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Effect of Additive of Polymetallic Ores' Tailings on Properties of Composite Cements

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Abstract

The article analyzes the use of polymetallic ores' tailings as a basis for production of composite cements and concrete, having protective properties against gamma and X-rays radiation, as well as high strength and lifetime. The main practically significant result is: the development of scientific and technological production bases of new high-tech type of multicomponent hydraulic binders for concretes – composite cements; the identification of new hydration products in composite cements with addition of polymetallic ores' tailings; the development of optimal compositions of composite cements for concretes. It is established that the composite cements, that developed by us on the basis of polymetallic ores' tailings, meet modern requirements i.e. its improve the construction-technical properties of material, have positive effect to the environment situation and allow to reduce the production cost of the final product. Their technology is low metal-intensive and power-consuming. Studies of physical-chemical processes of composite cements structure formation with addition of polymetallic ores' tailings have been conducted using methods such as chemical, X-ray phase, differential-thermal and electron-microscopic analysis methods.

1. Introduction

At the present stage of sustainable development of our country under conditions of continuous production scale growth and consumption of mineral raw materials, the problem of efficient and rational use of industrial technogenic mineral formations has a notably important national economic significance. The urgency of this problem is caused by limitation of mineral deposits, complicacy of mining and geological conditions concerning ore bodies' settings and appreciation of their extraction, deterioration of quantitative and qualitative composition of extracted ores from depths, fluctuations of prices of raw materials in the world market, as well as negative influence of accumulative technogenous resources on the environment, etc. All these factors determine the global and nationwide importance of questions, related to utilization and disposal of industrial waste. Therefore, the attention paid to these problems in industrialized countries of the world, is not accidental [1–4].

In many foreign countries the range of utilizable industrial technogenic mineral formations increases every year. The heap of rocks of mining enterprises, mill tailings and slags of metallurgical plants are intensivly involved to the processing. Engineering and organizational actions, aimed at multipurpose utilization of raw materials and technogenic waste of mining production, work towards this [3–7].

Technogenic mineral formations that existing in Kazakhstan used only in the limit of 6–7% of. Their extensive use in production cycle allows to increase the resource conservation on a large scale due to economy of operational and capital costs for exploration.

Currently it is observed the increase in construction but also deepening of its specialization. Each building and construction sector put demands to concrete of special purpose, which is used under certain operation conditions ("concrete for biological protection", "expansive cement concrete", etc.).

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Construction engineering companies have the goal to implement the technologies and obtain the advanced materials and products that far superior to the existing ones with minimal energy consumptions.

Market needs for cement grow every day, and according to estimates of the Ministry of Industry of the Republic of Kazakhstan it's approximately equal to 5000 tons. Therefore, the South Kazakhstan cement plants have the task to increase the production of operating production lines with simultaneous cost reduction of final products by using available local raw materials, including supplementary materials of their own and other industries.

In southern Kazakhstan the polymetallic ores' tailings are the most large-tonnage ones (more than 135 mln. tons), which can be used as mineral additives for producing of composite cements.

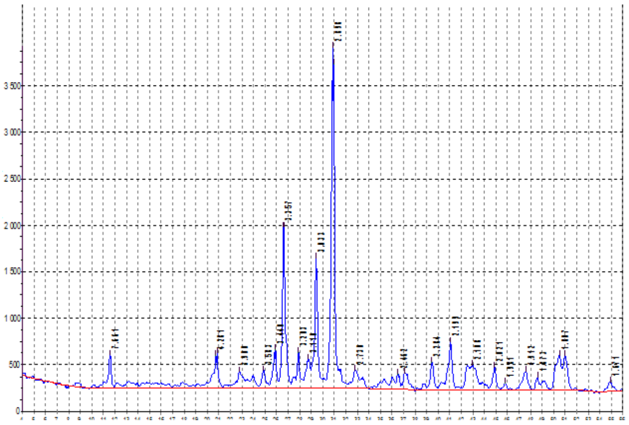
1.1. Raw materials

Polymetallic ore' tailings – carbonate – barium "tails" are fines, do not require an additional grinding before use (Fig.1).

