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Abstract

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The Influence of Gases on the Floatability of Certain Nonsulfide Minerals as a Function of Their Crystal Structure

The study of the influence of gases on the flotation of nonsulfide minerals made it possible to establish different adsorption and flotation properties of fluorite and barite, depending on the action of gases on them ([1]).

Thus, under flotation conditions in a pulp with a high concentration of dissolved oxygen, fluorite floats even in the absence of a collector; barite, even in a pulp maximally saturated with oxygen, passes into the froth product only in the presence of a collector.

It has been noted that prolonged treatment with nitrogen has no substantial effect on barite that has previously been subjected to the action of oxygen—barite stably retains the floatability initially acquired. The flotation activity of fluorite, in contrast to barite, decreases under conditions of oxygen deficiency in the pulp, and the flotation effect achieved is the greater, the higher the oxygen concentration in the solution. After thorough treatment with nitrogen, fluorite loses its ability to float, and the collector loses its ability to become fixed on the mineral.

Investigations carried out on a precision apparatus described earlier ([10]), on pure minerals—fluorite from the Transbaikalian deposit and barite from a deposit of the Turkmen SSR—confirmed the above propositions. The experiments were conducted on minerals with grain size 0.10-0.074 mm; mineral charge 20 g; sodium oleate dosage 50 g/t; flotation was carried out without alkali addition; solid:liquid ratio = 1:5.

Preparation of the mineral for the experiment, deoxygenation of the water, and flotation were carried out in a stream of argon (99.95% pure argon), as well as nitrogen (99.50% pure nitrogen), the latter being purified of oxygen impurities in an electric furnace filled with granulated copper oxide. Active copper was obtained by reduction with hydrogen while heating the furnace to 450° ([2]). For analysis of negligibly small oxygen concentrations in the purified gas, Mukdan' s colorimetric method was used ([3]). For the experiments, nitrogen was used in which no oxygen impurity was present.

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

The experiments showed that, as a result of flotation at a normal concentration of oxygen dissolved in the pulp (9.55 mg/l), 44% of the fluorite passes into the concentrate. After thorough cleaning of the mineral surface from oxygen adsorbed on it and lowering the oxygen concentration in the pulp to 0.2 mg/l, the floatability of fluorite decreases sharply—the recovery of the mineral into the froth product amounts to only 4-5%. As the oxygen concentration in the pulp increases to 7 mg/l, then to 33.88 mg/l, and finally to 41.35 mg/l, the recovery of fluorite into the concentrate increases, respectively, to 15.15; 53.20; and 81.20%. At a high oxygen concentration in the pulp, the flotation time is reduced by half: from 15-20 min to 6-10 min.

When conducting flotation experiments on barite whose surface had previously been altered by the action of oxygen, no noticeable decrease in floatability was observed in a nitrogen or argon medium under analogous conditions. In flotation in a pulp with the oxygen concentration reduced to the maximum extent (0.17-0.20 mg/l), the recovery of barite into the concentrate invariably remains at the level of 97-95.8%.

All this shows that the flotation activity of barite changes little with changes in the oxygen concentration in the solution, provided that oxygen has already been adsorbed on its surface. Conversely, the flotation properties of fluorite depend to a considerable extent on the oxygen content in the pulp: introduction of oxygen into the solution promotes better floatability of fluorite, increases the rate of attachment of particles to air bubbles, and reduces the flotation time. The collecting properties of sodium oleate increase when the oxygen concentration in one phase is raised.

Fig. 1. Projection of the structure of fluorite CaF_2 onto the cleavage plane (111)
Fig. 2. Projection of the structure of barite $BaSO_4$ onto the cleavage plane (010)

The dependence established above for the flotation behavior of fluorite and barite can perhaps be explained by features of their crystal structure, if one takes into account that the destruction of minerals during grinding occurs predominantly along cleavage planes—planes that have a definite crystallographic and crystal-chemical significance—and that the molecular-physical properties of the surfaces formed in this process are determined by their chemistry and topography.

