Effect of sodium lignosulfonate superplasticizer on the early hydration of cement with different contents of cubic C₃A

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Abstract. In this research, the influence of the sodium lignosulfonate superplasticizer (LS) on the early hydration of two types of cements containing different amount of cubic C₃A was studied. It is shown that at 0.1% addition of LS has no significant influence on the hydration, while at higher dosages LS contributes to the additional formation of ettringite. This phenomenon is observed for both types of cement. The higher ettringite formation was found for the cement containing higher C₃A amount. However, LS addition retards the hydration, which is indicated by the reduction of the portlandite amount formed.

1. Introduction

Lignosulfonates (LS) are one of the most popular superplasticizers (SP) in the market, since their first introduction in 1930s [1]. LSs are the by-product of the pulping industry. Thus, LS’s have a low price, and despite relatively low efficiency in comparison to polycarboxylate ethers, LS’s still remains highly demanded superplasticizers in concrete production [2].

LS is based on lignin – natural polymer presented in wood. Initially lignin is a water insoluble matter which undergoes sulfonating process in presence of sulfite or bisulfite salts containing various cations (Na⁺, Ca⁺², Mg⁺² etc.). Depending on its chemical composition LS differently influences on the properties of the fresh and hardened concrete [3]. Among others sodium and calcium lignosulfonates are the most common ones being used in the concrete industry.

Regardless of the type of the superplasticizers, most of them retard cement hydration. This shortcoming is a consequence of their performance. When introduced into water-cement paste SP is adsorbed on the cement particles. Then, depending on the SP’s nature, plasticizing effect is reached - either through the increment of the electrostatic forces or due to steric hindrance. Therefore, adsorption is a key interaction between SP and cement. Nonetheless, it is adsorption that causes retardation of the cement hydration due to the inhibiting the contact between the cement particles and water. It is known that cement minerals have a different affinity to the SP’s; the highest attraction exhibit C₃A and C₄AF phases [4]. Since C₃A hydrates way earlier than C₄AF, its content has a significant influence on the early-age hydration of cement.

Hydration of cement is an exothermic process, the typical heat flow curve obtained for the cement used in the current research is presented in figure 1. The retardation effect caused by SP’s application is usually associated with an increment of the stage II – induction period [5]. Since stage III is associated with the precipitation of C-S-H and portlandite, and the stage IV is associated with an intensive secondary ettringite formation caused be renewed C₃A dissolution [6], the influence of the LS

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introduction is appropriate to study right after these stages. Moreover, it was pointed out that $C_3A$ polymorphs significantly affect the performance of polycarboxylate ethers (PCE) and polynaphthalene sulfonate (PNS) superplasticizers [7].

The current study is to elucidate the effect of cubic $C_3A$ polymorph on the early-age hydration of the cement paste in the presence of sodium lignosulfonate. For this purpose, the hydration of two cements containing different amount of cubic $C_3A$ was stopped by the solvent replacement method and the hydration product was investigated by XRD.

2. Materials and methods

2.1 Materials

CEM I 52.5N supplied by Nesher Cement, Israel is used for this study. Its mineral composition is presented in table 1.

| Chemical composition | Cem_A (CEM I 52.5N) | Cem_B (model cement) |
|----------------------|----------------------|----------------------|
| Alite                | 61.02                | 58.31                |
| Belite               | 12.95                | 12.37                |
| $C_3A$ cubic         | 5.86                 | 8.81                 |
| $C_3A$ orthorhombic  | -                    | -                    |
| $C_4AF$              | 12.42                | 11.87                |
| Bassanite ($CaSO_4 \cdot 0.5H_2O$) | 1.87 | 2.97 |
| Anhydrite            | 0.28                 | 0.27                 |
| Portlandite          | 1.83                 | 1.75                 |
| Calcite              | 2.25                 | 2.15                 |
| Arcanite             | 0.97                 | 0.93                 |
| Aphthitalite         | 0.55                 | 0.53                 |

Model cement was prepared by mixing the industrials cement (table 1), laboratory made $C_3A$ cubic and calcium sulfate hemihydrate, which was added in order to compensate the acceleration of the setting time initiated by the $C_3A$ addition. The amount of hemihydrate added was chosen to keep the initial $C_3A$ to hemihydrate ratio as 73/27 by weight [8].

The cubic modification of $C_3A$ was synthesized from compacted powders of calcium carbonate (Spectrum) and alumina (Camag). The powders were mixed in plastic vials (50 ml) in a vortex mixer (Vortex-Genie 2 – Scientific Industries, Inc) and then compacted into pellets of about 3.5 g and 13 mm in diameter using a hydraulic press. The pellets were calcined at 900 °C for 1 hour and sintered at 1450 °C for 2 hours in Pt-crucibles in a high-temperature chamber (Nabertherm LHT 02/17 LB, Nabertherm, Germany) and finally quenched with a fan to a room temperature within minutes. The pellets were ground in a mortar and sieved. The obtained powders passed 45 µm sieve was retained. The obtained powder comprised 98.7 wt.-% of $C_3A$ and 1.3 wt.-% of free lime. The chemical composition of model cement (Cem_B) is presented in table 1.