Fig.1. Appearance of polymetallic ores' tailings.

Granulometric composition of waste is the following one: grains with the size less than 85 mcm are equal to 25–30%, 25–85 mcm – 55–65% larger than 200 mcm – 10–15%. The main minerals are included as compounds of "tails" are follows: the dolomite is 50–60%; limestone is 10–15%; barite is 10–20%; clayed substances are 5–8%; ore minerals are 2–3%. The mineralogical composition of "tails" enables to use them as limestone filler because they contain significant amounts of carbonaceous rocks.

X-ray phase analysis (Fig. 2) was performed to specify the mineralogical composition of polymetallic ores' tailings.



Start angle = 4; End point of angle = 56; Step = 0.05; Exposure = 0.38; Velocity = velocity_2; Max. number of imp. = 1744; S peaks = 4699; S general = 18635; K = 25.2%.

Fig. 2. X-ray diffraction pattern of polymetallic ores' tailings of JSC "Achpolimetall".

With the help of X-ray diffraction pattern there were identified several minerals based on polymetallic ores' tailings belonging mainly to dolomite (d = 2.898; 2.199; 1.807; 2.021 Å), calcite (d = 3.033; 2.284; 1.912; 1.857 Å) and quartz (d = 3.357; 4.281; 1.807; 2.284 Å).

Chemical composition of polymetallic ores' tailings of JSC "Achpolimetall" are characterized by stability and presented in mass %: SiO_2 – 4.34–6; Al_2O_3 – 0.98–1.2; Fe_2O_3 – 2.86–3.5; CaO – 27.79–29; MgO – 14.45–16.3; loss on ignition – 35.25–37; $BaSO_4$ – 12.7–13.5; FeS_2 – 1.39–1.5; $PbSO_4$ – 0.03–0.05; $PbCO_3$ – 0.09–1.2; PbS – 0.14–0.2.

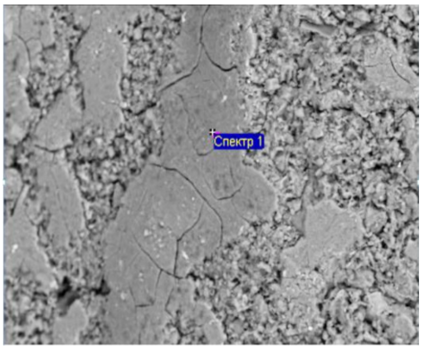
The mineralogical and chemical compositions have also been confirmed by research results using SEM.

The microphotographs of various spectra of polymetallic ores' tailings are presented in Fig. 3.

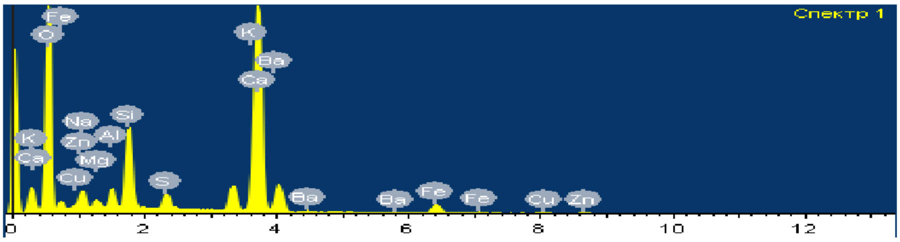
There are catalytic and modifying elements in the waste, mass %: Zn 0.01–0.05; Cu 0.002–0.004; Ti 0.03–0.05; Cd 0.002–0.003; barium and lead sulfates, lead and ferric sulfides, lead carbonate.

