

## **HYDRATION PROCESSES IN CALCIUM SULFOALUMINATE (CSA) AND CALCIUM SULFOALUMINATE - BELITE (CSAB) CEMENTS**

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### **Abstract**

The focus of this study is to analyze the evolution of the crystalline phases of the two types of cements, calcium sulfoaluminate (CSA) and calcium sulfoaluminate-belite (CSAB), during the process of hydration measured in days. X-ray diffraction (XRD) was applied to characterize the time evolution of the main peaks of ettringite, the key cause of high early strength. Scanning electron microscopy equipped with an energy dispersion system (SEM/EDX) was used for the topographical evolution of surfaces and chemical composition analysis. The XRD and SEM analysis revealed differences in the ettringite peaks between CSA and CSAB. The CSAB type shows more clear needle-like crystals of ettringite and well-shaped crystals. The results indicate microstructural differences in the crystalline and morphology structure between the two types of cement pastes, which affects the early strength values.

**Keywords:** *Characterization; sulfoaluminate cement; SEM/EDS; XRD*

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### **1. INTRODUCTION**

Ordinary Portland Cement (OPC) is a known hydraulic binder in the building industry. Its production accounts for approximately 2-3% of global primary energy use and 5% of manmade CO<sub>2</sub> emissions [1, 2]. In order to produce more environmental friendly binders, with lower CO<sub>2</sub> emissions and high early strength, a new type of cement based on calcium sulfoaluminate, known as CSA cement, has been developed in China in sixties. CSA is a promising high-performance material that exhibits a high resistance to free-thaw, rapid strength gain and excellent durability in a range of aggressive environment [2, 3]. Thus, CSA cements have been used as a binder for concrete in bridges, leakage projects, concrete pipes, precast concrete, prestressed concrete elements, shotcrete, construction on low temperature environment, etc. [4,5]. Calcium sulfoaluminatebelite, known as CSAB cement is a rapid setting, high early strength belite-based with addition of calcium sulfate. Both types, CSA and CSAB of cements were subject to this comparative study.

## **2. MATERIALS AND METHODS**

In this study, SEM/EDX (Scanning Electron Microscopy equipped with Electron Dispersion System of X-rays) and XRD (X-ray Diffraction) were used for material characterization. Pore structure and the pore sizes of hardened samples were characterized using MIP (Mercury Intrusion Porosimetry).

The specimens of both types of cements, CSA and CSAB, were prepared at the water to cement ratios (w/c) of 0.3 and 0.7, respectively. The w/c values were chosen according to the experimentally established respective water demands (0.27 and 0.61). The samples were cured for 24h and then stored in water for 2, 7 and 28 days. To achieve reliable compressive strengths measurements three prismatic samples, 40 x 40 x 160 mm<sup>3</sup> were cast from pastes of the two studied cements. The mixing protocol was as follows: 90 s at low speed, 30 s hands mixing, and again 90 s slowspeed mixing. The samples were cured for 24 hours in a standard climatic chamber ( $T = 21^{\circ}\text{C}$ ,  $RH \geq 95\%$ ). Then they were demoulded and stored under water until the start of the strength testing.

At the required age the samples were taken out from the water, broken in flexure into two halves, and each half was tested for strength with the compression machine at a maximum load of 4000 kN. The compressive strength was calculated as an average from 5 tested samples.

Samples for the MIP, XRD, and SEM were immersed in acetone for 24 h to stop the hydration process. Then they were dried in the oven at 30 °C for another 24 h. Samples for the SEM analysis were prepared from the broken bulk parts of the aforementioned flexural strength specimens. For the XRD analysis, the samples were prepared from the same bulk parts, but in a powder form.

