

UTILIZATION OF FERROUS-MAGNESIUM SLAG FOR PRODUCTION OF BINDING MATERIALS

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Abstract

Utilization of Pechenganickel, Severonickel and Norilsk Nickel smelter plants ferrous-magnesium slag for production of Portland slag cement, lime-slag cement and alkali-activated slag cement has been considered. Influence of mechanical activation of ferrous-magnesium slag, in air and in carbon dioxide atmosphere, on its binding properties has been studied. It has been shown that preliminary mechanical activation in CO₂ results in an increase of compressive strength of alkali-activated slag cement. Interaction between mechanically activated slag and liquid glass has been characterized using SEM and microprobe technique.

Introduction

The ferrous-magnesium slag is a waste of metallurgical processing of copper-nickel and lead-zinc sulphide ores. Stored on large areas, it adversely affects the environment. At present, only a small part of the ferrous-magnesium slag is utilized in road padding, filling of empty space in mines, etc. Utilization of the slag in the production of building materials would reduce the energy consumption of the building industry, extend its raw material base and diminish the load on the environment.

This work is concerned with utilization of the ferrous-magnesium slag of Kola (Pechenganickel, Severonickel) and Norilsk Nickel mining and smelting companies for the production of building materials. Since ferrous-magnesium slag interacts with water, calcium and sodium hydroxide solutions, liquid glass, and a mixture of calcium hydroxide and gypsum, it can be used in the production of lime-slag cement, Portland slag cement and alkali-activated slag binding materials.

Slag Characteristics

The slag of Pechenganickel and Norilsk Nickel Combines is produced by water-stream granulation, and that of Severonickel by air-stream granulation. The mineralogical composition of the slags is as follows: ferrous-magnesium glass – 90-95%, olivine – 2-8%, sulphides – 1-3%. The slags of Pechenganickel, Severonickel and Norilsk Nickel Combines are close in chemical composition and can be considered as members of a single series (Table 1). Besides, the slag contains trace amounts of nickel, copper and cobalt.

Table 1. Chemical composition of slag (in wt. %)

Oxides	Slag, sample №					
	Pechenganickel		Severonickel		Norilsk Nickel	
	1	2	1	2	1	2
SiO ₂	39.40	40.39	43.56	44.59	37.90	44.70
Al ₂ O ₃	7.04	7.20	5.59	5.88	6.57	6.88
Fe ₂ O ₃	3.00	5.58	4.32	2.98	46.30	-
FeO	32.14	26.27	23.21	22.67	-	27.14
CaO	2.13	2.74	5.04	5.51	7.02	4.69
MgO	13.65	11.02	11.99	12.60	5.67	11.74
S	0.25	0.80	0.34	0.44	0.83	0.36

Lime-slag Cement

Granulated ferrous-magnesium slag of the Pechenganickel Combine, limestone and dolomite burnt lime, and gypsum from an Archangelsk region deposit were used as raw materials. Burnt lime was obtained by calcination of limestone and dolomite at 1100°C and 1020°C, respectively. Table 2 shows the content of free calcium and magnesium oxides in limestone and dolomite lime. Chemical composition of raw materials for the production of lime-slag cement is given in Table 3.

It has been found that the optimal content of active (CaO+MgO) in lime-slag cement is 10-15 wt. %, the optimal content of gypsum for cements using limestone lime – 7 wt. %, using dolomite lime – 3-5 wt. % [1]. The bending and compressive strengths of 28 day-cured cement based on limestone lime (CaO_{free}-11.3 wt. %, SO₃ - 3.01 wt. %) of an optimal composition were, 3.2 and 10.7 MPa, respectively. For the cement based on dolomite lime (CaO_{free}- 5.91 and MgO_{free}- 5.04 and 1.54 wt. % SO₃) the corresponding values were, 3.1 MPa (bending strength) and 8.3 MPa (compressive strength).