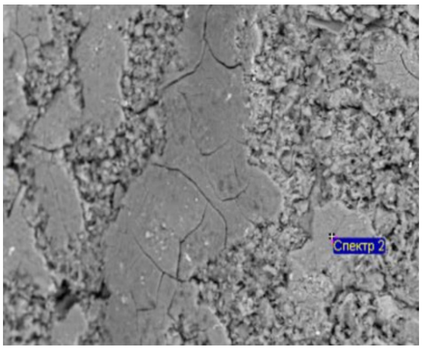
Low activity of radionuclides (53–55 Bq/kg), the absence of toxic emissions, low volatility of heavy metals indicates about radiation-environmental safety of waste. Portland cement of LLP "Standartcement" PC 500 D0 according to GOST 10178 – Portland cement 500 without additives, of normal hardening was used as a binder.

Portland clinker for production of composite cement must contain: the alite (C_3S) – more than 50%, C_3A – more than 5%, MgO – not more than 2.5%, the content of free lime and P_2O_5 – not more than 0.5 and 0.25%; requirements to multicomponent cements are as follows: loss on ignition not more than 0.5%, specific surface area is (Ssp., m^2/kg) – not less than 300, more preferably 350–400.

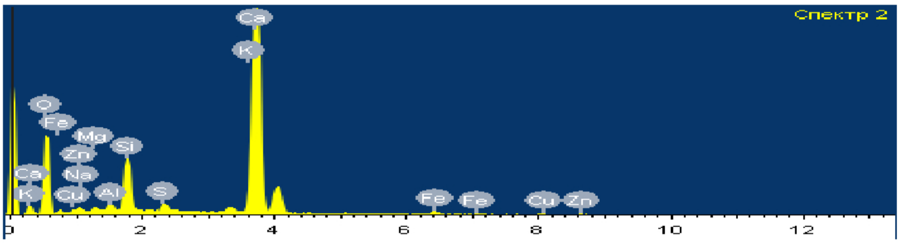


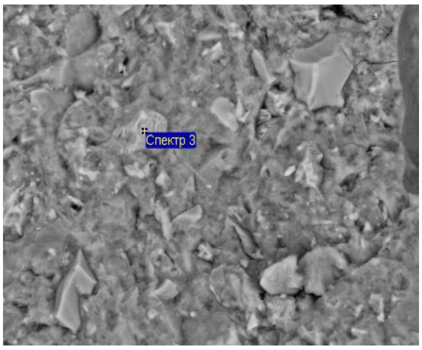
Element	Weight %	Atomic%
NA	2.78	2.93
Mg	14.22	14.17
Al	1.04	0.94
Si	6.70	5.78
S	0.67	0.50
Ca	22.51	19.66
Mn	2.90	1.28
Fe	4.26	1.85
O	34.92	52.80





Element	Weight %	Atomic%
O	20.08	40.97
Mg	1.69	2.27
Al	0.33	0.67
Si	5.36	6.23
S	21.63	25.08
Ca	2.77	2.25
Fe	1.17	0.68
Zn	43.75	21.85





Element	Weight %	Atomic%
Na	2.35	3.42
Mg	1.43	1.97
Si	3.69	4.39
S	12.01	12.51
Ca	2.93	2.44
Ba	47.01	11.43
O	30.58	63.85

