Construction and Building Materials 171 (2018) 197–204

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Rheology and apparent activation energy of alkali activated phosphorous slag

Hamideh Mehdizadeh, Ebrahim Najafi Kani *

Faculty of Chemical, Petroleum, and Gas Engineering, Semnan University, Semnan 3519645399, Iran

HIGHLIGHTS

- AAPS paste behaved like shear-thinning fluid and its rheological behavior obey the Herschel-Bulkley model.
- The shear stress of AAPS paste increased during the time due to higher dissolution rate of phosphorous slag and more gel formation.
- The shear-thinning behavior of AAPS paste was discovered to be independent of the chemical composition of activator.
- Apparent activation energy of the studied AAPS pastes was measured base on Arrhenius viscosity model in the range of 39.2–44.5 kJ/mol.
- Apparent activation energy decreased with increase of N/A molar ratio and decrease of S/N molar ratio.

ARTICLE INFO

Article history:
Received 5 January 2018
Received in revised form 14 March 2018
Accepted 17 March 2018

Keywords:
Rheology
Apparent activation energy
Alkali activated materials
Phosphorous slag

ABSTRACT

This paper focused on determining the rheological behavior and apparent activation energy of activated phosphorous slag (AAPS) with sodium silicate and NaOH at different SiO_2/Na_2O (S/N) and Na_2O/Al_2O_3 (N/A) molar ratios. The results showed that the AAPS paste behaved like a shear-thinning fluid, its rheological behavior obeyed the Herschel-Bulkley model, and its apparent viscosity decreased with increasing of shear rate. The chemical composition of activator affected the rheological properties and fluidity of AAPS paste but had no significant effect on shear thinning parameters. It was found that shear thinning behavior of AAPS paste was depend upon the changes done in the nature of phosphorous slag after activation process. It was observed that the initial rest time before increase of shear stress during the time was decreased as the S/N and N/A was increased due to increase in the slag dissolution rate and more gel formation. Increase in chemical composition of the activator also caused to accelerate the geopolymerization reactions and hence increased the shear stress. Apparent activation energy of AAPS paste based on Arrhenius viscosity model at temperatures of 10, 25, and 40 °C was measured in the range of 39.2–44.5 kJ/mol. It was found that lower silica content in the activator, i.e. decrease of S/N molar ratio, and higher alkaline content in the activator, i.e. increase of N/A molar ratio, result in decrease of the apparent activation energy. The accuracy of Arrhenius viscosity model was confirmed by determining the activation energy of OPC as the blank sample that was measured as 36.7 kJ/mol.

1. Introduction

Alkali activated materials (AAM) are a group of inorganic binders, which produce by chemical reaction between an aluminosilicate material and alkaline solution (usually acid salts, hydroxides, or metal silicate). Some specific engineering properties such as reduction of CO_2 emission and high resistance to acid environment of alkali-activated materials compared to ordinary Portland cement, put them as an alternative construction material [1–3]. Any change in the composition of the starting aluminosilicate material and the used alkali activator result in variation in reaction progress and microstructure of the products which could show good durability and suitable mechanical strength. However, future application of AAMs as concrete or grout depend on the rheological behavior, control of setting time and mechanistic aspects of geopolymerization of fresh paste in the process stages of pumping, injection, molding, and compaction [4–8].

Various techniques such as rheological characterization and determination of apparent activation energy are needed to analyze the geopolymerization mechanism in the early ages and control of setting times [9–12]. Rheological properties of cement based materials can provide viewpoint on hydration mechanism which affect their durability and mechanical properties [4].

* Corresponding author.
E-mail address: e_najafi@semnan.ac.ir (E. Najafi Kani).

https://doi.org/10.1016/j.conbuildmat.2018.03.130

In the rheological investigations, the formed flocs of cement grains break down as subjected to shear stress which causes the rotor speed to reduce, gradually. It is confirmed that cement pastes behave like a non-Newtonian fluid and its shear stress curve fit well with Bingham model (Eq. (1)) [7].

$$\tau = \tau_0 + \eta\dot{\gamma} \quad (1)$$

where η, τ, τ_0 and $\dot{\gamma}$ are the plastic viscosity (Pa·s), shear stress (Pa), yield stress (Pa), and shear rate (s^{-1}), respectively.

However, different models of Herschel-Bulkley and Power law have also been reported for rheological behavior of cement-like binders (Eqs. (2) and (3), respectively) [4].

$$\tau = \tau_0 + k\dot{\gamma}^n \quad (2)$$

$$\tau = k\dot{\gamma}^n \quad (3)$$

where k and n are the consistency coefficient (Pa.s), and dimensionless fluidity index, respectively.

Despite the more eco-efficient of alkali activated material than common Portland cement, in the literature, few researches on rheology of AAMs can be found. Primary investigations on the rheological behavior of alkali activated materials were done on alkali-activated fly ash and sodium carbonate-activated blast furnace slag [13,14]. Results showed that rheological behavior of activated fly ash fit with Bingham model [14].

Puertas et al. investigated the rheological behavior of alkali-activated blast furnace slag (AAS) with waterglass and NaOH–Na_2CO_3 (N/C activator) [15]. They reported that some process parameters such as nature and concentration of used alkaline solution affected the AAS pastes rheological properties. Their results showed that waterglass-activated slag had a better fit to the Herschel-Bulkley model, while AAS pastes activated with N/C activator behaved like Bingham model. Moreover, decreasing of Na_2O concentration leads to reduction the shear stress [15]. In other investigation, Palacios et al. confirmed that waterglass-activated slag had a better fit to the Herschel-Bulkley model [16]. These researches also showed that AAS pastes activated with sodium hydroxide (4 wt% Na_2O) fit with Bingham model.

