



Using of Citrogypsum in Alkali Activated Systems

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Abstract. A large amount of research and previously obtained experimental data allows us to conclude with a high degree of confidence that one of the key roles in the synthesis of alkali-activated binders, cement, concretes, etc. plays an alkaline component or activator, which, in fact, is the initiator of all structure-forming processes during the hardening of the system. In this study, we studied the features of the synthesis of alkali-activated binders with different component compositions using a complex of industrial waste “citrogypsum—electrometallurgical slag” as a solid-phase component. Based on the obtained experimental results, it was found that the addition of 10% citrogypsum promotes an increase in strength by 13% (from 4.9 to 5.54 MPa), i.e., a synergistic effect is observed. A similar trend: higher density values are provided with the combined action of the components (compaction up to 3–5%) versus similar values for the components that form a solid structure separately. The study of the effect of the type of alkaline activating agent showed that both activators used in the work (NaOH and Na₂SiO₃) do not have a significant effect on the strength indicators of synthesized alkaline-activated binders with citrogypsum. Moreover, the dosage of the introduced alkaline agent up to 5% reduces the compressive strength from 19% (for NaOH) to 43% (for Na₂SiO₃).

Keywords: Citrogypsum · Electrometallurgical slag · Alkali-Activated binder · Physical and mechanical characteristics

1 Introduction

Currently, quite a wide range of binders and materials for construction purposes is known, distinguished by their high efficiency in use and found their field of practical application. As a rule, a significant proportion of binders is occupied by multicomponent systems or composite binders/materials. It is important to note that the effectiveness of advanced

materials is due not only to their basic performance characteristics. Environmental and economic components are also very important [1–9]. Increasingly widespread use of multicomponent or composite systems is often due to the need to improve the operational characteristics of the resulting composite. In most cases, this is achieved through the mechanical action of the introduction in the form of grinding, mechanical activation, or mechanochemistry, as well as through the introduction of additional additives, modifiers, active fillers, etc. into the binder system [10–14].

Among the promising composite systems for the construction industry, it is necessary to highlight the binding systems of alkaline activation. Also, the literature review confirms that waste from the production of phosphoric acid and phosphoric fertilizers acts as one of the valuable modifiers in these systems [15]. Previously, Rashad [16] studied the possibility of processing calcined phosphogypsum as a partial replacement for fly ash in alkali-activated binders based on it. The results showed that the compressive strength increases with dosages of calcined phosphogypsum up to 10%. At the same time, an increase of this additive in the binder system up to 15% leads to a decrease in strength values. The effect of a complex additive of gypsum and phosphoric acid on the properties of an alkali-activated slag using sodium silicate (water glass) as an activator was studied in earlier works [17]. Phosphoric acid was used as a set time retarder and gypsum was used as a shrink-resistant component when drying the system. Bakharev et al. [18] presented the results of a study of concrete consisting of alkali-activated slag and gypsum additives (6% of the slag mass), which confirmed the shrink-resistant effect of gypsum.

Guo et al. [19] used a complex alkaline activator: sodium hydroxide and sodium silicate solution—for the synthesis of binders based on high-calcium (class C) fly ash and other Ca-containing additives such as Portland cement and gypsum-containing waste obtained during desulfurization of flue gases and water treatment. Due to their high strength values (up to 80.0 MPa), these alkali-activated binders can be used in various fields, in particular, for the production of building materials, as well as for hardening and “conservation” of hazardous waste, which allows us to speak about the environmental friendliness of these materials. Chinese scientists have established the possibility of the production of building materials using semi-aqueous phosphogypsum, the joint use of which provides both an environmental and economic effect. At the same time, a close analog of phosphogypsum, citrogypsum, is formed in the Russian Federation as a waste product. Citrogypsum is a waste product from citric acid production. This work aims to study the behavior of cytrogypsum in alkali-activated binders of different component compositions.

2 Materials and Methods

Methods. In the work, electrometallurgical slag (OEMK slag), (Russia) was used as an aluminosilicate component. The chemical composition of the raw solid-phase components: slag and cytrogypsum, was determined by X-ray analysis (XRF) using an ARL 9900 X-ray WorkStation diffractometer (Termo Scientific). X-ray diffraction spectra were obtained with an ARL X'tra diffractometer using CuK 1,2 radiation. Drying of raw materials was carried out in a laboratory oven BINDER FD-53 (Mettler, Germany).

Compressive strength tests were carried out using a PGM 100 hydraulic press machine (SKB Stroypribor, Russia).

Materials. In this study, two types of solid-phase components were used: OEMK slag and citrogypsum waste, the physicochemical characteristics of which are presented in Tables 1, 2 and 3.

