

Influences of Steelmaking Slags on Hydration and Hardening of Concretes

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Abstract. It is shown that the slag of metallurgical production can be used in the construction industry as an active mineral additive for concrete. This approach allows us to solve environmental problems and reduce costs for the production of binder and concrete simultaneously. Most often slag is used in the form of a filler, an active mineral additive or as a part of a binder for artificial conglomerates. The introduction of slag allows one to notice a part of the cement, to obtain concretes that are more resistant to the impact of aggressive sulfate media. The paper shows the possibility of using recycled steel-smelting slags in the construction industry for the production of cement. An assessment was made of their effect on the hydration of the cement stone and hardening of the concrete together with the plasticizer under normal conditions. In the process of work, we used the slag of the Zlatoust Electrometallurgical Factory. Possible limitations of the content of steel-slag slag in concrete because of the possible presence of harmful impurities are shown. It is necessary to enter slag in conjunction with superplasticizers to reduce the flow of water mixing. Slags can be used as a hardening accelerator for cement concrete as they allow one to increase the degree of cement hydration and concrete strength. It is shown that slags can be used to produce fast-hardening concretes and their comparative characteristics with other active mineral additives are given.

1. Introduction

Several studies have shown that the slag of metallurgical production can be reconstructed to produce a metal suitable for further processing and use [1-11]. In addition, slag is used in the construction industry as an active mineral additive (AMA) for concrete. In the South Ural region, the use of slag metallurgical production as AMA is high enough, as these solutions can simultaneously solve environmental problems and reduce costs for the production of binder and concrete. Most often, the slag is added as a filler, an active mineral additive, or as part of a binder for artificial conglomerates [12, 13]. The most demanded in this regard are blast-furnace granulated slags, which began to be used for the construction industry in the 70s of the 20th century in Germany [14,15]. However, in addition to blast-furnace ones, at the enterprises of ferrous metallurgy waste products are steel-smelting slags, whose annual output is about 25 million tons [15-17]. At the same time, steelmaking slags are used in the construction industry quite rarely, due to the variable chemical and mineralogical composition.

The use of blast-furnace and steel-smelting slags as an additive allows to bind free lime and to produce concretes more resistant to the action of aggressive sulfate media, in comparison with



Portland cement. The introduction of slag allows to replace part of the cement and to reduce its consumption [18].

In addition, the slag has a significant water demand. Introduction of slag into cement can greatly increase the water-cement ratio, so the slag must be used together with the plasticizer [19, 20].

The aim of the work is to study the possibility of using recycled steel-smelting slags (SS) in the construction industry for cement production and assessing their effect on the hydration of cement stone and hardening of concrete together with the plasticizer under normal conditions, as well as comparing them with other AMA, for assessment of the possibility of using the SS in the production of fast-hardening concrete.

2. Materials and methods of research.

In the process of work, the dump slag of the Zlatoust Electrometallurgical Factory (magnetic and non-magnetic fractions) was used. It had both previously passed solid-phase reduction procedure and not passed through this stage. The need for these activities is indicated in the work [21].

In the composition of the initial slag mixture, together with the crushed material, was introduced coke as a reducing agent in an amount of 10 wt. % by weight of the slag. The operating temperature in the laboratory induction furnace УПИ-60-2 was 1500 °C, the material was melted for 45 min, then for 25-30 min the solution was kept, after which the formed slag and metal melts merged.

A metallic solution (up to 30% of the weight of the starting mixture in the outlet) was examined for possible further use as charge materials for smelting structural steels, and the remaining slag material was subjected to research as an additive in the production of cement.

The work used portland cement CEM I 42.5 N manufactured by Dyckerhoff, which meets the requirements of state standard ГОСТ 31108-2003. As AMA, we used the Zlatoust steel-smelting slag (the chemical composition is presented in Table 1) at a dosage of 10%, metakaolin (MK) produced by «Пласт-Рифей» (TU 5729-095-51460677-2009) in dosage 3,5%, granulated microsilica (MS) (Novokuznetsk, Kemerovo region, TU 5743-048-02495332-96) at a dosage of 8%. As a plasticizing additive was used superplasticizer SP-1 of Novomoskovsk, at a dosage of 0.8% of the weight of the binder substance. AMA was administered in percent by weight, in excess of the binder's consumption. As a fine aggregate for concrete we used quartz sand of the Khleboborsky deposit with Mk 2.5, corresponding to state standard ГОСТ 8736-2014.

The studies were carried out using standard research methods and using the required number of samples of the same series to ensure a confidence probability of at least 0.95 on the certified equipment in a laboratory. The kinetics of strength were evaluated in accordance with state standard ГОСТ 10180 - 2012 "Methods for determining the strength of control samples," on cement stone (2x2x2 cm) and cement-sand specimens with beams (1: 3), 4x4x16 cm. The samples were hardened at a temperature of 20 ± 50C and a humidity of 95 -100% (normal conditions). Effect investigation of additives on the features of early hydration processes was studied by heat release using an isothermal calorimeter "TAMAir".

