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TOWARDS THE PROBLEM OF REPURPOSING INDUSTRIAL WASTES FOR DEVELOPMENT OF PUBLIC INFRASTRUCTURE

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Abstract

The use of polymetallic ore enrichment waste in the production of building materials improves the environment and increases resource conservation. These technologies include the production of composite cements based on industrial waste, used as active components of the binder. In the course of scientific research, the conceptual foundations of high-tech production of multicomponent composite cements based on hydraulic binders were developed. These cements have reduced cost and excellent construction and technical characteristics. Modern analytical methods were used to study the processes of structure formation in composite cements containing polymetallic ore enrichment waste. The mineralogical and chemical composition of these materials was established using X-ray phase analysis, microscopy and differential thermal analysis. The research results showed that the content of carbonates in waste from the enrichment of polymetallic ores, not exceeding 30%, does not have a negative effect on the strength of the samples. This opens up new opportunities for using these wastes as a component of composite cements, which not only reduces production costs, but also increases the environmental friendliness of the process.

Keywords: Building materials, composite cements, industrial waste, mineralogical composition, polymetallic ores, physicochemical processes

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1. Introduction

The use of technogenic waste in the construction industry allows to save natural resources (A. Z. Aimenov, Z. T. Aimenov, & B. K. Sarsenbaev, 2019) and improve the environment. In foreign countries, the use of industrial technogenic mineral formations is expanding every year. Dumps of rocks produced by mining enterprises, tailings from concentration plants and slags from metallurgical plants are increasingly involved in processing. This is facilitated by technical and organizational measures for the integrated use of raw materials and man-made mineral formations mining industry (Aimenov & Sarsenbayev, 2016; A. Z. Aimenov, Z. T. Aimenov, & B. K. Sarsenbaev, 2019; A. Z. Aimenov, N. B. Sarsenbaev, & Z. T. Aimenov, 2019).

2. Problem Statement

Technogenic mineral formations (Aimenov & Sarsenbayev, 2016; A. Z. A. Z. Aimenov, Z. T. Aimenov, & B. K. Sarsenbaev, 2019) available in Kazakhstan use no more than 6–7%. Their widespread use in industrial circulation will increase resource conservation by saving costs for exploration, production and processing of mineral raw materials. Currently, there is an increase in the scale of construction, and for the enterprises of the construction industry, tasks have been set to introduce technologies that make it possible to obtain materials and products with lower energy consumption not only with improved properties, but much superior to the existing ones (A. Z. Aimenov, N. B. Sarsenbaev, & Z. T. Aimenov, 2019; S. A. Y. Murtazaev & Salamanova, 2019).

The main advantages of the composite cement technology include wastelessness, conservation of valuable natural raw materials, and the possibility of using a variety of waste and non-metallic minerals as active components of a binder. At the same time, carbon dioxide and dust are not emitted into the atmosphere, as in the production of Portland cement.

3. Research Questions

The main valuable result is the development of scientific and technological foundations for the production of a new high-tech type of multicomponent hydraulic binders for concrete-composite cements. Their technology is eco-friendly and has little resource and energy consumption. The scientific value of the scientific research results consists in new patterns of mechanical dispersion in multicomponent systems on different grinding principles. Also, the identification of new products of hydration of mechanically activated composite cements with the addition of wastes of concentration of polymetallic ores and surfactants; development of new compositions of special and composite types of cement concretes.

4. Purpose of the Study

The main consumers of composite cement are enterprises producing concrete and reinforced concrete structures. The developed composite slag-alkali cements on the basis of polymetallic ore

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enrichment wastes meet modern requirements, improve the construction and technical properties of the material, have a positive effect on the ecological situation in the regions and reduce the product cost.

5. Research Methods

Investigations of the physical and chemical processes of the structure formation of composite cements with the addition of polymetallic ore enrichment wastes were carried out by modern methods using an X-ray diffractometer D & ADVANCE (Bruker) using Cu radiation and a synchronous thermal analyzer STA 409 P (Luxx Netzsch), the measurement period is 10 deg / min – platinum, medium-air, scanning electron microscopy.