Activation energy, like rheological properties, can also be used to investigate the geopolymerization mechanism of cementitious materials. This property usually is determined by the calorimetric data. Grazino et al. and Alonso and Palomo studied the effects of calcium addition and reaction temperature on reaction rate by isothermal conduction calorimetry (ICC) [10,17,18]. Moreover, the reaction kinetics of activated fly ash-slag blended with waterglass solution by isothermal calorimetry investigated by Chithirputhiran and Neithalath [19], while Ma et al. studied the reaction rate of alkali-activated fly ash [20]. Zhang et al. [21,22] also investigated thermodynamics and reaction kinetic of activated metakaolin with sodium hydroxide and sodium silicate by isothermal calorimetry. They also quantify the extent of reaction through the structural analogies between natural zeolites and metakaolin geopolymer binder.

Quasi-isothermal modulated differential scanning calorimetry has been employed to characterize the changes occurring in the heat capacity and heat flow of metakaolin-based geopolymer by Rahier et al. [9,11,23]. These results are also combined with rheological data to create a link between macroscopic properties and released heat due to chemical reactions. Najafi et al. [24] investigated the effect of calcium aluminate cement (CAC) as efflorescence control admixture and chemical composition of activator on reaction heat and apparent activation energy of natural pozzolan-based geopolymers. They showed that apparent activation energy decreased in the mixes containing CAC, but total heat of reaction is higher than the mixes without admixture [24].

Maghsoodloo and Allahverdi [3] also determined the apparent activation energy of activated phosphorous slag with two different activators of $Na_2CO_3 + Ca(OH)_2$ and $NaOH + Na_2CO_3$ by compressive strength data. Their results showed that the apparent activation energy of activated phosphorous slag was 60.7 and 35.6 kJ/mol for the two activator, respectively. Shi and Li also presented an investigation on compressive strength and apparent activation energy of phosphorous slag activated with water glass solution [25,26] and activated with NaOH [27]. They reported that 28 days compressive strength of AAPS binder was up to 120 MPa due to formation of calcium silicate hydrate gel (C-S-H) in the binder structure.

Authors of this work have not detected references in rheological behavior of alkali-activated phosphorous slag with sodium silicate and sodium hydroxide in the literature.

The important novelty of this work is the determination of apparent activation energy based on Arrhenius viscosity model. When conducting an increasing temperature (while frequency and oscillatory strain is constant), the apparent activation energy, E_a, could be determined over a limited temperature range by replacing the complex apparent viscosity, η, and absolute temperature, T, in the Arrhenius viscosity model. In this work, authors have studied and investigated the rheological behavior (shear stress, yield stress, Thinning index, and flow index), workability, and also the apparent activation energy based on rheological data of alkali activated phosphorous slag at different chemical composition of activator. Rheological behavior of OPC paste has also been investigated as the blank sample.

2. Experimental

2.1. Raw materials and sample preparation

The granulated phosphorous slag (PHS) is used in this work as the starting aluminosilicate material and obtained from an Iranian phosphoric acid production plant (Tehran, Iran). A Portland cement, CEM I 42.5R, is also used as a blank sample. The chemical composition and Blaine fineness (determined based on standard ASTM C311) for the PHS and cement are presented in Table 1.

The X-ray diffraction pattern of PHS and OPC is shown in Fig. 1. As seen, phosphorous slag is almost completely amorphous (calcite-manganoan, $((Ca,Mg)CO_3)$ and just a small amount of crystalline MgO during milling process exists in its structure.

The particle size distribution of phosphorous slag after milling process in a batch laboratory ball mill (110 mm radius and 380 mm length) is shown in Fig. 2. The particle size distribution of PHS is performed by a laser particle size analyzer (CILAS 1064, France). The mean particle diameter of PHS and OPC are 13.18 μm and 11.38 μm, respectively.

Analytical grade of sodium hydroxide (NaOH, 99% purity) and sodium silicate (32.87 wt% of SiO_2, 24.21 wt% of Na_2O, and 42.92 wt% of H_2O) are used for preparation of alkaline activator solutions all throughout the experiments.

For activated phosphorous slag mixes, named P1, P2, P3, P4, and P5 as described in Table 2, with three different levels of SiO_2/Na_2O molar ratios (Abbreviated as S/N) and Na_2O/Al_2O_3 molar ratios (Abbreviated as N/A) are prepared. The chemical composition of the binders was varied by changing the S/N and N/A molar ratio of the used alkali-activator. To prepare the activators, first, appropriate quantity of NaOH is dissolved in water, and then alkaline solution is added to the liquid sodium silicate. Finally, prepared activator solutions are mixed with the phosphorous slag precursor. The mixtures are all investigated at a constant total H_2O/Al_2O_3 molar ratio of 40 (with water to solid ratio of 0.54).The OPC paste as the blank sample is also prepared by mixing of Portland cement with water at a water/cement ratio of 0.45 all through the tests.

2.2. Determination of rheological properties

The OPC and AAPS pastes are tested for 30 min on a Brookfield DV3-RV rotational rheometer fitted with a small sample adapter (Spindle SC4-21) and operating at a constant shear rate of 50 s^{-1}.

Rheological behavior of AAPS pastes are specified by determining yield stress (τ_0), thinning index (TI) and flow index (n).

The specification procedure of yield stress consist of pre-shearing at 100 s^{-1} for 2 min, followed by ramping up from 0 to 10 s^{-1} in 45 s and from 10 to 100 s^{-1} in 45 s and then ramping down from 100 to 10 s^{-1} in 90 s as well as 10 to 0 s^{-1} at