Early hydration of C$_3$A–gypsum pastes with Ca- and Na-lignosulfonate

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ABSTRACT

The early age phase development during the hydration of C$_3$A–gypsum pastes with 1 and 4% Ca- or Na-lignosulfonate (CLS and NLS) was investigated using isothermal calorimetry, in-situ XRD, thermogravimetry, mass spectroscopy, and SEM analysis. With 1% CLS or NLS neither retardation of C$_3$A dissolution nor retardation of ettringite formation was observed. When LS was added in a concentration of 4%, C$_3$A and gypsum dissolution were slightly retarded. Gypsum depletion was delayed in all pastes containing CLS or NLS. 1% CLS or NLS increased the amount of AFm-phases formed within 24 h, while the amount of AFm was reduced with 4% CLS or NLS. The initial heat flow increased and the heat flow in the gypsum depletion peak was reduced with 1 and 4% CLS. With 4% NLS no initial heat flow was measured and the heat developed slowly within the first 15 min of hydration in the C$_3$A–gypsum paste.

1. Introduction

The raw materials used for cement production comprise mainly limestone (CaCO$_3$) and clay or shales (alumino-silicate minerals). Minor amounts of iron bearing minerals and sand may be added to regulate the composition [1]. Homogenising and heating the raw meal to temperatures of about 1450 °C results in the formation of cement clinker with the main phases C$_3$S, C$_2$S, C$_3$A and C$_4$AF. The hydraulic properties of Portland cement (PC) depends upon the variation in the amounts of these four phases, C$_3$A being the most reactive. Variation in the C$_3$A content of just some percentage points can affect the early hydration and properties of PC significantly [2]. When C$_3$A is mixed with water, calcium aluminate hydrate phases of different stoichiometry form immediately and the formation of these hydrates can cause hardening within seconds [2–4]. In PCs calcium sulphates are added to control the hydration of C$_3$A and hence the setting of the cement [5]. The chemical reaction between C$_3$A, calcium sulphate (e.g. gypsum) and water is of great relevance as it influences the early heat development in the cement paste. The first stable hydration product forming is ettringite (AFt-phase) which forms as long as there are enough sulphate ions in solution. When all gypsum is consumed and the sulphate ions reach a critical low value ettringite becomes unstable. Further reaction between ettringite and residual C$_3$A leads to the formation of monosulpho-aluminate hydrate (AFm) phases [6–9].

At different steps during the cement manufacturing process minor components like alkali metals, oxides or heavy metals might be introduced into the mineralogical composition of the clinker. Due to mainly cationic substitution, clinker minerals in industrial cements are impure which may change their reactivity. It is known for C$_3$A that the uptake of alkalis (Na$^+$, K$^+$) in the mineral structure changes the crystal lattice and the hydraulic reactivity [10,11]. Na-doped C$_3$A changes the crystal structure completely from cubic to orthorhombic if the Na$^+$ content goes beyond ~3.7%. At even higher Na$^+$ concentrations the lattice changes to monoclinic structure. Between 1.9 and 3.7% Na$^+$ cubic and orthorhombic modification can co-exist [12]. The structure of pure cubic C$_3$A consists of $(Al_6O_{18})^{18-}$ rings that are connected by Ca^{2+} ions [13]. It is reported that the hydration proceeds at a slower rate when C$_3$A is doped with Na$^+$ ions [10,12,14]. Typically PCs contain both modifications of C$_3$A.

C$_3$A has not only the highest hydraulic reactivity among the clinker minerals, but also it is the phase that seems to show the strongest interaction with plasticizing admixtures [15–18]. An often used plasticizing admixture is lignosulfonate, a complex anionic polymer obtained together with cellulose during acidic pulping of wood [19,20]. Lignosulfonates (LS) form a major percentage of the water-reducing/retarding admixtures used in the concrete industry [21]. LS in solution are high molecular weight materials. The molecular weight distribution is usually wide and the degree of sulfonation vary as well [19,22,23]. Increasing molecular weight usually increases the water reducing capacity [24].

