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The influence of sodium salts and gypsum on alite hydration

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ABSTRACT

This work aims to clarify the impact of alkali and sulfate on the hydration kinetics and microstructural development of alite. The plain alite system is compared to systems with addition of: i) gypsum, ii) Na_2SO_4, iii) NaOH plus gypsum and iv) NaOH. In all the cases a clear early acceleration of the hydration rate is observed. Alkalis increase the solubility of aluminate and this further inhibits the silicate reaction at later ages. This inhibition does not take place with sulfate, where ettringite is precipitated lowering the aluminate concentration in solution. Major differences in the morphology of hydrates are observed (C-S-H and portlandite). Sulfate uptake leads to a divergent needle-like C-S-H compared to the convergent needles in plain alite. In the presence of NaOH without sulfate, C-S-H tends towards a foil-like morphology. The highest mechanical strength obtained with the combination of alkalis and sulfate is not dependent on the morphology of C-S-H.

1. Introduction

Nowadays Portland cement clinker is increasingly blended with supplementary cementitious materials (SCMs) to lower the environmental impact of cement and concrete. SCMs react more slowly than Portland cement and this limits the levels of substitution possible to obtain reasonable early strengths. One of the main factors affecting the reaction of the SCMs is the alkalinity of the pore solution. However, alkalis do not only affect SCMs, but also the reaction of the clinker phases.

It is generally accepted that alkalis accelerate the hydration of cement (at least initially), which usually leads to a higher strength development at early ages. However, alkalis may have a detrimental impact on strength at later ages [1]. Some authors [2,3] reported a detrimental effect on compressive strength also at early ages. At present there is no clear explanation of the impact of alkalis. It is also possible that alkalis affect the structure and the intrinsic properties of the hydrates in addition to the rate of hydration. It has been speculated that the changes in the mechanical behavior in the presence of alkalis may result from changes in the morphology and changes in the composition of hydrates, especially C-S-H but also portlandite. However, this has not been systemically confirmed and findings in the literature are often contradictory [4–6].

The early acceleration by alkalis has been attributed to an enhancement of the rate of dissolution of the calcium silicate phases and precipitation of the hydrated phases [7–11]. Alite has received special attention as its dissolution controls the hydration in the early stages of the reaction. A recent study [4] reported that sodium hydroxide and sulfate (between 0.2–0.5 M) lead to a shorter induction period, a higher rate of hydration during the acceleration regime, an increase in the intensity of the main heat peak and a faster rate of deceleration. An increase in the alkalinity of the solution was found to promote a faster precipitation of portlandite (CH) as the amount of calcium ions needed in the solution to achieve the critical supersaturation level for portlandite precipitation is lower. In addition, the silicate concentration in the solution increases, which may lead to an earlier (and maybe more abundant) precipitation of the C-S-H product.

The morphology of early-age C-S-H is usually considered as “fibrillar” growth [12]. Mori and coworkers [8] reported that the addition of NaOH to C_3S favored the growth of a “coarser” C-S-H and Na_2SO_4 favored fine “acicular” C-S-H. The authors considered that the C-S-H was more “heterogeneous” in both cases compared to the C-S-H in plain cementitious systems. These changes in the morphology of C-S-H were related to differences in the pore structure. Alkalis were found to decrease the specific surface area of C-S-H (measured by N_2 adsorption) and the authors suggested that this was because C-S-H was not growing into the void spaces. Jawed and Skalny [1] reported in their review that the presence of alkalis in cement promoted the growth of long “straw-like” crystals starting after a few hours and persisting even after many weeks, proposing the formation of a better crystallized C-S-H with the addition of alkalis. Smaoui and coworkers [3] attributed lower strength to a more porous cement paste observed in the SEM but did not report any differences either in the chemical composition of C-S-H or in the characteristics of the air-void system. On the contrary, it has also been reported that the addition of alkali hydroxide to alite does not seem to induce any changes in the morphology

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of C-S-H [4]. In summary the descriptions found in the literature regarding the impact of alkali salts on the morphology of C-S-H are rather vague and ambiguous.

Changes in the morphology of portlandite have also been reported. Berger and McGregor [13] observed that a platelet-like morphology with a *c* and *a* crystallographic axis ratio below 0.5 was dominant when C_3S hydrated in the presence of sulfate and hydroxides [13]. At equal degrees of hydration, hydroxide and, to a lesser extent, sulfate were reported to induce the formation of smaller and more numerous particles. Way and Shayan [5] noted an increase in the rate of formation of portlandite when increasing the concentration of NaOH in mixing water. Gallucci and Scrivener [14] also reported that cement pastes with gypsum or alkalis seem to promote portlandite nucleation with a hexagonal platelet morphology which grows onto already existing clusters, and preferentially in the neighborhood of gypsum crystals. Recently, Galmarini et al. [15] studied the morphology of portlandite particles formed by coprecipitation with the addition of different ions and they also observed that the presence of sulfate endorses the formation of particles with a hexagonal platelet shape in which the relative growth speed in [00.1] direction is much lower than [10.0] direction. Moreover, Galmarini and coworkers reported the same effect but more enhanced in the presence of hydroxides, leading to more abundant but smaller particles. OH^- ions were conjectured to speed up growth in the direction of the plate edges ([10.0] surfaces) promoting thinner platelets compared to sulfate, which agrees with previous findings in Refs. [13,14,16].