Table 1 Chemical composition of OEMK slag and citrogypsum

Oxides content (wt%)											
CaO	SiO ₂	Fe ₂ O ₃	MgO	Al ₂ O ₃	MnO	Na ₂ O	Cr ₂ O ₃	TiO ₂	P ₂ O ₅	SO ₃	K ₂ O
40.78	24.55	15.03	12.51	4.18	0.92	0.49	0.3	0.2	0.18	0.17	0.11
30.6	0.75	–	0.25	–	–	–	–	–	–	44.7	–

Table 2 Mineral composition of OEMK slag

№	Mineral	Concentration, wt%
1	Ca ₂ SiH ₂ O ₅	20.42
2	γ-C ₂ S	17.65
3	Okermanite 2CaO·MgO·2SiO ₂	10.13
4	Merwinite 3CaO·MgO·2SiO ₂	8.26
5	α-quartz	2.4
6	Calcite	4.88
7	Wustite FeO	25.98
8	Magnetite FeO·Fe ₂ O ₃	10.26

Table 3 Compositions and properties of the «OEMK slag—citrogypsum» system

Composiption	Components, %			Citrogypsum	
	OEMK slag	Water	Citrogypsum	Yield compressive strength, MPa	Average density, g/cm ³
1	85.7	14.3	–	4.9	2.25
2	–	14.3	85.7	3.1	2.3
3	81.4	14.3	4.3	5.54	2.37

Preliminary treatment by additional drying is required for both wastes: OEMK slag and citrogypsum. This is justified by the fact that waste is, normally, stored in open landfills and, as a result, has excess moisture, which can complicate research, as well as adversely affect the properties of the synthesized compounds.

The drying procedure was carried out until the materials reached a constant mass, after which the materials were stored under laboratory humidity (35%).

3 Results and Discussions

Effect of the component composition on the physical and mechanical properties of the binder. To study the physical and mechanical characteristics of the binding system “OEMK slag—citrogypsum”, experimental compositions were molded (Table 3). The experimental mixtures were molded into cubes of 20 × 20 × 20 mm and left for hardening in ambient laboratory conditions (temperature 23 ± 2 °C; relative humidity—33 ± 2%). Compression strength and average density tests of the hardened specimens were carried out at the age of 9 days.

The results of the compressive strength given in Table 3 showed that the addition of 10% citrogypsum to the “OEMK slag—water” system leads to an increase in strength by 13% (from 4.9 to 5.54 MPa). Thus, there is a manifestation of a synergistic effect in structure formation during the interaction of these two wastes. This is confirmed by the fact that the hardening of slag and citrogypsum components separately demonstrates lower strength characteristics (3.1 MPa—for cement paste containing citrogypsum). Speaking about the average density of the composite system “OEMK slag—citrogypsum”, a similar tendency is observed: higher density values are achieved with the combined action of the components (compaction up to 3–5%) compared to the same values for the separately hardened components.

Effect of the type of alkaline activator on the physical and mechanical properties of the binder. Also, various additives, modifiers, fillers contained in the binder matrix are very important (if they have a reactive or chemical activity to the rest of the system). In this regard, at this stage of the work, the effect of two types of alkaline activators, such as liquid glass Na₂SiO₃ and sodium hydroxide NaOH, on the physical and mechanical properties of synthesized binders containing citrogypsum waste was studied (Fig. 1).

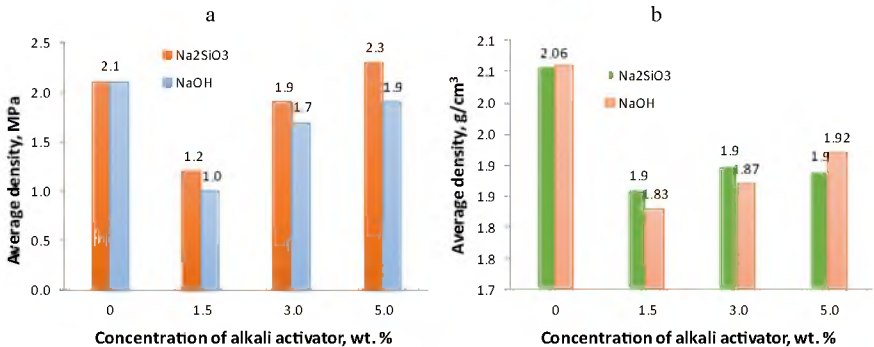


Fig. 1 Effect of the type and concentration of the alkaline activator on the physical and mechanical properties of, citrogypsum-containing binders: **a** compressive strength, **b** average density

The analysis of the results obtained, which are presented in Fig. 1, showed that both used alkaline activators (NaOH and Na₂SiO₃) do not have a significant effect on the strength characteristics of the synthesized alkaline-activated binders containing citrogypsum. Moreover, the dosage of the introduced alkali up to 5% leads to a decrease in the compressive strength from 19% (for NaOH) to 43% (for Na₂SiO₃). On the other

hand, the strength values of the experimental compositions at 5%-concentration of an alkaline activator of both types are comparable (1.9 and 2.3 MPa) with an alkali-free analogue (2.1 MPa). At the same time, for compositions with an alkali concentration of more than 5%, significant leaching is observed at the surface of the samples, and a longer period of hardening of mixtures and their transition to a consolidated state is observed, as well. Thus, a further increase in the alkaline component is technically in-efficient.

4 Conclusion

Based on the research presented in the article, the following conclusions can be formulated:—introduction of 10% citrogypsum additive into the “OEMK slag—water” system increases the strength of the cement paste by 13%, which indicates the manifestation of a synergistic effect when the interaction of these two types of waste. For density values, a similar tendency is observed: compaction is observed up to 3–5%);—Studies of physical and mechanical properties of the “OEMK slag—water—citrogypsum” system with various types and concentrations of alkaline activators showed that the dosage of the introduced alkali up to 5% causes a decrease in compressive strength from 19% (for NaOH) to 43% (for Na_2SiO_3).

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