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 BaSO₄ amounts to 76,11%. The impact of BaO and SO₃ 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 furnace 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 Magnitogorsk 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 | Loss on ignition | SC   |
|-------------------------|----------------------------------|------------------|------|
|                         | SiO₂   | Al₂O₃ | Fe₂O₃ | CaO   | MgO   | SO₃  |                  |               |
| 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 |                  |     |
|-------------------------|-------------------------------------|------------------|------|
|                         | SiO₂   | Al₂O₃ | Fe₂O₃ | CaO   | MgO   | SO₃  |                  |     |
| Magnitogorsk            | 20.53  | 6.39  | 3.39  | 64.14 | 4.34  | 0.15 |                  |     |
| Angarsk                 | 22.12  | 5.95  | 4.58  | 60.98 | 5.05  | 0.39 |                  |     |

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 BaSO₄. The basic oxides in the waste are BaO (50.00%) and SO₃ (26.11%), there are also SiO₂ (11.51%); CaO (5.75%); Al₂O₃ (1.20%) and Fe₂O₃ (0.50%); loss on ignition is 3.39%.
The transformations occurring with barite waste when heated (Fig. 1) have been studied. At temperature 723°C, CaCO$_3$ resoves when kept at temperature 1162°C, 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$^{2+}$ ↔ 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 1. The complex thermal analysis 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: \(\beta\)-C\(_2\)S (2.85; 2.29; 2.18 Å) and \(\alpha'\)-C\(_2\)S (2.89; 2.67; 2.72 Å). The reflections of \(\alpha'\)-C\(_2\)S 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\(_{\text{free}}\) is present in the amount of slightly exceeding the concentration of CaO\(_{\text{free}}\) in plain clinkers, and BaO in free condition is not revealed. It is clarified that in barium-bearing clinkers, the intensity and reflection surface 2.99 Å 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·2CaO·3SiO\(_2\) composition with main reflection 2.99 Å. It is possible to have the formation of solid solutions or compounds of 0.48BaO·1.52CaO·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\(_3\)A modified composition. In the barium-bearing clinkers under study, the significant decrease of basic reflection C\(_3\)A (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\(_2\)O\(_3\), forming barium mono-aluminate BaO·Al\(_2\)O\(_3\), 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·Al\(_2\)O\(_3\) 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·Al\(_2\)O\(_3\)·1.2BaSO\(_4\) and 2.75CaO·1.25BaSO\(_4\)·3Al\(_2\)O\(_3\), 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 oxide is slightly increased in comparison with the plain clinker.

Figure 2. The phase composition of Magnitigorsk (a) and Angarsk (b) clinkers depending on the amount of barite waste.
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 decreased 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$_3$A modified composition and some decrease of the alite amount. Barium mono-alluminate BaO·Al$_2$O$_3$ 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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