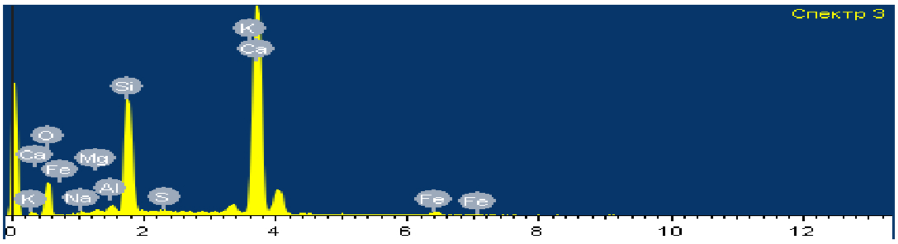
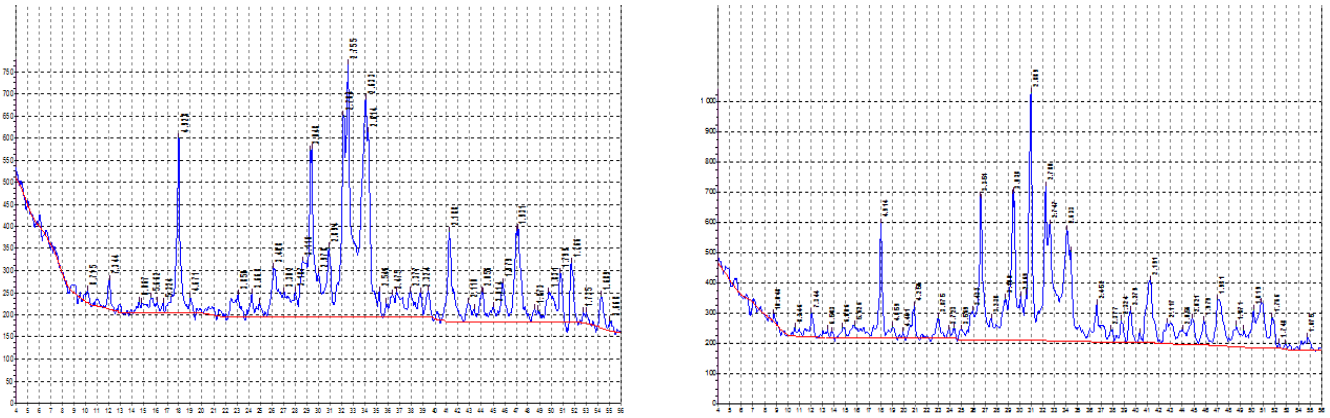


Fig. 3. Chemical composition of various spectra of polymetallic ores' tailings.



Start angle = 4; End point of angle = 56; Step = 0.05; Exposure = 0.38; Velocity = velocity_2; Max. number of imp. = 307; S peaks = 2344; S general = 13455; K = 17.4%

Start angle = 4; End point of angle = 56; Step = 0.05; Exposure = 0.38; Velocity = velocity_2; Max. number of imp. = 417; S peaks = 2781; S general = 14511; K = 19.2%

Fig. 4. X-ray diffraction patterns of products of Portland cement hydration: (a) Portland cement without additives; (b) Portland cement with additive of polymetallic ores' tailings and which was hydrated during 28 days.

2. Research methods

The following methods such as X-ray phase analysis method, electron-microscopic analysis method and differential- thermal analysis method were used for structure investigation, chemical composition of raw materials and hydration products; determination of specific surface area using KhD-12 was carried out, as well as determination of normal consistence and setting time using small apparatus "Vica" was made, Compression resistance was determined using hydraulic press HCP-10.

X-ray phase analysis of cement brick was carried out by powder diffraction technique. X-ray exposure was made using the apparatus "Dron-3" with copper anticathode and nickel filter within the interval of double reflection angles 2 degrees on filtered radiation CuK_d with Ni-filter.

The Electron-microscopic analysis was performed on scanning-electron microscope (SEM) JSM-6490 LV JOEL (Japan) with enlargement from 5 to 300000 times with sample preparation system STRVERS (Denmark). SEM is a device, the operation of which is based on television principle of scanning a thin beam of electrons over the surface of the sample under study. The beam of electrons, falling on the surface of the sample, is interacting with substance, resulting in origination of whole range of physical phenomena. After which a well-shaped picture of surface mapping on the screen is obtained. The elemental composition of the samples was determined by spectral analysis method of characteristical radiation emission is regenerated by electron beam in scanning-electron microscope. The calculation of elements content in sampling material was carried out with the help of the program, is attached together with the scanning-electron microscope.

2.1. Peculiarities of structure formation processes of composite cements based on polymetallic ores' tailings

Cements with microfillers or composite cements are produced by the addition to the portland cement of 10–50% additives in the form of milled rocks or industrial waste. The theoretical basis for producing of mixed cements is the fact that the Portland cement particles with the size more than 80 microns are hydrate even at the end of several years but only in small degree and they are basically its ballast component. So, the significant part of large particles of Portland cement can be substituted without much damage to its quality with grains of low-active substances of the same size [5–11].

Production of composite cements is a large consumer of polymetallic ores' tailings and may be launched near the sources of waste generation.

