

X-Ray Study of Synthesized Clinkers

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Annotation: X-ray examination made it possible to establish that the specified minerals were formed in the process of obtaining clinkers. At the same time, it was revealed that excess calcium sulfate contributes to the stabilization of the mineralogical composition.

Key words: sulfosilicate, sulfoaluminate, X-ray phase analysis, calcium sulfate, calcium aluminate, tricalcium silicate, dicalcium silicate, clinker diffraction patterns.

X-ray phase analysis of the synthesized clinkers made it possible to identify the following minerals by a set of interplanar distances (d) and relative intensities (J):

β -dicalcium silicate ($d=2,78; 2,75; 2,61; 2,189 \text{ \AA}$), calcium sulfoaluminate ($d = 3,75; 2,64; 2,16 \text{ \AA}$), calcium sulfate ($d = 3,49; 2,85; 2,32; 2,20; 1,86; 1,64 \text{ \AA}$), calcium sulfosilicate ($d=3,19; 2,84; 2,56; 1,889 \text{ \AA}$), calcium aluminate composition $C_{12}A_7$ ($d = 4,92; 2,68; 2,447 \text{ \AA}$), γ -dicalcium silicate ($d = 3,01; 2,755; 2,732; 1,911 \text{ \AA}$), tricalcium silicate ($d = 3,03; 2,776; 2,7; 2,602; 2,182; 1,765; 1,632 \text{ \AA}$).

It is known that the intensity of reflection is determined by the amount of a given mineral and the degree of perfection of its crystal lattice. The intensity value can be determined using the heights of the peaks or their areas. Identification of X-ray diffraction patterns of clinkers synthesized at 1573K showed that along with the formation of β -dicalcium silicate, calcium sulfoaluminate, calcium sulfate, there are minerals γ -dicalcium silicate, calcium aluminate of composition $C_{12}A_7$, calcium sulfosilicate. In clinkers that do not contain an excess of calcium sulfate, dicalcium silicate of and β -modifications is formed; β -dicalcium silicate dominates, while the proportion of γ -dicalcium silicate is not large, since the intensity of its very strong peak at $d=3,01 \text{ \AA}$ is inferior to the intensity of reflections of β -dicalcium silicate, which is expressed in an increase in the peak at $d=2,75 \text{ \AA}$ doublet ($d= 2,78; 2,75 \text{ \AA}$). For β -dicalcium silicate, a more intense peak at $d=2,78 \text{ \AA}$ of this doublet is characteristic, which is observed in clinkers containing an excess of calcium sulfate. This shows that the modification of β -dicalcium silicate is stabilized in the presence of calcium sulfate.

Since the intense lines of dicalcium and tricalcium silicates coincide, the identification was based on the middle lines. The following lines were selected as analytical: for tricalcium silicate line at $d=1,76 \text{ \AA}$ ($2\theta=51 \dots 52,5^\circ$); for β -dicalcium silicate line at $d=2,88 \text{ \AA}$ ($2\theta=31^\circ$), for γ -dicalcium silicate line at $d=3,01 \text{ \AA}$ ($2\theta=29,8^\circ$).

On the diffraction pattern of clinker containing 10% calcium sulfoaluminate and 90% dicalcium silicate, there is also a line of tricalcium silicate. The intensity of its reflections significantly decreases when the content of excess calcium sulfate in the clinkers, and the line of β -dicalcium silicate is intensified. Since an increase in the amount of β -dicalcium silicate from the presence of an excess of calcium sulfate is impossible, its crystal lattice is obviously improved. An increase in the amount of anhydrite by 30% leads to a slight decrease in the intensity of the lines of dicalcium silicate relative to clinker containing a 20% excess of calcium sulfate.

Diffraction patterns of clinkers containing 30% calcium sulfoaluminate, in the absence of excess calcium sulfate, are characterized by a decrease in the intensity of the doublet ($d = 2,75; 2,78 \text{ \AA}$). The extended peak reaches a significant intensity at the value of the interplanar distance $d=2,632 \text{ \AA}$, due to the superimposition of reflections of calcium sulfoaluminate, calcium aluminate composition $C_{12}A_7$, tricalcium silicate, β -dicalcium silicate. Under conditions of excess calcium sulfate, lines of β -dicalcium silicate are intensified.

The diffraction patterns of clinkers containing 50% calcium sulfoaluminate are characterized by a weak intensity of both the doublet and the peak at the value of the interplanar distance $d=2,62 \text{ \AA}$. With the appearance of an excess of calcium sulfate in the system, the intensity of the peaks of β -dicalcium silicate increases.

