Receiving Portland Cement from Technogenic Raw Materials of South Kazakhstan

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Abstract

A method of producing portland cement using the wastes of enrichment of polymetallic ores of "Achpolymetal" (Kentau, Kazakhstan) in the amount of 0.5 to 2.5% as a mineralizing additive in the raw mixture is proposed. This allows the clinker to be produced at a lower temperature (1300–1350 °C), resulting in lower fuel consumption and higher furnace productivity. The experimental clinker is better subjected to grinding, the electric power consumption for grinding cement decreases, the grinding bodies of cement mills decrease. In the waste, there are catalytic and modifying elements. Studies have shown that in the no-added raw mix the clinker formation processes are completed at 1450 °C. When 0.5 to 2.0% of the tailings are introduced, the complete binding of CaO is completed at 1400 °C, with the addition of 2.5% of tailings, lime binding is completed at 1300 or 150 °C lower than in the control non-additive raw mixture. In clinkers, only 1.09–1.32 % of free lime remains. The strength of cement when introduced into the raw mix from 0.5 to 2.0% of barite waste is increased. The compressive strength at 28 days of age for cement with an optimum dosage of 1‒2% of the tail increases from 414 kg/cm² to 430–432 kg/cm² or by 3.9‒4.3%. Similarly, the strength of steamed samples increases by 4.7‒5.7%.

Introduction

The rapid development of many industries leads to the depletion of non-renewable natural resources. Many industries generate a significant amount of solid waste polluting the environment. Nowadays, the cement industry is intensively uses many wastes (technogenic materials) in the production of cement [1–4].

However, despite significant progress in this direction, often the use of waste is accompanied by a certain decrease in the quality of cement. At present, there are numerous wastes in the form of slags, ashes, carbon-containing technogenic materials, waste tires and other types of waste that fall into dumps, occupying vast areas of useful land, polluting the environment. Therefore, the integrated use of technogenic materials with a simultaneous increase in production efficiency without reducing the quality of cement is of great importance.

The cement industry is one of the few industries in which a large number of industrial wastes of various industries can be used. The expediency of using waste is dictated by the development of resource and energy-saving technologies and the need to improve the environmental situation [5]. The cement industry belongs to one of the largest consumers of energy. At operating enterprises, the cost of fuel is 35%, raw materials – up to 25%, and electricity – up to 15%. Wide use of waste will increase the efficiency of cement production by reducing the consumption of fuel and electricity, while lowering the burning temperature and improving clinker grinding.

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that fall into dumps, occupying vast areas of useful land, polluting the environment. Therefore, the integrated use of technogenic materials with simultaneous increase in production efficiency without reducing the quality of cement is of great importance. In connection with the foregoing, the scientific studies of this article aimed at solving these problems are topical [6–8].

The authors [9, 10] have developed low-energy-intensive compositions of raw materials and economical technologies for the production of clinkers for general and special cements with the use of large-tonnage waste from coal mines of the Langer mines, granulated phosphoric and lead slags, dust from electrostatic precipitators of furnaces, igneous rocks. Tests conducted at «Standard Cement» (South-Kazakhstan region at «Sastobe Technologies» (South-Kazakhstan region) and «Shymkent Cement» plants (Shymkent, Kazakhstan) showed that the clinker formation processes are completed at temperatures of 1300–1350 °C, specific fuel consumption is reduced to 19%, the productivity of rotary kilns is increased, and CO₂ emissions are reduced.

A variation of the secondary resources poorly studied in cement technology is barium-containing waste from mining and processing enterprises and chemical enterprises.

Barium containing wastes in the territory of the South-Kazakhstan region are represented in the form of wastes of enrichment of polymetallic ores. They are a by-product of the processing of lead-zinc ores. In the South Kazakhstan region, the accumulation of such wastes is observed in two cities: Kentau and Shymkent. According to «Kazakh Himproyekt» (Shymkent), barium containing waste accumulated in the territory of «Achpolimetal» (Kentau) is not less than 1 million 800 thousand tons, and this is only in the city of Shymkent. The «Kentaulievdrudnik» («Achpolimetal») in Kentau accounts for 136 million tonnes, which, as shown by the study of their properties, are a universal technogenic raw material for the production of low-energy astringent materials for various purposes [7, 20].

