Peculiarities of physical and chemical processes of clinker formation in raw mixes with increased content of magnesium oxide in presence of barite waste

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Peculiarities of physical and chemical processes of clinker formation in raw mixes with increased content of magnesium oxide in presence of barite waste

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Abstract. The article considers the influence of barite waste on clinker formation processes in raw mixes with the increased content of magnesium oxide. A by-product of the barite concentrate manufacture of Tolcheinskoye deposit has been used as a barite waste, its predominant content of barium sulphate $BaSO_4$ amounts to 76,11%. The impact of BaO and SO_3 has been revealed, particularly the impact of barium oxide on clinker formation processes in raw mixes with the increased content of magnesium oxide. It has been clarified that the addition of barite waste into a raw mix causes the formation of dicalcium silicate in two modifications, reduces the amount of alite and influences on the composition of tricalcium aluminate. Barium mono-alluminate is formed in the composition of the intermediate material. Solid solutions with barium oxide are formed in clinker phases. The authors have determined the saturation speed of calcium oxide in magnesium-bearing raw mixes with saturation coefficient (SC) 0,91 and 0,80 in the presence of 2 and 3% barite waste in the temperature range 1300-1450°C.

1. Introduction

The cement industry is the most energy intensive of all manufacturing industries. The electricity costs of operating plants are rather high so the task aimed at saving energy resources seems to be of theoretical and practical importance. Clinker grinding is one of the most energetically demanding part of the cement manufacturing process. The clinker containing magnesium oxide within 3-5% is characterised by hard grindability that results in the increase of power consumption while grinding clinker, the increase of grinding media wear and the increase of the timeframe for remedial maintenance of cement grinding mills. This problem attracted a lot of interest among researchers [1], who studied the influence of mineralogical, chemical and physical properties on grindability of industrial clinkers which are high (more than 5%) in MgO. In addition, it is necessary to notice that having MgO in a raw mix, the clinker formation processes are accelerated [2-4], the conditions of protective coating formation in the furnance are improved [5], and the lining life is increased [6]. In the Russian Federation, the content of magnesium oxide in clinker is regulated by the State Standard and it is limited to 5%. In some countries for particular factories this limitation is higher and amounts to 6% or even 6.5%.

The cement industry is one of the few industries where it is possible to use a large amount of industrial wastes of different productions [8-12]. The reasonability to apply wastes is determined by

the development of resource- and energy-saving technologies and by the necessity of environmental improvement [13-15]. One kind of the wastes is a barium-bearing waste.

The aim of the given paper is to study the influence of barium waste on the clinker formation processes in raw mixes which are high in MgO (more than 2.5%).

2. Materials and methods

In order to conduct the research, the raw materials by Magnitigorsk and Angarsk cement plants have been used. The rated chemical composition of laboratory raw mixes and clinkers is presented in Table 1.

Table 1. The chemical composition of raw mixes and clinkers, %

Chemical composition of raw mixes								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Loss on ignition	SC
Magnitogorsk	13.15	4.09	2.17	41.09	2.78	0.09	35.94	0.91
Angarsk	14.77	3.97	3.06	40.71	3.37	0.26	33.24	0.80
The chemical composition of clinkers								
Magnitogorsk	20.53	6.39	3.39	64.14	4.34	0.15	–	0.91
Angarsk	22.12	5.95	4.58	60.98	5.05	0.39	–	0.80

The raw mixes based on the materials by Magnitogorsk cement plant were calculated for the saturation coefficient (SC) which was equal to 0.91. The saturation coefficient of the mix prepared from the raw materials by Angarsk cement plant was equal to 0.80. These raw materials contained the increased amount of magnesium oxide which resulted in clinker with high content of magnesium oxide, the amount of which approximated the upper bound of MgO limitation in clinker.

Originally, in order to study the influence of BaO on the grindability of the magnesium-bearing clinker, the mixes based on the raw materials by Magnitogorsk cement plant were made. The mixes were distinguished by the amount of barite waste ranging from 0.5 to 3% (in increments of 0.5%). In order to study the influence of a big amount of BaO on the cement properties, the concentration of the addition agent was increased up to 5%.

3. Experimental part

The research conducted on the raw materials by Magnitogorsk cement plant revealed the reasonability to apply this addition agent equal to 2, 3 and 5% in number. Therefore, the mixes based on the raw materials by Angarsk cement plant were calculated according to the stated content of barite waste.

Thus, within the scope of each series, the compositions distinguished by the amount of barite waste and MgO content were studied.

As a barium-bearing addition agent the authors used barite waste representing a finely-dispersed powdery product obtained when producing barite concentrates.

The mineralogical composition of the waste is mainly of barite $BaSO_4$. The basic oxides in the waste are BaO (50.00%) and SO_3 (26.11%), there are also SiO_2 (11.51%); CaO (5.75%); Al_2O_3 (1.20%) and Fe_2O_3 (0.50%); loss on ignition is 3.39%.

