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Investigation of the Influence of Barite Retreat to the Grindability Magnesium-Containing Clinker and Cement Properties

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Abstract: The way of saving energy and resources in the production of magnesium-containing cements, which is the use of barite waste as an additive in the feed mixture has an effect on the grindability of clinker and mechanical properties of the cement. Found that clinker containing more than 3% MgO, has a high resistance to crushing. The use of barite in the amount of waste 2-3% (1.52-2.28% $BaSO_4$) as an additive in feed mixture can improve the grindability of the clinker. This is accompanied by a reduction in the duration of grinding raw clinker and clinker with a high content of belite phase. Shown to improve the grindability of magnesium-containing clinkers synthesized with barite waste associated with the decrease in microhardness of clinker phases. It was determined that the introduction of barite departing optimizes granulometric composition of cement, increasing the amount of fine particles (1-5 microns) and high (5-35 microns) fractions and provides a more active hydration clinker.

Key words: Clinker · Barium waste · Magnesium oxide · Grindability clinker · Solid solutions

INTRODUCTION

The cement industry is the largest consumer of energy. At existing plants energy costs account for a significant amount of work therefore aimed at saving energy resources represent an important theoretical and practical problem. Clinker grinding - one of the most energy-intensive process of cement production. Clinker with a high content of magnesium oxide, which is a common impurity in the raw materials for cement production, different grindability most difficult, which leads to an increase in energy consumption in grinding the clinker grinding media wear increase and prolong maintenance campaigns cement mills. Interest in this problem is manifested in the work [1], which considers the influence of mineralogical, chemical and physical properties on the grindability of industrial clinkers with high (above 5%) content of MgO. Also note that the presence of MgO in the raw material mixture are accelerated clinkering [2-4], improving conditions for the formation of pack oven [5] is increased lining durability [6]. In Russia, the magnesium oxide content in the clinker regulated by the standard and limited to 5% [7]. For individual plants in some countries, this restriction is higher at 6 or even 6.5%.

The cement industry is one of the few industries in the enterprises which can be used by a large number of industrial wastes of various industries [8, 9]. The feasibility of using waste is dictated by the development of resource-and energy-saving technologies and the need to improve the ecological environment [10-12]. One of the types of waste are – barium-containing.

The study of changes in the properties of cements derived from raw mixes with the addition of various barium-containing waste dealt with by many researchers [13-17]. Most of the work in this area is devoted to the influence of barium-containing waste in the processes of clinker, the microstructure of clinker and cement activity. The studies were conducted on raw mixes with a saturation coefficient (SC) of 0.91 and mixtures with a low SC equal to 0.67-0.86. BaO mineralizing effect on the

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Table 1: The chemical composition of industrial clinkers%

Clinker	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O
Belgorod	21.77	5.33	4.42	66.69	0.70	0.16	0.54	0.23
Angarsk	20.50	5.60	4.60	63.60	4.70	0.30	0.60	0.10

Table 2: The chemical composition of clinkers,%

Clinker	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O
Belgorod	21.45	5.59	4.38	66.63	0.92	0.26	0.69	0.26
Magnitogorsk	20.53	6.39	3.39	64.14	4.34	0.15	0.97	0.10
Angarsk	20.26	6.45	3.19	63.65	5.25	0.36	0.66	0.18

process of clinker and cement activity was noted in [18]. Despite many studies, no consensus on the optimal concentration of BaO in the clinker has not developed.

In [19] noted that the barium-containing waste is introduced into the feed mixture improves the grindability of clinker. The authors explain this fact increases the porosity of clinker and simultaneously decrease the microhardness of clinker phases.

The aim of this work was to study the effect of withdrawal of barite on clinker grindability with magnesium oxide content greater than 3% and the properties of the cement.

The Main Part: The study of the influence of MgO on clinker grindability conducted on industrial Belgorod and Angarsk clinkers with SC = 0.92, differing content of MgO (Table 1).

