C-S-H are the main phases of hydrated cement pastes (HCP), about 40–60% in mass, and are often used as the more representative phase of HCP. The ζ values of C-S-H de-

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crease with the values of pH or calcium concentration of the equilibrium water. Nachbaur et al. [7] have found an isoelectric point (IEP) for $[\mathrm{Ca}] = 2\text{–}4 \times 10^{-3}\ \mathrm{mol\,L^{-1}}$ (pH about 11.6, estimated) and the IEP does not change when NaOH solutions are added to the system (0, 0.01, 0.02, 0.05, and 0.1 M of NaOH), showing that ζ also strongly depends on the calcium concentration in solution. Few modeling attempts have been developed to represent the evolution of the C-S-H surface chemistry [3–5, 8,9], and the surface charge of the C-S-H has been considered as the result of the ionization of silanol sites, mostly through deprotonation,

$$>\mathrm{SiOH} \rightleftarrows >\mathrm{SiO^-} + \mathrm{H^+}, \tag{1}$$

and by the sorption of $\mathrm{Ca^{2+}}$ on the silanol sites, bringing in addition a positive charge:

$$>\mathrm{SiOH} + \mathrm{Ca^{2+}} \rightleftarrows >\mathrm{SiOCa^+} + \mathrm{H^+}. \tag{2}$$

Other surface equilibria have also been suggested [4,5,9], with the resulting formation of $>\mathrm{SiOCaOH}$, or $(>\mathrm{SiO})_2\mathrm{Ca}$.

Nevertheless, Viallis-Terrisse et al. [8] and Pointeau [3] have assumed that only equilibria (1) and (2) dominated the surface chemistry of C-S-H and, thus, that the speciation of the C-S-H silanols sites will be dominated by $>\mathrm{SiO^-}$, $>\mathrm{SiOH}$, and $>\mathrm{SiOCa^+}$ surface complexes. Viallis-Terrisse et al. [8] have used the IEP value to calculate the constants of the two main surface equilibria with calculated $\log K$ values of -12.3 and -9.4, respectively, using the diffuse double-layer model (DLM) of SCM [10]. These values are in good agreement with the constant values obtained by acid titration of C-S-H in Pointeau [3] with $\log K$ of -12.0 and -9.2, respectively, using the same model. Using these two equilibria, Viallis-Terrisse et al. [8] have modeled the decrease of surface potential from +25 mV for surface of C-S-H with pH value of equilibrium water about 12 to −10 mV for lower pH values (about 9).

Heath et al. [4] have already tried to use ζ values measured in C-S-H and cement suspensions to model the interaction of the cement surface with equilibrated water, assuming that C-S-H dominated the surface chemistry of the HCP. But few ζ values were available to adjust the thermodynamic modeling and five surface equilibria were necessary to adjust experimental values. Furthermore, this first modeling did not take into account the fact that for *fresh* states of HCP,[1] ζ is negative [11–13]. For degraded states, Fujita et al. [14] have measured positive ζ (about +45 mV) for a CEM-I paste leached with specific groundwater and negative ζ (about −25 mV) for a HFSC paste (high flyash and silica fume-content cement), leached with the same s/w ratio as for CEM-I.

Thus, the aim of this study was to use a simple surface model of C-S-H to predict the evolution of the cement surface potential, from fresh states (with high pH) to highly degraded states (with pH close to 11).

2. Materials and methods

2.1. Cementitious materials preparation

CEM-I (ordinary Portland cement, OPC) and CEM-V (blast furnace slag and fly ash added to OPC) were used in this study. The clinker compositions, given by the manufacturer (Ciments d'Origny), are detailed in Table 1. The cements were cured as described in Pointeau et al. [15]. Shortly, a water/cement (w/c) ratio of 0.38 was used and the hardening pastes were kept for 4 yr after setting in saturated portlandite ($\mathrm{Ca(OH)_2}$ or CH) water ($\mathrm{W_{CH}}$) at 20 °C to provide samples free from carbonation. Both HCP were crushed and sieved in a glove box under argon and the fraction smaller than 50 µm was used. The elementary compositions have been measured in both fresh CEM-I and CEM-V HCP, whereas the initial amounts of cementitious phases have only been measured in fresh CEM-I HCP (see Table 1). The quantifications have been done by differential scanning calorimetry coupled to thermogravimetry (DSC/TG) analysis and by Rietveld's calculations of XRD diffractogramms.

Several leached states were considered for each cement paste, from fresh to highly degraded states. Fresh and degraded HCP states were obtained by mixing different amounts of the HCP powders with an artificial fresh cement pore water ($\mathrm{WHCP_{fresh}}$) and/or with degassed deionized water (DDW, Milli-Q water bubbled with argon for 24 h). The solid/water ratio (s/w) has been varied between 0.08 and 1000 $\mathrm{g\,L^{-1}}$, as reported in Table 2. $\mathrm{WHCP_{fresh}}$ was synthesized by dissolving 3.2, 12.34, and 0.033 g of NaOH, KOH, and CaO, respectively, in 1 L of DDW. After an aging period of 24 h, the solution was filtered (Nylon, 0.22 µm Millipore) and 1% diluted. All experiments and storages were carried out in HDPE bottles (high density polyethylene) or polysulfone (PSF) centrifuge tubes (with polypropylene screw closure) under argon atmosphere to prevent carbonation of the suspensions.

A kinetic study was performed for leaching experiments of HCP with DDW. The experiments was done by mixing CEM-I or CEM-V HCP powders with DDW in PSF centrifuge tubes with s/w ratios of 0.9 $\mathrm{g\,L^{-1}}$ with weak gentle stirring. The pH and the concentrations of Ca, Na, and K have been measured as a function of time between 1 and 30 days. The concentrations of Ca, Na, and K were measured by ion chromatography, after filtration (0.22 µm) and acidification with $\mathrm{HNO_3}$ (PROLABO, R.P. Normapure). The equipment was an Ion DX-120 chromatograph manufactured by DIONEX. An analysis cation column CS12 was used with a CG12 guard column. Methane sulfonic acid (MSA) 20 mM was used as eluent with a flow rate of 1.2 $\mathrm{ml\,min^{-1}}$. The pH values were measured at the end of the experiment in the suspension, with a combined microelectrode (Mettler Inlab, electrolyte filling KCl 3 M/AgCl saturated) calibrated at pH 7.01 (phosphate buffer as $\mathrm{KH_2PO_4/Na_2PO_4}$) and 12.65 (portlandite buffer suspension) at 20 °C. The uncertainty of pH measurement was estimated to be 0.05.

As few data exist on ζ measurements in literature on cementitious phases other than C-S-H, ζ measurements have also been made on two secondary cementitious phases in CEM-I

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[1] In the *fresh* state (unaltered cement pastes, $\mathrm{HCP_{fresh}}$), the cement contains alkali hydroxide, and the corresponding porewater is in equilibrium with portlandite and contains large amounts of Na and K, with pH of 13 or higher.