Effects of shrinkage-reducing admixtures on autogenous shrinkage in alkali-activated materials

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Abstract. This paper deals with possible solutions of chemical and autogenous shrinkage of alkali-activated blast furnace slag (AAS). Shrinkage is the main reason why AAS is not used in practice. One of the solutions how to reduce the shrinkage is the utilization of special chemical admixtures. In concrete technology, the use of chemical compounds based on hydrocarbon alcohols is well known, however the efficiency in AAS is still very poorly elucidated. Therefore, isopropanol was used in this study. The main aim of the work was to recognize and study the relations between chemical processes in the early stages of hydration. The effect of isopropanol on alkali activation was determined by calorimetric measurements and compared with the initial and final setting time of binder. It was found out that the presence of isopropanol additive had only insignificant effect on the setting time. On the other hand, the results indicated that an increasing amount of isopropanol deaccelerates the hydration process which was represented by smaller amount of primary CSH gel formation and delayed time of secondary binder phase formation.

1. Introduction

Current progress in development of new materials and technologies for reduction of waste forces cement industry to look for new building materials for example blast furnace slag (BFS). BFS is a secondary raw material that is produced in metallurgical industry and its bigger use in construction could reduce air pollution [1]. Although the cement industry uses a significant amount of BFS, still, enormous amount of BFS is not currently used. Therefore, its usage as alternative secondary binder is favorable action. Unfortunately, its utilization is limited by significant drying and autogenous shrinkage, which is substantially higher compared to OPC-based materials [1, 2]. Activated slag cement (ASC) which is a mixture of BFS and activator is one of the possibilities where to put BFS. Activator is a chemical compound that increases slag reactivity during hydration. Compared to OPC-based materials, ASC shows higher strength, lower porosity and heat evolution [3]. ASC exhibits higher chemical resistance, especially in acidic environment compared to OPC-based materials. This resistance seems to be based on the nature of the hydration products, rather than their porosity [4].

Concrete shrinkage is closely related to the increasing binder phase content. However, for some materials it is necessary to keep the content of binding phase, so it is favorable to use the shrinkage reducing admixture (SRA). The first mention about SRA reducing shrinkage of concrete during drying dates back in 1980’s. However, the use of SRA in concrete may have a negative effect...
on the hydration of the binder phase. It is also important to think about long-term concrete properties as leaching of SRA can eliminate long-term reduction in shrinkage [5]. SRAs are surfactants that reduce the surface tension of the pore solution and water films that are formed on the solid surface during the drying of the cement material. In 1983, Sato et al. studied the effect of SRA on cement materials and concluded that the reduction in shrinkage due to SRA occurred due to the reduction of the surface tension of the pore solution, from which the capillary force theory of drying shrinkage was derived [6].

However, even a smaller addition of SRA strongly influences the ongoing hydration processes. Calorimetric measurement showed that the pre-induction period is changed and the delay of the main hydration peak is prolonged up to several days [7]. The study of Bílek and coauthors [7] also showed that with the increasing dose of SRA intensity of the initial peak is reduced and it is divided into two almost separated peaks during calorimetric measurement.

2. Materials and Methods

2.1. Materials and Sample Preparation
As a solid precursor for the reference binder for measurement blast furnace slag (BFS) with a volume diameter of 12 μm was used. The amount of amorphous phase, melilite, merwinite, β–C2S and calcite was determined by X–ray diffraction. The chemical composition was determined by X–ray fluorescence using Rittvield method and it is presented in table 1.

| Chemical composition in wt. % | CaO   | SiO₂  | MgO   | Al₂O₃ | SO₃  | TiO₂ | K₂O   | MnO   | Na₂O | Fe₂O₃ |
|------------------------------|-------|-------|-------|-------|------|------|-------|-------|------|-------|
|                             | 41.1  | 34.7  | 10.5  | 9.1   | 1.4  | 1.0  | 0.9   | 0.6   | 0.4  | 0.3   |

Water glass with silica modulus of 1.86 provided by Vodní sklo, a.s. was used as an activator. Isopropanol in amount of 0.10, 0.25, 0.50, 0.75 and 1.00 wt. % of slag was used to reduce AAS shrinkage and to modify the AAS hydration. Following procedure of preparing samples was used: Isopropanol was added to mixture of activator and water. After homogenization of the mixture the BFS was added. The measurements were made on ASS pastes with water-to-binder ratio (w/b) 0.35. After the mixing, material was cast into the molds and moist cured for 24 hours. After that, the prisms (40 mm × 40 mm × 160 mm for mechanical strength and 25 mm × 25 mm × 280 mm for shrinkage measurement) were removed from the molds and placed into autogenous storage. Samples were prepared and stored in mild conditions with temperatures 25°C.

