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Energy Saving and Increasing the Strength of Cement Using Steel Slag as a Raw Material Component

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Abstract: Industrial tests showed the possibility of saving heat for clinker burning and reducing the emission of carbon dioxide into the atmosphere with up to 20% of slag of Oskol Electric Steel Combine (OESC) as a raw material component. However, there is a decrease in cement strength and technological difficulties arise caused by the necessity to prepare additional sludge with high coefficient of saturation (CS). Therefore, there is an alternative solution, which consists in getting batch of molten slag and chalk with a coefficient of saturation close to CS of raw sludge directly in the dumps of OESC. The method may provide not only the desired chemical composition of the batch and partial decarbonization chalk on cooling slag, but excluding the preparation of additional sludge with high CS and improve the strength of cement. Additional savings of heat for clinker burning may be up to 25%.

Key words: Energy saving · Saving heat · The molten slag · Decarbonization of chalk · Slag-containing raw mix · Process of clinker formation · Strength of cement

INTRODUCTION

Building materials industry belongs to one of the largest energy consumers and takes the third place after the thermal and metallurgical industries, therefore questions of energy savings are paramount. Burning is the most energy-intensive and difficult technological process in the production of cement clinker. The cement industry is one of the few industries in which enterprises the large number of waste from other industries can be used. In a related study, aimed at saving fuel, energy and material resources, represents an important theoretical and practical problem [1-3]. One of the efficient methods to solve this problem is to use a technogenic waste that has already been exposed to high temperature during production of the main product and contain a part low-basic calcium silicates [4-11]. The use technogenic materials will improve the environmental conditions and prevent further pollution by substances contained in waste or formed as a result of their storage [12]. One such type of waste is hydraulically inactive steel ungranulated slags of Oskol Electric Steel Combine (OESC).

Industrial Tests on the Use of Slags of Oesc as a Raw Component: Industrial tests on a closed joint-stock company "Oskolcement" (JSC "Oskolcement") have shown that on use of slag of OESC as a raw component considerable savings of heat for clinker burning are achieved [13]. Thus, upon edition into the furnace 12,5 and 19,2% calcined slag heat consumption decreased from 6270 to 5640 and 4990 kJ/kg clinker heat savings was 630 and 1280 kJ/kg, or 10,1 and 20,2%, respectively (Table 1). The volume of CO_2 in the waste gases fell from 1,18 to 1,07 and 0,95 nm^3/kg, that is 9,3 and 19,5%, respectively. However, using slag somewhat decreased cement strength in 28 days age hardening, namely from 51,5 to 47,2 and 45,2 MPa respectively. Furthermore, technological difficulties arose due to the necessity to prepare an additional sludge with high coefficient of saturation (CS), because the CS of slag is within 0,38-0,45.

Therefore, we propose an alternative solution is to obtain batch of molten slag and chalk with a coefficient of saturation (CS) close to ordinary sludge directly into slag pits of OESC. In future, it is recommended to submit the resulting partially decarbonise slag-chalk batch with ordinary sludge plant from the cold end of the furnace.

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Table 1:The main parameters of the furnace 5 × 185 m JSC "Oskolcement"

Name	Dimension	Value		
The share of burnt slag in clinker	%	0	12,5	19,2
Saturation coefficient:				
- slag	–	–	0,42	0,42
- sludge		0,91	1,01	1,05
- clinker		0,91	0,91	0,91
Heat consumption	kJ/kg	6270	5640	4990
Heat savings	kJ/kg	–	630	1280
	%	–	10,1	20,2
Waste gases:				
- the amount of CO_2	nm^3/kg	1,18	1,07	0,95
- reducing the amount of CO_2	%	–	9,3	19,5
Strength of cement:				
- 3 days	Mpa	30,3	31,2	24,1
- 28 days	MPa	51,5	47,2	45,2

Using the Heat of the Molten Slag: At present, according to technological regulations electrometallurgical combine with a temperature of molten slag 1500-1550°C is poured into slag pits where is exposed to water cooling. Proposed to pour the molten slag on the backsheet wet chalk, which will result not only provided the desired chemical composition of the charge, but also can be realized simultaneously drying and partial decarbonization chalk on cooling slag. This leads to further savings of fuel, which can reach 25%. In industrial conditions the degree of calcination chalk can vary widely. Therefore, further work was to study the influence of the degree of calcination of chalk for clinker formation, properties obtained clinker and cement strength when steel slag are used as a raw component.

