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THE EFFECT OF MODIFYING ADDITIVES ON THE PERFORMANCE PROPERTIES OF SLAG-ALKALI BINDERS AND CONCRETES

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Abstract: The results of the analysis and generalization of research on the problem of using man-made industrial waste for the production of composite slag-alkali binders and concretes based on them are presented. The disposal of industrial man-made waste and their use in the production of composite binders are issues of global importance. Therefore, much attention is paid to this issue in the industrialized countries of the world.The influence of waste products from the enrichment of polymetallic ores – carbonate-barium tailings on the performance properties (strength, water absorption, density, etc.) of composite slag-alkali binders and concretes based on them has been studied. Various methods of introducing modifying additives into the composition of composite slag-alkali binders and concretes based on them have been investigated. The optimal amount of introduction of modifying additives into the composition of composite slag–alkali binders - waste of carbonate-barium tailings and an efficiency indicator for the effect on the activity of concrete, depending on the type of alkaline component and hardening conditions, has been established. The methods of conducting experimental work to determine the operational properties of slag-alkali binders and concretes based on them are presented.

Keywords: waste of carbonate-barium tailings, composite slag-alkali binders, modifying additives, strength, water absorption, density

ВЛИЯНИЕ МОДИФИЦИРУЮЩИХ ДОБАВОК НА ЭКСПЛУАТАЦИОННЫЕ СВОЙСТВА ШЛАКОЩЕЛОЧНЫХ ВЯЖУЩИХ И БЕТОНОВ

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Аннотация: Приведены результаты анализа и обобщения исследований по проблеме использования техногенных отходов промышленности для производства композиционных шлакощелочных вяжущих и бетонов на их основе. Утилизация промышленных техногенных отходов и их использование в производстве композиционных вяжущих является вопросами глобального значения. Поэтому в промышленно развитых странах мира этому вопросууделяется большое внимание. Изучено влияние отходов производства обогащения полиметаллических руд – карбонатно-бариевых хвостов на эксплуатационные свойства (прочность, водопоглощение, плотность и др.) композиционных шлакощелочных вяжущих и бетонов на их основе. Исследованы различные способы введениямодифицирующих добавок в состав композиционных шлакощелочных вяжущих и бетонов на их основе. Установлено оптимальное количество введения в состав композиционных шлакощелочных вяжущих модифицирующих добавок – отходов карбонатно-бариевых хвостов и показатель эффективности по влиянию на активность бетона, в зависимости от вида

щелочного компонента и условий твердения. Приведены методики проведения экспериментальных работ по определению эксплуатационных свойств шлакощелочных вяжущих и бетонов на их основе.

Ключевые слова: отходы карбонатно-бариевых хвостов, композиционные шлакощелочные вяжущие, модифицирующие добавки, прочность, водопоглощение, плотность

1. INTRODUCTION

The problem of effective utilization of technogenic industrial waste has great importance due to the continuous growth of industrial production and consumption of natural mineral raw materials. Insufficiency and irreplaceability of deposits of natural raw materials, complication of mining and geological conditions of occurrence of ore bodies and rise in cost of their extraction, negative influence on the environment of accumulated technogenic wastes is an actual problem. Therefore, the application of industrial technogenic wastes in the production of composite materials is today the most important research questions of scientists.

The volumes of accumulated industrial wastes of production are significant in the Russian Federation and Kazakhstan, and their wide application for production of composite slag-alkali binders and concretes on their basis is expedient, and it requires their immediate accounting on a par with natural mineral resources. Development of composite cement and slag-alkali binders and concretes on the basis of industrial technogenic wastes promotes systematic and more intensive involvement of various types of technogenic mineral formations in the production process [1,2,3,4,5,5,6,7].

Currently, only an insignificant share of industrial anthropogenic waste in Russia and Kazakhstan is used in the production of construction materials. The widespread use of industrial waste in production turnover will allow to increase energy and resource saving on a large scale due to cost savings on exploration, extraction and processing of mineral raw materials. Application of accumulated technogenic industrial wastes (mining wastes, ashes of thermal power plants, phosphorus, metallurgical, steelmaking slags, non-ferrous metallurgy slags, alkaline-containing industrial wastes, etc.) as a component of cement is the main direction of modern development of cement industry both in Russia and Kazakhstan.