Technogenic waste of Achpolymetal JSC (carbonate-barium "tailings") is a finely ground product and does not require additional grinding for use. Waste has the following granulometric composition: grains less than 85 microns in size make up 25–30%, 25–85 microns – 55–65% and larger than 200 microns – 10–15%. The main minerals that make up the "tailings" are: barite – 10–20%, limestone 10–15%, clay substances 5–8%, ore minerals 2–3%, "dolomite" – 50–60%. “Tails” can be used as a limestone filler, since in terms of their mineralogical composition they consist of a significant amount of carbonate rocks (Aimenov et al., 2018; A. Z. Aimenov, N. B. Sarsenbaev, B. K. Sarsenbaev, et al., 2019; Sarsenbaev et al., 2019).

In order to determine the mineralogical composition of the above anthropogenic waste, X-ray phase analysis was carried out and minerals were identified that belong to dolomite (d = 2.898; 2.199; 1.807; 2.021 A), calcite (d = 3.033; 2.284; 1.912, 1.912, 1.857 A) and quartz (d = 3.357; 4.281; 1.811; 2.279 A).

As a binder used Portland cement LLP "Standartsement" PC500DO in accordance with GOST 10178 – Portland cement 500 without additives, normal hardening. The Portland cement clinker suitable for the addition of man-made waste of polymetallic ore concentration consist of: alite (C2S) content – more than 50%, CsA – more than 6%, MgO – no more than 2.6%, free lime and H2O5 content – no more than 0.6%, and 0.27%; requirements for multicomponent cements: p.p. not more than 0.48%, specific surface (Syg, m^2 / kg) – not less than 320, preferably 350–400.

The chemical composition of raw materials, their structure, hydration products were investigated using: microscopic, X-ray phase, differential thermal and analysis methods; specific surface area at PSKh-12 was determined; normal density and setting time on a small Vic device. The compressive strength was determined on a PSU-10 hydraulic press.

X-ray phase analysis of the cement stone was performed by the ionization method of recording the radiation intensity on a D & ADVANCE X-ray diffractometer (Bruker) using Cu – radiation. Thermal, thermogravimetric, and differential scanning calorimetry was carried out on an STA 409 P synchronous thermal analyzer (Luxx (Netzsch, Germany), measurement period 10 deg / min, medium – air, crucibles – platinum.

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6. Findings

Composite binders or cements with finely dispersed mineral fillers can be obtained by mixing 12–45% of powder additives from industrial waste or natural raw materials to the main component – Portland cement, a distinctive feature of which from chemically active mineral substances (granulated blast-furnace slags, CHP ash, clay, diatomites) consists in the weak absorption of calcium carbonates from its solution part. Filled cementitious systems are formed by hydration of very fine Portland cement clinker particles less than 80 microns in size. Higher grains remain unreacted even after many years and are in principle an inert constituent in cement stone, such as ballast. Therefore, without harming the activity of the binder, there can be used such a technological method as replacing the proportion of larger particles of portlane cement with the same proportion of low-active substances (Bikbau et al., 2008; S. A. Y. Murtazaev & Salamanova, 2018; S. A. Murtazaev et al., 2019; Rakhimova et al., 2007; Shubin et al., 2001; Salamanova et al., 2016; Sarsenbaev et al., 2019).

In developing filled multicomponent systems, it is advisable to use secondary products formed as a result of enrichment of polymetallic ores, and it is desirable to organize this production directly near the zone of accumulation of technogenic waste. Joint or separate grinding of this valuable product with Portland cement with varying binder constituents makes it possible to create new filled composite binder systems with definitely improved properties.

Separately ground clinker with gypsum was mixed with the wastes of the concentration of polymetallic ores. Physical and mechanical tests were performed on samples 40x40x160 mm from a cement paste solution 1: 3 (table 01).

Table 1. Physical and mechanical properties of a concrete

Composition, wt. %			Compressive strength of specimens at 28 days of age, MPa
	Cement	Number of the use of technogenic waste	
1	100	0	52,0
2	90	10	52,5
3	80	20	61,5
4	80	20	48,3
5	70	30	67,4
6	70	30	50,2
7	60	40	53,6
8	60	40	23,0

The tests showed that the introduction of polymetallic ore enrichment wastes up to 29% did not reduce the strength of the samples.

According to the X-ray phase analysis of the hydration products of Portland cement with and without the addition of polymetallic ore enrichment wastes, the following were identified: 2.110; 2.056; 1.668A); b) Portland cement with the addition of polymetallic ore enrichment wastes, low-base hydrosilicates CSH (d = 3.038; 2.780; 2.780; 1.819; 1.675A) hydrocarboaluminate (d = 3.875; 2.889;

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1.675A) edolomite (d = 2.889; 2.191; 2.021; 1.819 A) and calcite (d = 3.038; 2.267; 1.868 A) (A. Z. Aimenov, N. B. Sarsenbaev, & Z. T. Aimenov, 2019; Sarsenbaev et al., 2019).