Obtaining and Properties of Clinker Using Partly Decarbonized Slag-containing Raw Mix: As noted above, it is advisable to use the slag-chalk batch with a coefficient of saturation close to CS of ordinary sludge. Industrial tests that were carried out have shown that by supplying slag to furnace greatly facilitated sintering of furnace clinker and even with CS = 1 achieved a complete assimilation of lime. In this case, the silicate phase of the clinker was represented only by alite. Furthermore, with increasing CS observed increase of strength of cement in especially in the early stages. It is therefore proposed to prepare a batch CS = 0,95 ± 0,05; when you add it to the ordinary raw mix plant with CS = 0,91 saturation coefficient of clinker will be in the range 0,91-0,95. To investigate the clinker properties and clinker formation processes were used the raw materials that shown in Table 2. Phase composition of slag of OESC depends on the cooling conditions. On water cooling slag is mainly represented by hydrous silicate calcium $C_2SH(A)$, on air cooling – γ-C_2S. Considering irregularity of the cooling of the slag, it simultaneously contains $C_2SH(A)$ and γ-C_2S. Other phases are: C_7MS_4, C_5MS_3, FeO, Fe_2O_3, $C_2(A,M)S_2$, $CaCO_3$, $2C_2S{\bullet}CaCO_3$, $Ca(OH)_2$, MgO. Also for the first time we revealed in the slag the presence of solid solutions of 0,24 MgO•0,76 FeO with diffraction reflections d = 2,14 and 2,48 Å [14].

The optimum ratio for a given composition of the starting components was 54% of slag and 46% of chalk. In the test mix for 20% of calcined slag towards to the clinker content of ordinary raw mix and slag-chalk batch were, respectively, 74% to 26%. For comparison investigated control clinker obtained by burning of ordinary industrial raw mixture of the following components: chalk – 80,2%, clay – 15,6%, bauxite – 2,6% massive sulfide cinders – 1,6%.

Estimate mineralogical composition indicates that experienced clinker slightly differs from the reference by silicate minerals but contains less tricalcium aluminate and more tetracalcium alyumoferrita that caused by an increased iron oxide content in the slag (Table 2).

As previously noted, in industrial conditions, the calcination chalk in the interaction with the molten slag may be varied within wide limits, so research laboratory synthesized three slag-containing raw mixes #1-3 with a degree of decarbonization chalk 0, 50 and 100% (Table 3).

In addition, two additional slag-containing raw mix #4-5 are synthesized. It is connected with the fact that by supplying partially decarbonized slag-chalk batch from the cold end of the furnace with ordinary plant sludge contained therein free lime in an amount of 4,8% and 9,5% hydrates with the formation of $Ca(OH)_2$.

Table 2: Characteristic of components, raw mix and clinker

Material	Content,% (wt) LOI	CaO	SiO_2	Al_2O_3	Fe_2O_3 (FeO)	MgO	CS	n	p
Slag of OESC	10,0	38,8	23,3	4,1	15,1 (9,8)	8,1	0,41	1,2	0,3
Chalk	42,2	52,8	3,7	0,8	0,4	0,1	–	–	–
Slag-chalk batch	24,8	45,2	14,3	2,6	8,4 (5,5)	4,4	0,95	1,3	0,3
Experimental raw mix	32,3	43,5	14,1	3,4	4,2 (1,4)	1,7	0,93	1,9	0,8
Control raw mix	35,0	43,0	14,0	3,7	2,6	0,7	0,92	2,2	1,5
Clinker:									
- experienced	–	64,3	20,8	5,0	6,2	2,5	0,93	1,9	0,8
- control	–	66,2	21,5	5,7	4,0	0,9	0,93	2,2	1,5

	Mineralogical composition, %			
	C_3S	C_2S	C_3A	C_4AF
- experienced	62,4	12,5	3,0	18,5
- control	61,9	14,9	6,5	12,2

Table 3: Characteristics of slag-containing mixes

Name	Slag-containing mixes #1	#2	#3
The degree of decarbonization of chalk in slag-chalk mix, %	0	50	100
The share of decarbonated chalk in the experimental raw mix, %	0	8,5	17
The content of CaO_{sc} in slag-containing mix, % of clinker	0	4,8	9,5
The content of $Ca(OH)_{2sc}$* in slag-containing mix, % of clinker	0	#4	#5
		6,3	12,6

here and henceforth - the content of free lime in the experimental slag-containing mix.

