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Heavy concrete on cement with slag of low-carbon ferrochrome

Zyryanov, F. A.
Bukreev, *A. B.*
Department of a Financial Management, the Faculty of Economics and Entrepreneurship

Zyryanova, O. O.
South Ural State University (National Research University), Chelyabinsk
Email:oozyryanova@yandex.ru

ABSTRACT: This research work is aimed to determinate a possibility of stabilization of a low-carbon ferrochrome slag into a dry slag and further recycling it into a commercial product. Research was done with petrographic analysis of the structure of the artificial stone. The influence of a commercial product on constructional and technical properties of concrete and concrete mixture was determined according to the requirements of the standards for this product. As the result of the investigations of low-carbon ferrochrome slag the common regularities of formation of minerals of CaO-SiO2-Al2O3-MgO-Cr2O3 system in artificial stone were determined. Depending on the conditions of stabilization, the main minerals, formed during industrial stabilization of slag, and the structure of stabilized slag were studied in detail. The laboratory research was done and as the result new common influence patterns of fine powdered stabilized slag upon the properties of concrete mixes and concrete were reached.

KEYWORDS: Ferrochrome Slag, Structure, Mineral, Concrete mix, Properties, Additives.

1 INTRODUCTION

The Chelyabinsk region is the leader of the metallurgical industry. One of the wastes of metallurgical industry is a poorly explored low-carbon slag. During production of low-carbon ferrochrome, slag is produced up to 120,000 tons per year. This slag is a solid solution of a dicalcium silicate [3, 8, 12].

Depending on the cool-down conditions and used stabilizing additives the slag can be an artificial stone (β-C2S) or a fine powder (α-C2S), received as the result of belite's decay. A fine powder slag is of light grey color and doesn't have astringent properties in spite that its mineralogical and chemical compositions are close to the composition of clinker.[3, 13] High dispersion of slag is the result of its polymorphic transformations at slow cooling, such slag is called autodecomposing. Recycling of such waste can prevent the soil pollution with chromium and obtain a considerable saving of cement, if the structure of the slag will be stabilized. The main advantage is the presence of chromium oxide in slag, which lets to add the required amount of other stabilizers. [5, 6] Some research, having shown not only the advantages, but also disadvantages – infusibility, high residual contents of Cr2O3 and low degree of extraction of chromium, were carried out. One way to solve this problem is to analyze a five-component system CaO-SiO2-Al2O3-MgO-Cr2O3 [7, 14] and to ascertain areas of phase compositions of slag melts with necessary properties

of refractory raw materials and high technological parameters of the process of smelting low-carbon ferrochrome. The integration of new recycling technologies into metallurgical industry provides production of high quality slag materials. [4] Besides, new technology guarantees efficient use of raw materials, reduces the amount of waste, improves the ecological situation in the industrial districts greatly. The technology of slag stabilization includes the following steps: boric oxide is used as a stabilizer and put into a slag ladle; then slag is added; at temperature of slag about 1,700…1,800ºC diffusion establishes a uniform concentration of boric oxide in all parts of the slag melt and while melt is cooling it prevents slag's autodestruction and saves slag in the shape of ingot; slag is off-loaded from a slag car and broken in a crusher. As the result, minimum content of metal (up to 1 per cent) and production of dry slag with fraction 0…3 mm, 3…8 mm, 8…20 mm and value of 40,000 tons per month are provided. So the problem of slag recycling is very important and needs to be solved in a short time. In order to develop programs of slag recycling, its composition, structure, properties were explored.

The chemical composition of stabilized low-carbon ferrochrome slag contains a great amount of calcium oxide (not less than 35 per cent), silicon oxide (not less than 25 per cent), magnesium oxide (not less than

15%) and aluminum oxide (5…14 per cent) at such proportion, that provides creation of dicalcium silicate, having three polymorphic modifications, under conditions of slow cooling and crystallization of the melt.