At present, construction science and practice have accumulated a huge positive experience in the field of application of industrial wastes in the production of construction and silicate materials, but they have not been properly applied in production. In cement industry this direction includes development and research of glass- and slag-alkaline binders and concretes. In recent years, their new varieties have been obtained [7,8,9,10,11,12]. At the same time, alkaline-activated binders are very often proposed to replace cement and other binders [13,14,15]. They are formed by the reaction of aluminosilicate material with an alkaline agent such as sodium hydroxide [16,17]. The advantage of alkaline binders is that their use can reduce carbon dioxide emissions by up to 80% [18]. The use of alkaline binders can also reduce the cost of production of composite materials [19,20], reduce the heat of hydration [21] and strengthen the filler-matrix interface [13,19,22].

Research work on the production and study of composite slag-alkali binders with local mineral additives and concrete on their basis in recent years are conducted in the Research Institute of "Natural and Technical Sciences" at M. Auezov SKIU [11,12,23,24].

2. METHODS AND MATERIALS

Preparation and testing of composite slag-alkali binders was carried out in accordance with technical conditions TU 67-1020-89 "Slag-alkali binder. Technical conditions".

The made specimen beams were stored for 3 days in molds with the covered top surface in air-dry conditions, then unplugged and stored in normal-moisture conditions until testing. Testing of binder specimen beams was carried out

according to the accelerated method: specimen beams were made in accordance with the requirements of GOST 310.4-81 "Methods of determining the compressive and bending strength", taking into account the above changes, not earlier than 4 hours and not later than 12 hours after preparation. After manufacturing the specimens were subjected to heat and humidity treatment (HHT) in molds according to the regime 3+6+3 h at the temperature of isothermal heating 95±5 ºC. The specimens were subjected to testing one day after manufacturing.

For determination of construction-technical characteristics of concrete on the basis of CSB we used GOST 10180-90 "Methods of determination of strength by control samples", GOST 12730.0-78, GOST 12730.4-78 for determination of concrete density, GOST 12730.3 for determination of water absorption and characteristics of concrete porosity. For the grinding of different compositions of CSB and slag we used mills: Ml-1, Aktivator-4 m and SVM-3.

3. RESEARCH RESULTS

This section provides the results of research on the use of electro thermo phosphorus slags for the production of salt-slag binders. These include binders based on electro thermo phosphorus slags and natural salts (sulfates, chlorides, nitrites of alkaline and alkaline-earth metals) obtained by autoclave treatment of compositions [11].

The presence of ions CI- and SO-4 in the composition of salt-slag binders limits their application for the manufacture of reinforced concrete structures, as evidenced by the results of studies of corrosion of steel in concrete [25,26]. In these experiments it is shown that without special protection of steel reinforcement salt-slag concrete autoclave curing, prepared on salts of sodium sulfate, carnallite, magnesium chloride, can be used only at a relative humidity of up to 60%. In order to reduce corrosion of steel reinforcement, the same and other authors proposed to introduce into the composition of such concrete deficient and expensive additives of two substituted sodium orthophosphate and potassium bichromate, which does not solve the issue of their widespread practical application.

Currently, there is a deficit of conditioned alkaline components for the production of slag-alkali binders and concrete in Kazakhstan due to the lack of their production. Therefore, for production of composite slag-alkali binders and concretes various alkaline-containing wastes of technological processes and productions (for example, metallurgical and chemical industries) are used.

In particular, a very promising multi-tonnage alkali containing waste for production of slag-alkali concrete, especially in the region of Central Asia, is sodosulfate mixture - a waste of caprolautam production of Chirchik PO "Elektrokhimprom" (annual output is 14 million tons). The waste is a complex product of chemical composition: sodium sulfate - 30...35 %; sodium carbonate - 50...55 % and sodium chloride 10...15 %. 15 %. The research of the possibility of using this waste in the production of slag-alkali concrete has been devoted to a small number of works so far. The authors of works [23,24] showed the possibility of obtaining slag-alkali binders of grades 300, 400 on the basis of mixtures of sodium salts, weak and strong acids. On the basis of the developed binders the author obtained slag-alkali expanded clay concrete of grades 250, 400 with an average density of 1400, 1800 kg/m, respectively. The study of frost resistance and duration of reinforcement preservation in slag-alkali expanded clay concretes showed that the investigated characteristics of such concretes are most influenced by the type of alkaline component and the density of its solution [23].

