

The effect of added high-iron slag on the frost resistance of cement compositions

Gennadiy Ovcharenko¹ and Ekaterina Ibe^{2*}

¹Polzunov Altai State Technical University, Department of Building and technologies, 656038, Barnaul, Russia

²Khakass Technical Institute of Siberian Federal University, Construction department, 655017, Abakan, Khakassia, Russia

Abstract. Currently, it is of particular importance to study the possibility of increasing the durability of composite building materials by regulating the chemical and mineralogical composition. In this aspect, it is rational to consider the issues of increasing the frost resistance of cement concrete. It is known that to improve this property in concrete, it is necessary to create the correct structure of the hardened cement stone. The work aims to study the process of clogging the pores of a cement stone due to the formation of finely dispersed phases - ferrihydrite - in the process of hydration of composite Portland cement with the addition of high-iron slag of the established chemical composition. The paper analyzes the chemical and phase composition of concretes obtained based on of slag-containing binders with high values of frost resistance. It is shown that, based on this slag, concrete with frost resistance of 500 cycles has been obtained. Analysis of the hydration products showed that finely dispersed ferrihydrite of ferric iron are formed in the cement stone, which increases the density of concrete, plugging the defects in the microstructure of the C-S-H gel.

1 Introduction

As is known, to achieve a high class of concrete in terms of frost resistance, it is required to create a dense, impermeable cement stone with a uniformly distributed fine-pored structure. The currently known theoretical provisions that allow achieving a high indicator are as follows [1–4]:

- reduction of the water-cement ratio of concrete to a value of less than 0.38 to exclude the formation of capillary porosity;
- the use of air-entraining additives in the concrete mixture, allowing the formation of the correct structure of porosity;
- taking into account the formation of the microstructure of the cement stone, depending on the mineralogical composition of Portland cement.

At the same time, a significant reduction in the water-cement ratio leads to the fact that there is simply not enough water for the hydration of Portland cement, and a significant

* Corresponding author: katerina.ibe@mail.ru

proportion of unreacted grains remains in the cement stone, which is substantiated by the well-known theory of micro-concrete.

For the formation of the correct microstructure of the cement stone, providing high strength and deformation properties, the following requirements must be met:

- limiting the content of calcium aluminate in clinker, leading to the restructuring of hydroaluminates and a decrease in strength, as well as the formation of open porosity;
- the use of microsilica together with superplasticizers, which reduce the defectiveness of the microstructure of the stone due to the binding of portlandite and modification of the microstructure of the C-S-H (II) phase.

The first position is based on the fact that the forming calcium hydroaluminates have low water resistance and, if the content is high, lead to a decrease in frost resistance.

The second position is confirmed by the theory that concrete must be considered, including at the submicroscopic level, with the study of defects in the microstructure of hydration products, to which the C-S-H gel belongs.

Experimental studies [5, 6] cement (ash) slag concretes based on acidic fuel granular slag showed their frost resistance up to 1500 cycles.

Many works have shown the possibility of increasing the frost resistance of concrete through the use of an increased amount of sour granulated blast furnace slag in the composition of Portland cement and the use of air-entraining and plasticizing additives.

It is shown in paper [7] that when 45% of Portland cement is replaced with industrial waste, the compositions have a higher strength due to the increased formation of the so-called needle and rod-shaped crystals. There is also a more than two-fold decrease in the capillary porosity of the compositions modified with industrial waste.

Papers [8, 9] show the technical characteristics of a copper slag containing up to 60 % iron oxide and its effect on the properties of cement and concrete. The authors note that during hardening of cement compositions, up to 10% of copper slag, the maximum strength develops by 90 days of hardening, which is due to the slow hydration of iron oxide.

In work [10], the authors present the results of studies of high-strength concrete (HSC), including copper slag in the form of a large aggregate with great content of iron, at elevated temperatures. The authors note that high strength indicators are provided due to a strong interfacial bond between the slag and the cement matrix.

Some works have noted the role of iron nanoparticles in the formation of the properties of cement stone. Studies [11, 12] have shown that the compressive and flexural strength of cement slurries reinforced with SiO_2 and Fe_2O_3 nanoparticles is higher than that of simple cement slurries.

As is known, the very structure of calcium hydro silicate C-S-H has defects. The data obtained as a result of the experiment can confirm the theory of clogging of pores and defects due to the formation of finely dispersed phases - iron hydroxide $\text{Fe}(\text{OH})_3$ and other ferrihydrite. Coating the pores with finely dispersed ferrihydrite makes it possible to significantly compact the cement stone while increasing its frost resistance.

The use of iron salts to increase the density and impermeability of cement stone is known and used in practice. At the same time, in contrast to iron salts, the action of an active mineral iron-containing supplement has a different effect. Slag iron-containing binders during hydration form ferrihydrite, which are formed directly in the composition of the main phases of the cement stone.

2 Methods

For the experiment, we used slag Portland cement on a special nickel slag of increased basicity with chemical and phase compositions according to Tables 1 and 2.

Table 1. Chemical composition of high-iron slags.