Figures 1 and 2 give projections of the structures of fluorite and barite onto the cleavage planes (4-6)*. The decrease in the intensity of the shading indicates the degree to which ions are removed from the surface. The figures give the magnitudes of uncompensated electrostatic charges; the calculation of the latter for barite was made very approximately, without taking into account the degree of covalency of the bonds (7).

In fluorite, a uniform distribution of positive and negative charges of equal magnitude is observed. The displacement in the positions of their centers is small (0.785 Å, with ionic radii of calcium 1.04 Å and fluorine 1.43 Å). The voids above the fluorine ions of the underlying layer are comparatively small and are screened by ions of the overlying layers. Thus, the surface of fluorite is characterized by low relief, and its surface—The molecular field is characterized by uniformity and by a small magnitude of intensity (the magnitude of individual uncompensated electrostatic charges does not exceed 1/4).

The surface of barite, on the contrary, is distinguished by significant differences in the magnitudes of uncompensated charges and by a sharply expressed nonuniformity of their distribution within the boundaries of the unit cell. Together with the known "looseness" of the arrangement of ions and the presence of large irregularities (the protrusion of charge centers in the surface layer reaches 2 Å, with ionic radii of barium 1.38 Å and oxygen 1.36 Å), this determines the nonuniformity of the surface molecular field and its high intensity at the sites of localization of active centers—charges with magnitudes $> 1/2$.

From what has been said above there follows, first of all, an explanation of the difference in the hydratability of the two minerals. Thus, the low hydratability of the fluorite surface in comparison with barite, which in some cases permits one to speak of its natural floatability, is due, first, to the smaller magnitude of the uncompensated charges and, second, to the poorer ratio of the areas of the adsorbed water molecule and the "unit cell" of CaF_2 (8). The latter means that the landing area of the molecule is large in comparison with the area over which the action of the corresponding ion extends, and some molecules cannot at all approach the attracting ion to direct contact. In addition, the relative smoothness of the surface, together with the absence of strong charges, contributes to the weakness and mobility of the hydrate layer.

In the same way, the features of the surface molecular field determine the behavior of gases dissolved in the pulp, whose interaction with the mineral surface, if chemical effects are disregarded, is reduced to physical adsorption. As a result of the screening of the force field of the surface by adsorbed molecules, its total hydratability changes. In turn, the diffusion of gases to the surface that precedes adsorption depends on the ordering of the dipoles of the hydrate shell. A direct relationship between the degree of surface hydration and the adsorption of gases by it is evident.

The degree of increase in hydrophobicity as a result of the physical adsorption of gases from solution should, in general, be related to the magnitude of the surface-

* Imperfect cleavage along (010) was used as most clearly reflecting the nature of the energetic and topographic differences in the surface layer of the two minerals.

field intensity. The dependence is inverse: the smaller the field intensity, the greater the effect of its screening by adsorbed molecules. For example, oxygen in the absence of a collector does not affect the floatability of barite and quartz (^{1}) (a "strong" field) and significantly improves the floatability of fluorite (a "weak" field), up to the possibility of collectorless flotation under conditions of high pulp saturation.

The irreversibility of the effect of oxygen on the floatability of barite is probably associated with a special strength of attachment of some oxygen molecules at certain centers of the barite surface, the character of whose heterogeneity fully permits such an assumption. Here there is a case in which, in addition to the physical character of adsorption, it is also necessary to take into account the possibility of the superposition of a chemisorption effect. This question requires special consideration, and in the present work we shall confine ourselves to this remark.

In the case of oxygen—a strongly electronegative element possessing electron affinity—the superposition of chemisorption is undoubted, if one takes into account that most crystals contain all kinds of microdefects (^{9}), leading to heterogeneity of surface energy states and serving as adsorption centers. Chemisorbed ions or molecules of oxygen, evidently, in turn activate the surface of the adsorbent, at least certain areas of it, promoting the subsequent adsorption of collector molecules. It is precisely this aspect of the speci-

···of the chemical action of oxygen generally determines its greatest—compared with other gases—adsorption and flotation activity.

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