



# Use of Slags in the Production of Portland Cement Clinker

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**Abstract.** The use of technogenic raw materials as input products in the production of portland cement provides for considerable reduction of energy consumption during clinker burning. The study reveals the mineral formation features caused by the change of the liquid phase composition and crystallization of silicate phases. The use of slags in raw mixes increased the mechanical strength of cements by over 50%.

**Keywords:** Slag · Cement · Clinker phases · Microstructure

## 1 Introduction

Any waste can be considered as secondary material resources, which may be fully or partially (as additives) used in production (Klassen et al. 2003). In terms of their physical and chemical properties, slags are similar to igneous rocks used in the production of construction materials. Being exposed to high-temperature treatment and containing basic calcium silicates, they considerably reduce fuel consumption during clinker burning (Vvedensky 1978; Kopeliovich et al. 1998).

## 2 Methods and Approaches

The study included the methods of chemical analysis of input products and clinkers carried out according to GOST 5382-93. The X-ray phase analysis was performed via the powder diffraction technique using DRON-3 M. The polished sections were studied in reflected light using a universal polarizing microscope NU-2 by Karl Zeiss Jena. The etching of polished sections was carried out via the universal etching agent, i.e. M.I. Strelkov's reagent. The thermal test was carried out using the scanning calorimeter STA 449 F1 Jupiter® by NETZSCH in inert media. Thin slag structures were studied on a scanning electron microscope MIRA3 TESCAN.

### 3 Results and Discussion

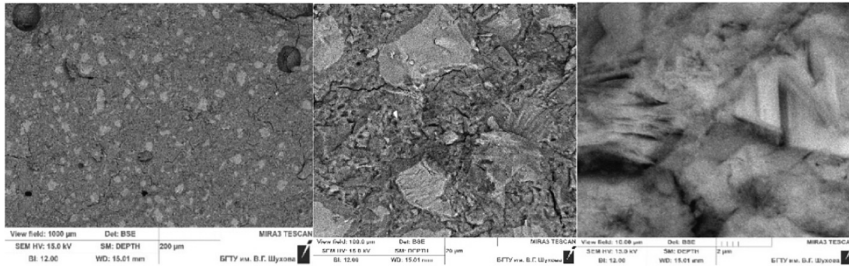
Besides others, the LLC South-Ural Mining and Processing Company utilizes smelter slags as input products. The chemical composition of slags and raw materials given in Table 1 indicates a possibility of replacing the natural constituent, i.e. clay, and slightly reducing the consumption of a carbonate component.

**Table 1.** Chemical composition of input products, %.

<i>Raw mix components</i>	<i>CaO</i>	<i>Al<sub>2</sub>O<sub>3</sub></i>	<i>Fe<sub>2</sub>O<sub>3</sub></i>	<i>SiO<sub>2</sub></i>	<i>MgO</i>	<i>PPP</i>
Blast furnace slag	39.70	8.80	2.09	39.08	4.08	0.17
Open-hearth slag	32.36	3.96	21.20	19.76	11.18	3.61
Limestone	52.12	0.24	0.18	1.53	0.48	43.11
Clay	7.57	12.8	6.32	50.45	3.97	12.80

According to X-ray phase analysis, the phase composition of dump blast furnace non-granulated and granulated slag differs only in the intensity of new crystal growths. The main identifiable minerals include gehlenite, akermanit, quartz and melilite minerals.

The DTA method of a dump blast furnace slag in the range of 600–700 °C demonstrates a slight vague exo-effect caused by ferrous iron oxidation. The same temperature range indicates the decomposition of a secondary calcium carbonate followed by the insignificant loss of a sample mass. At 840–900 °C the glass phase is crystallized with further heat release.



**Fig. 1.** Microstructure of dump blast furnace slag

The process of devitrification for the blast furnace granulated slag has more expressed exothermic maximum, which is caused by high concentration of a glass phase.