3. Research results and discussions.

A feature of steel smelting slags is a diverse number of metal inclusions, which can be used, first of all, as alloying components in the production of metallic melts. One of the research tasks was the complex processing of steelmaking waste, including magnetic separation, solid-phase and liquid-phase recovery of waste steel-smelting slags. Obviously, the effectiveness of the last recovery stages depends on the temperature conditions and the activity of the components, determined by the composition of the slag and the additives introduced [21].

After primary magnetic separation and final recovery, the steelmaking slag can be used as AMA for the production of building materials.

In the determination of the chemical and phase compositions of the processed steel-smelting slags, studies were carried out of physical and chemical samples of slag from various horizons of slag heaps at the Zlatoust Metallurgical Factory (Russian Federation, Chelyabinsk Region). Using the method of

local infrared spectroscopy and the Raman spectroscopy method, it was demonstrated that the slags have a heterogeneous composition: enstatite MgSiO_3 , ilmenite FeTiO_3 , augite $\text{Ca(Fe, Mg) \cdot Si}_2\text{O}_6$, plagioclase $(\text{Na, Ca}) \cdot (\text{Si, Al})_4\text{O}_8$, magnetite $\text{Fe(Fe}_2\text{O}_4)$, fayalite $(\text{Fe, Mg})_2\text{SiO}_4$ and hematite Fe_2O_3 [23]. X-ray spectral analysis of the investigated material was carried out on scanning electron microscopes JEOL JSM-7001 and JOEL JSM-6460 LV. Steel-smelting slag from different dump horizons, previously past magnetic separation and restored to a more homogeneous chemical composition, is presented in Table. 1.

The method of calorimetric analysis was used to determine the effect of additives on the hydration of cement stone. The study was carried out using an eight-channel isothermal calorimeter "TAM Air", operating in a milliwatt range. The measurement of the temperature of the cement paste was carried out automatically with an interval of 1 minute. The duration of the analysis was 100 hours, at a temperature of $20 \pm 0.02^\circ \text{C}$.

Table 1. Chemical composition of the dump steelmaking slag (wt.%)

Fe	Mn	Cr	Ti	Si	Ca	Mg	Al	S
12.94	3.08	4.20	0.66	19.71	32.69	9.42	6.08	0.20

With the help of calorimetric analysis, an assessment was made of the total heat release and the rate of change in the heat release of cement during hydration. The results of the studies are shown in Figure 1 and Table 2.

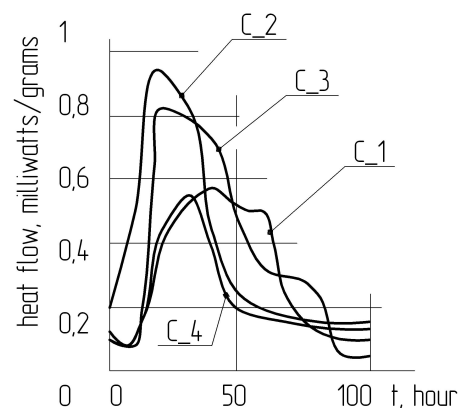


Figure 1. Effect of additives on the rate of heat release of cement.

Table 2. Effect of additives on the rate of heat release of cement.

№ in order	Name of additive	Heat generation, Q, kJ / kg, Conditionally at the age of 100 hours	
1	CEM I 42,5N+ SS+ SP-1	200	C-1
2	CEM I 42,5N+MS+ SP-1	204	C-2
3	CEM I 42,5N+MN+ SP-1	216	C-3
4	CEM I 42,5N+ SP-1	185	C-4

According to the results of calorimetric research, the acceleration of hydration is affected by complex additives, including MK and MN. In this case, the use of slag allows accelerating the hydration of $\beta\text{-C}_2\text{S}$ and contributes to the formation of low-basic weakly crystallized hydrate phases, which is confirmed by the appearance of a second intense peak in the 60-hour region.

The use of all the additives considered leads to an acceleration of the hydration of the cement, as evidenced by an increase in the main intense peak and an increase in the overall heat release effect.

The main criteria for the effectiveness of additives-accelerators, according to state standard ГОСТ 30459-2008, is acceleration the onset of setting by 25% or more at a temperature of 20 ± 5 °C, increase the strength of the solution or concrete by 50% or more on the second day on curing under normal conditions.

The results of studies of the effect of additives on the physic-mechanical characteristics of cement stone are given in Table 3.

Table 3. The effect of additives on the physic-mechanical characteristics of cement stone.

N	ND*	Experiment Response					
		Setting time, min.		Compressive strength of concrete, MPa		ρ , g/cm ³	WA, %
		B	E	2	28		
C-1	20	130	270	19,4	51,4	2,65	5,50
C-2	20	90	200	40,1	67,9	2,50	5,07
C-3	19	120	260	41,5	81,5	2,68	4,56
C-4	18	165	240	18,9	49,8	2,63	4,50

*ND - normal cement density, B - beginning of cement setting, E - cement setting end, WA - water absorption by mass.