Table 2. The content of free calcium and magnesium oxides in limestone and dolomite lime

Lime	CaO _{free} , wt. %	MgO _{free} , wt. %
Limestone	89,11	Traces
Dolomite	38,11	26,73

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Table 3. Chemical composition of raw materials for the production of lime-slag cement

Oxides	Chemical composition, (wt.%)			
	Slag	Limestone	Dolomite	Gypsum
SiO ₃	39,40	3,28	16,15	-
Al ₂ O ₃	7,04	1,23	1,57	0,48
Fe ₂ O ₃	3,00	0,20	1,57	0,48
FeO	32,14	-	-	-
CaO	2,13	52,38	28,49	35,96
MgO	13,63	Traces	18,08	-
SO ₃	-	0,80	-	43,37
S	0,64	-	-	-
R ₂ O	1,60	-	-	-
LOI*	-	42,30	35,56	18,90

* Loss on Ignition

The change in strength of lime-slag cement of optimal compositions, based on calcium and dolomite lime, during the process of curing is presented in Table 4. The samples were cured in wet conditions for up to 45 years.

Table 4. The change in strength of lime-slag cement of optimal compositions, based on limestone and dolomite lime, during the process of hardening

Curing time	Strength of lime-slag cement, MPa			
	based on limestone lime		based on dolomite lime	
	compressive	bending	compressive	bending
7 days	4.9	1.7	3.8	1.4
28 days	10.7	3.2	8.3	3.1
90 days	18.3	4.0	10.9	3.7
180 days	22.8	4.9	12.7	3.6
3 years	23.0	4.9	18.0	3.8
4 years	21.5	4.0	23.0	4.5
45 years	20.5	3.9	26.0	6.4

During the first 3 years, both compressive and bending strength of limestone lime-slag cement were increasing. Between 4 and 45 years, the compressive strength decreases but slightly (from 21.5 to 20.0 MPa), the bending strength remaining the same. The strength of dolomite lime-slag cement increases throughout the entire period due to formation of magnesium-containing compounds, since the rate of hydration reaction of MgO_{free} is much slower than that of CaO_{free}.

Portland Slag Cement

Granulated slags of the three mining and smelting combines mentioned above have been studied to develop a technology of Portland slag cement, with slag content varying between 20 and 70 wt. %. The Portland slag cement with slag content of 20 – 50 wt. % is general-purpose one. The Portland slag cement with slag content of 50 - 70% is used for filling of the empty mines. A batch of Portland slag cement has been produced at the pilot plant of the

GIPROTSEMENT Institute, by joint grinding the Pechenganickel slag and clinker. The characteristics of the experimental batch of the Portland slag cement are as follows: the clinker-to-slag ratio: 1:1; gypsum content – 2-7 wt.%; specific surface area 400 ± 20 m²/kg.

The data of Table 5 suggest the granulated copper-nickel slag can serve as a hydraulic additive for the production of Portland cement and Portland slag cement applicable for the production of various-purpose concretes, including for mine workings filling.

Table 5. Strength of concrete using Portland slag cement (the slag of Pechenganickel Combine, MPa)

Curing time, days	Articles		
	Slabs, covering	Slabs	Conduit
After steaming			
0.6	22.9	13.8	18.8
7	26.2	14.5	29.6
28	29.6	20.1	31.1
90	35.2	23.5	32.2
Normal hardening			
7	27.2	16.4	23.6
28	38.0	23.5	28.5
90	40.5	24.2	30.6

Alkali-Activated Slag Binding Materials

As shown by research carried out at Kola Science Center of Russian Academy of Sciences, the slag of the Pechenganickel Combine hardens under normal conditions in case of alkaline activation (see, for example, [2,3]). The maximum strength of alkali activated slag (AAS) binding materials can be achieved using the following conditions: Na₂O - 3÷5% (in relation to the mass of fine-ground slag), siliceous modulus of liquid glass - 1.5÷2.0, water-to-slag ratio of 0.20÷0.23.

