Effect of polyethylene glycol on the rheological properties and heat of hydration of alkali activated slag pastes

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Abstract. In this work the effect of two types of polyethylene glycol on the rheological properties of alkali activated slag pastes have been investigated. Polyethylene glycols were incorporated in the alkali activated slag pastes in quantities ranging between 0.5 and 5% by mass of slag. All rheological measurements were performed on all pastes with water-to-slag ratio of 0.4. Rheological parameters (shear stress and viscosity) of obtained fresh pastes were studied. Rheological behaviour of pastes modified with polyethylene glycols fits the Newtonian model. In this study also isothermal calorimetry test were performed with different amount of polyethylene glycols concerning time. Results showed that the heat flow generally decreases with increasing polymer dosage.

1. Introduction
Portland cement based materials are the most used construction materials worldwide. However, in recent years new systems have been developed to reduce the cement content due high energy consumption of Portland cement production and high greenhouse gas emissions. One of the alternative materials to Portland cement is alkali-activated slag (AAS), which has shown comparable performance while offering major reductions in CO₂ emissions compared to Portland cement [1-3]. However, AAS provides some challenges regarding its rheological properties, and the workability is considerably lower at the same water to solids mass ratio compared to Portland cement [4].

The rheological behavior of Portland cement pastes has been studied in detail. In the case of alkali activated materials this research field is ongoing yet. Chemical admixtures, which have been proved effective for cement-based materials, are not suitable for alkali-activated systems [5]. Very few studies have been conducted on alkaline activated slag pastes rheology. Palacios et al. [6] observed that polycarboxylate-based, melamine formaldehyde derivative, naphthalene formaldehyde derivative, vinyl copolymer, and shrinkage-reducing agent do not significantly modify rheological parameters. In other studies [7], the rheological properties and hydration process of slag-blended cement pastes in the presence of polycarboxylate superplasticizers with different structure were studied. Polycarboxylate-based admixtures do not modify significantly the plastic viscosity of any of studied pastes.

A.S. El-Dieb [8] investigated the effect of using water-soluble polymers as polyethylene glycol (PEG) and poly acrylamide. Investigation showed a denser microstructure and a lower tendency for microcrack formation. Basil M Joseph [9] studied influence of PEG 400 on the Portland cement concrete and found that the optimum dosage of PEG 400 for maximum strengths (compressive, tensile and modulus of rupture) is 1%.

Another important characteristic for cementitious materials is hydration parameters. These parameters are affected by polymers admixtures. Calorimetric tests are usually used to capture these hydration parameters. Isothermal calorimetry is used to monitor heat flow changes during alkali-
activation reaction. Group of authors [10] concluded that higher and earlier heat production rate due to hydration is found for higher amounts of polyethylene glycol added to the concrete.

Since AAS have an important disadvantage – significant shrinkage followed by formation of microcracks, the main aim of present study is to investigate the rheological behavior of AAS pastes in relation to the effect of polyethylene glycol’s amount and how heat release changes during time while changing rheological properties. The present study provides new information regarding the effect of polyethylene glycols and their dosage on the rheology and hydration process of AAS pastes by performing isothermal calorimetry.

2. Experimental

2.1. Materials
In this study Czech ground-granulated blast-furnace slag (Kotouč Štramberk, spol. s r.o.) was used as a primary raw material. The chemical composition of slag is given in Table 1. The specific surface of the slag was 380 m²/kg. The particle size, determined through laser granulometry was 19 µm (D50). The commercial solid sodium water glass SUSIL (SiO₂/Na₂O = 2.0) was used as an alkaline activator.

Table 1. Chemical analysis of blast furnace slag, [%].

|   | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | Na₂O | K₂O | MnO | Cl | LOI |
|---|------|-------|-------|-----|-----|------|-----|-----|----|-----|
|   | 39.66| 6.45  | 0.47  | 40.12| 9.5 | 0.33 | 0.55| 0.65| 0.05| 1.25|

The effect of two types of commercial PEG (ROTIPURAN®, Ph.Eur), with different molecular weight was used at different concentration: PEG 6000 and PEG 20000 as modifier. PEG is a water soluble linear polymer [11] condensed of ethylene oxide and water with the general formula H−(O−CH₂−CH₂)ₙ−OH, where n is the average number of repeating oxyethylene groups [12] with n=5–182 for typical PEGs (average molecular mass 200-8000 g/mol). PEG 6000 is powdery polymer with molecular mass 6000 g/mol. PEG 20000 is solid polymer in the form of scales with molecular mass 20000 g/mol. Both types of PEG were added at dosage from 0.5 up to 10% by mass of raw material.