Grindability were evaluated as clinker in a laboratory mill to a specific surface of 300±10 m^2/kg. In mill charged clinker fraction smaller than 2.5 mm. Every 5 minutes taken an average sample of clinker and its specific surface area was measured. The values obtained are presented in Figure 1.

Within 15 minutes the grindability of clinkers was almost identical. After this period was milled better Belgorod clinker grinding duration until its surface area was 300 m^2/kg 35 minutes, whereas the duration Angarsk clinker grinding to the same specific surface area – 45 minutes. Thus Angarsk clinker containing 4.7% MgO, milled significantly harder than Belgorod clinker, containing less than 1% MgO.

In industrial grinding clinkers can influence not only the magnesium oxide present in the clinker, but also the physicochemical [20] and technological factors. It should therefore create the same conditions for the synthesis of clinkers with different contents of MgO and to determine their grindability.

Clinkers was synthesized from raw mixes Belgorod, Magnitogorsk and Angarsk refineries. Choosing raw mixtures last two plants due to the fact that they use a feedstock with a high content of magnesium oxide. The chemical composition clinkers is shown in Table 2, saturation coefficient (SC) 0.91-0.92 clinker, lime module 2.1.

Clinkers burned in a laboratory furnace. The burning temperature was 1450°C, isothermal exposure – 40 minutes, a cool – sharp in the air. Clinker grinding was carried out before specific surface of 300 ± 10 m^2/kg. The data are shown in Figure 2.

Experiments showed that the grindability synthesized clinkers also depends on the content of MgO. With the increase of the MgO content of the clinker is deterioration of its grindability. If the duration of the Belgorod synthesized clinker grinding was 25 minutes, the duration of the Magnitogorsk grinding clinker containing 4.34% MgO, was 35 minutes and the Angarsk clinker containing

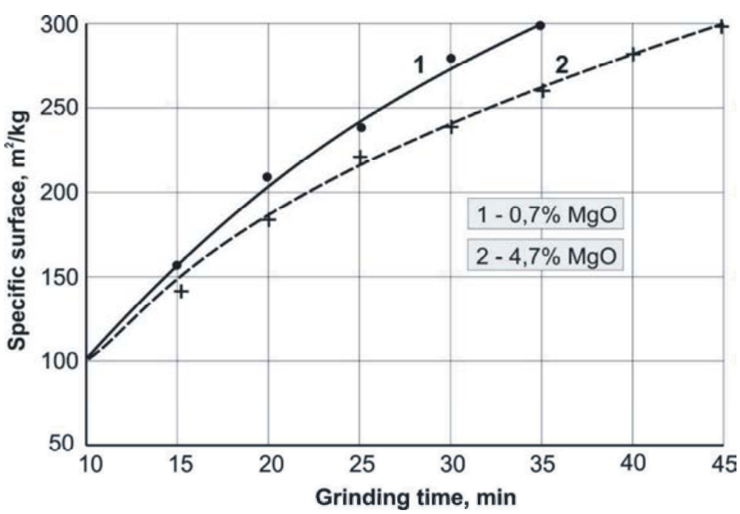

Fig. 1: Dependence duration Belgorod industrial grinding (1) and Angarsk (2) the amount of clinker magnesium oxide