The possibility of addition of polymetallic ores' tailings into cement composition during grinding enables to produce composite cements with special properties.

Separately milled clinker with gypsum was mixed with milled polymetallic ores' tailings. The physical-mechanical tests were performed on samples 4×4×16 cm from solution 1:3 and from hydrated cement. The results of physical-mechanical tests are presented in Table 1.

Table 1
Impact of polymetallic ores' tailings on the strength of Portland cement PC M500 D0

Type of initial materials	Amount of additive %	Compressive strength, MPa					
		3 days		7 days		28 days	
		$R_{bend.}$	$R_{compr.}$	$R_{bend.}$	$R_{compr.}$	$R_{bend.}$	$R_{compr.}$
PC M500 DO	-	6.0	31.5	6.2	42.0	6.52	49.5
PC M500 DO + polymetallic ores' tailings	10	6.24	32.3	6.33	41.8	6.62	51.4
	20	6.29	41.3	6.55	50.9	7.2	56.5
	30	6.36	42.9	6.7	58.7	7.9	60.8
	40	6.2	33.7	6.48	42.3	6.75	50.6

As can be seen from Table 1, the addition of polymetallic ores' tailings up to 30% did not decrease the strength of samples.

X-ray phase analysis of hydration products of Portland cement without additives (Fig. 4a) and with addition of polymetallic ores' tailings (Fig. 4b) was performed.

X-ray diffraction pattern of hydration products of plain Portland cement are identified by low-basic hydrosilicates CSH(B) (d = 3.048; 2.78; 1.799; 1.668 Å) and hydroaluminates (d = 3.850; 3.408; 2.784; 2.324; 2.110; 2.056; 1.668 Å).

X-ray diffraction pattern of hydration products of Portland cement with addition of polymetallic ores' tailings are identified by low-basic hydrosilicates CSH(B) (d = 3.038; 2.780; 1.819; 1.675 Å), hydrocarboaluminates (d = 3.875; 2.889; 1.675 Å), dolomite (d = 2.889; 2.191; 2.021; 1.819 Å) and calcite (d = 3.038; 2.279; 1.871 Å).

The data of table shows that the addition of polymetallic ores' tailings into Portland cement composition increases the strength of the binder for the additive amount: 10% – 3.8; 20% – 14; 30 % – 22; 40% – 2.2.

As can be seen from Table 1 the addition of polymetallic ores' tailings up to 40% did not decrease the strength of samples.

The composition of investigated cement is close to calcite Portland cement. The composition of carbonaceous portland cement includes up to 30% of floured carbonate component. Such cement was developed and studied by V.N. Uyng, A.S. Panteleyev and V.M. Kolbasov.

It is known [9] that the presence of calcareous rocks in various ways has an impact on hardening rate of certain clinker minerals. Dicalcium and tricalcium silicates, containing 25–30% of floured carbonate microfillers (limestone, dolomite, magnesite), hardens less intensively than in absence of additives.

In the course of alite phase hydration the substantial chemical interaction between the basic hydration product–calcium hydroxide and carbonate component does not occur. The surface of such filler is a substrate material for formation of hydrated newgrowths structure and possible epitaxial intergrowth of calcite and portlandite.

Clinker minerals such as C_3A and C_4AF in presence of carbonate microfillers enter in conjunction, lie in formation of complex compounds with the following composition: metastable carbonate analogue of ettringite $C_3A \cdot 3CaCO_3 \cdot 31H_2O$ and $3CaO \cdot Al_2O_3 \cdot MgCO_3 \cdot 11H_2O$, $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$.

Hydrocarboaluminates were identified by X-ray phase analysis in hydration products of investigated cements.

Well-developed hexagonal crystals of these compounds are intergrow together and with the grains of carbonate microfillers, forming a solid crystalline conglomerate, which provides the strength enhancement of aluminate and alumoferrite components of clinker.

Microphotographs that obtained from the chips of hydrated samples of Portland cement are presented in Fig. 5, the Portland cement with additive of polymetallic ores' tailings are presented in Fig. 6.