2.2. Rheological measurements
All rheology measurements were performed on all pastes with a water-to-slag ratio of 0.4. The reference (REF) AAS paste mix design represents mix of slag (300 g) and activator (60 g). Other tested (experimental) AAS pastes were modified by different types of PEG at dosage 0.5, 1 and 5% by mass of slag. The addition of 10% wasn’t used since the consistency of the mixture was stiff (at given w/s ratio) what is not sufficient for rheological measurements in used rheometer. The activator and polymer admixtures were dispersed and partially dissolved in water prior to mixing with slag.

Rheological measurements were performed at 25 °C on the stress-controlled rheometer Discovery HR-1. A gap thickness of 20 mm was selected for the paste. Rheological properties were measured using 2 program methods: Flow Sweep and Flow Ramp. For both program measurements, the pastes were initially mixed by hand in a plastic bowl with a spatula for approx. 2-3 minutes, depending on the polymer dosage (lower dosages required more time), and then they were inserted into the sample holder of a coaxial cylinder device mounted on the rheometer.

Flow Sweep procedure is based in measuring shear stress at changing shear rate. The rheological properties of AAS pastes were determined from curves at increasing and decreasing rates of shearing in the range 0.1–100 s⁻¹. The paste was pre-sheared for 60 s at 100 s⁻¹. After a rest period of 60 s, the rheological measurements were started. The testing routine consisted of a shear rate increase (from 0.1 to 100 s⁻¹) applied through 30 steps with 15 s of measuring time at each shear rate followed by a decrease of shear rate at the same conditions. The results were expressed as shear rate vs. shear stress.
With the Flow Ramp method shear stress at a constant shear rate in AAS paste was measured. This procedure started with pre-shearing at 100 s\(^{-1}\) for 1 min and was followed by ramping at the constant shear rate of 100 s\(^{-1}\) during 30 min. The results were expressed as shear stress vs. time.

2.3. Isothermal calorimetry test
TAM Air calorimeter (TA Instruments) was used to measure the generated heat in AAS pastes when different dosages of polyethylene glycol were used. For this purpose, several mixtures were prepared, containing slag (4 g), activator (0.8 g), water (2 g) and different types of PEG at dosages 0.5, 1, 5 and 10% by mass of slag. Mixing of each composition was performed in identical glass vials at 25 ºC, and then placed into calorimeter. Heat flow was measured at bath temperature of 25º C for 235 hours for each sample.

3. Results and discussions

3.1. Rheological properties
Figure 1 shows the shear stress versus shear rate flow curves for AAS pastes with addition of PEG 6000 and PEG 20000.

![Flow curves of AAS pastes with PEG 6000 and PEG 20000 at different dosage.](image)

The shear stress values found for pastes modified with PEG 6000 (figure 1a) at 0.5 and 1% dosages are lower than those observed for REF paste. The addition of 5% of PEG 6000 has higher value of shear stress. However, 0.5% of PEG 20000 reduces values of shear stress (figure 1b). Whereas the addition of 1 and 5% of PEG 20000 increases the shears stress values. 5 % of both types of PEG significantly change the viscosity of the pastes. Increasing the amount of PEG affected shear stress.