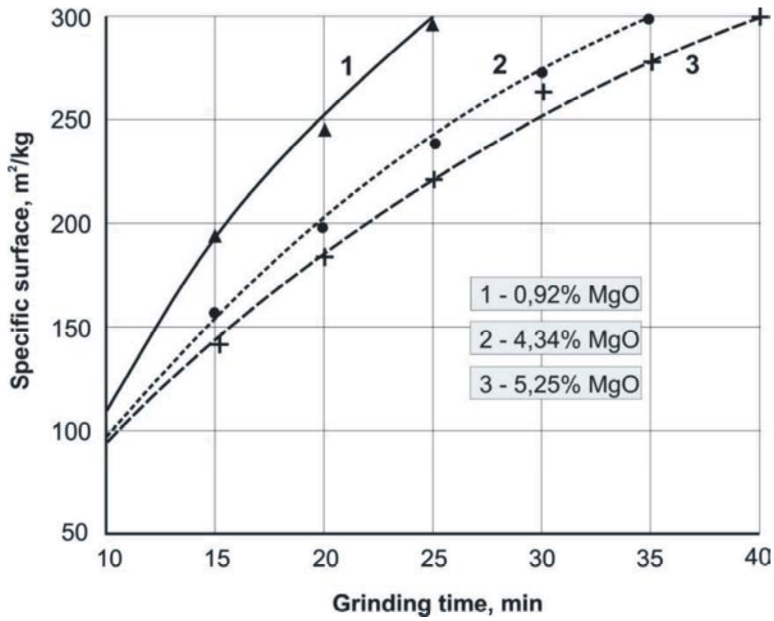

Fig. 2: The dependence of the duration of the grinding synthesized Belgorod (1), Magnitogorsk (2) and Angarsk (3) the amount of MgO clinkers

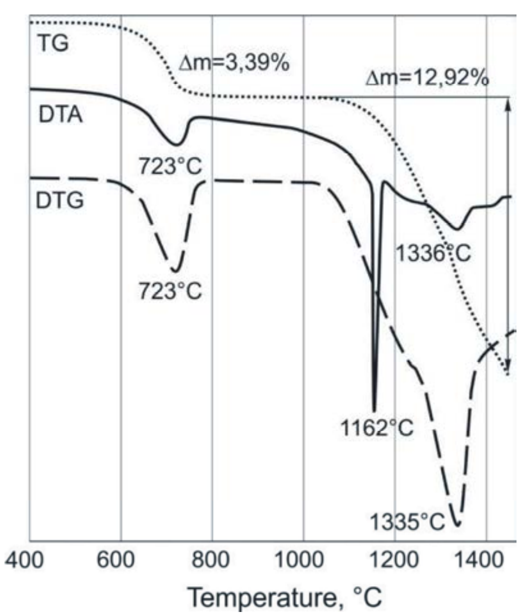

Fig. 3: Complex thermal analysis of barite waste

MgO 5.25% – 40 minutes. Therefore, the higher MgO content in the clinker, the greater the time required for its crushing.

Previously, it was shown [19] that the barium-containing wastes improve the grindability of clinker raw. It can be assumed that the waste containing barium may equally affect grindability and clinker with a high content of magnesium oxide.

Investigations were carried out on the synthesized clinker from raw mix of Magnitogorsk and Angarsk plants. As a barium-containing additives used barite waste, which is a fine powdery product obtained in the production of barite concentrate. The mineralogical composition of waste, mainly represented by barite $BaSO_4$. Basic oxides in waste BaO (50.00%) and SO_3 (26.11%), also contains SiO_2 (11.51%); CaO (5.75%); Al_2O_3 (1.20%) and Fe_2O_3 (0.50%), loss on ignition (LOI) are 3.93%.

Transformations occurring with barite waste when heated, are presented in Figure 3. At 723ºC decomposes $CaCO_3$, at 1162°C barite transition occurs from monoclinic to rhombic, which greatly increases its reactivity. It is well known that the net $BaSO_4$ melts at 1580°C [21]. The complex thermal analysis revealed was stated that $BaSO_4$ in waste in the presence of acidic oxides starts again, we offer a temperature range of 1100-1200°C with the loss of SO_3. With increasing temperature, weight loss and increased to 1450°C, reaches a value of 12.92%, accounting for 50% of total SO_3 content in the waste.

In the raw material mixture is added 2, 3 and 5% barite waste, which in terms of BaO 1.0; 1.5 and 2.5%, respectively. The raw mix of Magnitogorsk plant with SC = 0.91 with the addition of barite products containing 2.78-2.64% MgO or 4.16-4.05% MgO in the clinker. The raw mixture Angarsk plant with SC = 0.80 barite products containing 3.45-3.29% MgO or 4.92-5.25% based on clinker.

