Hydration of a silica fume blended low-alkali shotcrete cement

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A B S T R A C T

Ettringite and C–S–H are the main hydrates formed during the hydration of the low-alkali cement "ESDRED" consisting of 60% CEM I, 40% microsilica and 4.8% set accelerator. Small quantities of portlandite and hemicarbonate present as intermediate phases destabilise within a few weeks. The use of a set accelerator leads to massive ettringite precipitation, a moderate decalcification of C–S–H and reduction of pH due to presence of dissolved formate.

The slow reaction of the silica fume during hydration decalcifies the C–S–H and decreases the alkali concentration to 30 mM and the pH value of the pore solution to 11.5 after 1 year and longer. The further reaction of the silica fume is expected to be slow and to result in a decrease of pH to 11. Further, the destabilisation of ettringite to thaumasite is expected. The long-term stability of C–S–H and the pH of approximately 11 make ESDRED a good candidate for usage in contact with the clay-based barriers of a repository for radioactive waste.

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1. Introduction

Deep geological disposal is one of the preferred options to dispose of long-lived intermediate-level and high-level radioactive wastes. Clay-based geological barriers are expected to limit the ingress of groundwater and to reduce the mobility of radioelements. The high pH originating from the interstitial water of the cements used for the construction of the cavern (e.g. liner etc.) could lead to a local degradation of the clay-based barriers. In Portland cements (PC) pH values of 13.5 or even higher are often encountered (Lothenbach and Winnefeld, 2006; Rothstein et al., 2002). Cements with a lower pH value of the pore solution would improve compatibility with the clay barrier. Thus, "low-pH" cements have been developed and considered for application in radioactive waste disposal. The pH value of the interstitial solution of such low-pH cements should optimally be at 11 or lower in order to reduce the chemical gradients between the cementitious liner and the clay barrier. Low-pH values have been obtained in binary mixtures of Portland cement (PC) and silica fume (SF), but also in ternary mixtures with blastfurnace slags or fly ashes (Bach et al., 2012; Cau-dit-Coumes et al., 2006; Codina et al., 2008; Garcia Calvo et al., 2010; Lothenbach et al., 2012).

In this study the hydration of the low-alkali cement "ESDRED" consisting of 60 wt.% CEM I blended with 40 wt.% SF and an

aluminium salt as set accelerator was investigated. This 60:40 binary cement was originally developed in the framework of the EU-project Engineered Studies and Demonstration of Repository Designs (ESDRED) (Garcia Calvo et al., 2010).

The hydration of Portland cements (PC) is well investigated. The clinker phases react at various rates and calcium silicate hydrates (C–S–H[1]), portlandite, ettringite, AFm and hydrotalcite-like phases are formed. The blending of PC with SF and the addition of aluminium salts lead to a more complex system where the reactions of the PC, SF and the aluminium salt occur simultaneously and reciprocally influence the reaction rates of each other (Lothenbach et al., 2011). The blending of PC with SF can accelerate the hydration reaction of the PC clinkers due to the filler effect (Cheng-yi and Feldman, 1985a; Poulsen et al., 2009) as SF offers additional surfaces where the hydrates can nucleate. In addition, the use of SF, which reacts more slowly than PC at room temperatures, results initially in a higher effective water/cement ratio and thus a higher fraction of clinker can react. The reaction of the SF with water and $Ca(OH)_2$ increases the amount of C–S–H formed, leads to the formation of low Ca/Si C–S–H and decreases the amount of portlandite present in the cement. Low Ca/Si C–S–H leads to a reduction of the coarse porosity (Cheng-yi and Feldman, 1985b; Monteiro et al., 1989) and thus to a

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[1] Cement short hand notation is used: A: Al_2O_3; C: CaO; s: SO_3; c: CO_2; F: Fe_2O_3; H: H_2O, S: SiO_2. AFm (Al_2O_3–Fe_2O_3-mono): $Ca_2(Al, Fe)(OH)_6^{\pm}$ and anions and water in the interlayer: $X^- \cdot nH_2O$.

better durability. The blending of Portland cements with SiO_2 also lowers the pH value (Bach et al., 2012; Cau-dit-Coumes et al., 2006; Duchesne and Bérubé, 1994; Garcia Calvo et al., 2010) as less alkalis are present due to dilution of the Portland cement and as more C–S–H with a lower Ca/Si is formed. C–S–H with a low Ca/Si ratio can take up more alkalis (Hong and Glasser, 1999; Stade, 1989) so that less alkalis remain in the pore solution. The addition of SiO_2 lowers the alkali concentration and pH value more effectively than blast furnace slag or fly ash (Cau-dit-Coumes et al., 2006; Duchesne and Bérubé, 1994) as the large portion of SiO_2 and the better reactivity of the SF lower the Ca/Si ratio of the C–S–H efficiently.

The long-term reaction of binary mixtures with 60% PC and 40% SF without set accelerator has been investigated in the last years (Bach et al., 2012; Codina et al., 2008; Garcia Calvo et al., 2010) in the context of the development of low-pH cements for radioactive waste disposal. C–S–H and ettringite and relatively low pH values of 11.7–12.5 were observed after hydration for 3 months and longer. In some cases a small amount of portlandite was present (Codina et al., 2008; Garcia Calvo et al., 2010), while in another study portlandite was consumed completely (Bach et al., 2012).