In common conditions of melt's cooling dicalcium silicate transforms to γ-form with the increase of a value, that causes autodestruction of crystal lattice and slag to a fine powder. As the result this slag almost doesn't have any hydraulicity.

Rapid cooling of the melt or introduction of admixtures of boric oxide or chromium oxide or phosphorus oxide are necessary to stabilize slag. In such case dicalcium silicate is being stabilized in the form of β-2CaOxSiO2.

As is well known, β-C2S is one of the main minerals of Portland clinker [1] and can be characterized by medium activity in the early stage of the cement stone's maturing and by guaranteeing high technical qualities of the composite materials in the late stage of the maturing.

1.1 *Materials used*

In order to research a slag structure there were done petrographic investigations of dry slag, produced with stabilizer of boric oxide under the technology of JSC "Chelyabinsk electrometallurgical plant".

The results of petrographic investigations of samples (30 laps from 4 smelting patterns) show, that slag has densely porous structure with pore size 0.1…1 mm for round pores and 10…15 mm for different shapes of pores. The microstructure of slag is similar to porphyritic structure: relatively idiomorphic larger crystals of minerals (0.2…0.7 mm, in rare cases up to 1…1.5 mm) are included into less devitrified aphanite – 0.05…1.5 mm – mass of these minerals. In spite of that multioriented densely interdigitating and alternating units and aggregates dominate, single laps have a certain orientation of crystals.

2 RESULTS

2.1 *Materials used*

M20 grade In the studied samples simple and composite silicates, calcium aluminosilicate, magnesium aluminosilicate (larnite, enstatite, clinoenstatite, helenite) and complex metal oxides (spinel) prevail approximately in the same proportions. All these minerals, except spinel, are colorless and have high index of refraction, large relief and first of all they differ from each other in morphology and strength of birefringence.

Perhaps at first the enstatite MgOxSiO2 (the structural formula is Mg2 [Si2O6]) [5, 11, 12] was crystalized from the melt; it has relatively idiomorphic elongated, often elongate-prismatic and columnar forms of a grain up to 1.2…1.5 mm in length and 0.2…0.4 mm in width. Polysynthetic twins are typical for the enstatite. The enstatite with its rhombic system has straight extinction and weak birefringence (Ng–Np = 0.008) with grey up to pale yellow colors of interference. When the temperature drops the enstatite is replaced by the clinoenstatite, which is present in the form of individual grains, has monoclinic system and an oblique angle of extinction – 22…42o.

The depletion of a slag melting by magnesium causes the crystallization of larnite - β-2CaOxSiO2 (the structural formula is Ca2 [SiO4]), which often is in a dense intergrowth with the first crystals. Grains of the larnite have a roundish form with a specific hatching, caused by the presence of the polysynthetic twins. Such polysynthetic twins look like plagioclase twins in samples. The larnite has a monoclinic system and an oblique angle of extinction – 12…22o and medium – grey up to red-orange colors of interference (Ng-Np = 0,018).

On the morphology and well-developed fracturing crystalized with the larnite the helenite 2CaO-Al2 O3 -SiO2 (the structural formula is Ca2Al[(Si, Al)2O7]) is clearly visible in the samples.[2,11] Having the tetragonal system, the helenite is present in the form of short-prismatic and thin-tabular crystals with isometric shape in section. At the weak birefringence of the helenite (No-Ne=0,001…0,013) zonal grains with grey-blue colors of interference are present sometimes. Exactly fractures of the helenite contain inclusions of glass and ore minerals (ilmenite and chromite). In one of the samples around crystals of the helinite the accretion of the wollastonite (Ca [SiO3]) edge of acicular crystals and accumulation of the small dark-green diopside's (CaMg[Si2O6]) grains are observed.

In all samples there are crystals with the highest relief of chrome-bearing spinel of series Mg Al2 O4 - Mg Cr2 O4 with pale purple-pink up to bright red colors and of two lasings. Having a cubic system the spinel of the first generation is presented in the form of idiomorphic crystals up to 0.06…0.07 mm. The spinel of the second generation differs by pale-pink color and irregular shape of small grains (0.01…0.03 mm), which create accumulations with a size up to 0.2…0.5 mm in the form of chains along the fractures in the larnite and the helenite.