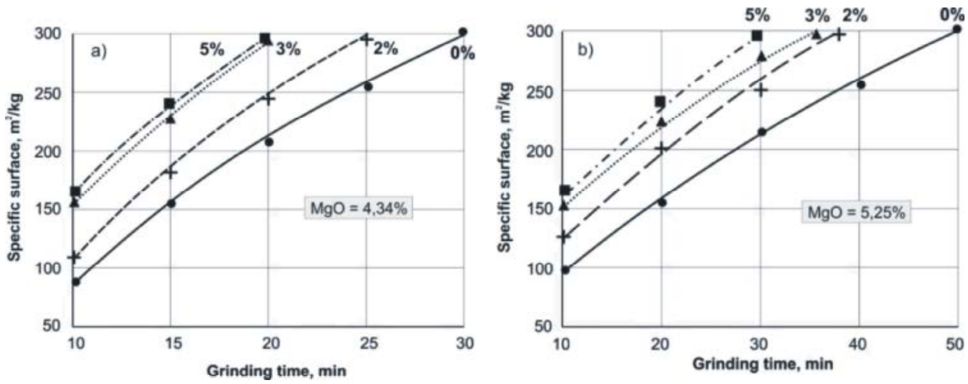

Fig. 4: Effect of the duration of barite departing grinding Magnitogorsk clinker SC = 0.91 (a) and Angarsk clinker CN = 0.80 (b)

Increasing the amount of waste in the raw material barite mixtures of 2 to 5% improves the grindability magnesium Magnitogorsk and Angarsk clinkers. Duration of barium-containing Magnitogorsk grinding clinker with SC = 0.91 is reduced by 5-10 min compared with without additional clinker (Fig. 4).

Duration of grinding without additional Angarsk clinker containing 34% belite, significantly more than without additional Magnitogorsk clinker and is 50 minutes (Figure 4). Introduction 2, 3 and 5% barite waste in Angarsk feed mixture shortens the clinker grinding for 13-20 minutes. It should be noted that the introduction of barite waste into raw material mixture, effectively increases the Angarsk grindability of clinker with high content of the most difficult grinds belite phase, compared with Magnitogorsk clinker.

Added to the raw mixture of barium deviation of 2% and reduces the duration of Angarsk clinker grinding for 13 minutes or 26% and the Magnitogorsk – 5 minutes, or 17%. When you add 3% barite waste into raw mix of Magnitogorsk clinker grinding length with SC = 0.91 and Angarsk clinker with SC = 0.80, reduced by about the same amount – 33% of the Magnitogorsk and 30% for Angarsk. By increasing the content of barite waste into a raw material mixture to a 5% duty grinding clinker Angarsk continues to decline, whereas the effect of improving the Magnitogorsk clinker grindability appears and remains on the same level as the introduction of 3% barite waste.

Therefore, the introduction of barite waste in the raw mix improves the grindability of clinkers and magnesium SC = 0.91 and SC = 0.80.

Grindability clinker depends on many factors, including – chemical composition, the cooling mode, character crystallization clinker phases, porosity clinker presence of various additives intensifying grinding. Can significantly affect the microhardness of clinker phases. Therefore, further to the PMT-3 microhardness by determination of microhardness of magnesium-containing clinker phases.

Microhardness measurements were carried out in phases Magnitogorsk clinkers with SC = 0.91. Of clinkers prepared based on the raw mixes Angarsk plant for the study were selected clinkers with SC = 0.80, because the definition of microhardness of clinker phases in the clinker with a high content of belite is of particular interest.

In the barium-containing clinker calculated SC = 0.91 with an increase in the dependence of the reduction of waste microhardness alit phase 19.5-26%, belite – by 17-24% and an intermediate – 8.5-17% compared with the phase without additional clinker. In clinkers with SC = 0.80 microhardness tricalcium silicate is reduced by 12-28% dicalcium silicate – 13-28% and an intermediate – 9.5-12.5% (Table 2).