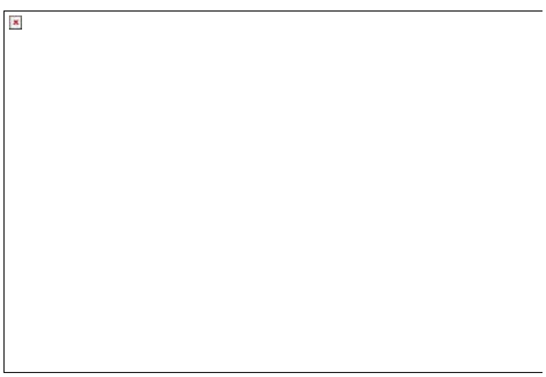

Fig. 1: The phase composition of clinker, depending on the amount of CaO_{sc} and $Ca(OH)_{2sc}$ in the slag-containing raw mix

Burning experienced and control clinkers are held at 1450°C with a 30-minute delay in the laboratory electric furnace. X-ray analysis was held to study the effect of CaO_{sc} and $Ca(OH)_{2sc}$ in slag-containing raw mix on the process of clinker formation. The results showed that same chemical composition of clinker mineralogical composition differs significantly from each other depending on the content CaO_{sc} in the raw mix with the (Fig. 1). In the absence of slag containing CaO_{sc} clinker raw mix has a smaller content of alite and tricalcium aluminate, as evidenced by less intensive reflection C_3S (line 3,04 Å) and C_3A (line 2,70 Å) and less distinct crystallization silicate minerals that confirmed by more blurred peaks C_3S and C_2S (line 2,75 Å). Aluminium-ferrite phase is enriched with iron oxides and is presented in the form of C_6AF_2 (line 2,66 Å) and C_2F (line 2,68 Å). When decarbonization slag-chalk batch of 50%, which match the content in the feed mixture CaO_{sc} = 4,8%, the number of alite and belite in the clinker increases and become close to the reference clinker by the degree of crystallization of minerals. However, the intensity of the reflections of calcium silicates in it is slightly smaller (lines 3,04 and 2,61 Å). The presence of $Ca(OH)_{2sc}$ in the slag-containing raw mix has a similar effect on the mineralogical composition of the clinker.

XRD data correlate well with the results of research of the microstructure of clinker. Thus, clinker structure has a pronounced more frequent clusters of fields uncrystallized belite grains in the absence of CaO_{sc} in slag-containing raw mix (Fig. 2).

The crystallization of minerals alite is predominantly medium, coarse, with a length of grains 40-50 micron. Clinker with the content of CaO_{sc} = 4,8% in the raw mix has a fine grained monadoblastic structure with precise crystallization of alite and belite and uniform distribution of the grains in the amount of the intermediate phase.

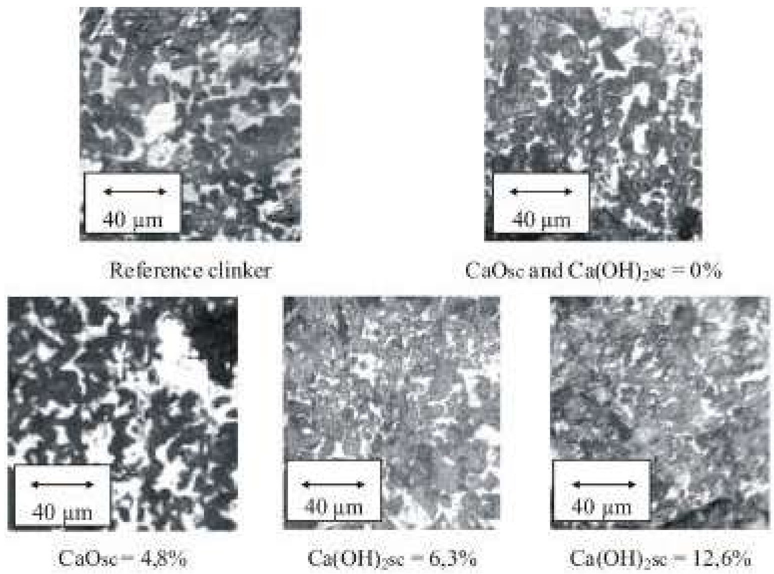

Fig. 2. Clinker microstructure depending on the amount ?aOsc and Ca(OH)2sc in slag-containing raw mix