All AAS pastes containing PEG display Newtonian fluid properties, since yield stress was not indicated. When the relationship between the shear stress \(\tau\) and the shear rate \(\gamma\) is a constant, the material constitutes a so-called Newtonian fluid [13]. Plastic viscosity was calculates using Newtonian model and presented in table 2. The viscosity of the activation solutions was determined by fitting the rheological data to the Newtonian flow model shown in equation (1):

\[
\tau = \eta \cdot \gamma
\]
Table 2. Viscosity of AAS pastes, depending on type and dosage of PEG.

| Type and dosage of admixtures | 0.5% | 1%  | 5%  |
|-------------------------------|------|-----|-----|
| REF                           | 4.23 | 4.23| 4.23|
| PEG 6000                      | 3.37 | 3.98| 5.99|
| PEG 20000                     | 3.80 | 4.69| 9.10|

Figure 2 and 3 shows the variations in shear stress at a constant shear rate in pastes with and without PEG 6000 and 20000. Shear stress is lower in REF pastes than in pastes with different amount of PEG 6000 (figure 2). In the AAS pastes the initial shear stress rose with concentration of PEG 6000. Furthermore, shear stress values for pastes with PEG 6000 decline slightly over time and by the end of the test progressively return to almost the initial values.

Figure 2. Shear stress versus time of AAS pastes containing PEG 6000.

Figure 3. Shear stress versus time of AAS pastes containing PEG 20000.

PEG 20000 raised the initial shear stress values with increasing its concentration (figure 3). The addition of 5% of PEG 20000 doubled the initial shear stress value in comparison with REF values (from 350 to 700 Pa). Also shear stress values for AAS pastes with addition of PEG 20000 decline over time to the end of the test. However, after 1200 s remained substantially constant for 1% and 5% contents.
3.2. Isothermal calorimetry

The isothermal test results of normalized heat flow of all different mixtures are illustrated in figures 4 and 5. The graphs are presented the initial heat peak for the first 3 hours (figure 4a and 5a) and peak which appeared in period from 20 to 120 h (figure 4b and 5b). The heat peak which was discovered after the first 30 min (figure 4a and 5a) is common to all alkali-activated systems as well as to the majority of other cements [14].

The addition of PEG 6000 reduced heat flow values in comparison with REF values (figure 4b). The addition from 1 to 10% of PEG 6000 shifted the heat flow peak to the left compared to the REF peak. However, PEG 6000 at dosage 0.5% did not change heat flow peak and heat flow value significantly. The greatest effect had 10% addition of PEG 6000. First peak was higher (figure 4a), however the second peak (figure 4b) was significantly lower and was significantly shifted to the left. It shows that heat generation accelerates with the increasing concentration of PEG 6000.

**Figure 4.** Calorimetric major peaks from 0 to 3 h (a), from 20 to 120 h (b) of sample with PEG 6000.

The addition of PEG 20000 at concentration 0.5, 5 and 10% showed that heat flow decreased compare to REF sample (figure 5b). 1% of PEG did not affect to the heat flow values. Results showed that mixtures with addition of PEG 20000 mostly shifted peaks to the left side of REF mix; however the addition of 0.5% didn’t shift significantly. Moreover, with the increasing the concentrations of PEG 20000 the peaks were shifted more to the left, which indicates accelerating effect on the hydration.

**Figure 5.** Calorimetric major peaks from 0 to 3 h (a), from 20 to 120 h (b) of sample with PEG 20000.
It can be concluded that alkali activated reaction in samples with addition of PEG 6000 and PEG 20000 starts earlier (second peak at figure 4b and 5b). At the same time intensity of reaction reduces to compare with REF sample, since the heights of heat peaks become lower and less sharp. This phenomenon can be explained, that PEG covers the slag grains what can lead to reduction the intensity of alkali activation. Due to the fact that the reaction of alkali activation take place on the slag surface and in the liquid regions [15] This reaction process will affect inter-particle forces what can result to slow formation of calcium-sodium aluminosilicate hydrate gel (the main product of alkali activation reaction) [16].

4. Conclusion

This paper presented procedures and analyses for elucidating rheological and hydration characteristics and the key conclusions are listed below:

- An analysis of the present findings showed that the polymers PEG 6000 and 20000 affected AAS pastes rheology depends on its concentration. The shear stress values were higher with increasing the concentration of both types of PEG. The rheological behaviour in AAS pastes fit a Newtonian model.
- An increase in both types of PEG dosage results in faster reaction in AAS pastes, with the calorimetric data showing main peak at earlier time than REF paste mix. However, the employment of PEG effects on reduction the intensity of reaction of alkali activation, since the height of main peak is higher and sharper of REF samples than peaks of modified samples by PEG.

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