The process and rate of hydration of some minerals of Portland cement clinker proceed taking into account the presence of carbonate rocks in the system (A. Z. Aimenov, N. B. Sarsenbaev & Z. T. Aimenov, 2019; Sarsenbaev et al., 2019). It should be noted that there is a decrease in the intensity of the hydration processes of the main minerals of dicalcium and tricalcium silicates, in the presence of up to 30% of finely dispersed carbohydrate-containing mineral powders from limestone, magnesite or dolomite in the binder. The study of the cement stone showed that there is no significant chemical interaction between such hydration products, calcium hydroxide and calcite in the alite phase. The process of structure formation of cement stone is based on hydrated neoplasms, and the surface of finely dispersed mineral additives serves as substrates for possible epitaxial intergrowth of calcite and portlandite crystals.

Clinker minerals: tricalcium aluminate and tetracalcium aluminoferrite (in the presence of a system of carb-containing finely ground powders) interact with the formation of complex compounds of a certain composition of metastable varieties of carbonate ettringite $C_3A{\bullet}3CaCO_3{\bullet}31H_2O$ и $3CaO{\bullet}Al_2O_3{\bullet}MgCO_3{\bullet}11H_2O$, $3CaO{\bullet}Al_2O_3{\bullet}CaCO_3{\bullet}11H_2O$.

Hydrocarboaluminates were identified in the hydration products of the studied cements by X-ray phase analysis. The hexagonal crystals of these compounds grow together with each other and with the grains of carbonate microfillers, thus forming a strong crystalline conglomerate, which causes an increase in the strength of the aluminoferritic and aluminate components of the clinker.

The micrographs obtained from the chips of the cement stone show calcium hydrosilicates and calcium hydraluminates. They show a dense structure of a cement stone with inclusions of pores of various sizes. Along with calcium hydrosilicates, calcium hydroaluminoferrite is also noted, calcium hydroaluminate and three-calcium silicate that has not reacted with water are noted. The pores are mostly filled with needle-like ettringite and hydrosilicates. The content of a large amount of such crystals leads to a high strength effect, but not to a bulking effect.

The use of man-made wastes of concentration of polymetallic ores contributes to the formation of a cement stone structure with a higher density. White spots in the micrograph indicate the presence of barium and iron sulfates in the composition of the cement stone and $CaCO_3$ is identified – a component of the wastes of concentration of polymetallic ores, besides it there are CSH – gel, tobbermorite, calcium hydroaluminate, rounded grains of calcium hydrocarboaluminate, calcium hydrosilicates on a carbonate substrate are also identified calcium.

Waste processing of polymetallic ores is relatively homogeneous, the particles of which, during hydration and hardening of cement clinker minerals, contribute to the acceleration of the formation of a crystalline structure. Thus, in the environment of hydrated cement, they are the centers of crystallization, and calcium aluminates form calcium carboaluminates and contribute to the acceleration of the hardening of the cement stone.

When replacing part of the cement with a limestone additive with the same degree of grinding in the binder, the total content of highly basic clinker minerals (C_3S, C_3A, C_3Al) decreases. Additionally, carbonate particles compact the structures of concrete or mortar, and as a consequence, increase their strength with significantly lower cement consumption.

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The formation of these compounds contributes to strengthening the structure and improve the strength of the cement stone. The barium sulfate introduced with the wastes of the concentration of polymetallic ores contributes to an increase in the protective properties of the composite cement against gamma X-ray radiation.

Thus, using the wastes of concentration of polymetallic ores as an additive, it is possible to obtain high-strength cement. The results of testing the strength of concrete samples containing wastes of concentration of polymetallic ores as an additive to cement are shown in table 02.

