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Abstract

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The Effect of Additions of Surface-Active Substances on the Intensity of Vibrational Grinding of Cement

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The effect of adsorption-induced lowering of hardness (strength) was discovered and studied for various solid bodies in the works of P. A. Rehbinder and co-workers ([1]). It is observed during wet grinding, for example, of refractory materials ([2]), dyes ([3]), and ores ([4]). For cement clinker, in particular, the effect was established and studied during wet and dry dispersion in ball mills ([5], [6]). It was shown that the introduction of certain surface-active substances makes it possible to increase significantly the fineness of cement. However, in some cases the increase in grinding intensity, along with the effect of adsorption-induced lowering of hardness, is also attributed to the deaggregating action of surface-active additives ([6]).

We investigated the influence of additions of surface-active substances on grinding intensity during the milling of Portland cement (Gigant plant; nominal initial specific surface area 3300 cm^2/g; chemical composition: SiO_2–32.8%, Fe_2O_3–3.85%, Al_2O_3–4.25%, CaO–52.6%, MgO–3.30%, SO_3–1.44%) in a laboratory vibrational mill of 10 l capacity. The volume of the grinding bodies (steel balls 10 mm in diameter) was 80%, and that of the material being ground was 32% of the volume of the grinding chamber.

Hydrophilizing additives of sulfite-spirit stillage–calcium lignosulfonates (SSB)–and hydrophobizing additives of soap naphtha, acidol-soap naphtha, and oleic acid were studied in amounts of 0.1-1% by weight of cement. The additives were introduced into the cement before grinding with thorough mixing: soap naphtha, acidol-soap naphtha, and oleic acid in pure form, and sulfite-spirit stillage in the form of a 50% aqueous solution.

The fineness of the cement was determined from the value of the nominal specific surface area S_1 of a layer of compacted powder by the air-permeability method of Kozeny–Carman, using an apparatus developed in our laboratory ([7]). The true values S_2, determined by us in individual cases by the method of low-temperature adsorption of nitrogen (the BET method) ([8]), were approximately 6 times greater than those indicated. Thus, for example, the true specific surface area of the initial cement, determined by the BET method, was 2.17 m^2/g, while the nominal value determined by the air-permeability method was 0.33 m^2/g.

Experimental data on the kinetics of dry grinding of cement at an oscillation frequency n = 3000 osc/min and amplitude A = 2.5 mm show that the introduction of surface-active substances has an intensifying effect on the dispersion of cement (Fig. 1). This is expressed in an additional increase in the specific surface area of the material compared with grinding without additives. Quantitatively, the increase in specific surface area ranges from 10 to 30%, depending on the nature of the additives, their concentration, and the grinding time. In this respect, the hydrophobizing additives are more active than sulfite-spirit stillage.

Thus, the introduction of surface-active additives makes it possible to reduce the grinding time of cement. Thus, for example, under the indicated

under the operating parameters of the vibratory mill, the duration of cement grinding to S_1 = 5000 cm^2/g is reduced by 20–40%; when grinding to S_1 = 6000 cm^2/g, by an average of 50%.

Determination of the particle-size distribution of the cements by sedimentometric analysis showed that the increase in specific surface area upon introduction of additives occurs owing to an increase in the fine fractions of particles (with radius up to 5 μ); the content of coarse particles (10–20 μ) decreases, while the content of particles of intermediate size (5–10 μ) remains practically unchanged (Table 1).

Table 1

Particle-size distribution of cements ground in the presence of surfactants; n = 3000 rpm, A = 2.5 mm, τ = 30 min.

Surfactant additive	<2	2–5	5–10	10–20
	Limiting radii of fractions, μ fraction content, %	**Limiting radii of fractions, μ fraction content, %**	**Limiting radii of fractions, μ fraction content, %**	**Limiting radii of fractions, μ fraction content, %**
Without additives	35	31	17	17
Mylo-naft, 0.3%	39	35	18	8
SSB, 0.2%	34	38	19	9

Figure 1. Effect of surfactant additives on the kinetics of cement grinding: 1 –without additives, 2 –sulfite-alcohol stillage, 0.2%, 3 –mylo-naft, 0.3%, 4 –acidol-mylo-naft, 0.3%, 5 –oleic acid, 0.2%.