Thus, it was found that the introduction of the raw material mixture in an amount departing barite 2, 3 and 5% significantly decreases the microhardness of both calcium silicates and intermediate in clinker with a high content

Table 2: Effect of the barite waste on the microhardness H (kg/mm²) clinker phases

Quantity%		Alit		Belit		The intermediate	
waste	BaO	H	ΔH, %	H	ΔH, %	H	ΔH,%
Magnitogorsk clinker SC=0.91, MgO=4.34%							
0	0	622	–	633	–	939	–
2	1.0	501	19.5	525	17.0	858	8.5
3	1.5	486	22.0	510	19.5	824	12.0
5	2.5	462	26.0	480	24.0	780	17.0
Angarsk clinker SC=0.80, MgO=5.25%							
0	0	690	–	722	–	960	–
2	1.0	609	12.0	629	13.0	870	9.5
3	1.5	540	21.5	569	21.0	852	11.0
5	2.5	494	28.0	520	28.0	839	12.5

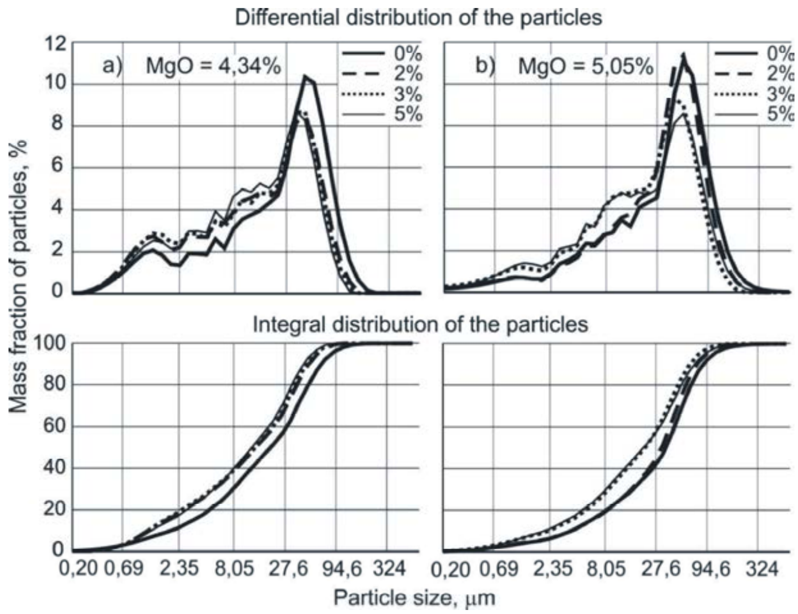

Fig. 5: Effect of barite on the size distribution of the waste Magnitogorsk cement with SC = 0.91 (a) and Angarsk cement with SC = 0.80 (b)

MgO. This relationship is stored in the clinker with SC = 0.91 and a clinker with a lower SC = 0.80 belite phase containing 36.3-34.8%.

It is known that the main cement minerals – silicates. aluminates, calcium alyumoferrity contain some impurities that replacing the main array elements – Ca, Si, Al and Fe by other elements form solid solutions, while changing the structure of the mineral hardness [20]. Depending on synthesis conditions, alite and belite include a lattice extraneous ions such as Al^{3+}, Mg^{2+}, Ba^{2+} and etc. In these phases, the most calcium and barium and calcium located in the periodic system of elements in a group have the same charges and similar properties. Barium ion Ba^{2+}, being an analogue of the calcium ion Ca^{2+}, replaces the latter primarily in the structure of calcium silicate.

However, calcium and barium ions have different ionic radius: ionic radius of Ba^{2+} is 1.37 Á, whereas the ionic radius of Ca^{2+} – 1.06 Á and the ionic radius of Mg^{2+} – 0.74 Á. The formation of solid solutions and to alite and belite with barium ions having large dimensions can affect the crystal microstructure and hardness.

Therefore, we can assume that the barium is introduced into the crystal lattice of the clinker phases and reduces strength deforming it and thereby a decrease in microhardness.

With the improvement of the grindability of magnesium-containing clinkers obtained with the addition of barite waste, by determination of the grain composition of cement. It is known that the activity of the cement can affect various factors, including particle size and optimized for the same surface area. Scientific studies [22] and studies in this field have shown that the desirable rather narrow granulometric composition, is minimized when the amount of as very fine grains – less than 1 micron and larger – more than 30-40 microns.

