

THE EFFECT OF CaO-RICH ADMIXTURES ON CONTROLLING DRYING SHRINKAGE OF ALKALI ACTIVATED MATERIALS

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Introduction

The worldwide production of Fe-Si-Ca rich residues is expected to increase and the development of suitable large-scale upcycling solutions is a pressing matter. Thus, alkali activation can be a viable valorization route and has attracted increasing attention. Still, alkali activated materials (AAM) are highly susceptible to shrinkage and as such can potentially limit their attractiveness for real-life applications. In cement industry, the swelling potential of oxide-based admixtures has been successfully used to counteract shrinkage effects. Nonetheless cement and AAM chemistry are entirely distinct and calcium compounds can affect the polymerization process and products formed.¹ Further, the scarce existing literature on the use of oxide-based admixtures to control AAM shrinkage is focused on precursors with low-iron content;^{2,3} appreciable levels of the latter will interfere with the polymerization reaction and increase the complexity of the reactions' mechanisms involved. Hence, the present work assessed the feasibility of using CaO-based admixtures to mitigate drying shrinkage phenomena on Fe-rich AAM, while simultaneously investigated their impact on fundamental properties of fresh pastes and hardened specimens.

Experimental

A synthetic glass (PS), mainly composed of (in wt.%) SiO₂ 35, CaO 23, Fe₂O₃ 23, Al₂O₃ 16, and 2% loss on ignition (LOI), was used as the main precursor. Silica fume (SF, Elkem, >95% SiO₂) was used to increase Si availability, while a CaO-rich material was used as expansive agent (EA). The EA is composed of > 70 wt.% CaO with trace amounts of calcite and portlandite being detected in XRD patterns; possible due to partial hydration and subsequent carbonation. Three EA dosages (1, 2 and 3 wt. % of solid precursors) were added to the reference paste (EA0), and the corresponding samples termed as EA1, EA2 and EA3, respectively. An activating solution with 0.74

SiO₂/K₂O molar ratio and 80 wt.% H₂O was used. The reference paste (EA0) is described in Table 1. All samples were synthesized following the procedure described by Ascensão *et al.*⁴, modified by employing 2 extra minutes for mixing the EA.

Table 1: Mix proportions of the reference paste, EA0.

Code	Mixture portion (wt.%)		
	PS	SF	Solution
EA0	72.1	4.1	23.8

Setting time was determined as prescribed by EN196-3:2016. For each formulation, six samples (2x2x16 cm³) were produced according to EN12617-4:2002. The samples were kept for 24 h at 20±0.5 °C and 95±1 % RH, being afterwards demolded and cured at room conditions (20±1 °C; RH=65±5 %). Length and weight variation were monitored up to 28 days. A second batch of samples (4x4x16 cm³) was prepared and cured under the same conditions. Samples' volume and bulk density were determined according EN12390-1 and EN12390-7:2007, and used to estimate water absorption and open porosity.⁴ For each formulation, flexural and compressive strength of two samples was determined according to EN196-1:2016.

Results and discussion

EA addition aimed to counteract shrinkage by combining its swelling potential with the reduction of free water in the system. Still, it was possible that calcium compounds affect polymeric gel formation and/or result in the formation of calcium silicate hydrate phases or calcium hydroxide precipitates depending on the medium conditions.⁵ Under highly alkaline conditions, Ca-forms rapidly dissolve and precipitate, providing extra nucleation sites accelerating the formation of polymeric networks.⁶ On the other hand, (i) the formation of calcium silicate hydrates removes silicate species from the activating medium and (ii) the formation of Ca-precipitates decreases the pH of activating solution due to the removal of OH⁻ ions, hindering further the dissolution of more stable Si elements. These competing effects influence the reaction kinetics and products formed, which ultimately determine AAM properties. Seeking to minimize the disturbance of reaction mechanisms, EA was introduced only after the precursors' initial wetting/dissolution phase. Rising EA content was shown to accelerate setting time, suggesting that increasing calcium availability enhances the reaction kinetics and promotes the formation of the consolidated structures, Figure 1a. Final setting varied between 90 and 79 min, for EA0 and EA3, respectively, representing a reduction of 12 %. The impact is even more significant to the initial setting where a maximum reduction of 26 % was observed. These results were in line with the findings of Guo *et al.*¹ who observed that even a small addition of calcium compounds rises setting and early yield stress. EA2 and EA3

present the most shortened but comparable initial setting times. When higher EA levels were attempted, flash setting occurred, thus limiting EA dosage.