The porosity measurements were performed using a Pascal 140 and 440 porosimeter with a maximum pressure of 400 MPa. XRD analyses were performed with an X'PERT Pro MPDPW 3040/60 Diffractometer from Panalytical, working in Bragg-Brentano geometry. The X-ray tube with a copper anode was operated at 40 kV and 40 mA. The  $2\theta$  range was from  $7.5^{\circ}$ - $80^{\circ}$  with a step of  $0.013^{\circ}$  in reflection geometry. The crystal phase quantification procedure involved the identification and quantification of major and minor phases using the X'Pert High Score Plus software. The analyses were done on dry powders using the back-loading technique to minimize preferred orientation. For this purpose, X-ray diffraction combined with the Rietveld method was utilized for the identification of phases in the pasts and their changes over time [6]. Since the Rietveld quantitative phase analysis only considers the crystalline phases and normalizes their sum to 100%, successful strategies that account for the potential amorphous or minor non-identified crystalline phase were adopted. In the present work, the internal standard methodology is used [7, 8]. To perform quantitative analysis and identify the amorphous content in the cement, 20 wt.% of ZnO (zincite - Z) standard was used in the XRD sample preparation procedure. Before the SEM studies, the samples were coated with a thin conductive carbon film. The SEM investigation was performed by an XL 30 ESEM - Philips at 30 kV. The Blaine fineness of the commercially produced cement was measured with an air permeability apparatus.

### 3. RESULTS AND DISCUSSION

The chemical compositions of the CSA and CSAB cements in concern, examined by the EDX technique are presented in Table 2. The Blaine fineness of CSA and CSAB were 0.464 m<sup>2</sup>/g and 0.652 m<sup>2</sup>/g, respectively.

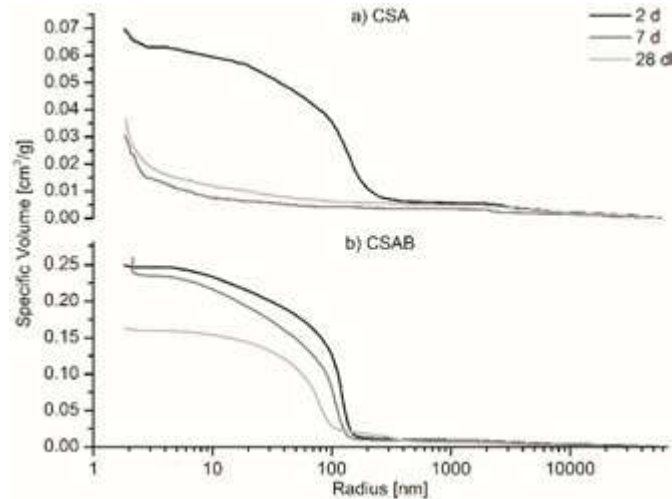
The results from the MIP measurements, presenting the pore size distribution of a) CSA and b) CSAB after 2, 7, 28 days of hydration, are depicted in Figure 1. The notable difference in the overall porosity between CSA and CSAB could be associated with the different w/c ratios used for the mixtures. Figure 1a shows that the pore size distribution of the CSA undergoes pronounced changes with increasing hydration time. Here, it is evident that a significant sample volume contains pores with a radius ranging from 2 to 200 nm. The porosity of the CSA cement decreases significantly during the first 7 days, meaning that the pore reduction due to crystallization hydrated phase formation starts to occur between 2 and 7 days. Furthermore, the porosity slightly increased again between 7 and 28 days. Figure 1b) shows the pore size distribution of the CSAB cement. Herein, the pore size ranges from 2 to about 100 nm.

**Table 2.** Chemical composition (EDX measurements) of sulfoaluminate cements in weight %

Compound	CSA (wt.%)	CSAB (wt.%)
SiO <sub>2</sub>	4.44	10.40
Al <sub>2</sub> O <sub>3</sub>	39.09	17.82
Fe <sub>2</sub> O <sub>3</sub>	1.98	2.02
CaO	43.83	51.66
SO <sub>3</sub>	8.71	16.39
TiO <sub>2</sub>	1.31	0.70
MgO	0.48	0.64
K <sub>2</sub> O	0.15	0.37

The graph clearly shows that the measured overall porosity gradually decreases with time due to hydrated phase formation. Also, one could see that the larger radius pores are gradually reduced between day 2 and day 28. These findings could be explained with the continuous hydration of the cement that results in the filling of pores, thus reducing the porosity [9–11].

The XRD patterns (not shown here) of the unhydrated and hydrated cement pastes, cured for 2, 7 and 28 days, allow identification of the following CSA phases: Y-ye'elimite (C<sub>4</sub>A<sub>3</sub>S), G-gehlenite, M-mayenite (C<sub>12</sub>A<sub>7</sub>), R-rutile (TiO<sub>2</sub>).