Cements investigated by laser particle size on MicroSizer 201. We studied two series of cements: Magnitogorsk with SC equal to 0.91 and Angarsk with SC equal to 0.80. Each series consists of three barium-containing cements and one control – without additional.

It is known [23] that the content of fine fractions (˜ 2 to 30 microns) in fixed, determines the activity of the cement in the early and middle periods of hydration. In this case, it is optimal amount of fines in the range of 60-70%. Early strength cement in a 2 or 3-day-old defines the content of fine grains of a class size of less than 5 microns and strength in the 28-day-old – the number of grains of the middle class (5-30) mm. In connection with this assessment of the grain composition was carried out, focusing on these fractions. Found that barium waste, improving magnesium clinker grindability, at the same time optimizes the size distribution of the cement.

Differential and integral curves of the mass distribution of cements containing barium shifted the curves without further cements to higher dispersion (Fig. 5), indicating a higher content in the fine fraction of them.

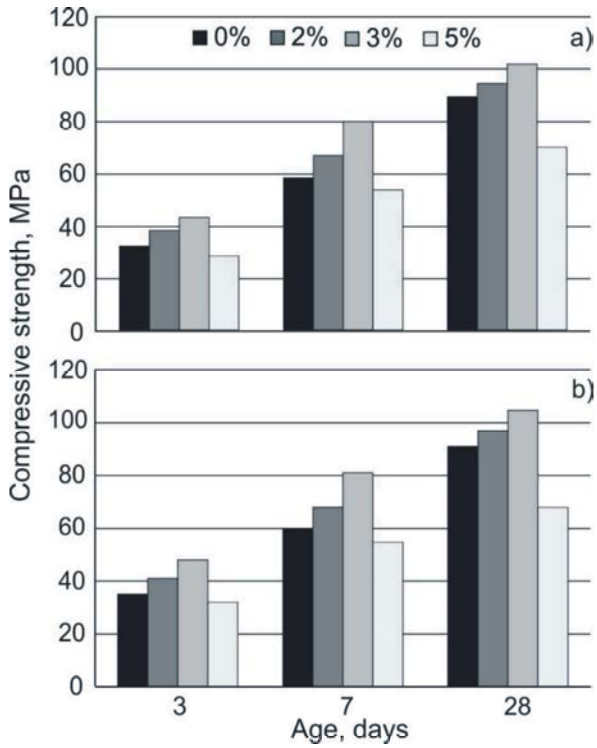

Fig. 6: The influence of additives on the strength of barite waste Magnitogorsk (a) and Angarsk (b) of cements with SC = 0.91

Table 3: Effect of barite on the size distribution of the waste cement

Quantity, %		The content of particles, %			
waste	BaO in mix	< 1 mkm	1-5 mkm	5-35 mkm	> 35 mkm
Magnitogorsk cement SC=0.91, MgO=4.34%					
0	0	3.2	14.4	45.3	37.1
2	1	3.6	20.1	48.1	26.1
3	1.5	3.5	23.1	49.1	24.3
5	2.5	3.4	22	53.3	21.3
Angarsk cement SC=0.80, MgO=5.25%					
0	0	2.2	9	36.5	52.3
2	1	2.5	8.6	41	47.9
3	1.5	3.5	13	48.2	35.3
5	2.5	3.2	14	45.3	37.1

The mass distribution of barium-containing cement particles by size (Table 3) indicates a more optimal particle size distribution.

The cement additive synthesized barite waste a quantity in excess particulate fraction with particle size less than 1 micron virtually unchanged and is within 3.5% and also reduces the content of large grains larger than 35 microns, which do not participate in the formation of both primary and grade strength.

Magnitogorsk barium-containing cement of fine fraction (1-5 mm) for the growth strength in the early stages of solidification increases to 20.1-23,1% as compared with no extension – 14.4%, i.e. almost 1.5 times. Angarsk cement containing barium content of said fraction is increased up to 13-14% as compared with no extension – 9.0%, i.e. by 44-55.5%, respectively. Magnitogorsk cements obtained barite waste, the amount of particles (5-35 micron) forming brand strength increases to 48.1-53.3% as compared with no extension – 45.3%, i.e. at 6-17%. In Angarsk cements containing barium content of the particles is within 41.0-48.2% and no extension – 36.5%, i.e. increased by 12-32%.