Corrosion of reinforcement in slag-alkali expanded clay concrete is caused by penetration of stimulant ions CI^- and SO^-_4. The samples showed rust spots and the degree of corrosion of reinforcement in concrete was estimated at 3 points. The authors [23,25] recommend the introduction of $NaNO_2$ corrosion inhibitors or lowering the density of sodium sulphate carbonate solution to 1050 kg/m^3.

Despite the fact that the paper [12] noted the influence of the type and density of the alkaline component on the physical and mechanical properties of concrete. However, there is no systematized data on the optimization of the structure of concrete on soda-sulfate mixture, as well as there is no information on some construction and technical characteristics of heavy slag-alkali concrete in relation to different types of construction.

The influence of different methods of carbonate-barium tailings (CBBT) additive introduction on the performance properties of slag-alkali concrete was investigated. Studies were conducted using Portland cement clinker, phosphorus slag, modifying additive of waste carbonate-barium tailings and aqueous solution of soda-sulfate mixture. In the first case phosphorus slag and additive waste-carbonate-barium tailings were subjected to separate grinding to the residue on the sieve 008 10 % (300 m^2/kg on PSX-12). In the second case phosphorus slag, Portland cement clinker and waste carbonate-barium tailings - together. The joint grinding of the components of CSB was carried out for the time required for grinding without additive, grinding fineness up to Sud 300 m^2/kg. The obtained results are shown in Figure 1.

Compared to separate milling, co-milling is more efficient. The milled CSB compositions obtained by separate and joint grinding methods show higher activity results and have a wider range of "possible" and "effective" replacement of carbonate-barium tailings waste with modifying additive, higher density by 1.7 % and lower water absorption by 9.8 % as compared to unmilled samples. At separate grinding of components (the amount of Portland cement clinker is accepted - 5 % Const) the range of replacement of phosphorus slag by modifying additive of waste carbonate-barium tailings, in which the composition on CSB is not inferior to additive-free, is 4-6 %. At joint grinding of CSB constituents this area increases up to 10 % and it is possible to get a binder with increased activity in comparison with control compositions. It is established that, depending on the type of hardening and alkaline component in comparison with the control composite compositions of CSB on phosphorus slag, modifying additive of waste carbonate-barium tailings of Portland cement clinker, obtained by joint dispersion, have higher activity by 60.0-70.0 MPa.

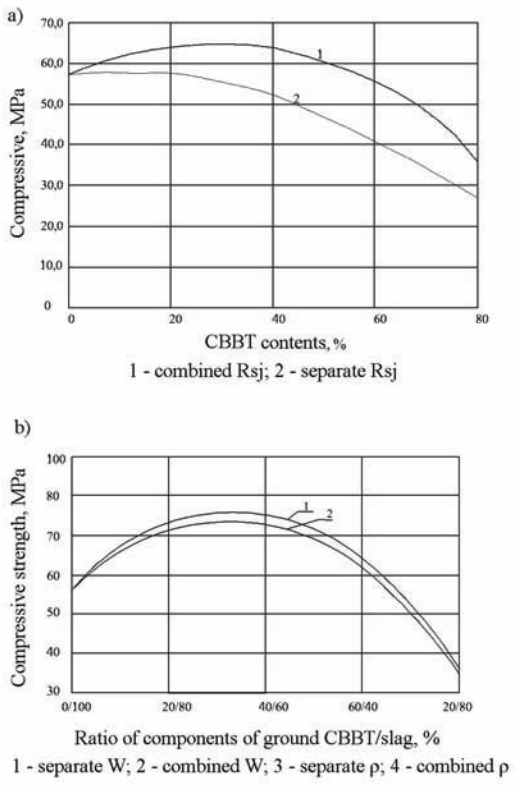

Figure 1. Dependences of strength (a), density and water-absorption (b) of CSB stone on the content of waste carbonate-barium tailings and the method of additive introduction

Introduction of a modifying additive of waste carbonate-barium tailings at co-milling with phosphorus slag gives a great effect, it is achieved for the following reasons. From the results of the study, it is known that Portland cement clinker is crushed lighter than phosphoric slag and at the same time is crushed to Sud 1.2 times more than phosphoric slag. When co-milling with a modifying additive of waste - carbonate-barium tailings to Sud 300 m^2/kg, particles of phosphoric slag are not ground and have a size in the composition of CSB than in a sample of pure phosphoric slag with the same grinding fineness.