Thus, this work is due to the need for significant savings in fuel and energy resources, the expansion of the raw material base of the cement industry, the improvement of mineral formation and the strength values of clinkers.

Using the above mentioned waste as an additive to the raw mix will significantly reduce electricity consumption for cement production during clinker grinding and improve its quality, as well as improve the ecological situation in the country.

1. Raw materials

The object of the study was the wastes of enrichment of polymetallic ores of «Achpolimetal» (carbonate-barium tails) and synthesized clinker. Their influence on clinker formation processes and the quality of cement was assessed, and the cost of electricity was reduced by grinding clinker by improving the clinker grind ability.

Waste of enrichment of polymetallic ores – carbonate-barium "tails" is a finely divided product that does not require additional grinding before use. The main minerals that make up the "tailings" are: dolomite 50–60%; limestone 10–15%; barite 10–20%; clay substances 5–8%; ore minerals 2–3%.

The chemical composition of the wastes of enrichment of polymetallic ores of "Achpolimetal" is characterized by the stability of the composition and is presented in Table 1.

In the waste there are catalytic and modifying elements, wt. %: Zn – 0.01-0.05; Cu – 0.002-0.004; Ti – 0.03-0.05; Cd – 0.002-0.003; barium and lead sulfates, lead and iron sulfides, lead carbonate.

Low activity of radionuclides (53–55 Bk/kg), absence of toxic emissions, low volatility of heavy metals indicates the radiation-ecological safety of waste [20].

2. Research methods

To solve the tasks set in the work, complex physical and chemical studies of the initial components, raw mixtures containing barite waste, clinkers synthesized with their use were used. At the same time, chemical, petrographic, spectral, X-ray phase and other analyzes were used [11–13].

During the research, raw mixtures were prepared, differing in the amount of barium-containing components introduced therein. Mixtures were prepared on the basis of raw materials used at «Cement Plant Semey»: limestone, clay, pyritic cake (Table 2). As barium containing component, wastes of enrichment of polymetallic ores of "Achpolimetal" were used. Mixtures differed by the amount of input of this component from 0.5 to 2.5%.

All raw mixtures were prepared by dry method. Crushed (until completely passing through a sieve #008) raw materials mixed in the propor-
tions indicated in Table 3, within 20 min. Initially, a four-component raw mixture with a saturation coefficient of 0.97 was prepared without additives. Next, a certain amount of the barium-containing component was administered. The total weight of each raw mixture was 25 g.

The chemical analysis of the raw mixture obtained on the basis of the above raw materials is presented in Table 4.

### 3. Results and its discussion

The resulting non additive mixture was tested to confirm the correctness of the calculation of the raw mixture. From the obtained raw mixtures on press LPG 20 at a pressure of 20 atm. were compressed pellets for roasting. After that, all the samples obtained were fired in an electronic high-temperature muffle furnace SNOL 12/15. Each mixture was fired in the temperature range from 700 to 1450 °C and isothermal aging for 20 min, the cooling of the cakes was sharp in the air.

Portland cement clinker is a product of sintering when burning a raw mix of the proper composition, which ensures the predominance in it of highly basic calcium silicates tricalcium silicate and dicalcium silicate. The chemical analysis of the additive portland cement clinker is presented in Table 5.

The evaluation of the properties of the clinker was carried out according to ST 461-1917-27-TOO-4-04-2011 Portland cement clinker (technical conditions [14]).
A study of the microstructure of the Portland cement clinker on the Clinker S-7 microscope showed the quantitative content of minerals in the sample under study. Figure 1 shows the microstructure of the Portland cement clinker.

The reactivity of the investigated raw mixtures was evaluated by the degree of assimilation of calcium oxide at burning temperatures from 700 to 1450 °C, which was determined by the ethyl glycerate method [11]. The results are shown in Table 6.

Burned at a temperature of 1450 °C, raw mixtures with the addition of enrichment wastes from polymetallic ores in the amount of 0.5 to 2.5% were also examined, as was the resultant additive clinker.

