Increasing the activity of cements during mechanical activation of raw materials

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Abstract. The article is devoted to the study of the influence of dispersion of raw mixtures on the properties of Portland cement clinker. The study established that the mechanical activation of raw mixtures by hydrodynamic effects significantly accelerates the processes of mineral formation during the synthesis of clinkers. In this case the microstructure and phase composition of clinkers changes. Clinkers from activated mixtures are characterized by clear crystallization of minerals, their uniform distribution and increased content of the alite phase. This determines the high mechanical strength of cements based on these clinkers. At the use mechanical activation of waste it is possible to obtain high level activity one.

1. Introduction
The problems of modern construction require an increase in the manufacture of multicomponent cements for the production of which high active clinker is needed. The production of such clinkers is largely associated with an increase in the reactivity of row mixes. However, the increasing attention to environmental issues has made the building materials industry one of the main consumers of industrial wastes, which often do not possess the necessary chemical activity. In addition, the depletion of reserves of natural active components and the involvement of local low-quality raw materials to increase the volume of cement production, lead to the need to find ways to increase the activity of raw materials [1-5].

One of them is the optimization of raw mixes, the introduction of modifying additives in the synthesis of clinkers [6-9]. However, as a rule, each plant works on specific types of raw materials of relatively stable chemical composition, therefore, ways to increase the reactivity of raw materials by changing its composition are limited.

There is another direction for improving the quality of clinker associated with improving the preparation of raw mixes [10-12].

The main technological action in the preparation of mineral raw materials, which makes it possible to transfer the raw materials to a chemically active state and to ensure an intensive and complete course of the reactions of clinker formation, are crushing and grinding. Fine grinding of materials is one of the methods of mechanical activation [13-15].

However, to solve this problem, the use of traditional grinding units, such as a ball mill, as a rule, is not economically rational because of the disproportionately large increase in energy costs relative to the growth of dispersion of the material being crushed, and the grinding units: jet, roller, vibratory and other...
mills are mainly focused on grinding dry materials, while up to 60% of cement plants in Russia work in a “wet” way. There is an obvious need to develop and study the technology of grinding raw mixes using new grinding units for the existing conditions of cement production.

The purpose of this work was to study clinker formation during the firing of conventional and mechanically activated raw mixtures, determination of the properties of clinkers from raw mixes of different dispersion.

2 Experimental procedure

2.1 Materials and sample preparation

In carrying out the research, raw materials of JSC “Sukholozhskcememt” were used: limestone, argillite, tripoli, and chemical industry waste - pyrite cinders. Raw mixtures with the following characteristics: the saturation coefficient - 0.93; silicate module - 2.0 were prepared. The chemical composition of the components is presented in Table 1.

Raw mixtures were prepared by joint grinding of raw materials in a laboratory ball mill in an aqueous medium for 60 minutes. Then the sludge was dried up to moisture content of ~ 1% . Then prepared cylinder samples measuring 20 mm in diameter and 20 mm in height by pressing under a pressure of 20 MPa. The prepared samples were fired at 1450 °C in a laboratory kiln for 1 hour.

| Table 1. Chemical compositions of raw materials |
|-----------------------------------------------|
|             | Limestone | Argillite | Tripoli | Pyrite cinders |
| Loss of ignition, %                          | 40.8      | 6.46      | 9.81    | 1.15           |
| SiO₂, %                                       | 4.82      | 66.14     | 74.4    | 9.42           |
| Al₂O₃, %                                      | 1.69      | 14.16     | 7.52    | 4.52           |
| CaO, %                                        | 49.58     | 4.29      | 2.72    | 2.59           |
| MgO, %                                        | 1.16      | 1.62      | 1.5     | 1.05           |
| SO₃, %                                        | 0.03      | 0.15      | 0.43    | 4.19           |
| Fe₂O₃, %                                      | 0.82      | 5.39      | 2.8     | 75.13          |
| Others, %                                     | 1.10      | 1.79      | 0.82    | 1.95           |

The firing samples were ground in a laboratory mill to obtain a Blaine specific surface area of 3800 cm²/g.

2.2 Methods

For mechanical activation of materials the rotary pulsation device was used. Rotary pulsation devices, which combine the principles of operation of dismembrators, disintegrators, colloid mills and centrifugal pumps, provide the appearance of developed hydrodynamic flows, as well as an effective grinding (dispersing) effect on the processed medium.

The working elements of such devices, as a rule, are two or more sets of hollow coaxial cylinders (cones or disks) with holes or slots of various shapes (Fig. 1). When one set of cylinders rotates relative to another or when both sets are rotated in opposite directions, a rapid alternation of alignment and non-alignment of the slits occurs, which entails a synchronous change in the velocity of the medium being processed through the slits, i.e. the occurrence of a pulsating fluid with a high frequency. As a result, the processed medium is exposed to large shear stresses arising in narrow radial gaps between rotating and stationary cylinders due to significant velocity gradients, hydraulic shocks, cavitation, small scale pulsations in a wide frequency range. These factors in combination with intensive mechanical effects significantly increase the speed of technological processes in homogeneous and heterogeneous liquid systems.
To determine the effectiveness of the activation of the individual components of the Portland cement raw mixture, formulations were prepared that contained either limestone or argillite, subjected to hydrodynamic activation. Also a mixture composed of individual components was activated. 4 mixtures were examined (table 2).

Clinker samples were examined by chemical analysis, XR- diffraction and optical microscopy. The change in the composition of clinker, the nature of the crystallization of minerals was studied. To determine the compressive strength of cements from laboratory clinkers, they were mixed with the necessary amount of water, and then samples were prepared with a size of 10x10x30 mm. They hardened in water for 28 days.