Diffraction reflections of calcium sulfoaluminate (analytical line $d=3,75 \text{ \AA}$) are directly dependent on the content of this mineral in the clinker. With an excess of anhydrite, the intensity in the calcium sulfoaluminate line increases, but up to certain limits. With the same amounts of β -dicalcium silicate and

calcium sulfoaluminate, the reflection intensity of the latter is three times greater than that of β -dicalcium silicate, which indicates a more perfect crystal structure of calcium sulfoaluminate.

The intensity of anhydrite reflections (analytical line at $d=3,49 \text{ \AA}$) increases with an increase in the content of calcium sulfoaluminate in the clinkers. The formation of calcium aluminate composition $C_{12}A_7$ is evidenced by characteristic diffraction reflections. A very strong peak was chosen as the analytical line at the value of the interplanar distance $d=2,68 \text{ \AA}$. On individual X-ray patterns, there is a change in the value of the interplanar distance within certain limits Δd . Accordingly, a range appears in the value of θ , that is, an extension of the reflections. This is a consequence of a violation in the periodicity of the structural, caused by the static displacement of atoms and arising as a result of the conditions of formation at not quite favorable ratios of the ionic radii of the elements.

In this case, Δd is $0,05 \text{ \AA}$, so a very strong peak at $d=2,68 \text{ \AA}$ appears at $d=2,76 \text{ \AA}$, which makes it difficult to determine due to the superposition of β -dicalcium silicate on the line.

Calcium aluminate composition $C_{12}A_7$ is formed in clinkers that do not contain excess calcium sulfate, as evidenced by its intense lines, which increase with increasing content of calcium sulfoaluminate. In the presence of excess calcium sulfate, the reflections of calcium aluminate of composition $C_{12}A_7$ decrease. Calcium sulfosilicate is formed in small amounts in clinkers containing an excess of calcium sulfate, as evidenced by reflections at interplanar distances $d = 2,84$ and $3,19 \text{ \AA}$ of medium and low intensity.

Repeated firing of the synthesized clinkers led to some changes in the nature of the reflections. So, on the X-ray patterns of all clinkers, the peak at $d=2,78 \text{ \AA}$ of the doublet is more intense than the peak at $d=2,75 \text{ \AA}$, which corresponds to β -dicalcium silicate. The intensities of diffraction reflections of single and double firing clinkers do not change significantly. Only in clinkers containing 40 ... 50% calcium sulfoaluminate, double firing contributes to some decrease in the intensity of reflections of β - dicalcium silicate. Weak reflections of γ -dicalcium silicate are present on X-ray diffraction patterns of clinkers that do not contain excess calcium sulfate.

On the diffraction patterns of re-fired clinkers, the intensity of the lines of calcium aluminate with the composition $C_{12}A_7$ decreases. In the absence of excess calcium sulfate, $C_{12}A_7$ reflections are somewhat more intense.

The intensity of diffraction reflections of calcium sulfate ($d = 3,49 \text{ \AA}$) of re-baked clinkers somewhat decreases, which is associated with partial decomposition of anhydrite. This difference increases with an increase in the content of calcium sulfoaluminate in the clinkers.

X-ray diffraction patterns of clinkers synthesized at different temperatures (1523...1673K) made it possible to establish the dependence of the intensity of diffraction reflections of minerals on the firing temperature.

Thus, the intensity of mineral reflections of synthesized clinkers containing 10% calcium sulfoaluminate and 90% dicalcium silicate changes as follows. With an increase in the firing temperature, the reflections of tricalcium silicate slightly increase, β -dicalcium silicate, starting from 1623K, weaken, the intensity of reflections of calcium aluminate composition $C_{12}A_7$ increases, and calcium sulfate sharply decreases. In the absence of an excess of calcium sulfate, the reflections of calcium sulfoaluminate increase, and calcium sulfosilicate does not change, but when the content of excess calcium sulfate in clinkers is 10 ...30%.

The dependence of the diffraction reflections of minerals on the amount of excess calcium sulfate in the clinkers is as follows: with an increase in the content of calcium sulfate, the reflections of tricalcium silicate do not change. β -dicalcium silicate, calcium sulfate, calcium sulfosilicate and calcium sulfoaluminate are enhanced, calcium aluminate composition $C_{12}A_7$ is weakened.

Thus, the X-ray study made it possible to establish that the specified minerals were formed in the process of obtaining clinkers.

At the same time, it was revealed that excess calcium sulfate contributes to the stabilization of the mineralogical composition.

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