Investigation of the effect of additives on the properties of the cement test made it possible to establish that the introduction of additives leads to an increase in its water demand by 11%, which is due to the high specific surface area of the MS and slag. The use of MK leads to an increase in the water requirement of the mixture by only 6%, which is explained by the low dosage of the additive (3.5% by weight) and some with the effect of plasticization, because MK is the dehydration product of kaolin clays.

The use of SS, MK and MS allows to reduce the beginning of setting of cement paste from 21 to 45%, in addition, on the second day of hardening, these additives provide a cement strength increase of more than 50% of the brand strength.

Some increase in water absorption of cement stone with the introduction of additives may indicate an increase in its open porosity, which is associated with an increase in mixing water due to the fine fraction of additives and the formation of pores during the recrystallization of unstable hydrated phases of cement stone.

To confirm the results on cement stone, the effect of additives on the strength of cement-sand bars, manufactured and hardened according to the requirements of state standard ГОСТ 310.4-81, was studied. The rod samples were made on mixtures of equal mobility. The results of the studies are shown in Figures 2 and 3.

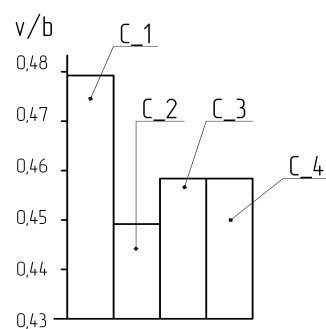


Figure 2. The ratio of water to the binder (v/b).

The physical and mechanical tests of cement-sand samples confirm the results obtained on the cemented stone. So the additive SS allows to increase the strength on the 2nd day of concrete hardening by 91% in comparison with the composition, including only SP-1. Since the strength on the

second day of concrete modified by additives SS and SP-1 is 50% of the strength at grade age, this additive can be used to produce fast-hardening concretes. On the 28th day of hardening, the strength with the use of the SS is 7% higher, compared with the composition comprising only SP-1.

The most effective accelerators of concrete are MS and MK, because they allow to get from 50 to 61% of the brand durability of concrete on the 2nd day of hardening. On the 28th day of hardening strength with the use of these additives is higher by 53-67% compared with the composition, including only SP-1.

4. Conclusions

1. Physico-chemical analysis of the dump steelmaking slag indicates a significant heterogeneity in the distribution of chemical elements and compounds. In this case, after pre-held magnetic separation, recovery and averaging with shutter, slag includes active compounds suitable for use as an active mineral additives (AMA) for concrete, such as silica, calcia, alumina, etc. The steel-smelting slag includes an insignificant amount of harmful impurities, including chromium oxide. Therefore, it is necessary to limit the content of steel-smelting slags to concrete to no more than 10%, and to introduce them together with superplasticizers, in order to reduce the flow rate of mixing water.

2. Since steelmaking slag allows to increase the degree of hydration of cement and the strength of concrete, it can be used as a hardening accelerator for cement concretes.

3. Since the slag allows you to gain more than 50% of the brand strength of concrete for 2 days, it can be used to produce fast-hardening concretes, which will lead to an increase in the formwork turnover at the construction site or plant, accelerate construction time and lead to a reduction in material costs.

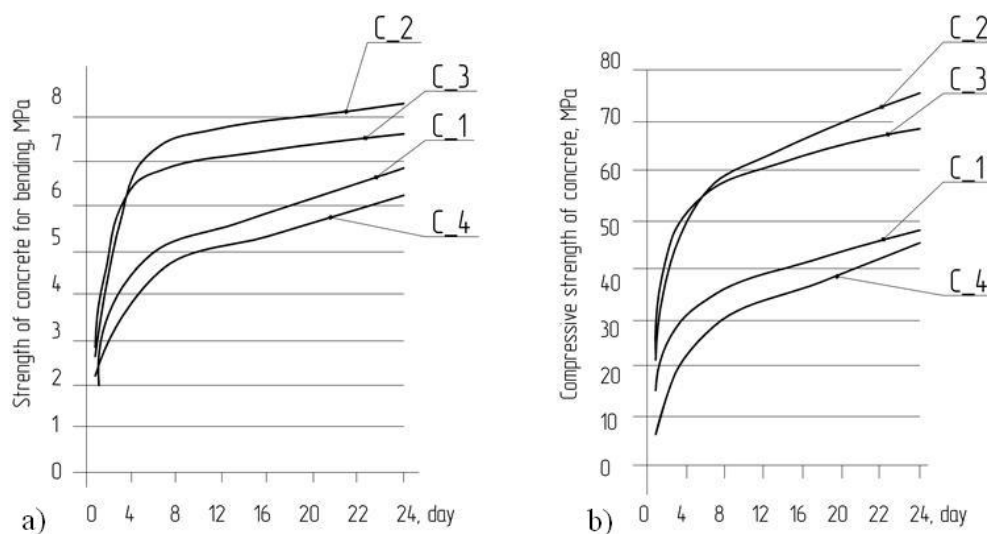


Figure 3. Strength of cement-sand beams: a) Strength of concrete for bending; b) Compressive strength of concrete

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