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Understanding the relationship between composition and rheology in alkali-activated binders

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Abstract. Based on the knowledge that exists today, it is generally accepted that there are basic parameters and characteristics to obtain effective mixtures for their use in 3D printing. Rheological behavior and setting time (initial and final) are those characteristics that determine workability, as well as the speed and nature of hardening of the molded pastes and, as a result, the final framework and the integrity of the resulted structure. Among the promising options for 3D printing, the literature often contains information on alkali-activated binders. In this work, an alkali-activated binding system based on electrometallurgical slag, as well as citrogypsum, a waste of the industrial production of citric acid, was studied. Some rheological characteristics of experimental binders were considered: the nature of the mixture flow under the action of torsional loads and their initial and final setting times. It was found that the joined use of both components in the experimental system "slag - water": an alkaline activator and citrogypsum, promotes the transition of the character of the system from thixotropic to mixed: dilatant-thixotropic (for the Na_2SiO_3 activator) and dilatant (for the NaOH activator). It was found that the addition of alkaline activators and citrogypsum to the binding system separately in both cases helps to reduce the initial and final setting times from 18 and 22 hours to 1 hour and 1.5 hours. Also, experimental results have shown that the jointed action of both components: an alkaline activator and cytogypsum, has a synergistic effect on the setting time.

1. Introduction

Keeping track of the dynamics of the development of the construction industry not only in recent years but also over the past decades, indicate a constant intensive change in trends that were relevant in different periods. So, in different periods of time, the following factors were the priority indicators in the production of building materials and the construction of buildings and structures:

- *when choosing raw materials:*



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1) the use of quality natural raw materials, which will ensure the high quality of the finished product;

2) the use of modifying additives that increase the efficiency of the main raw materials of medium and low quality;

3) the use of cheaper and more accessible raw materials in the form of by-products and waste, but not inferior in quality to natural analogues in order to preserve the quality of the final product;

4) the use of multicomponent composite compositions that combine cheaper and more affordable raw materials together with cheap and affordable modifiers, the jointed action of which ensures high quality of the finished product

- *when choosing a production technology:*

1) technologies that ensure the simplicity and reliability of building materials and the construction of structures;

2) technologies that provide maneuverability in the production of building materials and the creation of structures in situ;

3) technologies that provide maneuverability and tight lines in the production of building materials and creation of structures;

4) technologies that allow to create structures of complex configuration in a short time.

Thus, based on the above points No. 4 in the paragraphs "when choosing raw materials" and "when choosing a production technology", which represent modern requirements for construction technologies and the production of building materials and structures, the constantly growing interest in 3-D printing, and building mixtures for them is explained [1–3]. The rheological characteristics of 3-D printing mixes are key, which determine workability and mobility under various operating conditions, as well as taking into account the duration of operation until the moment of setting/hardening of the mix. One of the main challenges to be addressed in the implementation of 3D printing in the development of a clear understanding of how a material can be liquid enough to flow through a hosepipe without clogging, while still having sufficient viscosity to maintain its shape after the printing process [4]. For this, the developed concrete mixture must be thixotropic, for which it must demonstrate a high yield strength at rest and low viscosity during flow. These ideas are formulated based on a large number of rheological studies of concrete mixtures of different compositions. Le et al. [5, 6] established the key concept of fresh concrete properties such as workability and extrudability of fresh concrete, the period until the fresh mix sets, satisfying the requirements for 3D printing of concrete, and simplicity in the assembly of precast elements. The proposed concept is that the composition of the raw mixture influences the rheological properties, i.e. the ratio of the components, the presence of modifying additives, for example, superplasticizers, retarders / set accelerators, reinforcing fibers, etc. As the literature review shows, a significant proportion of mixtures that are positioned as raw materials for 3-d printing are based on pure Portland cement or a complex cement-based compound containing various additives and modifiers. In terms of rheological flow, classical cement systems are characterized as thixotropic. It is known that thixotropy manifests itself as a decrease in viscosity at increased shear stress or shear rate over time. The process is reversible. [7, 8]. As a rule, thixotropic materials transform into a more mobile fluid when shear stress is applied, and when the stress is removed, they change back to a more viscous state. In other words, resting flocculation and stress deflocculation play an important role in 3D printing. Alkali-activated systems such as slag-alkaline types of cement and geopolymers can be used as another no less promising material for creating mixtures for 3D printing.

There are different opinions about the rheological behavior of cement and alkali-activated systems. According to [9, 10], in contrast to cement mixtures, alkali-activated analogs, as a rule, do not exhibit thixotropic properties since in the process of chemical reactions there is no interaction of components at the colloidal level.

A recent study has shown that the rheology of alkaline activated systems is more related to the viscous nature of the alkaline activating agent and, to a lesser extent, to the interaction of particles [6, 11–12]. However, some works [10, 13] have established that freshly prepared geopolymer and cement

pastes can be considered as suspensions of particles in a continuous liquid (solution of an alkaline activator). Cement suspensions exhibit the following features: Newtonian behavior, which is characterized by constant apparent viscosity at rest; liquefaction/decrease in apparent viscosity with increasing shear rate; or an increase in apparent viscosity with increasing shear rate. The type of rheological behavior depends on the nature of colloidal interactions, which are caused by electrostatic interaction forces, weak van der Waals forces, as well as closer interactions that are created due to hydrodynamic forces and direct contact of particles with each other. Due to these interactions, cement pastes can be described as Bingham (non-Newtonian) fluids.