**Figure 1.** Results from the MIP measurements: pore size distribution of: a) CSA and b) CSAB measured on 2, 7, 28 days as specific volume in cm<sup>3</sup>/g

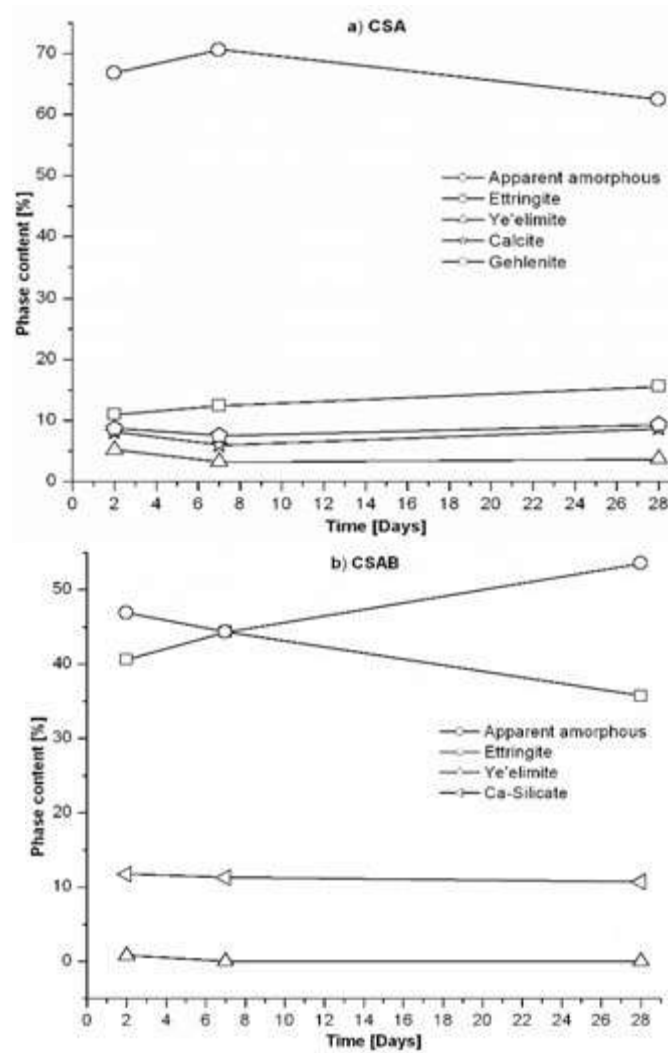
and C-calcite (CaCO<sub>3</sub>). Whereas for CSAB: Y-ye'elimitite (C<sub>4</sub>A<sub>3</sub>S), G-gehlenite, M-mayenite (C<sub>12</sub>A<sub>7</sub>), A-anhydrite (CS), Ba-bassanite (CS), B-belite and C-calcite (CaCO<sub>3</sub>).

The evolution of the phase composition over time, deduced from the results of the quantitative XRD analysis for the two cement pastes, CSA and CSAB, are presented in Figure 2a) and 2b), respectively. In both figures, the apparent amorphous content refers to the amorphous phase, including the minor non-quantified crystalline content [12]. Furthermore, the peak intensity values of the most dominant maxima were extracted from the diffractograms.

As observed in Figure 2a), the apparent amorphous content slowly increased between days 2 and 7. However, between 7 and 28 days the quantity of the apparent amorphous decreased. It is also evident that the ettringite content slightly increases over time.

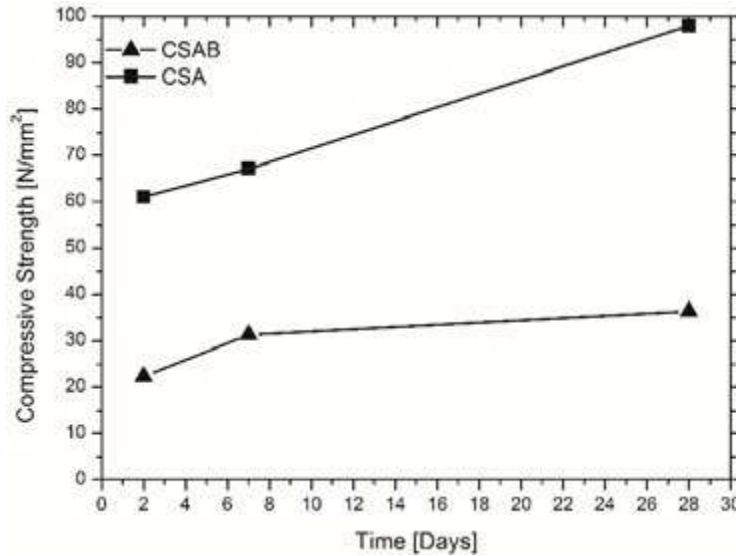
For CSAB quantitative phase evolution (Figure 2b) the period between 2 and 7 days from hydration is characterized by continuous precipitation of ettringite, while a decrease of the apparent amorphous phase is observed. Afterward, a slightly linear decrease of the ettringite content follows, while the apparent amorphous content increased.