We cannot exclude the possibility of interaction of waste carbonate-barium tailings in the solid

phase and the formation of aggregates or "complexes", doped as a result of breaking and compensation of bonds on the surface-active particles, changes in their curvature and relief, and the formation of new mechanical bonds.

Based on the experimental results, the combined milling of phosphorus slag, Portland cement clinker and modifying additive of waste - carbonate-barium tailings to produce CSB was accepted in further studies.

The activity of CSB samples and concrete on their basis was determined on the samples made on the basis of phosphorus slag, Portland cement clinker and with modifying additive of waste carbonate-barium tailings, aqueous solutions of soda-sulfate mixture and soda ash, after TVO (mode 4+3+6+3 h at the temperature of isothermal heating 95±5 P.). Fine milled CSB with modifying addition of waste carbonate-barium tailings is 300 m^2/kg. The results of the study are presented in the form of Figure 2. It follows from the data of the figure that fluctuations in the composition of additives do not significantly affect the level of activity of CSB stone with modifying additive of waste carbonate-barium tailings. The content of modifying additive of carbonate-barium tailings waste has a great influence on the strength. The content of carbonate-barium tailings additive in the composite binder is 10 % regardless of the nature of the alkaline component

When using soda ash, the strength increase was 22,1-26,1 %, soda-sulfate mixtures - 19,2-20,4 %. Introduction of carbonate-barium tailings waste modifying additive up to 10 % into CSB composition allows to obtain equal strength cement stone CSB with modifying additive of carbonate-barium tailings waste in comparison with non-additive one. In CSB, increasing the content of carbonate-barium tailings waste modifying additive up to 15 % reduces the activity of cement stone samples. CSB with carbonate-barium tailings waste additive on soda ash - 32,2-38,2 % and on soda-sulfate mixture - 31,3-39,2 %. At the optimum content of modifying additive of carbonate-barium tailings waste - 10 % efficiency index on the effect on the strength of stone obtained by co-milling up to 600 m2/kg depending on the type of alkaline component and curing conditions is in the range of 1.2-1.41.

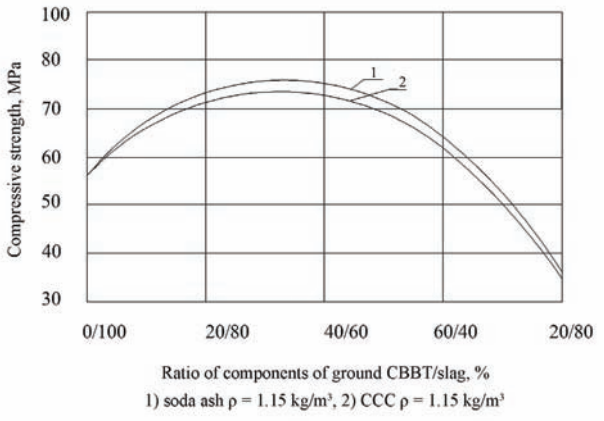

Figure 2. Influence of type and content of milled CBBT on the strength of CSB stone specimens after TVO, made on aqueous solutions, %

4. CONCLUSIONS

1. It is established that the amount of modifying additive of carbonate-barium tailings waste has a great influence on the strength, with the content in the composite binder being 10% regardless of the nature of the alkaline component.

2. It is determined that for CSB compositions without additive and with additives the dependences of properties are described by minimum regularities with maximum values of average density and strength and minimum values of water absorption in the area of grinding fineness 6,0-7,0 m^2/kg irrespective of the nature of alkaline component and curing conditions.

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