In works [14, 15], it is shown that the viscosity of a typical geopolymer based on metakaolin, in comparison with the viscosity of cement paste, is characterized by lower values. To a large extent, the viscosity of the system determines the viscosity of the alkaline activator solution and, to a lesser extent, the interaction between the particles of the solid phase. The literature review has shown that alkali-activated systems using a wide range of raw materials have been studied as a binder for the production of mixtures for 3D printing

In [14], studies of geopolymer mixtures based on fly ash and microsilica, granulated blast furnace slag for 3D printing by the extrusion method are presented. The work studied the effect of microsilica on the rheology of mixtures. The work found that the introduction of silica fume has a positive effect on the yield strength and viscosity of mixtures at an early stage, as well as an effective extrusion process. The authors explain this by the large surface area and the spherical shape of the particles.

2. Materials and methods

The raw materials used were electrometallurgical slag (Russia) as the main binder and citrogypsum as a mineral additive. Sodium hydroxide NaOH (98% of purity) and sodium silicate Na₂SiO₃ (water glass) with a silicate modulus of 2.75 were used as alkaline activating agents. The rheological characteristics of the experimental alkali-activated pastes were studied using a Fungilab Rotational Viscometer (Spain). Determination of the setting time and normal thickness of the experimental alkali-activated pastes was determined using a standard technique using a Vicat apparatus according to Russian Standard GOST 310.3-76

3. Results and discussions

3.1 Rheological characteristics

For rheological studies, samples of alkali-activated pastes were used, the compositions of which provide the highest values of compressive strength when hardening in ambient conditions at the age of 9 days (Table 1).

Table 1. Compositions and characteristics of alkali-activated pastes.

Samples	Components, %					Characteristics	
	Slag	Water	Citrogypsum	Alkaline activator		Yield compressive strength, MPa	Average density, kg/m ³
				NaOH	Na ₂ SiO ₃		
1	84.5	15.5	-	-	-	0.6	1900
2	80.3	15.5	4.2	-	-	0.6	194
3	74	13.7	8.2	4.1	-	1.8	2050
4	74	13.7	8.2	-	4.1	4	1990
5	82.2	13.7	-	4.1	-	2.33	2352
6	82.2	13.7	-	-	4.1	2.04	2033

The study of the viscous-plastic characteristics of experimental alkali-activated pastes was carried out using a disk-shaped spindle R5 with a disk diameter of 21 mm (see Figure 1).



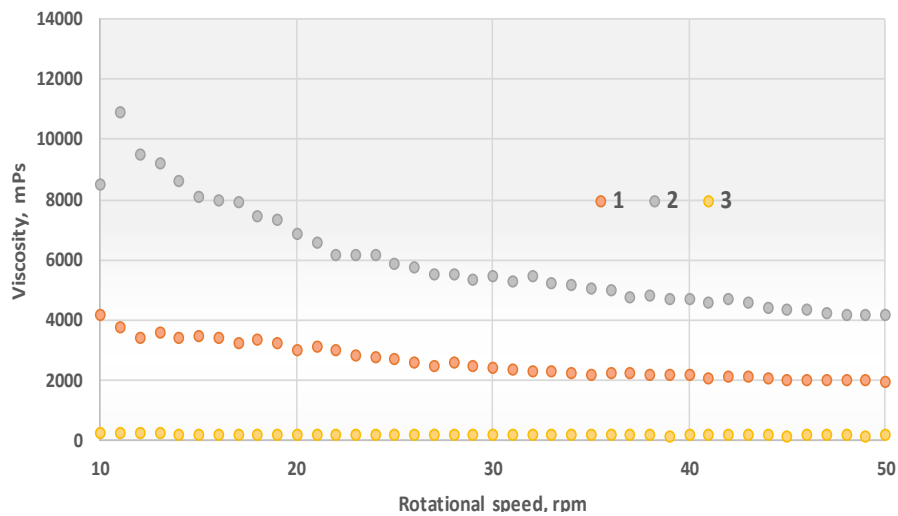
Figure 1. The appearance of the disc-shaped spindle R5 used as a tip for the Fungilab Rotational Viscometer.

During the experiment, the following shooting mode and parameters were used: rotation speed spindle is from 1 to 50 (rpm); the duration of the experiment was 120 s.



Figure 2. The testing process for alkali-activated paste with a Fungilab Rotational Viscometer.

The rheological curves obtained as a result of the test are presented in Figure 3.