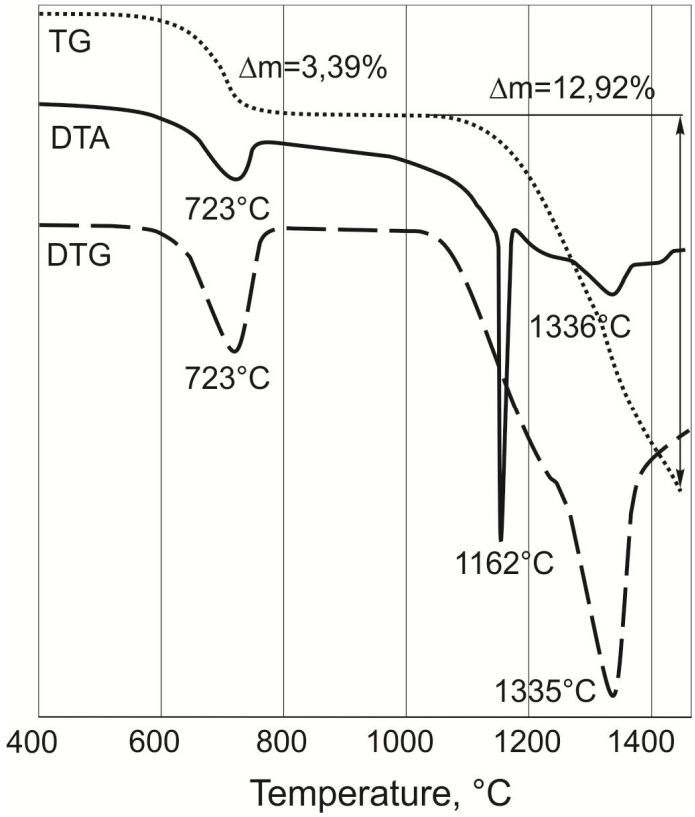

Figure 1. The complex thermal analysis of barite waste

The transformations occurring with barite waste when heated (Fig. 1) have been studied. At temperature 723ºC, $CaCO_3$ resoves when kept at temperature 1162ºC, barite changes from a monoclinic modification into a rhombic one that considerably increases its capacity of reaction.

It is known that pure $BaSO_4$ melts at 1580°C. The complex thermal analysis revealed that in the waste, $BaSO_4$ starts resolving in the presence of acid oxides at temperatures between 1100-1200°C with the loss of SO_3. With increasing temperature, the weight loss also increases and at temperature 1450°C, it reaches the value of 12.92% that amounts to 50% of the total content of SO_3 in the waste.

The studies of mineral formation processes in clinkers were conducted by means of X-ray diffraction analysis of the sintered materials obtained.

It is known that Ba^{2+} ion, being an analogue of Ca^{2+}, replaces the latter in the structure, first of all, of calcium silicate [16]. However, according to isomorphous replacements $Ca^{2+} \leftrightarrow Ba^{2+}$, it is possible to suggest that barium can be present in silicates as well as in aluminates and calcium aluminate ferrites since calcium is a component of any clinker phase.

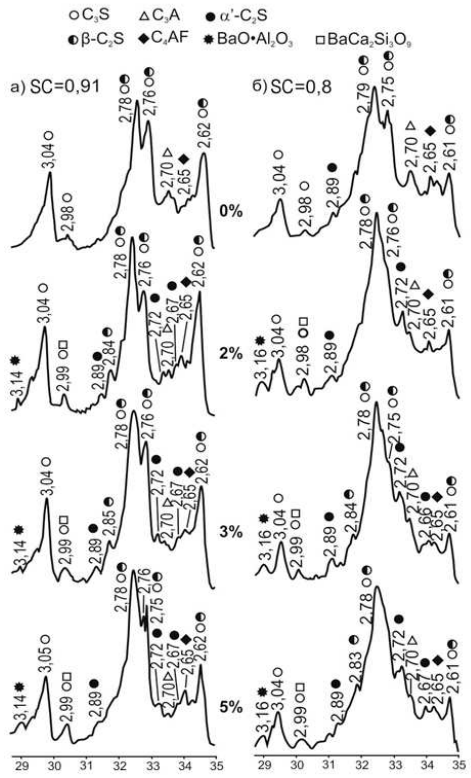

Figure 2. The phase composition of Magnitigorsk (a) and Angarsk (b) clinkers depending on the amount of barite waste

When studying the influence of barite waste on the clinker formation process in raw mixes with the increased content of MgO, it was revealed that there were all clinker phases present in clinkers; free BaO was not found (Fig. 2). The addition agent of barite waste reduces the intensity of the main alite reflections (3.04; 1.76 Å). Dicalcium silicate in barium-bearing clinkers is present in two modifications: β-C_2S (2.85; 2.29; 2.18 Å) and α'-C_2S (2.89; 2.67; 2.72 Å). The reflections of α'-C_2S are displayed more in Angarsk belite clinkers (Fig. 2b)