Figure 5 shows Microphotographs that obtained from chips of cement stone, where the calcium hydrosilicates and calcium hydroaluminates are clearly seen. The structure of cement stone is compact with pores inclusion of various sizes (Fig. 5a). Microphotographs shows not only the calcium silicate hydrate (is presented by CSH-gel in the form of needle-shaped particles and in the form of rounded masses with protruding needles and tobermorite in the form of fine, needle-like crystals) but also the calcium hydroalumoferrite is present (Fig. 5b). In Fig. 5c there is has been observed the tricalcium silicate which is non-reacted with the water. Figure 5d presents the calcium hydroaluminate. Microphotograph (Figs. 5e and 5f) presents the pore, which is mainly filled with hydrosilicates and needle-shaped ettringite. Content of large number of these crystals results in the effect of high strength, but not in the effect of volume increase.

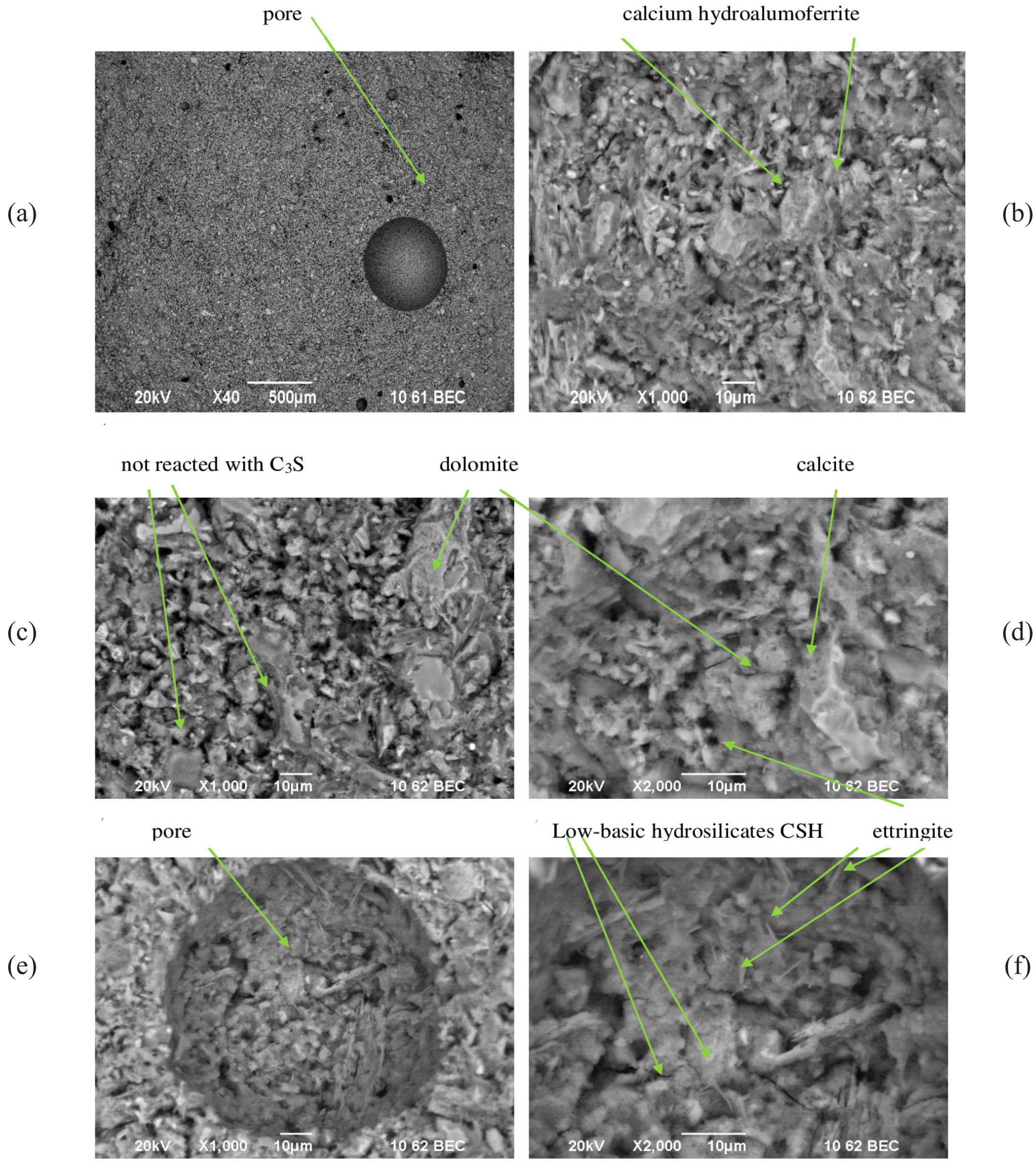


Fig. 5. Microphotographs, obtained from chips of cement brick without additives with various enlargement

Addition of polymetallic ores' tailings promotes the formation of more compact structure of cement brick, and this can be seen in Fig. 6a. White spots in the microphotograph prove the presence of iron and barium sulfates in the composition of cement brick. In Fig. 6b, $CaCO_3$ – a component of polymetallic ores' tailings is identified, in addition, there are presented CSH-gel, tobermorite, calcium hydroaluminate, rounded grains of calcium hydrocarboaluminate.