2.2. Surface tension
Samples with weight of 20 g consisting of waterglass and water were placed to the six plastic vials. Isopropanol was added to each vial to give the resulting concentration of 0, 0.1, 0.25, 0.5, 0.75, 1.00 wt. %. The prepared solutions were homogenized for 3 minutes and the surface dynamic tension was measured on bubble-pressure tensiometer KSV Sigma 701.

2.3. Shrinkage measurement
Shrinkage tests were performed on 25 mm × 25 mm × 285 mm beams, which were stored at 25°C under autogenous conditions. Shrinkage was measured almost daily using to ASTM C490 apparatus, three samples from each mixture were prepared.

2.4. Mechanical strength testing
Samples for measurement of mechanical properties were stored under the same conditions as samples for shrinkage measurement. The bending strength was tested on mortar samples with dimensions 40 mm × 40 mm × 160 mm and compressive strength tests were performed on broken parts from flexural testing. Flexural and compressive strength were performed at the age of 1, 7 and 28 days.
2.5. Isothermal calorimetry
The effect of isopropyl alcohol on AAS hydration was studied by isothermal calorimetry (TAM Air, TA Instruments). BFS (4 grams) and mixture of liquids were tempered separately inside the calorimeter at 25°C, after that, components were mixed together and mechanically stirred for three minutes.

2.6. Thermogravimetric analysis
Using thermogravimetric analysis (DSC SDT Q600, TA Instruments), influence of SRA on hydration, rate and amount of hydration products was studied. The measurement conditions were as follows: temperature set to 30°C, temperature ramp 10°C per minute to 1 000°C. After compressive strength measurement part of the samples was ground and put into the isopropanol to stop hydration processes.

3. Results and discussion

3.1. Surface tension
Surface tension plays a very important role in many physical-chemical processes and therefore the influence of alcohols on surface tension has been extensively investigated [9, 10, 11]. The surface tension measurement in figure 1 illustrates that the surface tension is decreasing with the increasing addition of SRA.

![Figure 1. Effect of isopropanol addition on surface tension of porous solution.](image)

3.2. Isothermal calorimetry
The heat flow curves for measured samples are shown in figure 2. The course of the hydration curves of the reference mixture corresponds to the description Shi and Day [8], where the first peak indicates the dissolution of the BFS. The second peak is assigned to the pre-induction period and the formation of the primary C-S-H gel, this pre-induction period lasts from 30 minutes to 9 hours of hydration. After that a secondary C-S-H gel is formed, which starts to form after 100 hours after hydration at the highest dose of isopropanol. The addition of isopropanol significantly influences the course of the hydration curves. While at the first peak, isopropanol influence is greatly varied due to a large number of possible acting factors. At the second peak, which is shown in more detail in figure 2
(right), it is evident that the heat flow decreases with the increasing SRA dose. Also, the distribution of this peak corresponding to primary C-S-H formation was observed here and the distribution was more apparent with the increasing dose of isopropanol. This may mean that there are 2 possible reactions during the pre-induction period, which overlap in the reference sample and therefore cannot be distinguished from each other. This phenomenon was also observed with the application of SRA based on hexylene glycol [7]. In both cases the first peak maximum is reached around 1 hour after the start of the mixing process and the second peak has a maximum about after 3 hours. However, while for hexylene glycol, the second peak was dominant, for the use of isopropyl alcohol the first peak was more dominant. The effect of increasing isopropanol additions on the change of position of the third peak can be observed. At low doses of isopropanol, only minimal retardation of hydration on formation of the secondary C-S-H gel occurs. With the increasing dose of isopropanol, the hydration retardation increases and at the maximum dose, hydration is delayed up to 160 hours. Also, with the increasing dose, not only the third peak is delayed, but also the main stage of overall secondary CSH gel formation takes longer time.

