The role of aluminum and iron hydroxides in the formation of concrete properties

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Abstract. Aluminum and iron hydroxides, formed in the stone during the hydration of cement with the addition of special slags, significantly improve the properties of concrete. The addition of low-basic calcium aluminates CA₂ and CA₆, in the form of high-alumina slag, which releases a large amount of Al(OH)₃ during hydration, increases the strength, density, water resistance, frost and corrosion resistance of hydraulic concrete. A compressed mixture of concrete scrap and high-alumina slag based on low-basic aluminates makes it possible to obtain durable and frost-resistant materials and pavement structures. A special nickel slag of increased basicity in a mixture with Portland cement ensures the formation of ferric hydroxide during hydration. Concrete on such Portland slag cement shows frost resistance for more than 500 cycles without special measures.

1. Introduction
As you know, the cement stone structure is a combination of not fully hydrated initial cement particles, the resulting hydration products, as well as pores of various sizes. The composition of products during hydration of Portland cement depends on the chemical and mineralogical composition of the cement, as well as on several other factors, including the temperature at which the components interact, and the degree of environmental influence.

The performance properties of concrete are directly determined by the properties of the cement stone; the most important are strength, frost resistance, and corrosion resistance. Due to the low frost and corrosion resistance of concretes used in construction, accidents, and unacceptable deformations of critical structures operating in special conditions often occur. This makes it necessary and relevant to find solutions related to increasing the durability of concrete composites.

Since the structure of the cement stone plays the main role in matters of durability, special attention, in addition to reducing the W/C and the technology of correct concrete placement, must be paid precisely to the formation of the structure.

The study of the frost resistance of cement concretes allowed scientists to formulate several universal provisions that are used today in the practical design of super-resistant materials. The main provisions for obtaining highly frost-resistant concrete are as follows [1–4]:

- it is necessary to reduce the W/C of concrete until the disappearance of capillary porosity in it (less than 0.38);
- it is necessary to ensure air entrainment into the concrete mixture, which contributes to the good work of the stone in conditions of freezing and thawing;
- the parameters of air entrainment should be such as to obtain a certain amount, pore diameter (less than 250–300 microns) and the distance between them;
- it is necessary to take into account the formation of its microstructure of a stone of a particular mineralogical composition.

The last provision includes:
- a ban on the use of cement with a high aluminate content in the clinker, leading to open microporosity;
- the use of silica fume 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.

In many works, it is said that the most durable is concrete, which has a dense structure of cement stone impermeable to aggressive components [5], which, according to the well-known provisions on the clogging of pores of cement stone [6–8], can be formed due to the formation of in the process of hydration of gel-like bridging phases.

2. Materials and methods

Previously, we carried out studies to optimize the compositions of materials containing high-alumina or high-iron slags. [9]

To study the formation of aluminum hydroxides in the products of cement hydration, pressed samples were prepared based on concrete scrap and high-alumina slags. Concrete scrap in the form of pieces of 200–300 mm was obtained during the processing of scrap structures at the precast concrete plant (Barnaul) by a specialized organization. For contact hardening binders, concrete scrap in the laboratory was crushed and scattered into fractions 0–1.25, 0–2.5, 0–5.0, and 0–10 mm.

In the course of the work, sample cylinders with a diameter and height of 50 mm were made. Molding was carried out at pressing pressures of 20–100 MPa. The samples were tested 1 hour after molding, after 28 and 90 days of normal hardening or steaming at 80 °C according to the 3+6+3 hours mode.

To study the formation of iron hydroxides in cement hydration products, special cement were prepared with the addition of nickel slag. The experiment used slag Portland cement-based on a special nickel slag of increased basicity.

Special 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.

The phase analysis of the cement stone was carried out by Mössbauer (Varian spectrometer, type 60), thermal (Paulik derivatograph, Erdei), X-ray methods.

3. Results and discussions

High-alumina slag (HAS), introduced as a binder component for the production of hydraulic concrete, changes both the rheological properties of the concrete mixture and the composition of new formations of Portland cement. Water separation of a concrete mixture made using composite Portland cement with complex mineral additives containing high-alumina slag is 14 times lower than water separation of a concrete mixture with no additives Portland cement; there is a rapid formation of a gel-like phase.

Calcium aluminates of the CA₂ and CA₆ types, contained in high-alumina slag, upon hydration form complex hydrated phases such as alumino-substituted silicates, as well as a certain amount of aluminum hydroxide. The existing endothermic effect at a temperature of 310 °C with a weight loss of 5.6% proves the formation of aluminum hydroxide (Fig. 1).
Figure 1. Derivatogram of cement stone obtained by hydration of composite Portland cement with the addition of high-alumina slag

This fact determines the effect of clogging of the pores, due to which there is a decrease in concrete permeability and an increase in operational properties. Concretes made using HAS are characterized by high corrosion resistance and strength in the late periods of hardening.

However, the introduction of HAS into the composition of the binder for hardening under normal conditions has some limitations due to a partial decrease in strength during hydration as a result of the recrystallization of calcium hydroaluminates. According to the results of X-ray phase analysis, it was revealed that over time, cubic calcium hydroaluminates are observed in the hydration products of composite Portland cement (Fig. 2).

Figure 2. X-ray diffraction pattern of composite Portland cement with HAS additive
If for hydraulic concrete of massive structures this is a less important limitation, since the strength is estimated at the age of 180 days, then for conventional structures this factor is of great importance. The experiment showed that during the initial hardening period, concrete based on a composite binder containing HAS quickly gained strength. Then there is a decline and a further slow increase in strength.

To eliminate the problem of strength decay during recrystallization, it is necessary to create conditions in which this process will occur quickly, without deterioration of construction and technical properties. Research on the development of materials for road bases made of concrete scrap [9] showed that the use of HAS very effectively affects the properties of materials obtained by pressing at high pressure.