Kumar and coworkers [4] found that the stoichiometry of C-S-H did not change significantly in alite pastes with NaOH (0.1, 0.2 and 0.5 M) in the mixing solution. All the pastes had a Ca/Si ~ 1.7 at 30 h of hydration.

The effects on the degree of hydration (DoH) at later ages remain unclear as most studies are focused on the earlier stages of hydration. The present work studies the impact of NaOH and Na_2SO_4 (with equivalent sodium content), as well as gypsum (with equivalent sulfate content), on the hydration kinetics and microstructural development of alite, the most important constituent of cement. The present study focuses not only on early ages but tries to clarify how the changes induced by alkalis at the first hours of hydration may have an impact on the properties of the systems at later ages.

2. Materials and methods

2.1. Materials

Two batches of alite (substituted C_3S) were synthesized in the laboratory by mixing 81.4 wt.% of calcium carbonate (precipitated GR for analysis, Merk), 16.6 wt.% of silica (highly dispersed extra pure, Merk), 1.3 wt.% of magnesium oxide (GR for analysis, Merk) and 0.6 wt.% of aluminum oxide (anhydrous, Merk). Powders were homogenized for 24 h in a ball mill with deionized water and the blend was dried at 90 °C for 24 h. The dried mass was pressed into pellets and burned at 1500 °C for 8 h. The pellets were quenched in air, ground using a ring grinder and sieved at 100 μm. Batch A was used for calorimetry, TGA and microscopy analysis. Batch B was used for the mechanical strength tests. The particle size distributions (Fig. 1) of both batches are very similar. The calorimetry curves (Fig. 2) show that the hydration rate of Batch A is slightly higher than that of Batch B. However, these differences at early ages have a minor impact on the DoH at later ages. Therefore, the two batches of alite were considered to be comparable. Free lime was undetected in the XRD pattern for both Batches A and B, considering that it was under the detection limit in both cases (<0.5 wt.%).

Alite pastes were prepared at a constant water to solid ratio (w/s) of 0.35 using de-ionized water (DI–water) or the appropriate aqueous solution of NaOH (>98%, Reagent grade, Sigma-Aldrich) or Na_2SO_4 (>99%, ReagentPlus, Sigma-Aldrich). When required (see Table 1) 5 wt.% (by alite mass) of gypsum (>98%, AcrosOrganics) was added.

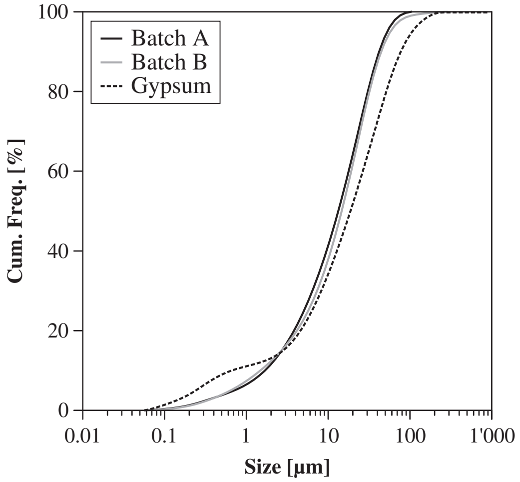

Fig. 1. PSD of the two batches of alite synthesized and the gypsum.

Both sodium salts were dissolved in water prior to the mixing to ensure a homogeneous distribution. The compositions were selected to be equivalent in sodium and sulfate content. The pastes were mixed 2 min by hand. The samples were stored in sealed conditions at 20 °C and care was taken to minimize exposure to the air to limit carbonation. The formulations studied are given in Table 1.

2.2. Experimental methods

2.2.1. Isothermal calorimetry

The heat release was recorded with an isothermal calorimeter from Thermometrics. The ambient temperature was 20 °C and the measurements were carried out for 25 days. 3 g of paste was placed in a glass vessel and then into the calorimeter. An enthalpy of hydration of 513 J/g was used to calculate the degree of hydration of the alite. As a first approximation it was assumed that the alkali salts do not significantly change the enthalpy of reaction.

2.2.2. Thermogravimetric analysis

The hydration was “stopped” by immersion in isopropanol for 7 days (exchanging the solvent twice during the first 24 h) and further vacuum drying for at least 2 days. Thermogravimetric analysis (TGA) was carried out on 50 mg of powdered sample (in pure alumina crucibles) with a Mettler-Toledo TGA/SDTA 851 balance using a 10 °C/min ramp from 30 °C to 1000 °C under a 30 ml/min flow of N_2. The tangent method

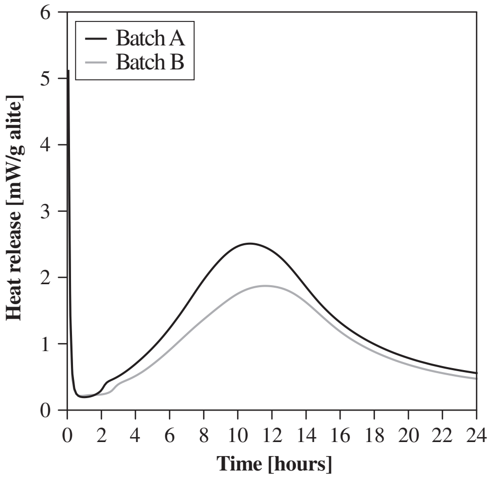

Fig. 2. Calorimetry curve of the two batches of alite synthesized.