![Figure 2. Influence of isopropanol addition on hydration of BFS and amount of heat flow during hydration.](image-url)

3.3. Autogenous shrinkage

The shrinkage development depending on the age and the mortar composition during the first 50 hours is shown in figure 3 (left). It is clear that isopropanol at the dosages of 0.10% and 0.25% did not significantly affect shrinkage (there is a 20% reduction in shrinkage) of the samples and after 32 hours of hydration, the shrinkage of these samples was very similar to the reference sample. For samples with isopropanol addition of 0.50% and 0.75%, there were more than half shrinkage values compared to reference sample in the beginning. A similar course of shrinkage as in the reference was observed after 48 hours of hydration. The biggest differences in shrinkage values compared to the reference were recorded at the maximum dose of 1.0% SRA. At this concentration the shrinkage decreased by 87% after 48 hours. However, within a time interval of 48 to 120 hours, sample of isopropanol 1.0% performed high increase of shrinkage and after 12 days (from beginning of mixing) the shrinkage was same as for the reference sample, which could be observed in figure 3 right. It can also be concluded that the resulting shrinkage for mixtures of isopropanol 0.10%, 0.25% and 0.50% was the same (and had a similar course) as the reference.
3.4. Flexural and compressive strength

Figure 4 (left) shows the development of flexural strength and influence of SRA addition. As can be observed, there is only minimal difference between samples because they have a small flexural strength after 24 hour. At seven-day strength testing, it is already possible to observe a decreasing tendency with increasing isopropanol additions. The decline in strength is closely related to the hydration processes. The lowest strength is achieved in the sample with 1.0% of SRA, because secondary C-S-H gel formation has not occurred yet. After 28 days hydration of all the mixtures proceeded significantly resulting in a partial equalization of the strengths.

The compressive strength results given in figure 4 (right) showed a similar trend as the flexural strength. For strength values after 24 hours, there is a decreasing trend with an increasing isopropanol dose. These one-day strength values were affected by the delay of the pre-induction period and formation of the primary C-S-H gel. For seven-day strength measurements, the compressive strength values are similar for the samples apart from the sample with 1.0% isopropanol addition, where C-S-H gel is not formed yet. Measurement after 28 days shows, that samples have very similar compressive strength values and therefore the addition of isopropanol only affected the course of hydration, not the resulting mechanical properties.
3.5. Thermogravimetric analysis

TG-DTA analysis was used to determine amount of hydration products and ongoing chemical processes. From the TG curves, mass decay and decomposition temperatures were found. An example of a TG-DTA curve is shown in figure 5 (left). At an elevated temperature, the first weight loss occurs at 106°C, which is caused by the dehydration of water from the C-S-H gel [12, 13]. Another weight loss is caused by dehydroxylation of the C-S-H gel and decomposition of hydrotalcite [14]. This weight loss occurs very slowly and begins at 200°C and ends at about 600°C. Decreasing intensity of these peaks with increasing isopropanol dose is consistent with calorimetric outcomes. Mass losses taking place beyond 600°C are related to carbonates decomposition. In the case of present study, two separated peaks between 650–700°C and 750–800°C were observed. It was reported [15] that the region of carbonates decomposition in cementitious materials can be significantly modified when organic solvents are used for stopping the hydration resulting sometimes even in two separated peaks [16]. This would be also the case of the present study where isopropanol was used not only to stop the hydration but also as an additive during the mixing process of fresh pastes. It is worth mentioning that these weight losses increase with an increasing isopropanol dose, except for one-day samples, which would be related to different hydration degree of the samples at early ages. Nevertheless, further research is needed to deeply investigate this issue.

From figure 5, noticeable exothermic peak can be observed around 800°C which is likely related to recrystallization of decomposed C-S-H phase to Wollastonite structure [13, 17].
4. Conclusion
According to the interpretation of the obtained data, the addition of isopropanol has a significant effect on hydration of AAS. From the surface tension measurements, it is clear that isopropanol reduces the surface tension of the pore solution, but this addition does not have a significant effect on the autogenous shrinkage of AAS from the long-term point of view. Only in the initial stages, the autogenous shrinkage is reduced in presence of isopropanol, which is, however, not due to reduction of surface tension, but due to a considerable delay in hydration, that could be observed also by isothermal calorimetry and thermogravimetric analysis results. The difference is also evident in the development of strength values, with a difference during the initial days depending on the isopropanol addition, while the strengths after 28 days were very similar.

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