Figure 1: Figure 1. Effect of surfactant additives on the kinetics of cement grinding: 1 –without additives, 2 –sulfite-alcohol stillage, 0.2%, 3 –mylo-naft, 0.3%, 4 –acidol-mylo-naft, 0.3%, 5 –oleic acid, 0.2%.

Surfactant additive	<2	2–5	5–10	10–20
Mylo-naft, 0.3% in 10% solution of Na_2CO_3	49	28	16	7

The effect of a surfactant, in particular oleic acid, on grinding increases as its relative content in the cement rises within the range 0.1–0.5% (Fig. 2). A further increase in the acid content does not lead to an increase in the effect of its action during short-term grinding (up to 20 min), but does cause an additional increase in specific surface area during grinding for about 1 hour.

Thus, for the initial stage of grinding the optimum content of oleic acid is 0.5%, whereas at the end of grinding, to obtain the maximum increase in specific surface area, 1% acid is already required. It follows from this that, depending on the required fineness of the ground product, there exists an optimum content of surfactant, corresponding to the maximum increase in specific surface area.

Fig. 1. Effect of surfactant additives on the kinetics of cement grinding: 1 –without additives, 2 –sulfite-alcohol stillage, 0.2%, 3 –mylo-naft, 0.3%, 4 –acidol-mylo-naft, 0.3%, 5 –oleic acid, 0.2%.

Thus, in 30-minute grinding of cement the optimum content of oleic acid is 0.5%, and the increase in specific surface area is already 50% compared with grinding without the use of surfactant additives.

The influence of the effectiveness of surfactant additives on the kinetics of cement grinding as a function of the frequency–

the frequency and amplitude of oscillations of the mill housing. Grinding of cement at $n = 1500$ osc/min and amplitudes from 1.9 to 6.5 mm (the power expended on grinding $W = 0.85 \div 8.0$ kW) showed that under these conditions the dispersing effect from the introduction of surface-active additives is practically

Fig. 2. Effect of the concentration of oleic acid on the kinetics of cement grinding:
1–0%, 2–0.1%, 3–0.2%, 4–0.5%, 5–1%

Figure 2: Effect of oleic acid concentration on the kinetics of cement grinding.

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absent. In grinding cement in the case $n = 3000$ osc/min ($W = 1.4 \div 4.5$ kW), it was established that at small amplitudes, of the order of 1.0 mm, surface-active substances have practically no influence on grinding; the effectiveness of the additives appears at $A > 2$ mm, and in this case it reaches a maximum at $A \sim 2.5$ mm. Thus, the influence of surface-active additives becomes clearly pronounced in the region of optimal parameters of vibratory grinding at sufficiently high frequency and amplitude.

This circumstance makes it possible to conclude that the observed intensification of vibratory grinding of cement under the influence of surface-active additives is caused not by the prevention of aggregation of particles of finely dispersed material, i.e., not by their stabilization, but by the primary effect of adsorption-induced lowering of hardness, since the stabilizing (deaggregating) action of surface-active additives is obviously not connected with the grinding mechanism.

The adsorption character of the process of intensification of cement grinding is confirmed by its dependence on the concentration of the additive. A calculation carried out using the true specific surfaces of cement, determined by the BET method ([8]), shows that, for the formation of a saturated monolayer of oleic acid on cement, the following are required: for the initial material, 0.4%, and for the final product, 0.8% of surface-active additive by weight of cement, which agrees well with the experimental data (Fig. 2).

The experimental results make it possible to consider that the main factor responsible for the intensification of cement grinding due to adsorption-induced lowering of hardness is a sufficiently high frequency of oscillations. The power expended on grinding, irrespective of the oscillation frequency, apparently plays a secondary role. Thus, at $n = 1500$ osc/min, $A = 6.5$ mm, the power consumed is 8.0 kW; at $n = 3000$ osc/min, $A = 2.5$ mm, the power is 3.6 kW; however, the effect of surface-active additives is observed only in the second case.

These results are in agreement with the ideas of P. A. Rebinder and co-workers[1] on the role of hardness reducers under periodic destructive actions on solid bodies.

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Note: Figure translations are in progress. See original paper for figures.