In some samples and in several parts of slag the content of the spinel, especially of the second generation, cementing silicates, reaches 30…50%, it causes even macroscopic grey slag to get light pink shade. In common, the content of spinel is not more than 5…15%. Nowadays a pilot lot of stabilized slag of low-carbon ferrochrome was received on JSC "Chelyabinsk electrometallurgical plant". The optimal dosages of the stabilizing additive of the boron oxide (0.6% by weight of the melt), guaranteeing the maximum hydraulic activity of the stabilized slag (10.2 megapascals), were obtained. [8,9,10].

Table 1 – Compositions of concrete mixtures

Water-binder proportion (project grade of concrete)	Source materials, kg/m^3				
	Cement	Sand	Macadam	SP-1	Water
0,6 (200)	311	804	1122	1,56	187
0,5 (300)	368	766	1135	2,21	184
0,4 (400)	450	740	1100	3,15	180

As expected, the received slag has a low activity in the early stage of the maturing and cannot be used as a low-grade binder. But this slag is similar to cement in composition, therefore it can be a component of composite binders.
In order to identify the main regularities of influence of the stabilized slag
on the properties of concrete mixes and concrete, the series of experiments with subsequent mathematical processing and obtaining mathematical dependences of the influence of slag content in different water-binder proportions on the properties of concrete mixtures and concrete were carried out.[15]
During research there were variable factors:
The content of powdered slag with the specific surface 4100 cm2/g (0; 20; 35; 50%);
The water-binder proportions (0.6; 0.5; 0.4).
The main source materials were: cement CEMII 32,5R (Korkino cement plant), natural sand of Kalachevo deposit (a fineness modulus is 1.98), granodiarite macadam 5…20 mm, superplasticizer SP-1.
The experimental determination of the strength properties of concrete was done at the age of 7, 28, 90, 180 and 360 days for concretes, hardened under normal conditions, and 7, 28, 90 days for concretes, which were hardening during 8 hours at temperature 800C under conditions of steam curing.
The purpose of such research, aimed to determine the concrete's strength properties during the term, is to get the main inference about a stability of an artificial stone of a binder based on a composite binder.
The source compositions of concrete mixtures are shown in table 1.
It should be noted that the proposed compositions were tested at the plants of production concrete mixtures many times.

During research the influence of slag content on the workability of concrete mixture was received (Figure 1).