Figure 6c presents the microphotograph where the calcium hydrosilicates at substrate from calcium carbonate are identified.

Based on authors' researches [8] it was found that new formations arising from hydration of $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ in presence of calcium and magnesium carbonates, considerably differ from hydration products of pure clinker minerals. According to X-ray analysis and petrographic analysis the cubical hydroaluminate C_3AH_6 with light refraction index N = 1.604+0.2 is the main phase of hydration products C_3A and C_4AF. This crystalline hydrate contains in hydrated mixtures C_3A and C_4AF in less amount with calcium carbonate and magnesium. However, these mixtures have a new crystalline phase with interplanar distance to which corresponding the diffraction maxima 7.7; 3.77; 2.85; 2.51 Å, etc.

The study of hydrated suspensions under microscope reveals that this phase is crystallized in the form of hexagonal platelike and needlelike chrystallohydrates with light refraction indexex Ng = 1.553+0.003 and Np = 2.527+0.002.

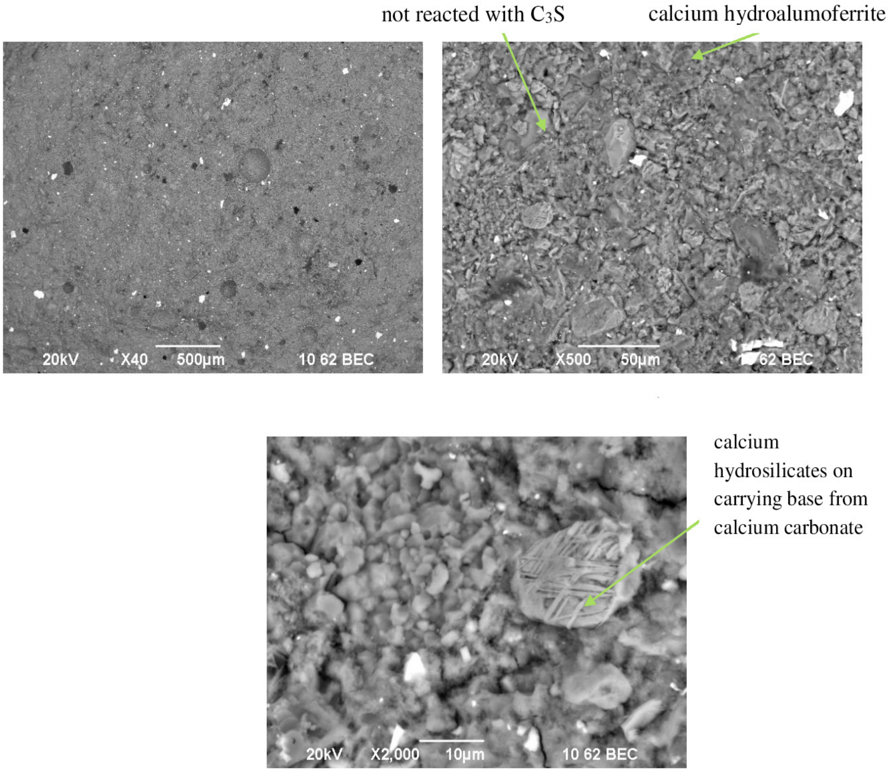


Fig. 6. Microphotographs, obtained from chips of cement brick with addition of polymetallic ores' tailings with various enlargement.

