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## Abstract

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## PHYSICAL CHEMISTRY

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# THE EFFECT OF CAUSTIC SODA SOLUTIONS ON THE ABSORPTION BAND OF SURFACE HYDROXYLS OF CERTAIN SILICATES

Minerals of rare elements belonging to the class of silicates can be divided into two groups according to their capacity for flotation. Silicates with isolated $SiO_4$ tetrahedra in crystal structures with close packing of ions float without preliminary preparation, and oxyhydryl reagents are well fixed on their surface. Silicates with ring anionic radicals require preliminary treatment with hydrofluoric acid, solutions of sodium silicofluoride or caustic soda ([1], [2]). Mixed crystals are encountered more often in ores, and their silicate structures undergo changes in the process of genesis, which worsens their flotation properties. Disturbances in the crystal lattice lead to the fact that adsorbed water remains in the pores and cracks of a particle; this water can characterize the surface participating in the flotation act ([3], [4]).

Representatives of such silicates are beryl and zircon, on whose surfaces the corresponding radicals are exposed when the ore is split and crushed. For the experiments, particles of natural minerals smaller than $5\,\mu$ were selected from an aqueous medium by the sedimentometric method. Part of the powders was treated with a caustic soda solution at a rate of 3 mg/g. Leaching was carried out five times over 2 hours at 20°. The ratio of the solid phase to the liquid was $1:50$. After leaching was completed, the preparations were washed with distilled water until the alkaline reaction disappeared. Untreated and treated samples were dried over calcium oxide to constant weight. Zircon particles were deposited on sodium chloride plates by spraying from air. Weighed portions of beryl powder were pressed into metal frames of known thickness. A 3% solution of medicinal vaseline oil in petroleum ether was used as the binding substance. Pressing was carried out at pressures up to 100 atm.

Spectrograms in the infrared region were recorded from 2 to $4\,\mu$ on IKS-11 and

IKS-12 instruments. The instruments used sodium chloride prisms, calibrated by the spectra of polystyrene, ammonia vapors, atmospheric water, and carbon dioxide ($^5$).

Figure 1 presents the infrared absorption spectra of zircon and beryl powders. Zircon particles, with a layer thickness of 0.3 mg/cm$^2$, give a narrow and strong absorption band at $3340 \pm 10$ cm$^{-1}$ ($2.99\,\mu$), independent of treatment with NaOH solution. A plate made from beryl powder, with a thickness of $1.02 \pm 0.02$ mm, shows a broad absorption band at $3620 \pm 10$ cm$^{-1}$ ($2.77\,\mu$), the intensity of which decreases after treatment with NaOH solution.

Work by a number of investigators has established that silicates are capable of chemically binding and adsorbing molecules of water, ammonia, alcohol, and other substances. By the method of infrared spectroscopy it has been shown that, upon adsorption of water on the surface of microporous glass, there are three layers forming the hydrate shell of the particle and possessing characteristic po-

absorption bands (6–9): 3749 cm$^{-1}$—absorption of the fundamental frequency of surface OH groups; 3670 cm$^{-1}$—absorption of perturbed OH groups of adsorbed water molecules; 3450 cm$^{-1}$—absorption of the fundamental vibrational frequency of water molecules in the capillary-condensed phase.

On the surface of the silicate, the existence of two types of adsorption centers was found: hydroxyl OH groups and valence-unsaturated silicon atoms ($^{10}$). Owing to the anionic structure of the radical or to disruption of the structure of the crystalline tetrahedra, the formation of valence-unsaturated silicon atoms is probable. However, their action must extend first of all to neighboring atoms, namely to hydroxyl groups, increasing their proton-donor, acidic properties. In this case the energy of formation of the hydrogen bond increases sharply, approaching that of a chemical bond. Water molecules adsorbed on activated hydroxyl groups can be removed by chemical reactions or by severe physical methods. Therefore, in the case of beryl, removal of the quasi-crystalline water film that hinders adsorption of oxyhydryl reagents on the particle surface is accomplished by chemical means. Formation of ONa groups on the surface is possible, or else the mechanism is associated with leaching of surface valence-unsaturated silicon atoms.

**Fig. 1.** Infrared spectra of zircon and beryl in the 3-micron region for particles smaller than 5 $\mu$: **1**—absorption band of zircon $ZrSiO_4$ at a loading of 0.3 mg/cm$^2$; **2**—absorption band of beryl $Al_2Be_3[Si_6O_{18}]$ (pressed plates $S = 1.02 \pm 0.02$ mm); **3**—the same band after treatment of beryl grains with NaOH solution (3.0 mg/l).

The absorption bands of hydroxyl OH groups make it possible to judge the capacity of silicate minerals for flotation. The presence in the sample studied of an absorption band near 3640 cm$^{-1}$, detected when recording the infrared spectrum in pressed plates made from powder, indicates the need for preliminary treatment of the silicate with inorganic activators.

Fig. 1. Infrared spectra of zircon and beryl in the 3-micron region for particles smaller than 5 $\mu$: 1 –absorption band of zircon ZrSiO4 at a loading of 0.3 mg/cm$^2$; 2 –absorption band of beryl Al2Be3[Si6O18] (pressed plates S = 1.02 ± 0.02 mm); 3 –the same band after treatment of beryl grains with NaOH solution (3.0 mg/l)

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