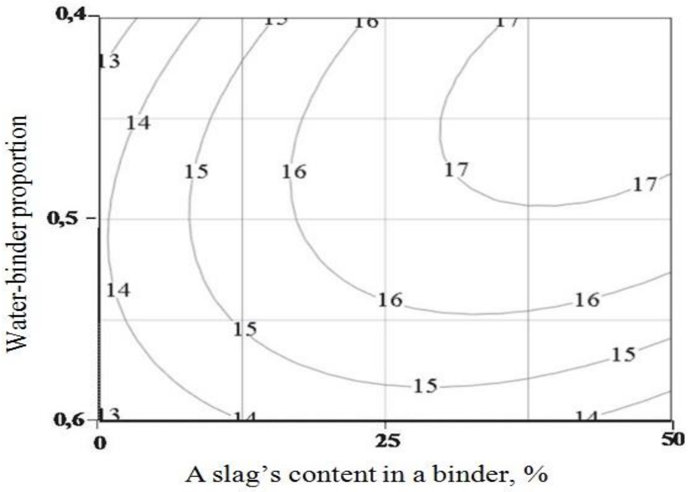
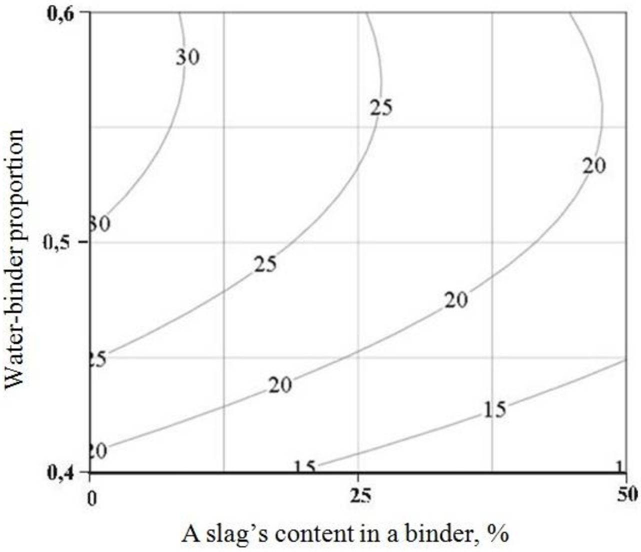
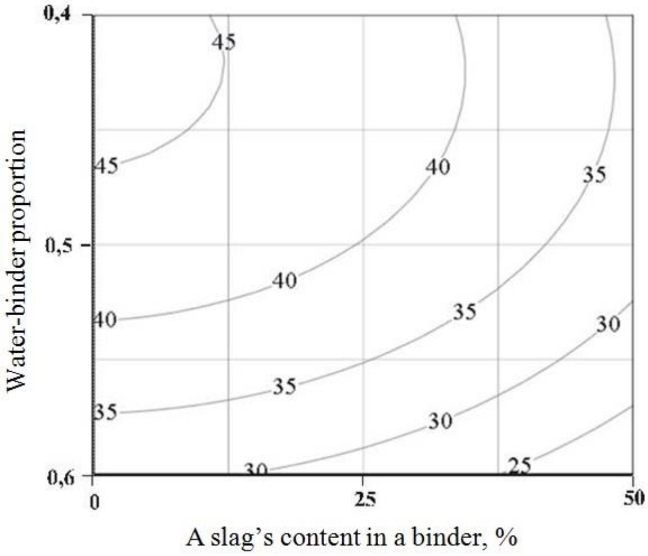


Figure 1 - The influence of slag content and of water-binder proportion on the workability of a concrete mixture

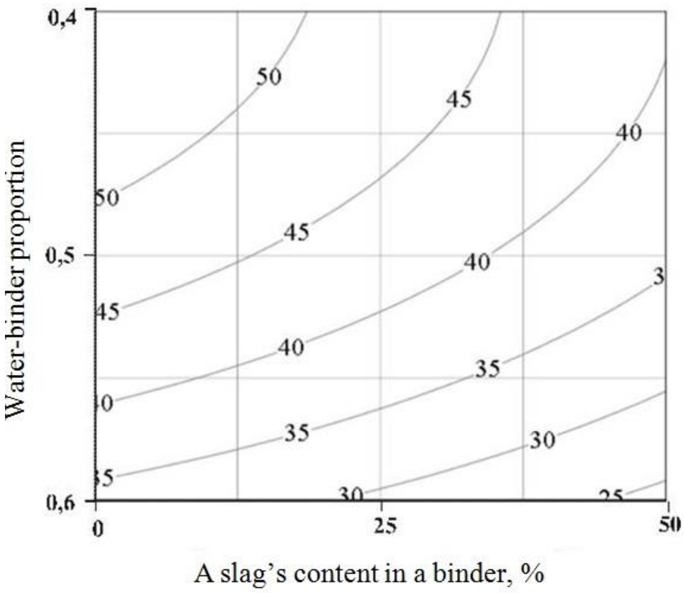
It is worth mentioning that after introduction of stabilized ferrochrome slag the storability of concrete mixtures has increased for the slump of 10…15 mm and has reached 90 minutes with 50% slag content, that is in three times longer, then for concretes based on a pure cement.
It should be noted that after addition of stabilized ferrochrome slag the density of concrete mixtures practically has not changed, but it has increased by 10…20 kg/m3 only with 50% slag content.
Strength properties of investigated compositions are shown as received with mathematical data processing isolines of compressive strength on figures 2-3.