Superplasticizer was commercially available sodium lignosulfonate (Sodyum Lignosülfonat) produced by Likit Kimya, Turkey.

All cement pastes were prepared at a water to cement ratio w/c = 0.4. Sodium lignosulfonate superplasticizer was preliminarily dissolved in the mixing water and then added to cement.

2.2 Methods

2.2.1 X-ray diffraction (XRD)
The XRD analysis was performed using a Malvern PANalytical EMPYREAN X-ray diffractometer. The XRD scans were analyzed using the HighScore Plus software. Analyzes were performed using the external standard method. As a standard was used α-Al₂O₃ with 100 % crystallinity. Commercial name is CR1 produced by Baikowski, France.

Sample preparation: for each XRD sample, the hydration of LS-cement suspensions was stopped using the solvent replacement method [9]. After 12 hours of hydration, cement paste (5 g) prepared at w/c = 0.4 were gently ground by mortar and immersed in iso-propylalcohol (IPA) for 5 min and then moved in a chamber for 24 hours, 35 °C, low vacuum 500 mbar. The dried powder was milled and sieved, particles passed 75 μm were retained and analyzed by XRD.

2.2.2 Isothermal calorimetry
Calorimetric measurements were performed using the Isothermal Calorimeter TAM Air model (TA instruments). Measurement precision of the heat flow was ±4 μW at a 95% confidence interval. Fresh pastes consisting of cement (5 g) and deionized water (2 g) were prepared and mixed by vibration at 60 rpm for 10 s. The samples were then introduced into the calorimeter, which measured the heat flow for 48 hours, providing 6 measurements per minute. All the tests were conducted at 21ºC with three independent mixes for each LS dosage in the cement paste.

2.2.3 Particles size distribution
The analysis was performed by means of Particle Size Analyzer Malvern Mastersizer 2000 in iso-propylalcohol (IPA).

3. Results and discussion
The particle size distribution of the cements, gypsum hemihydrate and cubic C₃A is shown in figure 2. It can be seen that the model cement (Cem_B) is almost similar to the reference Cem_A. The only difference is a small “tail” of the particles bigger than 100 μm, that is evidently caused by hemihydrate addition.

![Figure 1. Heat flow of OPC (Cem_A).](image1)

![Figure 2. Particle size distribution.](image2)

The hydration of both cements was stopped after 12 hours of hydration. The XRD scans of the cement prepared with different LS dosages are presented in figure 3 (a), (b). The quantitative composition of the obtained phases is presented in figure 4.

The addition of higher LS dosage significantly oppressed the hydration of alite and consequently the formation of portlandite, that naturally induces an increment of the induction period (stage II in figure 1), i.e. the more alite remains, the less portlandite is formed, and the longer retardation of hydration.
Figure 3. XRD curves from $2\theta = 5^\circ$ to $55^\circ$; (a) Cem_A; (b) Cem_B. Hydration was stopped after 12 hours. Displayed peaks: AFT - ettringite; CH – portlandite; C3S – alite; C2S – belite; C3A – aluminate cubic; F – aluminoferrite; C – calcite.
Simultaneously, the amount of cubic C₃A is slightly reduced. Interestingly, that irrespective to the cement type the amount of ettringite formed is increased with a LS dosage. Evidently, an increment of LS dosage promotes the intensive formation of ettringite.

Recently this phenomenon was pointed out for the ettringite formation in the presence of calcium lignosulfonate [10], [11]. Obviously, this phenomenon repeats for the cement paste prepared with sodium lignosulfonate. The increasing of the C₃A and gypsum contents naturally boost the amount of ettringite formed. At the same time, the difference in alite amount (figure 4 (a), (b)) is related to the initial difference between the cement used (table 1). It is worth noting that up to 0.1% LS addition the amount of portlandite and alite remains the same for both types of cement. At the higher dosages the portlandite amount is decreased meaningfully, that evidently extends the induction period of hydration. Since the C₃A has a higher affinity to the LS than other phases, it is expected that an increment of C₃A amount reduces the retardation effect.

4. Conclusions
In the current research the influence of sodium lignosulfonate on the early hydration products was investigated. The hydration of two type of cements with similar mineral composition, but different amounts of C₃A and calcium sulfate hemihydrate, were stopped after 12 hours of hydration. It was found that the influence of 0.1% LS addition on the development of the hydration products appears to be negligible. At higher dosages LS induces acceleration of the ettringite formation that was detected for both cement types. The highest increment of ettringite was found for the LS dosage of 0.5%. At the same time, LS retards the hydration of cement by extending the induction period. The retardation is embodied in reduced portlandite formation. Evidently, LS is consumed by alite that inhibits its hydration. The increasing of cubic C₃A (Cem_B) content results in higher ettringite formation and at the same time does not significantly affect the portlandite formation up to the LS dosage 0.3%. Therefore, it can be concluded that LS presumably is adsorbed by the cubic C₃A phase.

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