



# Impact of NaOH and Na<sub>2</sub>SO<sub>4</sub> on the kinetics and microstructural development of white cement hydration

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## ABSTRACT

This work clarifies the impact of NaOH and Na<sub>2</sub>SO<sub>4</sub> on the kinetics and microstructural development of cement hydration to better understand their effect on the mechanical properties. Na<sub>2</sub>SO<sub>4</sub> and NaOH accelerate hydration and strength development during the first hours but lower strength values later on. For the same degree of hydration of cement, the addition of Na<sub>2</sub>SO<sub>4</sub> leads to the same compressive strength as the alkali free system while NaOH clearly lowers it. Compressive strengths closely correlate to the total capillary porosity of the cement paste, which relates to the total volume of hydrates. Na<sub>2</sub>SO<sub>4</sub> promotes the precipitation of a higher volume of hydrates, especially ettringite. A higher volume of hydrates can better fill the space, decrease porosity and consequently increase strength. Contrary, NaOH lowers the total volume of hydrates, mainly the volume of ettringite. Strength differences are not dependent on the bulk density, chemical composition or morphology of C-S-H.

## 1. Introduction

Lerch was one of the first to notice that alkali salts accelerate the hydration of cement [1]. Some years later, Jawed and Skalny [2] reviewed the effect of alkalis on cement hydration and reported an acceleration effect with alkalis, at least initially, which has been confirmed by more recent works [3–6]. The early acceleration of hydration by alkalis has been attributed to an enhancement of the rate of dissolution of the calcium silicate phases and precipitation of the hydrated phases [3,7–10]. Recent studies show that sodium hydroxide [5] and sodium sulfate [10] (both between 0.2 and 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.

The early acceleration of the hydration of cement by alkalis usually leads to a higher strength development at early ages. However, alkalis are usually found to have a detrimental impact on strength at later ages [2]. Some authors [11,12] reported a negative effect on compressive strength also at early ages. Fig. 1 shows strength values collected by Holcim [13] at 2 and 28 days for different cements (ground to the same fineness and adjusted to the same gypsum content) containing alkali sulfate. It indicates that higher contents of alkali sulfate lead to higher compressive strengths at early ages but lower at later ages. They also observed that the addition of NaOH not only does not increase the

compressive strength at early age but also the lowering of the compressive strength at later ages is more pronounced than with the addition of alkali sulfates [13]. Sant et al. [14] found a lower rate and extent of strength development at later ages in presence of 0.5 M NaOH and 0.5 M KOH and Shayan and Ivanusec [15] observed that an increasing addition of NaOH from 0.5 M to 4.5 M gradually lowered the compressive strength of cement mortars at 7, 28 and 90 days.

In many studies on alkali, additions are made to cements which already contain significant levels of alkalis, and this complicates the understanding of the mechanism behind the lower late age strengths observed in the presence of alkalis. For instance, Shayan and Ivanusec [15] made additions to a cement with a high alkali content of 0.8% Na<sub>2</sub>O<sub>eq</sub> (Na<sub>2</sub>O equivalent defined as %Na<sub>2</sub>O + 0.658 × %K<sub>2</sub>O).

To understand why the addition of alkali salts may have a negative impact on strength at later ages it is necessary to look at their effect on the total porosity and its distribution. Sant et al. [14] observed that 0.5 M NaOH led to a coarser porosity in cement pastes at 28 days. Smaoui and et al. [12] and Shayan and Ivanusec [15] attributed lower strength to a more porous and less dense cement paste based on SEM observations in secondary electron mode at 7 days. However, it is subjective to judge the porosity of a cement sample from micrographs of fractured surfaces. Although it is widely claimed in the literature that porosity is affected by alkalis, there are very few studies which characterize these changes quantitatively or identify the mechanism behind

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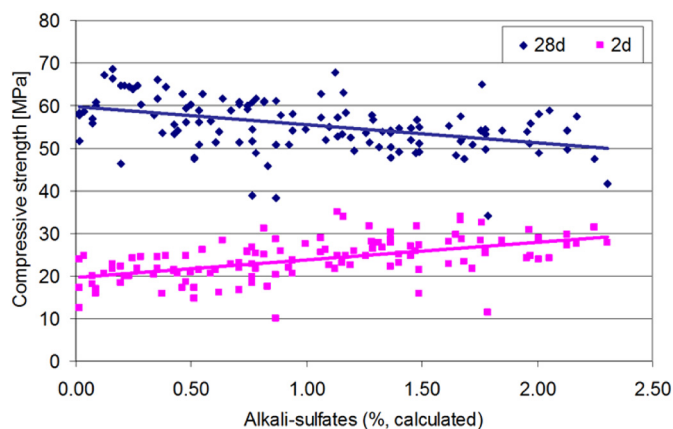


Fig. 1. Data collection of the compressive strength values for different clinker systems containing alkali sulfates at early (2 days) and later age (28 days), based on EN 196 standard mortars (internal data from Holcim [13]).

them. Many authors suggest that changes in porosity are related to a changes in the morphology of C-S-H [2,5,8,12,16] or portlandite [17–21], but such hypotheses were not investigated quantitatively.

Alkali salts increase the pH of the pore solution and lower the Ca/Si ratio, by lowering the calcium and increasing the silicon concentrations in solution [22–25]. This might be expected to affect the composition and morphology of the C-S-H formed. However, Kumar et al. [5] 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.