Slag number	SiO ₂	Al ₂ O ₃	Fe	CaO	MgO	SO ₃
13 (sour nickel slag)	31,3	4,5	58,3	3,4	1,1	3,5
1	25,4	9,9	40,5	25,4	2,6	3,5
4	25,9	8,4	42,1	24,2	2,9	3,6
20	23,6	7,2	39,2	29,4	2,4	4,1

Table 2. The phase composition of granulated slag No. 1 according to microprobe data.

Phase	SiO ₂	CaO	MgO	Al ₂ O ₃	Cr ₂ O ₃	FeO	Total content
Gross slag composition	24,3	27,0	7,8	4,7	-	31,9	95,9
Glass	34,9	34,9	7,1	4,3	-	17,2	97,8
Magnetite	-	0,5	8,0	5,4	6,7	71,6	92,2
Chromite	-	0,4	19,3	6,4	20,1	53,5	95,9

Note: The microprobe was unable to estimate the composition of wustite dendrites with a size of about 0.5 μm, contained in an amount of about 20%.

The phase analysis of slags was carried out by X-ray (DRON 2), micro-X-ray spectral (microprobe, Kameka MS-46), and chemical methods. Phase analysis of the cement stone was carried out by Mössbauer (Varian spectrometer, type 60), thermal (Paulik derivatograph, Erdei), X-ray methods.

Slag Portland cement was obtained in laboratory and industrial ball mills based on clinkers from the Achinsk and Norilsk plants with a slag content of 30%. Cement in all respects met the requirements of GOST 10178-85. With a residue on sieve No. 008 of 9-10%, their specific surface area was 300-320 cm²/g. The activity of the slag Portland cement at 30% slag was 33.2 MPa.

Concrete mixtures with a slump of a cone 5 cm had the next composition (in kg/m³):

- crushed stone - 1200;
- sand - 680;
- slag Portland cement 300-400;
- LST - 0.8;
- START - 0.05.

Detailed formulations are given in Table 3.

3 Results

Sour slag No. 13 (Table 1) according to XRD data is mainly represented by glass with insignificant crystallization of fayalite Fe₂[SiO₄] and olivine (Mg, Fe)₂[SiO₄] (hereinafter, the interplanar distances in crystals are given in 10⁻¹⁰ m: 3.35; 2.81; 2.49; 1.77), magnetite Fe₃O₄ (3.019; 2.542; 2.083). Slag No. 1 contains wustite FeO (2.46; 2.13; 1.50), magnetite Fe₃O₄ (2.94; 2.51; 2.13), okermanite Ca₂Mg[Si₂O₇](C₂MS₂) (2.94; 2.51). In slag No. 20: wustite, magnetite, insignificantly okermanite, and more significantly merwinite Ca₃Mg[SiO₄]₂(C₃MS₂) (2.66; 1.92; 1.85; 1.54) and β-C₂S.

Micro X-ray spectral analysis showed the presence of phases in slag No. 1 according to Table 2.

Additionally, wustite dendrites are noted in the slag, which is not detected by the microprobe due to the small crystal size of 0.5 microns.

Concrete mixtures (Table 3) based on slag Portland cement with 30% slag No. 1 and Achinsk clinker hardened during steaming and under normal conditions (Table 4).

The problems of the heat-shielding properties of the structures under consideration are primarily due to the presence of heat-conducting inclusions in the form of metal brackets. Also, heat-conducting inclusions are dowels for fixing insulation, window slopes, balcony slabs, outlets for fixing scaffolds.

Table 3. Compositions of concrete mixtures with the slump of the cone 5 cm

Component	Component content in the composition (kg/m ³)				
	1	2	3	4	5
Crushed stone (20-40 mm)	520	490	465	490	490
Crushed stone (5-20 mm)	780	740	700	740	740
Sand	680	650	620	650	650
Slag Portland cement	300	400	500	400	
Achinsk Portland cement	-	-	-	-	400
LST	-	-	-	0.8	
SNV				0.05	
Water	180	193	197	162	204

Table 4. Compressive strength of concrete

Duration of steaming at 80 °C, hour	Curing time by normal conditions, days	Composite number				
		1	2	3	4	5
4	without	13.1	21.6	28.7	-	23.8
4	28	24.7	30.7	43.6	33.5	35.5
without	7	14.5	22.1	28.7	-	25.4
without	28	18.6	25.6	37.2	32.3	31.8

4 Discussions

According to the results of the experiment may be noted the greatest increase in strength was noted for compositions subjected to heat treatment with an additional hardening period under normal conditions. It follows that under the conditions of heat and moisture treatment, a finely dispersed structure is formed in the composition of hydrate phases, which is characterized by increased resistance during cyclic freezing. The effect of increasing frost resistance is also facilitated by a decrease in the amount of water for composition No. 4, which leads to an improvement in the pore structure.