Shotcretes are widely used in tunnels, bridges and other underground constructions. Set accelerators used to accelerate the setting of the shotcrete generally contain calcium chloride, carbonate, silicate, aluminium, alkali metal hydroxide, and/or organic chemicals. Alkali-free admixtures have been developed to improve mechanical stability, safety and to lower the environmental impact. In this study an alkali-free accelerator on the basis of aluminium sulphate and formate was used. Little has been published on the influence of such alkali-free accelerators on the composition of the hydrate assemblage and the pore solution. Paglia et al. (2001, 2004) showed that the addition of an aluminium sulphate-based accelerator leads to an increased dissolution of C_3S, C_3A and $C_2(A,F)$ during the first hours of hydration, while Xu and Stark (2005) observed no significant influence on the dissolution of the clinker phases. The addition of such an accelerator leads to a strong increase in the amount of ettringite and to a reduction of the amount of portlandite (Maltese et al., 2007; Paglia et al., 2001; Xu and Stark, 2005), as portlandite is consumed along with the aluminium and sulphate supplied by the accelerator for the formation of ettringite. The use of such an accelerator lowers the pH and sulphate concentration and increases calcium and aluminium concentrations in the pore solution (Maltese et al., 2007; Pileggi et al., 2002; Xu and Stark, 2005).

In the framework of the Cement Clay Interaction (CI) project carried out at the Mont Terri rock laboratory in St. Ursanne, Switzerland, different cements were emplaced in 2007 in Opalinus Clay (OPA) to study the interaction with a clay-based barrier. Complementary to the field experiments the hydration of cements has been studied in detail in laboratory experiments using the same formulations as in the field experiments with the difference that no sand and gravel were added in order to simplify sample handling for mineralogical analysis. Furthermore, the laboratory study was carried out at 20 °C instead of the 15 °C prevailing at the Mont Terri rock laboratory. The present study describes the main findings of the laboratory study with the binary ESDRED cement (60 wt.% PC, 40 wt.% SF plus an aluminium sulphate-based set accelerator). The composition of the solid and the liquid phase were investigated for hydration times between 1 h and 3.5 years. Changes in the compositions of the hydrate assemblages and the pore solutions of the cement were determined by X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy coupled to energy dispersive X-ray spectroscopy (SEM/EDX), ^{29}Si nuclear magnetic resonance (NMR), pH measurements, and inductively coupled plasma-optical emission spectroscopy (ICP-OES), respectively.

2. Materials and methods

2.1. Materials

The experimental procedures were identical to those reported elsewhere (Lothenbach et al., 2012), and they are briefly summarised as follows. The chemical compositions of the materials as given in Table 1 were determined by X-ray fluorescence (XRF). Sulphur and carbonate were determined using a LECO C/S analyser, and free lime was determined according to (Franke, 1941). The fraction of "total" alkalis in CEM I was determined with ICP-OES in a solution, obtained by digesting 0.20 g of the cements in 20 ml HCl (3%) for several hours (Gunkel et al., 1970). The mineralogical composition of the unhydrated cement was quantified by Rietveld analysis (Le Saout et al., 2011). The chemical compositions of the set accelerator and the polycarboxylate superplasticizer were determined by ICP-OES and the content of dissolved organic carbon (DOC) was determined using a Shimadzu TOC-Analyser. The solid contents of the SP and the set accelerator were determined according to EN 480-8 (heating of 2 g for 4 h at 105 °C). The results are compiled in Table 1.

2.2. Hydration experiments

Hydration experiments were carried out at 20 °C at a water/binder ratio of 0.5, which corresponds to the water/binder ratio used in the Mont Terri field experiments. The polycarboxylate based superplasticizer (1.2 g/100 g binder) and the set accelerator (4.8 g/100 g binder) were added to the mixing water (deionised water). A conduction calorimeter (Thermometric TAM Air) was used for the determination of the rate of hydration heat liberation. A small portion was mixed externally and placed in a sample holder into the calorimeter at 20 °C. Homogeneous internal mixing was not possible due to the presence of the accelerator and the high fraction of silica fume. Thus mixing was done externally and the heat generated during the first 30 min was not recorded and therefore not displayed in the plots.

The compositions of the cement pastes were investigated from 1 h to 1310 days of hydration. For each time interval individual cement paste samples were prepared. Samples consisting of 1 kg cement and the appropriate amount of water and admixtures were mixed twice for 90 s according to EN 196-3. The pastes were cast in 0.5 and 0.1 L PE-bottles, sealed (to exclude the ingress of CO_2) and stored at 20 °C until further use.

2.2.1. Analysis of solid phases

After appropriate hydration times, a small disc was cut from the single 0.1 L paste samples, crushed, immersed for 20 min in acetone to stop the hydration process, dried for 2 days at 40 °C and manually ground and sieved to particles with diameter <63 μm. The crushed material was used for XRD (first day only), TGA, and NMR measurements. After the first day, when the pastes had been sufficiently hardened, XRD measurements were performed on solid disk cut from the 0.1 L bottles, immediately after cutting.

A Mettler Toledo TGA/SDTA 8513 was used for TGA. Samples of approx. 10 mg crushed material were heated under a nitrogen atmosphere at 20 °C/min from 30 to 980 °C. The amount of bound water in the pastes was calculated from the total water loss up to 550 °C. The amounts of portlandite and calcite were estimated from the weight loss between 400 and 520 °C and between 600 and 700 °C, respectively.

X-ray diffraction data were collected using a PANalytical X'Pert Pro MPD diffractometer in a $2\theta-\theta$ configuration employing the Cu Kα radiation ($\lambda = 1.54$ Å) with a fixed divergence slit size 0.5° using a rotating sample stage and a X'Celerator detector. The samples