Thus, it is established that the barium-containing cements compared with no additional increase of the content of the fractions 1-5 microns, have a decisive influence on the growth of strength in the initial period of hardening, fractions 5-35 microns, which mainly affects the brand strength. Fractions cement than about 50 microns, which are practically ballast in the barium-containing cements far fewer than without further.

Further cements were synthesized physical and mechanical tests, which showed (Fig. 6) that the introduction of the feed mixture with SC = 0.91 barite departing at 2 and 3% (1 and 1.5% BaO) increases the strength of cement compared with the strength without further cements.

In Magnitogorsk barium-containing cement, synthesized with 2 and 3% barite waste, the strength characteristics of the age of 3 days increase to 38 and 43 MPa as compared to cement without additional – 32 MPa, i.e. at 19-34%, respectively. At the age of 7 days strength increases to 67 and 80 MPa compared with no extension cement – 58 MPa, i.e. on 15.5-38%.

A similar dependence was observed for the Angarsk cement. In the cement obtained with 2 and 3% barite waste, strength increases to 41 and 48 MPa compared with no extension cement – 35 MPa, i.e. at 17-37%. At 7 days of barium-containing cements strength increases to 68 and 81 MPa compared to without additional – 60 MPa, i.e. at 13-35%.

In 28 days no additional strength Magnitogorsk and Angarsk cements are respectively 89 and 91 MPa, whereas additive 2 and 3% of barite increases the strength departing Magnitogorsk cement to 98 and 102 MPa strength cement Angarsk to 97 and 105 MPa. Consequently, the average increase in strength of 10-15%.

CONCLUSION

A process for producing magnesium-containing cement with barite waste in an optimal amount of 2-3% (1.52-2.28% $BaSO_4$) as an additive in the feed mixture, allowing a clinker, which is better exposed to crushing, which may result in be reduced electricity consumption for grinding. Introduction of barite waste in the raw mix to optimize particle size distribution of cement and provides more hydration activity of clinker.

Findings:

- The possibility of intensifying the magnesium-containing grinding clinker grindability differs difficult, due to the introduction of barite waste into raw material mixture. The use of barite departing improves grindability of clinker with a high MgO as a saturation coefficient 0.91 and the amount of clinker with a high belite phase. At the optimal concentration in the feed mixture of barite waste constituting 2-3% (1-1.5% BaO), the duration of grinding clinker with SC = 0.91 is reduced by 17-33 %. Introduction of barite in the waste feed mixture in an amount of 2-5% (1-2.5% BaO) reduces the duration of belite clinker grinding at 26-40%.
- It is found that with increasing amounts of barite waste in the raw mixture is reduced microhardness main clinker phases from the substitution of ions Ca^{2+} and Mg^{2+} to ions Ba^{2+}, having larger ionic radius and the formation of additional defects in the crystal lattice of silicate, aluminate and alyumoferrite calcium. In this regard, grinding of the crystals is easier and therefore faster clinker is ground.
- Determined that barite waste, improving magnesium clinker grindability while optimizing particle size distribution of cement. In the barium-containing cements increases the amount of fine fractions (1-5 microns), providing initial strength and quantity of the fraction of average size (5-35 microns) providing brand strength. Simultaneously, cements derived clinkers synthesized barite waste, reduces the content of particles larger than 35 microns.
- It is established that the introduction of barite waste into raw mix can be enhanced activity of cement at the age of 3 days at 18-35% in 28 days – by 10-15%. Physical and mechanical tests indicative exist, that the activity of barium-containing cement with SC = 0.91 increased by the addition of up to 3% barite waste. The increase in barite waste to 5% reduces the strength of the cement. The strength of cements with SC = 0.80 is increased in the presence of 2-5% of barite waste into a raw material mixture.

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