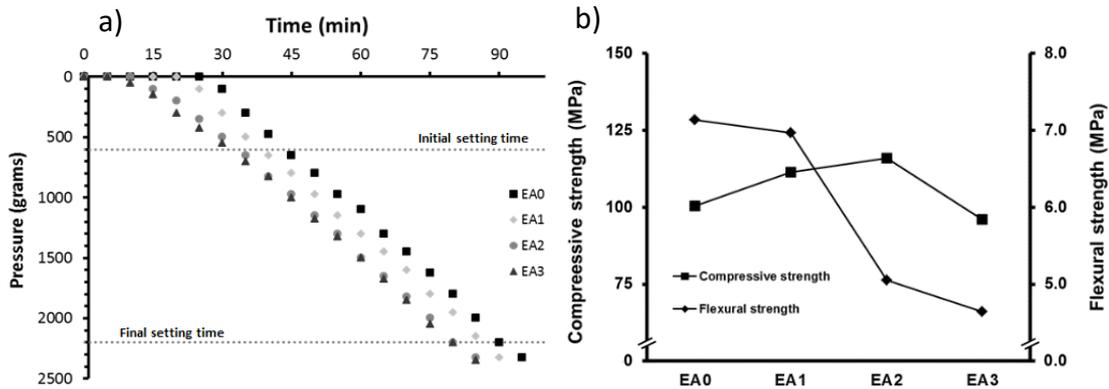


Figure 1: (a) Pastes setting time and (b) IPs mechanical properties after 28 days of curing.

Figure 2 shows the results of drying shrinkage and mass loss, and as can be seen, all samples lose their mass and shrink continually during the testing period. Still, the rate in the initial seven days was considerably more pronounced. EA0 presents the highest linear length reduction, while risen EA content considerably improves volumetric stability (up to 62.1%) and decreases the mass loss (up to 25%). All samples presented low open porosity (< 4 %) and water absorption capacity (< 2 %), and increasing density as EA rises, from 2.22 up to 2.32 g/cm³. Increasing Ca content can cause the refinement of structure resulting in denser and more compact matrixes.^{1,6} In fact, EA2 achieved the highest compressive strength while EA0 presented the best flexural performance (Figure 1b). With the exception of EA3, compressive strength increased as the EA content rose, while the flexural strength exhibited the opposite trend.

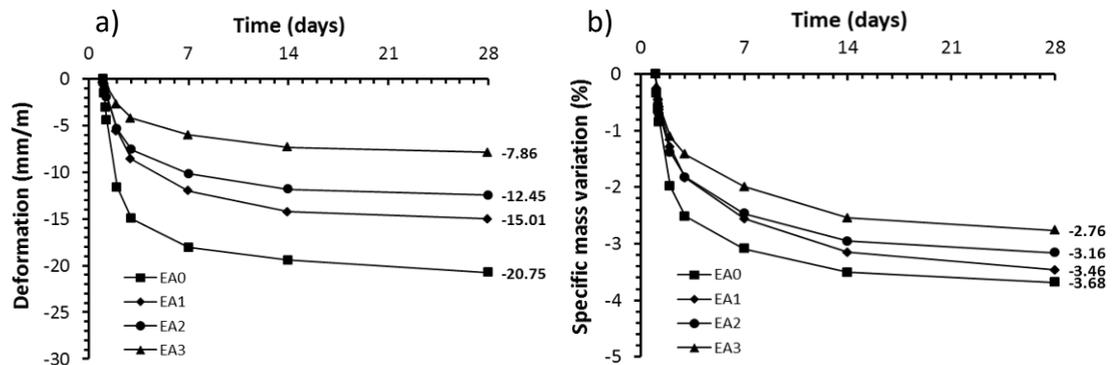


Figure 2: (a) Drying shrinkage and (b) specific mass variation as function of EA content.

As suggested by Temuujin *et al.*⁶, the fine microstructure produced by CaO addition may cause heterogeneous nucleation and crystallisation. Also, EA3 shortened setting did not give time for proper casting and de-airing, contributing to decrease its mechanical performance. In general, the results indicated that EA had a positive impact on compressive strength development while the increase of rigidity of

structures lead to the decrease of its flexural strength.⁷ This trend was similar to what was observed when calcium was added in metakaolin^{1,7} and fly-ash^{1,6} - based systems but in contrast with findings reported for blast furnace slag systems.² The latter is probably linked to the already high content of Ca available in the system. The distinct strength development of different systems stretches the necessity to fully establish the reaction mechanisms, comprehend the role of cationic elements and elucidate the relation of its content and form with the reaction products formed.

Conclusions

Inorganic Fe-Si-Ca rich binders were synthesized and the effect of CaO-rich admixtures (EA) on the setting time, volumetric stability and strength development was investigated. Results have shown that EA addition is an effective and relatively inexpensive way to partially mitigate shrinkage. The reduction (up to 62.1%) was almost proportional to the EA content but high levels were shown to considerably hasten pastes' setting times. The produced AAM presented low open porosity (< 4.0%) and water absorption (< 2.0%), and considerable flexural (up to 7 MPa) and compressive strength (up to 116 MPa) after 28 days. The results seem to suggest an optimal EA dosage between 1.0 and 2.0 wt.%. At this dosage, the compressive strength increased up to 15.5 %, flexural strength was maintained above 5 MPa, shrinkage was reduced up to 40 %, while a sufficiently long setting time was achieved.

Acknowledgements

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