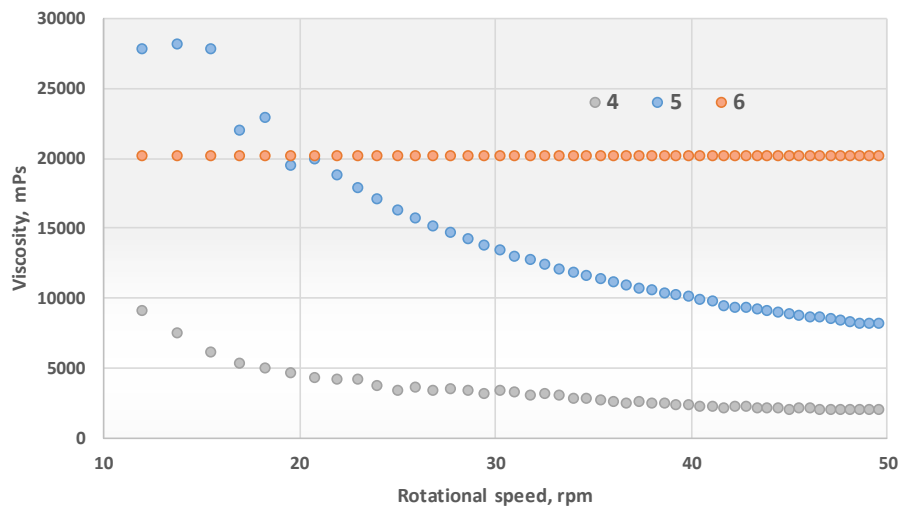


Figure 3. Rheological curves of alkali-activated binders with different compositions: 1, 4 - reference binding system "slag-water"; 2 - "slag - water - Na_2SiO_3 "; 3 - "slag - water - Na_2SiO_3 - citrogypsum"; 5 - "slag - water - NaOH"; 6 - "slag - water - NaOH - citrogypsum".

According to the dynamics of the obtained rheograms, the type of alkaline modifier does not affect the flow pattern of the binding system based on slag, as well as the values of the initial viscosity. For systems that do not contain citrogypsum, predominantly thixotropic behavior is characteristic, as for classical cement systems [16]. For the NaOH-based system, dilatant behavior occurs in a narrow range of initial velocities from 10 to 13 rpm. In turn, the introduction of an additive of citrogypsum significantly affects the nature of the flow of the curves, transforming the system based on liquid glass Na_2SiO_3 into a dilatant-thixotropic one (curve 3), and the system based on NaOH into a dilatant one (curve 6), similar to ceramic [17] and geopolymer [18] systems. For systems based on NaOH for the rheological curve, dilatant flow is observed in a wider range of velocities (from 10 to 23 rpm), followed by a transition to thixotropic flow.

3.2 Setting test

One of the main indicators of mixtures that meet the requirements of construction (3D) printing is rather short setting times, which ensure the preservation of the original shape of the "printed" structure. The studies were carried out according to the Russian standard methodology, as reflected in GOST 125-79. The results are shown in Table 2.

Table 2. Values of setting times for alkali-activated binders with different compositions.

№	Composition	Setting time, hours	
		initial	final
1	"Slag – water"	at least 18	22
2	"Slag – water – citrogypsum "	16	20
3	"Slag – water – NaOH"	5	21
4	"Slag – water – Na_2SiO_3 "	1 hour 45 min	3
5	"Slag – water – NaOH – citrogypsum"	3	19
6	"Slag – water – Na_2SiO_3 – citrogypsum"	1	1 hour 30 min

According to the data in Table 2, the addition of citrogypsum to control composition No. 1 (Slag - water) shortens the initial and final setting times by approximately 2 hours (composition No. 2). A similar trend is observed when both alkaline activators NaOH and Na_2SiO_3 are introduced into the control system, however, these components have a more significant effect on the onset of the setting time: a reduction in the time period from 18 (for control composition No. 1) to 5 hours and 1 hour 45

minutes for compositions on based on NaOH and Na₂SiO₃, respectively (compositions No. 3 and 4). The combined introduction of an alkaline activator and cytogypsum into the system has a synergistic effect on the setting time. There is a reduction in the initial setting time to 3 hours and 1 hour and the final setting time to 19 hours and 1.5 hours for cementitious systems based on NaOH and Na₂SiO₃, respectively (compositions No. 5, 6). Analyzing the data on the setting time, the decisive influence of Na₂SiO₃ (Compositions No. 4, 6) on the reduction of the initial and final setting times in comparison with citrogypsum and NaOH activator is clearly expressed.

4. Summary

The obtained results of the experiments made it possible to formulate the following conclusions:

- The combined introduction of both components into the "slag-water" system: an alkaline activator and cytogypsum, promotes the transition of the character of the system from thixotropic to mixed: dilatant-thixotropic (for Na₂SiO₃ activator) and dilatant (for NaOH activator);
- The introduction of alkaline activators and citrogypsum into the binder system "slag - water" separately in both cases helps to reduce the initial and final setting time. A more obvious effect of shortening the setting time is characteristic of Na₂SiO₃, which makes it possible to reduce the time of the beginning and end of the setting from 18 and 22 hours to 1 hour and 1.5 hours;
- The combined action of both components: activator and cytogypsum, has a synergistic effect on the setting time.

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