We have studied the effect of mechanical activation (MA) and MA medium, on the properties of the AAS binding materials. MA of the Pechenganickel slag was carried out in a laboratory centrifuge planetary mill AGO-2 at 40 g centrifugal factor in air and in carbon dioxide atmosphere (P(CO₂)=10⁵ Pa). Specific surface area of the ground slag was measured by air permeability method. During MA experiment the vial with sample (10 g) and balls (200 g) after every 30 sec of grinding was repeatedly filled with CO₂ from balloon at P=10⁵ Pa. The samples prepared by mixing of ground slag and liquid glass using described above conditions were molded and cured at room temperature in a humid atmosphere.

Slag specific surface area (S_{sp}) change in the course of MA in air and in CO₂ atmosphere is shown in Fig. 1. It is seen that for up to 200 sec of MA S_{sp} is virtually not sensitive to the grinding medium, then MA in CO₂ results in slightly slower S_{sp} values.

Compressive strength values of AAS samples prepared using slag ground in air and in CO₂ to approximately 450 and 750 m²kg⁻¹ are given in Table 6. For all curing times MA of slag in carbon

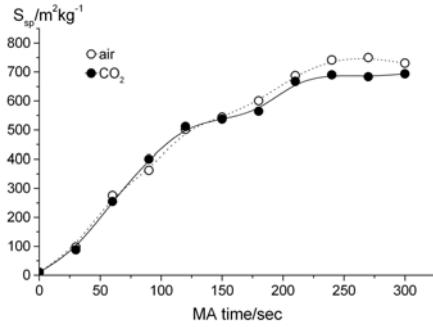


Figure 1. Specific surface area (S_{sp}) of Pechenganickel slag as a function of mechanical activation time in air (open symbols) and in CO_2 atmosphere (solid symbols).

dioxide atmosphere results in larger compressive strength at comparable S_{sp} values in comparison to MA in air. It is known that grinding of Ca and Mg silicates is accompanied by enhanced sorption of carbon dioxide from the environment by the mineral particles in the form of carbonate ions [4]. Increased carbonization of the outer layer of the slag particles during MA in CO_2 obviously leads to rise of its reactivity in hydration processes.

Table 6. Compressive strength (MPa) of alkali activated slag samples

S_{sp} of slag m ² kg ⁻¹	MA atmosphere	Curing time, days		
		7	28	180
410	Air	40.1	51.9	78.6
450	CO_2	41.5	59.9	80.9
750	Air	55.5	63.2	73.6
730	CO_2	66.6	107.8	104.4

Figures 2 and 3 demonstrate typical polished surfaces of cured AAS samples. It is clearly seen that in morphological characteristics, the samples produced in carbon dioxide (Fig. 2) and in air (Fig. 3) are similar. Along with polydisperse, irregular-shaped particles distributed throughout the volume of the hardened cement phase (the dark background) one can see spherical formations with the diameter of 30-200 μm (Fig. 2(a) and 3(a)). The spherical inclusions may have appeared as the result of the following processes. The paste, when poured into the mould, is penetrated by air bubbles. The emerging pores get gradually filled with the liquid phase containing microparticles of slag, which later hardens. The presence of slag microparticles is visible in Fig. 3(a).

It is interesting to trace the effect of the MA atmosphere on the composition of cement phase during the hardening of AAS samples. According to XRD data (not shown), the structure of new formations is colloid or pseudo-crystalline one. Table 7 shows the averaged composition of new formations in AAS samples obtained by grinding slag in CO_2 and in air according to the microprobe analysis data, without account for the water. Analysis was performed at points of inter-grain spaces, in cracks filled with the cement phase, and in spherical inclusions.