When added to the cement–water system LS immediately adsorbs on the surfaces of C$_3$A while the adsorption on C$_3$S does not start before 4–5 h [25]. A film of the adsorbed molecules on the mineral surfaces is supposed to cause deflocculation of cement particles but also retardation by preventing further hydration reactions with water. When Ca- or Na–LS is added to the C$_3$A–water systems (i.e. without gypsum)

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several authors reported delayed initial C_3A hydration and retarded conversion of the hexagonal hydrates C_2AH_8 and C_4AH_{13} to the cubic phase C_3AH_6 [21,26–31]. When LS was combined with Na_2CO_3 the C_3A hydration was completely blocked for a certain amount of time being proportional to the LS concentration [28,31]. The retarded conversion of hexagonal calcium-aluminate hydrates to the cubic C_3AH_6 phase was explained by measuring adsorption–desorption isotherms. There was evidence for an irreversible adsorption of LS on the hexagonal hydrate phases. The authors concluded that LS intercalates in the interlayer spaces thus stabilizing the hexagonal hydrates [29,30]. When gypsum was added to the C_3A–water systems several authors showed a similar retardation effect on the hydration reactions in the presence of LS. With LS both the initial ettringite formation as well as the transformation of ettringite to monosulpho-aluminate phases were retarded [26, 30,32,33]. In contrast, during hydration of PC pastes in the presence of LS evidence was found for an initial acceleration of ettringite formation and hence C_3A hydration during the hydration of cement pastes [34–37]. Thus, the initial hydration retardation of C_3A in C_3A–gypsum pastes due to the addition of LS stands in contradiction to the C_3A hydration with LS in cement. It is known that plasticizing admixtures can influence the morphology of hydrate phases. In case of C_3A hydration without gypsum it was reported that the first hydration products (C_2AH_8, C_4AH_{13}) crystallize in needle like morphology instead of hexagonal platelets when LS is present in the system. The hexagonal AFm phases formed in the hydration of C_3A with gypsum showed also a needle like crystal habit when LS was added [38].

Even though extensive studies on the hydration retardation of cements or single clinker phases with LS have been performed, there is still a lack of understanding the mechanisms. The general aim of the paper is to increase the understanding of the interaction between LS and C_3A and the influence of LS on the early age phase development and hydration of C_3A–gypsum pastes. As mentioned before C_3A is the most reactive mineral phase in the cement clinker. Most papers in literature claim that organic admixtures mainly adsorb on the surface of C_3A and that this is mainly responsible for the retardation of PC hydration. In a previous study on the influence of LS on the PC hydration it was shown that both C_3S and C_3A hydration are retarded [37]. It was not completely clear which of the two phases was most retarded. The same Ca–LS based on softwood is used in this study to further investigate the effect of LS on the hydration of the C_3A–gypsum system only.

This study aims to clarify the extent of C_3A retardation by the used LS. In addition Ca-version of LS (CLS) studied earlier a Na-version of the LS (NLS) is used to investigate possible influence of the cation on the hydration process. In preliminary studies it was observed that the hydration of cubic and orthorhombic C_3A is affected similarly [39]. Therefore, this article discusses the effect of CLS and NLS on the early hydration of cubic C_3A only. Commercial lignosulfonates can contain significant amounts of different impurities such as sugars. Sugars are well-known for their retarding action on cement hydration [40,41]. To reduce the effect of sugars only purified low sugar lignosulfonates were used in this study.

2. Experimental

2.1. Materials

The chemical composition of the softwood based, purified (low sugar) Ca- and Na-lignosulfonate (CLS & NLS) can be seen in Table 1.

The sugar content of the CLS sample was reduced by fermentation of the sugars using yeast. Yeast and lignosulfonate was separated by centrifugation. CLS was converted into NLS by a simple ion-exchange process, adding sodium carbonate and precipitating calcium sulphate. Hence, the difference in carbonate content between CLS and NLS.