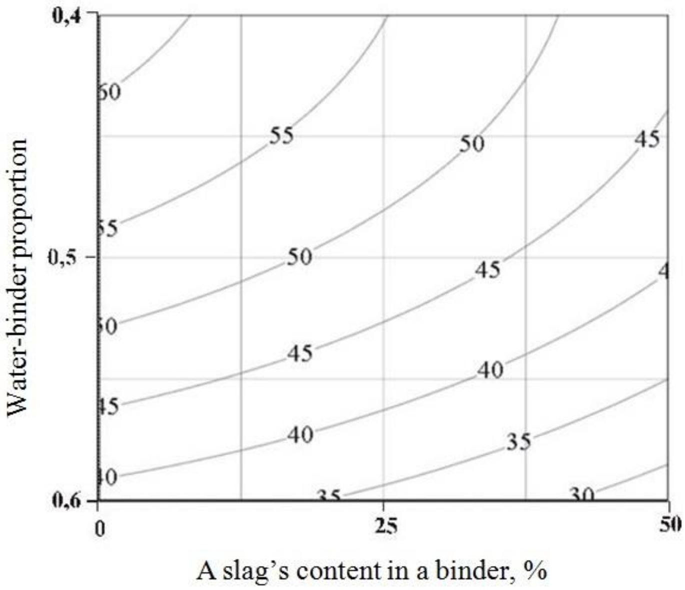
a) 7 days



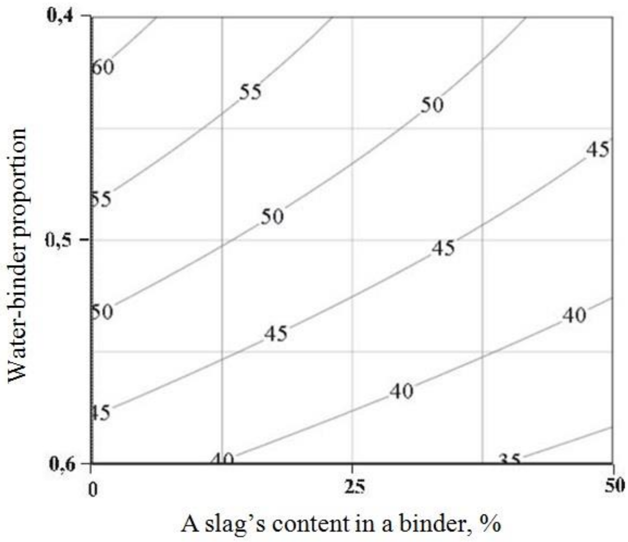
b) 28 days



c) 90 days



d) 180 days



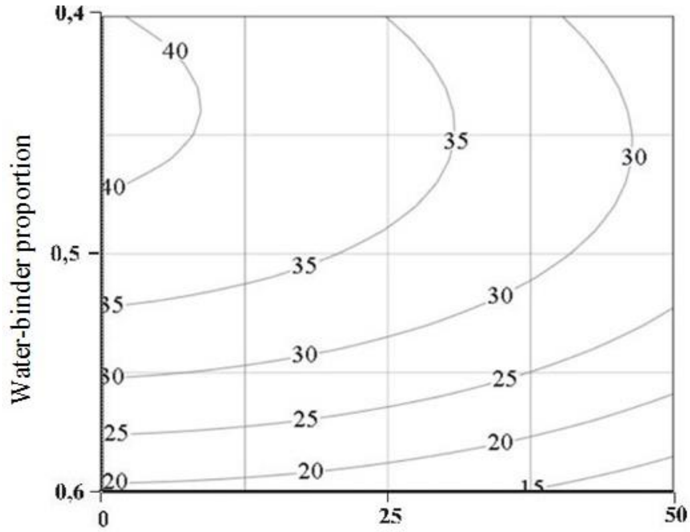
b) 360 days

Figure 2 – Isolines of compressive strength of concretes, hardened under normal condition