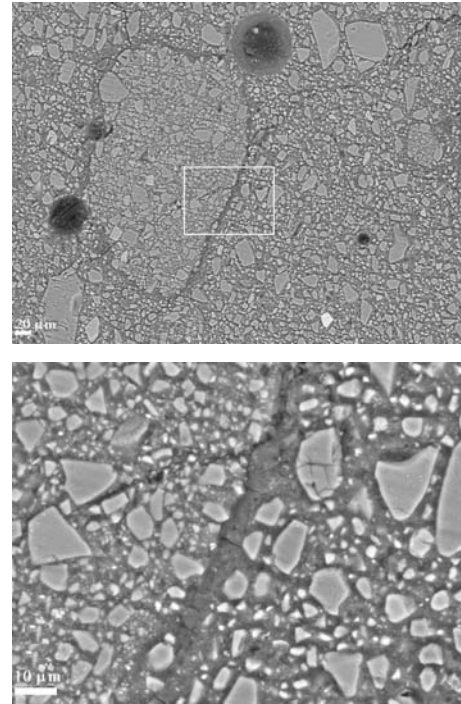


Figure 2. SEM images of cured alkali activated slag samples based on the slag ground in carbon dioxide (Fig. 2(b) – the highlighted rectangular area in Fig. 2(a) (top image))

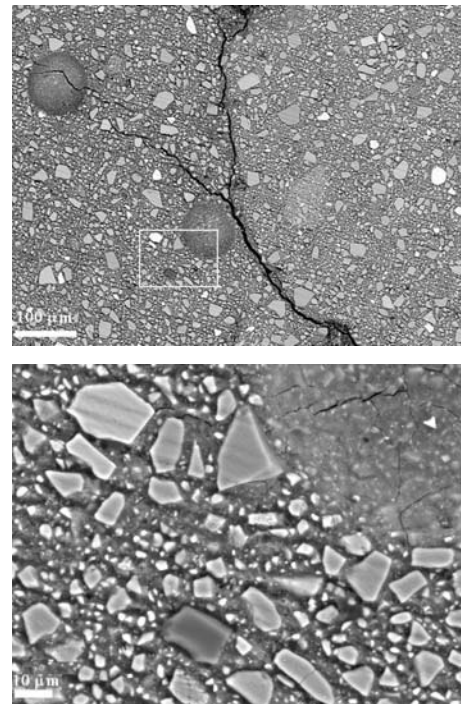


Figure 3. SEM images of cured alkali activated slag samples based on the slag ground in air (Fig. 3(b) – the highlighted rectangular area in (Fig. 3(a) (top image))

Table 7. Composition of cement phase in alkali activated slag samples (wt. %) according to the microprobe analysis data (without account for H₂O)

Constituent	Grinding medium			
	CO ₂		Air	
	Location of the point of analysis			
	In the crack	Between the grains	Spherical inclusions	Between the grains
CO ₂	19.1	16.1	16.9	8.3
MgO	7.8	6.8	9.4	7.8
SiO ₂	41.2	41.2	40.1	41.8
FeO	16.2	22.7	16.9	25.7
Al ₂ O ₃	6.0	5.8	7.0	8.3
CaO	4.6	2.7	2.2	2.8
Na ₂ O	3.4	2.9	6.3	3.5
K ₂ O	1.1	0.91	0.75	0.84
TiO ₂	0.70	0.81	0.52	0.79

As it follows from Table 7, with CO₂ as the grinding medium the compositions of the cement phase at the points of analysis are similar. For the AAS sample obtained using slag ground in air the main difference in the composition of the cement phase in comparison to that with CO₂ as MA atmosphere is a lower (2 – 2.5 fold) carbonate groups content. Apparently, the effect of adsorbed carbon dioxide on the strength of AAS samples is due to the more intensive interaction of liquid glass with the outer, highly reactive carbonized layer of the ground slag particles. It is not ruled out as well that in case of CO₂ as MA atmosphere sodium silicate solution in contact with the ground slag is additionally decomposed forming sodium carbonate and silica gel. The presence of the latter accelerates the formation of hydrosilicates.

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