By the results shown in Table 6, it can be seen that in the no-additive raw mixture the clinker formation processes are completed at 1450 °C, the content of CaO free at the same time is 0.25%. Tailings of enrichment of polymetallic ores have a strong mineralizing effect on clinker sintering processes. With an increasing dosage of tailings, the binding of CaO to clinker minerals is accelerated, the process occurs much more rapidly and at lower temperatures. When 0.5 to 2.0% of the tailings are introduced, in fact, the complete binding of CaO is completed at 1400 °C, and when 2.5% of the tailings are introduced, lime binding is completed at 1300 or 150 °C lower than in the control non-additive raw mixture. In clinkers, only 1.09–1.32% of free lime remains.

The chemistry of the acceleration of clinker formation with the introduction of 1–2.5% tail is due to the presence in the waste of catalytic and modifying elements – zinc, copper, titanium oxides, etc. Tails also contain barium and lead sulfates, lead and iron sulfides, lead carbonate, which in optimal dosages have a mineralizing effect on the burning process and a modifying effect on the crystalline structure of the main minerals; in their presence, fine, well crystallized crystals of minerals of regular shape are formed and with faces. The hydraulic activity of such crystals is higher, so the strength of cement with tailings increases.

The study of the processes of mineral formation in clinkers was carried out by X-ray phase analysis of the obtained specks (Fig. 2).

All clinker phases are simultaneously present in the analyzed clinkers: tricalcium silicate $C_3S$, dicalcium silicate $C_2S$, tricalcium aluminate $C_3A$, and cobalt 4-calcium aluminate $C_4AF$. No free barium oxide was found in the clinkers. This is explained by the fact that the $Ba^{+2}$ ion, being an analog of the $Ca^{+2}$ ion, replaces the latter in the structure primarily of calcium silicates [15].

Two calcium silicate $C_2S$ in synthesized clinkers is present in two polymorphic modifications: $\beta$ and $\alpha'$. X-ray diffraction patterns show reflec-
of overlapping of diffraction peaks against each other, including reflections of other phases, for example, to a greater extent alite.

Petrographic studies made it possible to evaluate the morphological characteristics of the clinker microstructure, the size of the grains of the mineral phases (alite and belite), and also to make a quantitative analysis of the phase components (alite, belite, intermediate phase, clinker porosity), calculate the saturation coefficient, and determine the percentage of free calcium oxide. The petrographic analysis of synthesized clinkers showed that the phase composition of synthesized barium containing clinkers varies. Figure 3 shows micrographs of synthesized clinkers at a temperature of 1450 °C.

Based on the results of the petrographic analysis, the clinker saturation coefficient was determined; the share of alite, belite, intermediate substance and pores is determined (Table 7).

The petrographic analysis found that the presence of barium-containing waste in the raw mixture leads to a decrease in the amount of alite by 6.5%; the content of belite in the synthesized clinkers is increased by 18.2% and the liquid phase by 9.8%. At the same time, the increase in crystal size in synthesized clinkers was determined under the influence of the additive containing barium. The alite crystals increased from 18 to 32 μm; there are also large individual ones up to 42 μm. The sizes of belite increased from 8 microns (no additive) to 32 microns; single larger crystals up to 37 μm are encountered.

Table 6

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Name</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>1</td>
<td>Free flowing clinker (25 g sludge)</td>
<td>0.70</td>
</tr>
<tr>
<td>2</td>
<td>0.5% «tails» (25 g + 0.77 g tails)</td>
<td>0.82</td>
</tr>
<tr>
<td>3</td>
<td>1.0% «tails» (25 g + 1.60 g tails)</td>
<td>0.87</td>
</tr>
<tr>
<td>4</td>
<td>1.5% «tails» (25 g + 2.37 g tails)</td>
<td>0.94</td>
</tr>
<tr>
<td>5</td>
<td>2.0% «tails» (25 g + 3.21 g tails)</td>
<td>1.15</td>
</tr>
<tr>
<td>6</td>
<td>2.5% «tails» (25 g + 3.98 g tails)</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Fig. 3. The microstructure of Portland cement clinkers.
Physical and Chemical Characteristics of Cobalt Catalysts