In this case, the effect of low-basic calcium aluminates in the composition of HAS has an extremely positive effect, since when the raw mixture is pressed under a pressure of 60–100 MPa, the hexagonal hydroaluminates are rapidly rearranged into cubic C₃AH₆ and the gel of aluminum hydroxide Al(OH)₃ is formed in parallel. Al(OH)₃ gel contributes to the formation of a dense, hardened structure of pressed products.

Compositions of concrete scrap with the addition of HAS provide the necessary characteristics of road products in terms of strength and frost resistance at a pressure of 20 MPa (Fig. 3).

Moreover, the strength of the pressed stone increases with an increase in the specific pressing pressure and the time of the normal holding of the compacts.

![Figure 3. Compressive strength of a compressed composition of concrete scrap and HAS](image-url)

The use of iron salts (sulfates, chlorides, nitrates) in the manufacture of concrete is also justified by the strengthening effect, however, chemical additives cannot participate as actively in the hydration process as mineral ones, for example, high iron slags.

Experimental studies [10, 11] cement slag concretes based on acidic fuel granular slags showed their frost resistance up to 1500 cycles (without loss of strength - up to 1000 cycles). Using up to 30% high-iron nickel slag in the composition of Portland slag cement made it possible to increase the strength of concrete from 32 to 46 MPa after 523 cycles of frost resistance testing without destruction. This fact allows us to conclude that iron oxides are directly involved in the hydration and formation of the structure of the cement stone. The study of the cement stone of the hardened cement showed that, in addition to the typical hydration phases in the form of portlandite and C-S-H gel,
goethite FeOOH or, in new terminology, ferrihydrite are determined in the hydration products: DTA – 300 °C. It is confirmed by the data of Mössbauer spectroscopy (Fig. 4).

The original acidic slag contains divalent iron cations Fe\(^{2+}\) in the glass phase and olivine (curve 1). The hydration of this slag in the composition of the Portland slag cement does not lead to a noticeable change in the charge of iron cations and their coordination for oxygen (curve 2). A different picture is observed with iron-containing phases in lime-containing slags of increased (in terms of lime) basicity. The original slag contains trivalent iron cations (curves 3 and 5), the proportion of which significantly increases upon hydration (curves 4 and 6). This is due to the spontaneous oxidation of iron ions with an increase in the basicity of slags, as well as in the process of its hydration. That is, we can talk about the formation of a large number of ferrihydrite of ferric iron, providing the formation of finely dispersed iron-containing phases.

The concrete on the experimental Portland slag cement (Table 1) (based on high-calcium ferrous slag, composition 1) was not inferior in strength to the concrete on the Achinsk no-additive Portland cement (compositions 4 and 5). This, among other things, is due to a 20% lower water demand for mixtures based on Portland slag cement. But concrete with air-entraining additives on Achinsk cement withstood only 250 cycles of frost resistance, and composition 4 – after 523 cycles, increased its strength to 46 MPa and showed no signs of frost destruction.

![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)](image)

**Figure 4.** 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)
Table 1. Compressive strength of concrete, MPa

| Duration of steaming at 80 °C, hour | Curing time (normal conditions), days | Concrete composition 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 |

High-iron slags of increased basicity with a content form in the cement stone an increased amount of ferrihydrite of ferric iron, which provides concrete at such Portland slag cement with frost resistance of more than 500 cycles.

As in the case of Al(OH)$_3$, the finely dispersed ferrihydrite of ferric iron formed during the hydration of the Portland slag cement clog the pores and microstructure defects of the cement stone, significantly strengthening it.

4. Conclusions

1. Thus, according to the results of numerous experiments, it can be argued that to increase the operational properties of concrete (frost and corrosion resistance), it is necessary to form a dense hardened structure, which can be provided by the formation of gel-like finely dispersed aluminum and iron hydroxides formed during the hydration of Portland cement, containing additives high-alumina and high-leather-iron slags.

2. In this case, high-alumina slags play a special role in ensuring the properties of contact-condensation materials. When concrete hardened under normal conditions, high-alumina slags increase the corrosion resistance of concrete, however, due to recrystallization, they can reduce the strength.

References

[1] Pigeon M 2014 Durability of Concrete in Cold Climates. CRC Press, London
[2] Boos P and Giergiczny Z 2010 Proceedings of the Silesian University of Technology 2, 41-51
[3] Stark J and Wicht B 2004 Durability of concrete [in Russian]. Oranta, Kiev
[4] Shestoperov S V 1997 Technology of concrete [in Russian]. Higher School, Moscow
[5] Kuznetsova T V and Talaber J 1989 Alumina Cement [in Russian]. Stroiizdat, Moscow
[6] Rakhimbaev Sh M, Tolypina N M, Khakhaleva E N and Tolypin D A. 2018 Bulletin of BSTU named after V.G. Shukhov [in Russian] 3, 18–23
[7] Rakhimbaev Sh M, Tolypina N M, Khakhaleva E N and Tolypin D A. 2020 Materials Science Forum 974, 26-30
[8] Fedosov S V, Rumyantseva V E, Krasilnikov I V, Konovalova V S and Evsyakov A S 2018 Magazine of Civil Engineering 7, 198–207
[9] Ovcharenko G I, Volobueva A V and Ibe E E 2020 IOP Conference Series: Materials Science and Engineering 918, 012116
[10] Pavlenko S I 1997 Fine-grained concretes from industrial wastes [in Russian]. Publishing House of the DIA , Moscow
[11] Avtushko E A. and Pavlenko S I 2005 In Young Researchers’ Forum: Proceedings of the International Conference held at the University of Dundee, Scotland, UK Thomas Telford Publishing, 137–143