We recently reported [6] that the addition of NaOH, Na<sub>2</sub>SO<sub>4</sub>, or gypsum, to alite pastes modifies the morphology of C-S-H. In alkali free systems C-S-H formed as convergent needles. On the addition of Na<sub>2</sub>SO<sub>4</sub> or gypsum this changed to divergent needles and NaOH promoted a more planar or foil-like morphology. However, there was no apparent impact of these changes in morphology on the mechanical strength. At the same degree of hydration, the addition of Na<sub>2</sub>SO<sub>4</sub> enhanced the compressive strength whereas the addition of gypsum did not, despite having the same divergent C-S-H morphology [6]. However, alite is a single phase and may not be fully representative of cement [6,26]. Cement is more complex as it contains other phases such as C<sub>3</sub>A, which will influence the distribution of the porosity and the hydrates in the matrix. These effects are studied here. To isolate the impact of NaOH and Na<sub>2</sub>SO<sub>4</sub>, a cement with a very low alkali content was used (0.09% Na<sub>2</sub>O<sub>eq</sub>). The novelty of this study lies in the complete analysis of evolution of the phase assemblage and consequent development of porosity, in relation to mechanical strength. The use of <sup>1</sup>H NMR brings new insights on the impact of alkalis on the amount of water and density of C-S-H.

## 2. Materials and methods

### 2.1. Materials

White Portland cement (from Aalborg Portland A/S) was used in this study to minimize paramagnetic species (e.g. Fe<sup>3+</sup> ions) that can enhance relaxation in <sup>1</sup>H NMR experiments. It only contains 0.32 mass % of Fe<sub>2</sub>O<sub>3</sub>. Moreover, it contains a low amount of alkali oxides, which is an advantage to study the impact of alkali salts on the hydration. Table 1 shows the mineralogical composition by XRD-Rietveld and the oxide composition by XRF (ARL Instrument calibrated for UniQuant in fused bead form, APC-Solutions) of the white Portland cement. Fig. 2 shows its cumulative particle size distribution (Mastersizer S, Malvern) using isopropanol as dispersant solvent [27].

Table 1

Mineralogical composition (by X-ray diffraction and Rietveld) and oxides composition of white Portland cement (by X-ray Fluorescence).

| Anhydrous phase  | Content [mass %] | Oxide                           | Content [mass %] |
|------------------|------------------|---------------------------------|------------------|
| C <sub>3</sub> S | 72.4             | SiO <sub>2</sub>                | 24.40            |
| C <sub>2</sub> S | 18.6             | Al <sub>2</sub> O <sub>3</sub>  | 2.16             |
| C <sub>3</sub> A | 3.5              | Fe <sub>2</sub> O <sub>3</sub>  | 0.32             |
| Gypsum           | 1.2              | CaO                             | 68.12            |
| Basanite         | 2.3              | MgO                             | 0.56             |
| Other            | 1.7              | SO <sub>3</sub>                 | 1.94             |
|                  |                  | Na <sub>2</sub> O               | 0.05             |
|                  |                  | K <sub>2</sub> O                | 0.06             |
|                  |                  | Na <sub>2</sub> O <sub>eq</sub> | 0.09             |

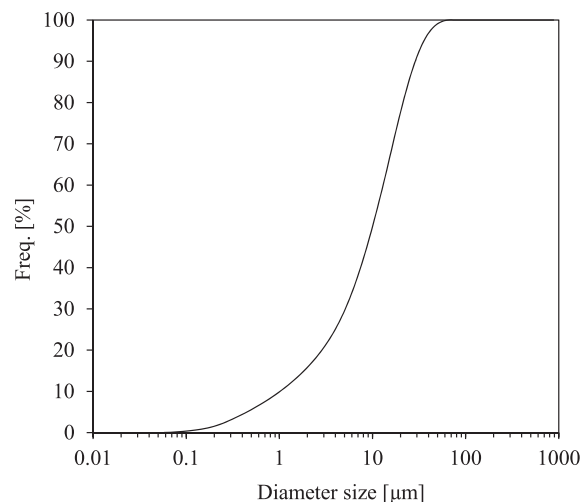


Fig. 2. Cumulative PSD of white cement.

### 2.2. Experimental methods

#### 2.2.1. Preparation of pastes

Na<sub>2</sub>SO<sub>4</sub> (> 99%, ReagentPlus, Sigma-Aldrich) or NaOH (> 98%, Reagent grade, Sigma-Aldrich) were dissolved in water prior to the mixing to ensure a homogeneous distribution. The compositions were selected to be equivalent in sodium content. For all the experiments, 80 g of cement were mixed with the corresponding amount of deionized water or alkali solution to ensure a water to cement ratio (w/c) of 0.4. The formulations studied are given in Table 2. The pastes were mixed for 2 min at 1600 rpm. They were stored at 20 °C in sealed conditions in individual plastic containers (well-sealed with parafilm) for each testing time to minimize exposure to the air and limit carbonation.

#### 2.2.2. Mechanical strength tests

Mortar prisms were prepared according to EN-196. 2 prisms of 160 × 40 × 40 mm were tested for the flexural strength and 4 prisms of 40 × 40 mm section for the compressive strength. Flexural and compressive strength measurements were carried out at 1, 3, 7, 14, 28 and 90 days. The error bars in the graphs with compressive and flexural strength tests of this work represent one standard deviation of the results.

Table 2

Formulations of the white cement systems studied.

| Material              | Mixing solution                         | Nomenclature in figures           |
|-----------------------|---|-----------------------------------|
| White Portland cement | Deionized water                         | W alkali-free                     |
| White Portland cement | 0.725 M Na <sub>2</sub> SO <sub>4</sub> | W Na <sub>2</sub> SO <sub>4</sub> |
| White Portland cement | 1.45 M NaOH                             | W NaOH                            |

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