Table 7
Mineralogical composition of synthesized clinkers containing wastes of enrichment of polymetallic ores

<table>
<thead>
<tr>
<th>Quantity of waste, %</th>
<th>Alite</th>
<th>Belite</th>
<th>Intermediate substance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>60.7</td>
<td>15.2</td>
<td>18.4</td>
</tr>
<tr>
<td>0.5</td>
<td>58.9</td>
<td>17.4</td>
<td>20.1</td>
</tr>
<tr>
<td>1.0</td>
<td>58.4</td>
<td>17.5</td>
<td>20.5</td>
</tr>
<tr>
<td>1.5</td>
<td>57.4</td>
<td>18.2</td>
<td>20.4</td>
</tr>
<tr>
<td>2.0</td>
<td>57.3</td>
<td>18.3</td>
<td>20.4</td>
</tr>
<tr>
<td>2.5</td>
<td>56.7</td>
<td>18.6</td>
<td>20.4</td>
</tr>
</tbody>
</table>

It is determined that with increasing input of the amount of barium containing waste, the amount of pores in the analyzed synthesized clinkers is increased. In the no-additive clinker, the pores are 26%, and with the introduction of waste, the pore volume increases from 26 to 34%.

The grinding of raw materials and finished clinker in the cement industry is considered to be the most energy-intensive operation, on which not only energy but also metal is consumed. However, cement workers not only do not intend to abandon it but on the contrary increase the fineness of the ground cement, thereby guaranteeing significant acceleration and a relatively fast growth rate of the hardening cement strength after two days.

The grinding of the clinker depends on a large number of factors, including chemical composition, cooling regime, the nature of the crystallization of clinker phases, the porosity of clinker, the presence of various additives that intensify grinding, can significantly affect the microhardness of clinker phases.

The authors of [16–18] found that the introduction of barite waste in the amount of 2.3% and 5% into the raw mix significantly reduces the micro-hardness of both calcium silicates and an intermediate substance. The authors suggested that barium is introduced into the crystal lattice of clinker phases, deforming and softening it, as a result of which the microhardness decreases. In order to find out whether barium is being introduced into the crystal lattice of clinker phases, the elemental composition of each phase of synthesized clinkers was made, namely, without additive and with a maximum input of wastes of enrichment of polymetallic ores.

The spectra obtained for the tricalcium silicate phase in the no-additive and barium-containing clinkers. The spectra show that barium appears in the alite phase. Characteristic lines have a very low height, in comparison with the height of the lines in the phases of belite and intermediate substance, which indicates a less quantitative content of the element in the alite.

The definition of the elemental composition of belite in synthesized clinkers. The analysis revealed the presence of barium in the dicalcium silicate of barium-containing clinkers. The diffraction lines characteristic of barium manifests themselves more clearly than in the alite, which may indicate its greater amount in the phase of dicalcium silicate. The determination of the elemental composition of the tricalcium aluminate and the four calcium alumoferrite together, since the determination, was separately difficult. A study of the distribution of elements in the intermediate phase showed that barium is present in sufficient quantities in its composition.

Thus, during the determination of the elemental composition, it is clarified that barium is introduced into all clinker phases, which leads to a decrease in their microhardness. Consequently, with the introduction of Ba²⁺, which has a larger ionic radius than that of calcium ions, the softening of clinker minerals results in their softening, and grinding the clinker with such microstructure will be much easier.

To confirm the decrease in microhardness, the clinker grind ability was determined by the specific surface reached after a certain interval of grinding time in a laboratory mill. The results of the experiment are presented in Table 8.

Table 8
Dependence of the specific surface area of cements on the duration of grinding of synthesized clinkers

<table>
<thead>
<tr>
<th>Name</th>
<th>Specific surface of cements, m²/kg, through</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 min</td>
</tr>
<tr>
<td>Without additional</td>
<td>248</td>
</tr>
<tr>
<td>2.5% of the input of &quot;tails&quot;</td>
<td>268</td>
</tr>
<tr>
<td>2.5% of the input of barite</td>
<td>277</td>
</tr>
</tbody>
</table>
The initial fractional composition of the clinkers and the mass were the same. The grinding ability of the synthesized clinkers was estimated by the duration of the grinding of the clinkers to the specific surface $S_{ss}$ of $320 \pm 10 \text{ m}^2/\text{kg}$, which corresponds to the specific surface area of industrial clinkers.

