Influence of Carbon Dioxide in the Calcite-Sodium Oleate Flotation System

FATTY acids are usually employed in the flotation of carbonate minerals as collectors; among them oleic acid in the form of sodium oleate is important. Mortenson and Ljokjell¹ reported that flotation of calcite using sodium oleate as the collector is improved by conditioning the pulp with carbon dioxide. Biswas² pointed out that the improvement due to the use of carbon dioxide is not related solely to the lowering of pH but is largely attributable to the surface chemical reaction in the system. We report further studies on this system.

To study the calcite-carbon dioxide-water system transparent calcite crystals were wet ground and sieved. About 20 g of moist samples of -120 + 140 ASTM mesh size range were treated with 150 ml. of distilled and deionized water in a 500 ml. reagent bottle and then carbon dioxide was bubbled through the system for various times at a constant rate of 3 l./min. The bottle was shaken for 30 min and kept in a thermostat (operating at $30 \pm 0.1^\circ \text{C}$) for 1 h. For each set, the slurry was filtered and the Ca^{++} , CO_3^{--} and HCO_3^- concentrations in the filtrate estimated.

Calcium estimation was done by the ammonium purpurate method described by Williams and Moser³. The pH was maintained at 11.3 and percentage absorbance was measured at 505 m μ . It was established that neither carbon dioxide nor sodium oleate interferes with the estimation of calcium by this method. Carbonate and bicarbonate were estimated by titration⁴; the results are presented in Table 1.

Table 1. CALCITE-CARBON DIOXIDE-WATER SYSTEM

Time of bubbling of carbon dioxide at the specified rate (min)	Carbonate (moles/l.)	Bicarbonate (moles/l.)	Calcium (moles/l.)	$[\text{Ca}^{++}][\text{CO}_3^{--}]$	pH at the end of the experiment
0	2.87×10^{-3}	—	0.19×10^{-3}	54.5×10^{-3}	7.26
5	0.10×10^{-3}	1.26×10^{-3}	1.56×10^{-3}	15.6×10^{-3}	—
10	0.18×10^{-3}	1.17×10^{-3}	2.30×10^{-3}	41.4×10^{-3}	—
20	0.20×10^{-3}	0.16×10^{-3}	3.35×10^{-3}	67.0×10^{-3}	5.56
30	0.13×10^{-3}	0.12×10^{-3}	3.48×10^{-3}	45.2×10^{-3}	5.80

To study the calcite-carbon dioxide-sodium oleate-water system a similar set of experiments was performed with moist calcite immersed in 100 ml. of sodium oleate solution of known concentration and the procedure already described was followed.

In this set of experiments, estimations of sodium oleate and calcium ion were made at different stages. A method of colorimetric estimation of sodium oleate using Nile blue as the complexing reagent was developed on the basis of earlier findings by Goffin and Conchand⁵. It was necessary to buffer the solution at pH 11.2. Colorimetric estimation at a wavelength of 620 m μ was found to be unaffected by the presence of carbon dioxide. Presence of carbon dioxide was found not to interfere with the estimation of sodium oleate. The data obtained are given in Table 2. These results suggest the following.

(a) As more carbon dioxide is bubbled through the calcite suspension, the concentrations of Ca^{++} and HCO_3^- in the solution increase, presumably as a result of a surface chemical reaction. The equilibrium constant values for the various dissociative reactions in this system were worked out by Garrels and Christ⁶. According to them, if a calcite suspension is equilibrated with pure water without any gas such as carbon dioxide, the ionic concentration values should be 0.126×10^{-3} , 0.398×10^{-3} and 0.891×10^{-3} moles/l. for Ca^{++} , CO_3^{--} and HCO_3^- , respectively. It should be pointed out that, according to Mellor⁷, the solubility of CaCO_3 is 0.0014 g/100 ml. of water at 25°C and thus the concentration of Ca^{++} at equilibrium should be 0.14×10^{-3} moles/l. Our data reported in Table 1 (0.19×10^{-3} moles/l.) is slightly higher. Garrels and Christ⁶ further postulated on the basis of equilibrium constants that

Table 2. CALCITE-CARBON DIOXIDE-SODIUM OLEATE-WATER SYSTEM

Initial concentration of sodium oleate solution: 9.85×10^{-4} moles/l.					
Time of bubbling of carbon dioxide at the specified rate (min)	0	5	10	20	30
Concentration of calcium (moles/l.)	0.32×10^{-3}	0.66×10^{-3}	1.02×10^{-3}	1.71×10^{-3}	2.49×10^{-3}
Initial concentration of sodium oleate solution:	2.35×10^{-4} moles/l.				
Time of bubbling of carbon dioxide (min)	0	5	10	20	30
Final concentration of oleate (moles/l.)	1.61×10^{-4}	0.54×10^{-4}	1.74×10^{-4}	0.41×10^{-4}	1.04×10^{-4}
Amount of oleate adsorbed (moles/g)	—	—	—	0.39×10^{-4}	—
Initial concentration of sodium oleate solution: 4.70×10^{-4} moles/l.					
0	1.13×10^{-4}	0.52×10^{-4}	0.89×10^{-4}	2.20×10^{-4}	2.72×10^{-4}
5	—	—	—	2.80×10^{-4}	—
Initial concentration of sodium oleate solution: 9.40×10^{-4} moles/l.					
0	1.02×10^{-4}	3.03×10^{-4}	—	5.35×10^{-4}	3.94×10^{-4}
5	—	—	—	—	—

equilibration with atmospheric air containing carbon dioxide (partial pressure $10^{-3.5}$) would raise the concentrations of Ca^{++} and HCO_3^- to 0.398×10^{-3} and 10^{-3} moles/l., respectively, and lower the carbonate concentration to 0.126×10^{-3} moles/l. These trends are reflected and established in data presented in Table 1. The value for the ionic concentration product $[\text{Ca}^{++}][\text{CO}_3^{--}]$, however, was not constant in the experimental conditions, and differs widely from the theoretical value: 0.2×10^{-6} . This inconstancy and discrepancy reflect non-attainment of equilibrium conditions.

(b) Even in the presence of sodium oleate, this surface chemical reaction mentioned is evident. The concentration of calcium in the solution increases as more carbon dioxide passes (Table 2). The slower increase in calcium concentration could be caused by an adsorbed layer of oleate hindering the diffusion of carbon dioxide or by the parallel precipitation reaction which results in the formation of calcium oleate.

(c) Adsorption of sodium oleate on calcite increases with a greater initial concentration of sodium oleate and with the use of a limited amount of carbon dioxide. With more carbon dioxide, however, a process of desorption is initiated.

The difference in the adsorption of oleate on calcite in the carbonated and uncarbonated pulp is pronounced for low concentrations of sodium oleate, for example, 2.35×10^{-4} moles/l. For a high concentration such as 9.4×10^{-4} moles/l., adsorption actually decreases with the use of carbon dioxide.

(d) Thus it seems plausible that bubbling a limited amount of carbon dioxide increases the concentration of the calcium in the solution through surface chemical reaction, which in turn induces heightened adsorption of collector (oleate) and increases flotability. The beneficial effect of carbon dioxide (in terms of collector adsorption and flotation) is discernible only at low collector concentration².

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