3. Experimental results and discussion

The mixtures were burned in a laboratory furnace, and the in the obtained samples the content of CaO_free was determined (Figure 2). Also the change in the size and weight of the samples before and after firing was determined. According to the obtained data, the density of the fired samples was calculated (table 3).

Differences in the nature of the sintering of raw mixtures are confirmed by optical microscopy studies. So, clinker 1 has a vague crystallization of minerals. Their distribution over the area of the polished section is uneven: the areas containing alite are alternated with the areas of belite aggregation. Alite crystals for the most part do not have the correct forms, part of them has collapsed, as evidenced by the rim around them, consisting of the smallest belite grains. Some alite crystals have inclusions of residual belite grains (Figure 3). The size of the crystals is 30-90 microns. The composition of clinker consists of 55-60% alite, 20% belite and 25-30% of the intermediate phase. Belite is presented by grains of an angular form. Intermediate phase has a high reflectivity. The distribution of the intermediate phase over the polished section is uneven. Single grains of free calcium oxide are found.
Table 2. Composition of mixes

| Mix    | Description                                      |
|--------|--------------------------------------------------|
| 1      | All the components are not activated             |
| 2      | Only limestone is activated                      |
| 3      | Only argillite is activated                      |
| 4      | All components are activated                     |

Table 3. Sample density

| No mix | ρ<sub>b</sub> before firing, g/cm<sup>3</sup> | ρ<sub>a</sub> after firing, g/cm<sup>3</sup> |
|--------|---------------------------------------------|--------------------------------------------|
| 1      | 1.822                                       | 1.639                                      |
| 2      | 1.966                                       | 1.689                                      |
| 3      | 1.906                                       | 1.712                                      |
| 4      | 2.004                                       | 1.786                                      |

Figure 2. The dependence of CaO<sub>free</sub> in the samples on the isothermal firing at 1450 °C

Clinker 2 has a distinct crystallization of minerals. Alite is represented mostly by crystals in the form of elongated prisms, hexagonal plates, often they knit among themselves. The edges of the crystals are often slightly broken. The size of the main mass of crystals is 25-30 microns; large crystals of about 75 microns are found. Belite is observed only as inclusions in alite crystals. The intermediate phase in reflectivity in polished section is heterogeneous: the "light" and "dark" intermediate is different. Moreover, the content of the intermediate phase with low reflectivity is quite a lot; sometimes it has the form of angular, clear crystals. The mineral composition of clinker consists of 60-65% alite, 20% belite and 15-20% of the intermediate phase (Figure 4).

Clinker 3 in microstructure practically does not differ from clinker 2. Alite is represented by clearly decorated crystals, often fused together. Their edges are also slightly destroyed. The sizes of crystals lie in the range of 5–50 µm, crystals with a size of 20–25 µm predominate (Figure 5). Belite is observed only as inclusions in Alita grains.

Compared to previous samples, the crystallization of minerals in clinker 4 is more distinct. Alite crystals are of regular geometric form. There are crystals with a border of the smallest grains of belite. The sizes of alite crystals are from 5 to 60 microns, their main mass has a size of 25 microns. Belite is represented by angular, less often rounded grains, their preferred size is 30-40 microns (Figure 6). The intermediate phase is presented, in the main, "light" variety, interspersed with the smallest points with low reflectivity. According to analysis, clinker lacks free calcium oxide.
Thus, a change in the phase composition, improvement of the microstructure of clinkers obtained by roasting raw mixtures subjected to hydrodynamic effects predetermine an increase in the hydration activity of cements based on clinkers data (Table 4).

### Table 4. The results of cement tests

| Cement on clinker | 1  | 2  | 3  | 4  |
|-------------------|----|----|----|----|
|                   | Flexural strength, MPa |    |    |    |
| 1 day             | 3.18 | 3.69 | 3.77 | 3.81 |
| 3 days            | 6.26 | 6.59 | 6.82 | 8.11 |
| 7 days            | 9.31 | 9.6  | 9.62 | 10.62 |
| 28 days           | 13.03 | 15.29 | 16.04 | 16.85 |
|                   | Compressive strength, MPa |    |    |    |
| 1 day             | 9.8  | 11.6 | 12.0 | 12.3 |
| 3 days            | 23.2 | 23.8 | 24.5 | 25.7 |
| 7 days            | 34.7 | 36.6 | 38.4 | 39.6 |
| 28 days           | 65.9 | 69.9 | 70.1 | 73.4 |
As can be seen from the presented data, cements obtained from activated clinkers have high strength during almost all curing time. Moreover, cement obtained from the entire activated raw mix has the highest values. This is obviously due to the fact that when the components are jointly activated, a better homogenization of the material occurs.

4. Conclusion

It has been established that the processing of materials by hydrodynamic action results in their fine grinding and homogenization of the raw mix, as well as the mechanical activation of the particles. High dispersion and change in the internal structure of raw materials causes an increase in their reactivity. Correspondingly, calcium oxide is absorbed faster in activated mixtures. (the absence of CaO_free in clinker already at a temperature of 1400 °C).

Clinker from activated raw materials are characterized by a distinct fine-grained microstructure, a high content of alite phase.

Cements prepared on the basis of activated mixtures are characterized by a faster set of strength both in the early stages of hardening and have high strength properties with long-term hardening.

The highest activation efficiency in the RPA is observed during the processing of the least reactive component – the argillite and during the processing of the entire mixture.

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