It is stated that the clinkers synthesized with 2 and 3% of barite waste have a reduced concentration of alite; at the same time, CaO_{free} is present in the amount of slightly exceeding the concentration of CaO_{free} in plain clinkers, and BaO in free condition is not revealed. It is clarified that in barium-bearing clinkers, the intensity and reflection surface 2.99Å increase, whereas all other main reflections belonging to tricalcium silicate phase decrease. It gives grounds for the supposition that there is a formation of barite solid solutions of $BaO \cdot 2CaO \cdot 3SiO_2$ composition with main reflection 2.99Å. It is possible to have the formation of solid solutions or compounds of $0.48BaO \cdot 1.52CaO \cdot SiO_2$ composition with the main reflections 2.77 and 2.84 Å, which are overlapped by the reflections of the calcium silicate phases on clinker radiographs. It is defined that barium oxide in clinkers causes the formation of C_3A modified composition. In the barium-bearing clinkers under study, the significant decrease of basic reflection C_3A (2.70 Å) in comparison with the plain clinker was noticed. It is likely that some part of BaO appearing in the process of burning is spent on the formation of phases which are not present in usual Portland clinker. When the temperature is increased, $BaSO_4$, containing in a raw mix resolves and starts interacting with Al_2O_3, forming barium mono-alluminate $BaO \cdot Al_2O_3$, that is confirmed on the radiographs by the appearance of barium-bearing sintered materials of the strongest reflection of this compound which is 3.15 Å. Reflections 2.24, 1.58 and 1.35 Å also belonging to $BaO \cdot Al_2O_3$ were revealed. There were no such reflections revealed in plain clinkers.

It is stated that triple compounds, the analogues of calcium sulfoaluminate of $4.2BaO \cdot Al_2O_3 \cdot 1.2BaSO_4$ and $2.75CaO \cdot 1{,}25BaSO_4 \cdot 3Al_2O_3$ composition, are not formed.

The capacity of reaction of the raw materials under study was evaluated due to the saturation degree of calcium oxide at temperatures 1300-1450°C, which was defined by means of the ethyl-glycerate method (Table 2).

Experimental data reveal that in Magnitogorsk raw materials with saturation coefficient 0.91 in the presence of 2 and 3% of barite waste (1 and 1.5% BaO) at temperatures 1300 and 1400°C, the content of free calcium oxode is slightly increased in comparison with the plain clinker.

Table 2. The influence of barite waste on CaO saturation intensity

Clinker	Amount of barite waste in mix %		Content of CaO,% at burning temperature, °C		
	%	with BaO, %	1300	1400	1450
Magnitogorsk SC=0.91	0	0	8.84	3.74	0.22
	2	1.0	9.20	4.84	0.33
	3	1.5	10.23	5.90	0.80
	5	2.5	13.10	6.7	2.10
Angarsk SC=0.80	0	0	1.80	0.70	0.30
	2	1.0	1.40	0.59	0.18
	3	1.5	1.16	0.35	0.10
	5	2.5	0.90	0.20	trace

The increase of the addition agent amount of barite waste up to 5% results in even a bigger amount of CaO_{free} at the specified temperatures that is confirmed by X-ray diffraction analysis of the given clinker, in which the intensity of the main diffraction lines of calcium oxide is increased – 2.41 and 1.69 Å. When increasing the temperature up to 1450°C and cure time – to 40 minutes, the content of CaO_{free} in clinkers reduces, and for both plain clinkers and the clinkers synthesized with 2 and 3% of barite waste, it fluctuates within one value, which is equal to 0.2-0.8% for Magnitogorsk clinkers. The content of CaO_{free} in clinkers synthesized with 5% of barite waste (2.5% BaO) amounts to 2.1%, that is much higher than in plain clinkers. The increase of CaO_{free} amount is probably connected with the increase of the clinker melt viscosity and with the fact that the significant amount of barium makes difficulties for forming tricalcium silicate with the appearance of free calcium oxide.

The saturation speed of free CaO is increased in Angarsk raw mixes with the dicreased saturation coefficient (SC=0.80) in the presence of the addition agent of barite waste amounting to 2, 3 and 5%.

4. Conclusion

The possibility to apply barite waste as an addition agent for a raw mix with the increased content of magnesium oxide has been revealed. The peculiarities of physical and chemical processes of clinker formation in raw mixes with the increased content of magnesium oxide in the presence of the given waste have been determined.

5. Summary

While studying the influence of barite waste on the clinker formation process in raw mixes with the increased content of magnesium oxide it was revealed that the waste addition causes the formation of dicalcium silicate in β- and α' modifications, C_3A modified composition and some decrease of the alite amount. Barium mono-alluminate $BaO{\cdot}Al_2O_3$ is formed in the composition of the intermediate material. Solid solutions with barium oxide are formed in clinker phases. It was clarified that ternary compounds with barium sulfate are not formed.

The saturation of calcium oxide in raw mixes with saturation coefficient 0.91 in the presence of 2 and 3% barite waste in the temperature range of 1300-1450°C becomes slightly slower. With the temperature increase up to 1450°C, there is an insignificant amount of CaO_{free} in the specified barium-bearing clinkers, which is comparable to the content of CaO_{free} in the plain clinker. The addition of 5% barite waste makes the saturation of CaO_{free} considerably slower and at temperature 1450°C it amounts more than 2%.

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