Cubic C_3A was synthesized by high temperature sintering of the respective oxides. CaO ($CaCO_3$) and Al_2O_3 were mixed in a molar ratio of 3:1 and homogenised for 2 times 2 min in a vibratory disc mill from Retsch. Before sintering the powders were decalcified for 4 h at 1000 °C. Subsequently the decalcified powder was sintered 2 times for 4 h at 1350 °C. Between the de-calcination and sintering steps the powder was milled and homogenised in the vibratory disc mill one more time. After the second sintering step the powder was milled down until all material passed a 45 μm sieve. The oven used for the synthesis was a Nabertherm LH 60/14 chamber furnace. Particle size distribution and BET surface area of the cubic C_3A and PC is shown in Table 2.

Particle size distribution was measured in isopropanol with a Microtrack Bluewave instrument. BET surface measurements were performed on a Tristar 3000 from Micromeritics.

The PC used was a CEM I 42.5 R provided by Norcem, (Brevik, Norway). Details about chemical and physical data can be found in Danner et al. [37]. The cement contains 2.4% cubic and 3.2% orthorhombic C_3A as well as 2.8% limestone.

Gypsum used for paste experiments with C_3A was laboratory grade obtained from Merck Company.

Cement pastes were mixed with a constant water to cement ratio (w/c) of 0.4. A 1% lignosulfonate solution was prepared and the lignosulfonates were added directly with the mixing water in a concentration of 0.4% by weight of dry cement (bwoc). Mixing was performed by hand for 90 s in a 100 ml beaker. The batch size was 21 g.

For C_3A hydration experiments dry powders of cubic C_3A and gypsum were mixed in a molar ratio of 1:1.5. The batch size for C_3A–gypsum pastes was between 4 and 10 g. The water to solid ratio was kept at 1.0. Lignosulfonate was directly dissolved in the mixing water and added in concentrations of 1 and 4% by weight of dry solid (bwos). The high concentration of LS was chosen in the assumption that all the 0.4% LS bwoc added to the cement pastes are consumed by the C_3A and sulphate phases in the cement. The C_3A and sulphate phase content in the used cement make about 10% of the total cement composition. That means 4% of LS on C_3A as maximum amount and smaller amount of e.g. 1% if other species like C_3S consumed LS.

2.2. Methods

2.2.1. Isothermal calorimetry

Isothermal calorimetry of cement and C_3A–gypsum pastes (C_3A–pastes) was carried out at 20 °C using a TAM Air (TA Instruments). For cement pastes mixing was performed outside the calorimeter for 2 min and the measurements started 5 min after mixing.

For C_3A–paste experiments mixing was performed inside the calorimeter using the TAM Air Admix ampoule. Internal mixing was chosen to monitor the initial reaction from injecting the water/lignosulfonate solution. Mixing was performed for 2 min. The cumulative heat of cement and C_3A pastes was determined with an accuracy of ± 0.5 J/g. All measurements on C_3A and PC pastes were repeated three times. It is reported that different mixing methods can have an influence on the hydration curves [42].

2.2.2. Thermogravimetry

C_3A–pastes without LS and with 4% CLS or NLS were mixed by hand for 2 min and distributed into 10 ml glass vials. The glass vials were sealed and samples were cured at room temperature (23 °C) for 5, 15, 30 min, 1, 2, 5 and 24 h. Subsequently, the hydrated C_3A–pastes were frozen in liquid nitrogen to quench hydration. The frozen samples were then thawed and washed with ethanol to eliminate unbound water and finally dried in a vacuum-freeze drier for 5 h. The dried samples were milled down to a fine powder and stored in the desiccator until measurements were performed. Samples of about 600 mg were analysed with a Mettler Toledo TGA/SDTA 851 in two steps. First, the samples were dried in the apparatus for 3 h at 40 °C and then heated from 40–900 °C with a heating rate of 10 °C/min. In both steps nitrogen (N_2) with a flow of 30 ml/min was used to avoid carbonation during the analysis. The amount of physically and chemically bound water after the