Table 2. Strength of concrete samples (10x10x10 cm), using Portland cement with the addition of polymetallic ore enrichment wastes

Binder composition, %		**Test terms, in a day**					
Cement	**Addition of wastes of concentration of polymetallic ores**	**1**	**3**	**7**	**28**	**90**	**180**
		Compressive strength, MPa					
		Aggregate – granite sand and crushed stone					
100	-	18	22	30	32	32	36
90	10	20	24	36	36	36	48
80	20	21	27	38	41	41	52
75	25	19	26	36	40	40	46
100	-	22	28	30	34	34	40
90	10	26	32	38	38	42	52

When a part of the cement is replaced by wastes from the concentration of polymetallic ores, the strength of concrete in the early stages of hardening almost does not change, and in some compositions, the strength of concrete on granite sand is higher as the proportion of the additive in the composition of the binder increases, the strength of concrete decreases at a later date. However, even with the replacement of up to 24% of the amount of cement for the wastes of the concentration of polymetallic ores, concrete of grade 300 and higher can be obtained.

Comparisons in all periods of hardening of the phase composition of the cement-sand mortar of cement and wastes of concentration of polymetallic ores show that during the hydration of the cement stone, mainly high-strength low-basic (toward to CaO) compounds are formed, providing high strength with a smaller amount of cement. Waste enrichment of polymetallic ores in the composition of the hardening cement-water system plays the role of a catalyst that promotes the formation of these compounds. Particles of wastes of concentration of polymetallic ores are additionally micro-fillers, on the surface of which the hydration and hardening of cement minerals and the formation of crystalline intergrowth of stone with high strength take place.

Increasing the strength of concrete when replacing cement with wastes of concentration of polymetallic ores as additives and the use of carbonate aggregates is based on the following: high strength of carbonates and a rough surface of its particles, which adhere well to hydrated cement particles, and also absorb part of the concrete water, create a high-strength structure of cement stone. A homogeneous high-strength concrete structure creates by a carbonate aggregate, which occupies up to 80% of the concrete volume, and the wastes from the concentration of polymetallic ores in the form of an additive

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Experimental studies provided for the distribution of prototypes in batches, depending on the hardening conditions.

The first batch of samples was placed on the top floor of the building for direct exposure to solar radiation and hardening in air-dry conditions; the second batch of prototypes hardened in normal humidity conditions, and after 28 days of age they were moved for storage in natural conditions on the covering of the building. The last batch of samples after manufacturing was subjected to heat and moisture treatment for 12 hours (3 + 6 + 3) at a temperature of 80 ± 5 °C, after which they hardened in natural conditions.

The test results showed that the use of a mineral additive in a binder system at a dosage of up to 25% and normal humidity conditions of hardening led to an increase in the strength characteristics of concrete at all test periods in comparison with no additional cements. Replacement of particles with a size of more than 80 microns in a dosage of up to 20–25% with wastes of concentration of polymetallic ores contributed to a significant gain in strength at a later age of hardening, in comparison with the strength characteristics of concrete without additives. It is possible to identify the most optimal storage conditions for concrete based on carbonate-containing additives, which is water and normal moisture hardening.

Heat and moisture treatment increases the strength of concrete in the early stages, subsequently, during hardening in natural conditions, the rate of concrete hardening slows down. Concrete hardened for 28 days under normal and natural conditions, in the late hardening periods, gains strength almost equal to the strength of normal hardened concrete by these terms.

7. Conclusion

1. Using X-ray phase chemical and electron microscopic methods of analysis, it was found that in the wastes of concentration of polymetallic ores, the content of carbonates is 50–70%, which makes it possible to use them as a carbonate-containing additive to cement.

2. The granulometric method of analysis established that in the wastes of concentration of polymetallic ores, the main modulus of size is made up of grains with a size of 25-85 microns.

3. Clinker minerals C3A and C4AF interact with carbonate microfillers to form the following complex compounds: metastable carbonate analogue of ettringite $C_3A{\cdot}_3CaCO_3{\cdot}31H_2O$ and $3CaO{\cdot}Al_2O_3{\cdot}MgCO_3{\cdot}11H_2O$, $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$.

4. It has been established that the presence of barium sulfate, introduced with the wastes of enrichment of polymetallic ores, can increase the protective properties of composite cement against gamma and X-ray radiation.

5. Comparison of the phase composition of the cement-sand mortar of cement and cement with the addition of wastes of concentration of polymetallic ores in all periods of hardening show that in the process of hydration products of the cement stone mainly high-strength low-basic (in relation to CaO) compounds are formed.

6. It has been established that when replacing 10–20% of cement in the composition of hydraulic concrete 1:1, 5:2.5 with a water-binding ratio of 0.4 for wastes of concentration of polymetallic ores, frost resistance of the samples does not decrease; the concrete has a frost resistance grade of 400 and

corresponds to samples suitable for the production of hydraulic products used in water management construction.

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