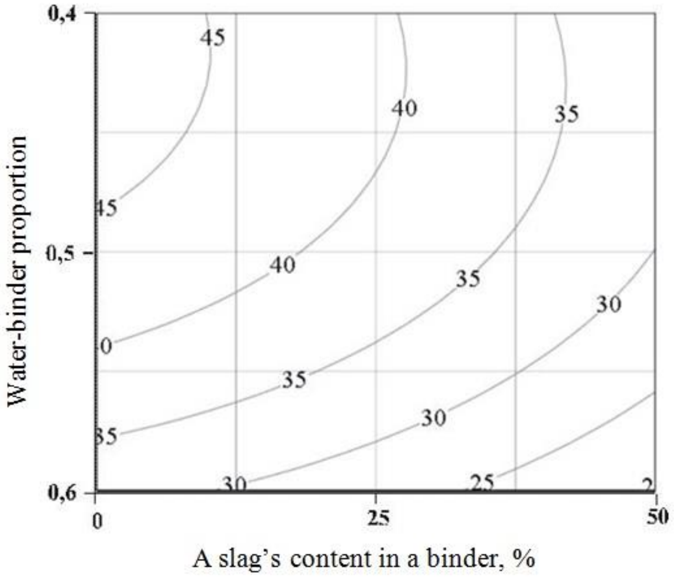
3 DISCUSSION

The main conclusions about the results of determining the strength characteristics of concrete:

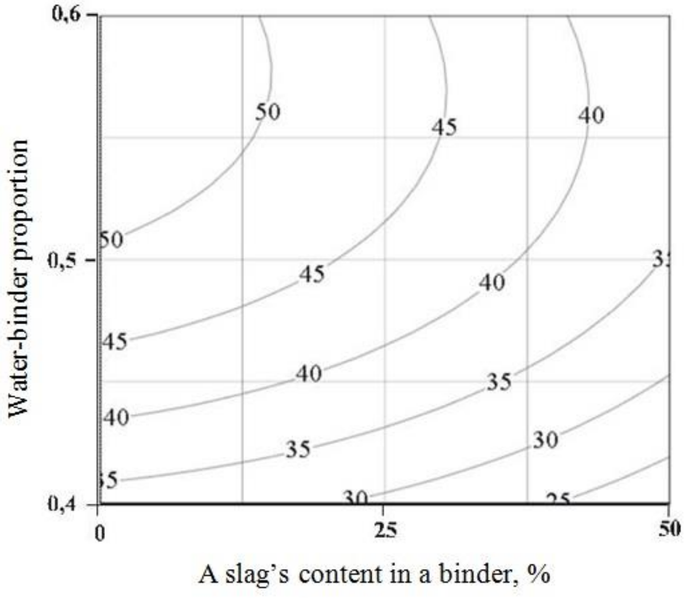
1. The introduction of stabilized ferrochrome slag reduces the strength properties of concretes in all terms of hardening. Besides it should be added, that with introduction of 50% of slag at the age of 7 days strength reduces to 50% and at the age of 360 days reduction in strength in proportion to cement amounts 22…25%. This fact indicates a low, but stable kinetics of slag's hydration on the later stages of hardening. So we can get concretes with higher strength properties because during the slag hardening low-basic hydrated calcium silicates are segregating and able to seal pores.



a) 7 days



b) 28 days



b) 360 days

Figure 2 – Isolines of compressive strength of concretes, hardened under steam curi

2. When comparing data on the strength of concretes at the age of 7 days, hardened under normal conditions and under steam curing it can be concluded that steam curing activates the process of slag's hydration. So when the content of slag is 50% the relative decrease of strength of concretes, hardened under normal conditions, is about 50% and for concretes, hardened with steam curing, the relative decrease is 30…35%.
3. The inverse function of the fined ferrochrome slag's influence and strength properties of concrete samples is set as the result of the comparison of the strength research of the concrete samples at the age

of 7, 28 and 90 days, hardened under normal conditions and under steam curing.