The open-hearth slag acts as a correcting ferrous additive, besides hematite and magnetite is rich in calcium ferrite, monticellite, diopside and magnesium oxide in the form of a periclase.

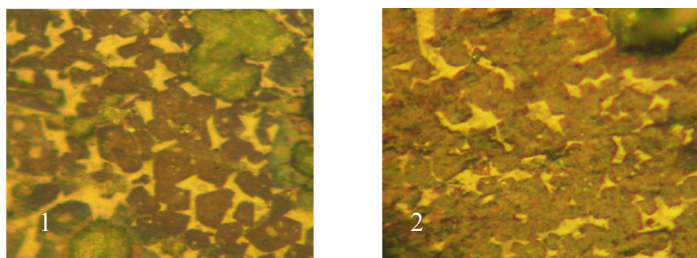
Figure 1 shows the structure of dump slags representing the conglomerate of crystalline phases and melting particles. The phase formation analysis was carried out in raw mixes having similar chemical composition with various ratio of clay and slag components (Table 2).

**Table 2.** Raw mixing ratio

Raw mix, No.	Limestone	Clay	Blast furnace slag	Open-hearth slag
1	75%	22%	0%	3%
2	61%	0%	33%	6%

The clear exo-effect is observed in a clay-based raw mix (No. 1) at 1227 and 1256 °C caused by the formation of belite phase, as well as endothermal melting effects at 1288 and 1300 °C. According to (Kougiya, Ugolkov 1981), the exotherm of belite mass crystallization at higher temperatures improves the synthesis of alite and its formation in a fine-crystalline state.

Within sintered materials cooled at 1250 °C the crystallization of phase C3A and C4AF is recorded, the reflection intensity of aluminat phase considerably increases with temperature rise. When clay is replaced with slag in a mix the exothermal processes characterizing the formation of silicate phases are weakly expressed within the range of 1000 and 1200 °C. The melting in these mixes is recorded at 1259 and 1308 °C.



**Fig. 2.** Micrographs of polished section of sample clinkers: identifications are given in Table 1

Within sintered materials №2 cooled at 1250 °C the aluminat phase prevails thus leading to the appearance of ferrous phases – C6A2F and C4AF with temperature rise. The basic clinker fusion is formed at 1327 °C. These differences in A-F formation are clear with the increase of slag concentration in raw mixes. The gehlenite and mayenite is observed at 1200 °C in clay-containing mixes along with belite phase, which is not observed in slag-containing samples. The introduction of slag intensifies the formation of belite phase at early burning stages. Some changes in the composition of a ‘liquid’ phase, which increase its temperature and molten viscosity with the increase of slag composition in a raw mix, also affect the features of crystallization of clinker phases.

Figure 2 shows micrographs of polished sections of sample clinkers, which demonstrates the crystallization difference of alite phase.

Clinkers from clay-based raw mixes have clear monodispersive texture. Clinkers from slag-based raw mixes are different in terms of the number of alite growths.

The strength of cements was defined in small samples from cement paste (1:0) with water-cement ratio of 0.28. The results given in Table 3 show that the use of slags in raw materials instead of clay positively affects the activity of clinkers. The strength improvement within a 28-day interval at full replacement of a clay component with slag made 62%. The heat burning input of limestone-slag mixes may be reduced by over 0.85 MJ/t.

**Table 3.** Cement stone strength, W/C = 0.28

<i>Mix No., Identifications are given in Table 1</i>	<i>Tensile strength, MPa, days</i>		
	2	7	28
1	7	14	32
2	30	37	52

## 4 Conclusions

The integral analysis of raw materials and calcined products indicates the possibility of full replacement of clay in a raw mix for the production of portland cement clinker. This contributes to the improvement of qualitative parameters of a calcined product and to the reduction of its production cost.

**Acknowledgements.** The study is implemented in the framework of the Flagship University Development Program at Belgorod State Technological University named after V.G. Shukhov, using equipment of High Technology Center at BSTU named after V.G. Shukhov.

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