The concrete on the experimental slag Portland cement (based on high-calcium ferrous slag No. 1) was not inferior in strength to the concrete on the Achinsk non-additive Portland cement (compositions No. 4 and No. 5). This, among other things, is due to a 20 % lower water demand for mixtures based on slag Portland cement. At the same time, concrete based on Achinsk Portland cement, containing air-entraining additives, showed a frost resistance value of only 250 cycles. The considered experimental Portland cement (composition No. 4) showed an increase in frost resistance up to 530 cycles without destructive signs.

The study of the hydration products of cement stone obtained during hardening of slag Portland cement carried out by analyzing the data of Mössbauer spectroscopy (Fig. 1), showed the difference between new formations and typical hydrated phases of Portland cement. Together with portlandite, calcium hydro silicate C-S-H, goethite FeOOH is formed, which corresponds to the endothermic effect -300 °C. [13-16]

The considered iron-containing acidic slag contains divalent iron cations Fe²⁺ in the glass phase and olivine (curve 1 in Fig. 1). During the hydration of Portland slag cement, there is no noticeable effect on the change in the charge of iron cations and their

coordination to oxygen (curve 2, Fig. 1). In the case of hydration of Portland cements with the addition of highly basic (by lime) iron-containing slags, the hydration products change significantly.

Initial slags No. 1 and No. 20 contain trivalent iron cations (curves 3 and 5, Fig. 1), the proportion of which significantly increases upon hydration (curves 4 and 6, Fig. 1). This effect may be due to the spontaneous oxidation of iron ions in the case of increased basicity of slags. In the process of hydration of slag Portland cement, this effect increases, which may indicate the formation of a significant amount of ferric hydroxide - ferrihydrite, which is the cause of clogging of the pores of the cement stone.

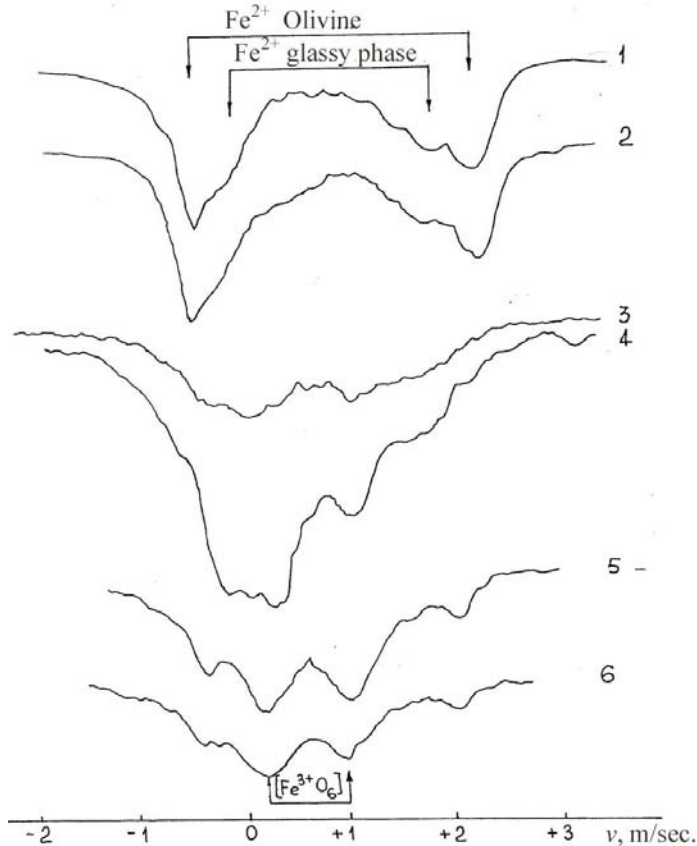


Fig. 1. Mössbauer spectra of the initial and hydrated Portland slag cement on slags of different basicity (1, 3, 5 - original Portland slag cement; 2, 4, 6 - hydrated Portland slag cement at the age of 28 days)

The formation of a dense crystalline structure of the cement stone due to the formation of ferrihydrite contributes to an increase in the frost resistance of the stone [17, 18].

Processes similar to those described are possible when using fuel slag and ash in cement concretes, especially medium calcium concretes containing 10–15% $\text{Fe}_2\text{O}_3 + \text{FeO}$ and 20–30% CaO and SiO_2 . Therefore, the data of [5] could be achieved, in part, and because of this effect. The resulting finely dispersed ferrihydrite are embedded in the structure of the C-S-H gel. As a result, the permeability of the cement stone by aggressive components is reduced.

As a result, note the essential provision that high-iron slags can increase the frost resistance of concrete due to the formation of a correct pore structure. In this case, reserve

porosity is formed in the structure of the cement stone due to the increased amount of the gel phase during the steaming process, which allows moisture to be redistributed during the freezing of concrete.

5 Conclusions

The research performed allows us to draw the following conclusions:

1. High-iron nickel slag can be used as a component of mixed Portland cement.
2. High-iron slag of increased basicity with a content of 25–29 % CaO, about 25 % of silica, and 40 % of iron oxides upon hydration in the composition of the Portland slag cement form an increased amount of ferrihydrite of ferric iron in the cement stone
3. Ferrihydrite provides the concrete on such the Portland slag cement with frost resistance of more than 500 cycles.

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