Primary crystallization of these new formations at the surface of carbonate grains is characteristic, and as a result the last ones are "overgrown" by fascinated together well developed crystals of new phase.

Thermograms of hydrated compounds also indicate the fact that the addition of finely dispersed calcium carbonates results in change of phase composition of hydration products of alumosilicate minerals of Portland cement clinker.

In thermograms of hydrated mixtures C_3A and C_4AF with calcium and magnesium carbonates besides the endothermic effects, corresponding to the initial components, endothermic effects at temperature 180 °C and 230 °C, relating to new hydrated phase, are observed.

With the help of X-ray phase analysis, petrographic analysis and DTA it has been found that C_3A and C_4AF in the process of hydration interact with calcium and magnesium carbonates, this leads to the change of phase composition of hydration products of these minerals in cement. Whereas calcium carbonate and dolomite in polymetallic ores' tailings are the main components.

The observable peculiarities of phase changes of hydration products of calcium aluminates and alumoferrites explain the peculiarities of the change of strength characteristics of composite cements. It is characteristic that in the process of hardening, hexagonal forms of calcium carboaluminate and carboalumoferrite are formed and their phase transition into cubic sorts of crystallohydrates is not observed. Presence of calcium carbonate in the system promotes the stabilization of hexagonal carbon compounds.

Strength increase of composite cements is explained by the following reasons:

– firstly, particles of calcium carbonate and dolomite in polymetallic ores' tailings at hydration and hardening of clinker minerals of cement promote the acceleration of nucleation of crystal structure, i.e. in hydrated cement medium they act as centers of crystallization. Calcium aluminates form calcium carboaluminates and thereby accelerate cement brick hardening;

– secondly, by replacing part of cement with polymetallic ores' tailings with the same degree of grinding in the binder composition, the total content of highly basic minerals of clinker (C_3S, C_3A, C_4AF) decreases. Furthermore, carbonated particles compact the structure of concrete or mortar, and thereby increase their strength with significantly less consumption of cement.

Such changes in ratios of highly basic minerals in the composition of composite cements at hydration and hardening of cement minerals contribute to formation of mainly calcium hydrosilicates of low-basic form of CSH (B) type, which are more high-strength than their highly basic forms.

Thirdly, at grinding the particles of carbonate form small crystals and they firmly fix the hydrated minerals of cement on the roughened surface.

The formation of these compounds contributes to structure hardening, strength increase of cement brick. Presence of barium sulfate, being added with polymetallic ores' tailings, can increase the protective properties of composite cement against γ and X-ray radiation. The protective properties can be improved also due to the content of chemically bound water, which is the moderator of neutrons.

3. Conclusions

Performed studies enable to recommend the use of polymetallic ores' tailings as mineral additive to clinker during its grinding, this opens the following possibilities:

– enhancement of strength quality of cement, which exceeds the strength of check samples on Portland cement without additive due to formation of calcium hydrocarboaluminates and hydrocarboalumoferrites;

– enhancement of protective properties of concretes against radioactive effect due to the presence of chemically bound water, which is the moderator of neutrons, in calcium hydrocarboaluminates and hydroalumoferrites and also due to presence of barium sulfate, being added with the polymetallic ores' tailings;

– improvement of environmental situation of the region because of reduction of clinker component in cement, decrease of quantity of CO_2, being evolved at clinker firing;

– cost decrease of Portland cement and concrete because of reduction of power-consuming clinker component and transport expenses at delivery of tailings.

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