Alite crystals characterized by a rectangular prismatic shape with an average length of 10-15 microns, which is 3-4 times lower than in clinker without CaO_{sc} in the original raw mix. Intermediate phase is considerably larger, structure is less porous. Incorporating small (to 5 microns) alite grains are observed in clinker pores. A similar dependence was observed in the presence of $Ca(OH)_{2sc}$ in slag containing raw mix. Increasing amounts of $Ca(OH)_{2sc}$ also leads to the formation of clinker fine-grained structure.

The strength of the cement depending on the degree of decarbonation of chalk raw slag-containing mix.

Cement strength is determined by the adopted methodology in small samples [15]. Experienced, control and industrial clinkers was milled with 5%-gypsum in a laboratory ball mill until equal specific surface, 300 ± 10 m^2/kg. Cube samples were prepared from these cements in normal density test with edge size equal 1,41 cm which harden in standard conditions for 2, 7 and 28 days. Based on a comparison of test results for the industrial cement to GOST 310-76 and in small samples was set the conversion factor, which amounted to 0,5.

Analysis of test results showed the strength of cement (Table 4) that for the same chemical composition of the experimental mechanical properties of cement of clinkers produced with different contents CaO_{sc} the slag-containing raw mix differs significantly. On the dependence of the strength of the cement on the degree of pre-decarbonation of chalk has of an extreme character.

Thus, when the content of CaO_{sc} = 4,8% in the slag-containing of the raw mix cement has the highest strength, which is equal to 28 days of hardening and even exceeds strength of the reference cement. Considering that in the experimental clinkers is design low content C_3A = 3,0% and increased C_4AF = 14,8%, it is natural that there is some reduction in strength in the early hardening time as compared to the control sample. At the same time in all the experimental cements there is a high rate of increase of the strength from 2 to 7 days, particularly in the sample content in the raw mix CaO_{sc} = 4,8%. The strength of this cement to 7 days is up to 57,7 MPa, what is 98% of the 28-day strength and superior to the final strength of the control cement equal 54,9 MPa. A similar effect on strength cement exerts presence of $Ca(OH)_{2sc}$ in the slag-containing raw mix.

CONCLUSION

The results indicates the possibility of saving heat for clinker burning and improvement of the strength of cement with using up to 20% of slags of OECS as a raw component. It is established that the optimum content of free lime in the slag-containing raw mix is about 5%, that corresponds to 50% degree of decarbonation of chalk in the slag-chalk batch. Hydration of free lime contained in the slag-containing raw mix in the kiln of wet method of production will not negatively impact on the clinker formation process, properties of clinker and cement strength.

- Industrial tests on JSC "Oskolcement" have shown that the use of up to 20% of slag of OESC as a raw component achieves a reduction of heat consumption for clinker burning by 20% and reduce CO_2 into the atmosphere by 19,5%. If you are using molten slag for drying and partial decarbonation for the wet chalk on sailings of OESC then savings in heat for clinker burning can be achieved up to 25%.
- Partial decarbonization of chalk in the slag-containing raw mix significantly affects on the phase composition and microstructure of the clinker. At optimal levels of free lime ~ 5% the formation of fine-grained structure of clinker with increasing amounts of C_3S and C_3A by compared with the calculated is provided and offset alumin-ferrite phase in the direction of the enriched iron oxides.
- The possibility of increasing the strength of cement by partial decarbonation of chalk by heat of the molten slag. Cement, slag-containing produced from the optimum raw mix with the content of free lime ~ 5%, is very strong in all periods of hardening. In the 7-day-old it is 57,7 MPa or 98% of 28-daily strength and durability exceeds strength of the control sample equal 54,9 MPa at 28 days of hardening.
- Hydration of free lime contained in the slag-containing raw mix in the kiln of wet method of production will not negatively impact on the clinker formation process, properties of clinker and cement strength.

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