Every 5 min, the mill was unloaded, an average sample was taken, the specific surface of the clinker was measured, then the material was returned to the mill to the house. Based on the obtained data, the graph shown in Fig. 4 was constructed.

As can be seen from the graph in Fig. 4, the duration of the grinding of the additive clinker to a specific surface of $\sim 320 \text{ m}^2/\text{kg}$ was 30 min. When adding an additive – enrichment wastes of polymetallic ores in an amount of 2.5%, the clinker grinding time decreased by 5 min compared to the no-dough, that is, the grinding time was reduced by 16.6%.

The introduction of 2.5% of barite into the raw mix also significantly affected the grind ability of the clinkers in comparison with the no-dough. The additive reduces the duration of the clinker grinding to 20 min, which is 66.6% of the grinding time of the clinker without additives.

According to the proposed method for producing barium containing clinker, a different amount of BaSO$_4$ was introduced into the raw mixture. In this regard, it is necessary to study the effect of barite waste on the hydration activity of cement.

Synthesized cement were subjected to physical and mechanical tests. The clinker was ground in a spherical laboratory mill with 5% gypsum in conditions close to industrial tests. The results of physical and mechanical tests of the samples made in accordance with the requirements of GOST 310.4-81 (State standard) [19] are given in Table 9.

Thus, the activity of ordinary cement can be increased by introducing into the raw mixture from 0.5 to 2.0% of barite waste. The compressive strength at 28 days of age for cement with an optimum dosage of 1–2% of the tail increases from 414 kg/cm$^2$ to 430–432 kg/cm$^2$ or by 3.9–4.3%. Similarly, the strength of steamed samples increases by 4.7–5.7%. Further increase in the concentration of tailings in the raw mix causes a decrease in the strength parameters of cement.

Table 9

<table>
<thead>
<tr>
<th>Cements</th>
<th>Designation of samples</th>
<th>Amount of components</th>
<th>Strength at steaming, kg/cm$^2$</th>
<th>Strength in 28 days of age, kg/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>bending</td>
<td>compression</td>
</tr>
<tr>
<td>1</td>
<td>Without additional</td>
<td>1500 g sand + 500 g cement</td>
<td>50.3</td>
<td>296</td>
</tr>
<tr>
<td>2</td>
<td>0.5 % «tails»</td>
<td>1500 g sand + 500 g cement (12.84 g tails)</td>
<td>52.7</td>
<td>303</td>
</tr>
<tr>
<td>3</td>
<td>1.0 % «tails»</td>
<td>1500 g sand + 500 g cement (25.68 g tails)</td>
<td>53.0</td>
<td>308</td>
</tr>
<tr>
<td>4</td>
<td>1.5 % «tails»</td>
<td>1500 g sand + 500 g cement (38.52 g tails)</td>
<td>53.1</td>
<td>313</td>
</tr>
<tr>
<td>5</td>
<td>2.0 % «tails»</td>
<td>1500 g sand + 500 g cement (51.36 g tails)</td>
<td>52.9</td>
<td>310</td>
</tr>
<tr>
<td>6</td>
<td>2.5 % «tails»</td>
<td>1500 g sand + 500 g cement (64.2 g tails)</td>
<td>50.8</td>
<td>298</td>
</tr>
</tbody>
</table>
4. Conclusions

The involvement of technogenic raw materials in the production of cement allowed to reduce:
1. Fuel consumption for clinker burning, due to reduction of the burning temperature to 1300 °C;
2. Electricity consumption for clinker milling;
3. The release of CO₂ and NOₓ into the environment by reducing the roasting temperature, thereby improving the ecological situation in the country and obtaining a cement of appropriate quality that meets the requirements of GOST for products.

References