4.

5.

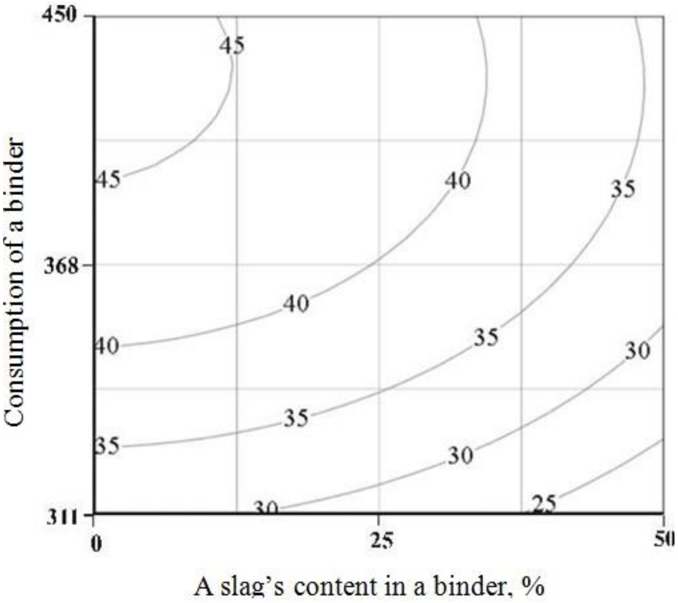


Figure 4 – The influence of consumption of a binder and a slag's content on the strength properties of concretes

6. Thus, concretes made with the identical consumption of a binder and fined ferrochrome slag and hardened under normal conditions, have the limit of compressive strength by 15…30% more, than concretes, hardened under steam curing, due to the formation of more dense structure of the stone as the result of a synergetic effect (figure 4). This effect can be characterized as a compaction of the primary crystal frame of hydrate forming, which crystalized during hydration, with the products of the fined ferrochrome slag hydration, received at the later stages. Such sequence of hydration and hardening of the multi-component binder is due to the difference between mineralogical compositions of it. In particular, fined low-carbon ferrochrome mostly contains the β-form of dicalcium silicate, which hydrates during the later stages of a hydration, unlike the α-form of tricalcium silicate, and compacts the frame, produced by tricalcium silicate.
7. The analysis of isolines of concrete's strength, pictured on figure 2, shows that while a time of a concrete's hardening is increasing, the function of fined ferrochrome slag's influence and strength properties of concrete samples is changing. So at the earlier stages of hardening non-proportional change of strength of concretes with different water-binder proportions is observed depending on the content of slag. At the age of 7 and 28 days the reduction of strength of concretes, produced with the water-binder proportion 0.6 amounts 16… 20 per cent if to compare with non-slag concretes and 25…40 per cent with the water-binder proportion 0.4. At the age of 360 days the proportional change of concrete, depending on the slag's content and water-binder proportions, is obvious.
8. The stability of stone of a composite binder leaves no doubt – it is stable with time. During the hardening researched concretes increased their strength properties, this fact indicates an absence of any destructive phenomena.
9. It should be noted that on the basis of the obtained data the test of results and additive has been carried out by the LLC "BC Legion" and LLC "Betomix" (Chelyabinsk).

4 CONCLUDING REMARKS

1. It is proved that the hydraulic activity of stabilized slag was increasing while temperature of steam curing of materials was growing up.
2. The optimal content of the powdered stabilized slag of low-carbon ferrochrome has been got, its level is up to 35 per cent of a binder's mass. In such cases the insignificant reduction of a concrete strength can be marked, especially after heat and steam curing.
3. The stability of strength properties of stability of strength properties of concrete, based on the analyzed composite binder, is proved.

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