Finally, the results of the compressive strength tests, presented in Figure 3, show the strength evolution as a function of the curing time (2, 7 and 28 days). From Figure 3 it appeared that the strength of both CSA and CSAB cements increases with the curing time. The strength of the 28-day sample for the CSA cement is about 100 MPa, while as for CSAB it is relatively low, about 35 MPa. The difference in the strengths could be associated with the different w/c ratio used for the hydration process of CSA and CSAB. It is a known fact that the porosity of the samples prepared with high w/c is higher and therefore the compressive strength is lower [14–16]. Also, Figure 3 shows that the development of the compressive strength of CSAB decreases after 7 days, while for CSA the strength continues to increase until 28 days. The near-linear evolution of the compressive strength of the CSA pastes could be related to the significant changes in the pore structure for up to 7 days. Since the porosity does not undergo any considerable changes after day-7, the further increase in the compressive strength should be sought in the mineralogical changes that occur in the later stage (between 7 and 28 days).



**Figure 2.** Relative change of the phase contents with time. a) CSA, b) CSAB

The XRD relative changes of the phase contents from Figure 2 revealed a correlation between the porosity of the CSA cement (Figure 1a) and the content of the amorphous phase. The comparison of both figures implies that as the content of the amorphous phase increased during the first 7 days, the porosity of the paste decreased. Furthermore, it is evident that between days 7 to 28 the content of the amorphous phase slowly decreased while the porosity slowly increased. Comparison of Figure 2b) and Figure 1b) pertaining to cement CSAB, on the other side, show that during the entire observed period (2-28 days) the amorphous phase increased, but the porosity decreased. Furthermore, from Figure 2 it is evident that the increase of strength with the hydration time of CSA could be ascribed to the slow growth in ettringite phase (E). Finally, the increase in the compressive strength of CSAB with the curing time is consistent with the results of the MIP measurements, that revealed a decrease in porosity over time. Due to the space restriction with the curing time, full crystallization of the ettringite crystals becomes less viable. Moreover, the XRD peak analysis from Figure 2b showed that the ettringite content of CSAB after 7 days decrease with the curing time, presumably turning into an amorphous phase, therefore contributing to a further hardening of the microstructure, which is in line with the findings of other authors [5, 17, 18].



**Figure 3.** Compressive strength progression with the curing time for CSA and CSAB cements

#### 4. Conclusions

The results obtained by MIP, XRD and SEM methods indicated that there are microstructural differences in the crystalline and morphology structure between the two types of cement pastes, CSA and CSAB. The notable difference in the overall porosity between CSA and CSAB could be ascribed to the different w/c that influence the compressive strength. Hence, the cement paste of a higher porosity (CSAB) is less strong.

The small quantity of water used in the case of CSA did not allow the main phase ye'elinite to form crystalline ettringite, which remains rather amorphous due to the constraints within the dense paste structure (cf. low w/c) [19, 20]. In CSAB, on the other side, the larger amount of water allows the formation of needle-shaped ettringite crystals. The SEM images revealed that the crystallinity of both types of cement CSA and CSAB progresses with time since more crystals are evident after 28 days. The XRD analysis of the CSA pastes revealed slight growth of ettringite at the expense of ye'elinite. To the contrary, the XRD-peak analysis of CSAB showed a decrease of the ettringite peak with hydration time, while a simultaneous growth in an amorphous hump has been observed, which implies that at later hydration stages ettringite crystals transform to an amorphous phase that is presumably favorable for the growth in the compressive strength. Finally, the comparative compressive strength of both CSA and CSAB remains to be studied for longer curing/aging times in a future study.

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#### Compliance with Ethical Standards

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Conflict of Interest: The authors declare that they have no conflict of interest.

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