The Kinetics of Dissolution of Cubanite in Aqueous Acidic Ferric Sulfate Solutions

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When sintered disks of synthetic cubanite (CuFe$_2$S$_3$) were leached in acidified ferric sulfate solutions, the following reaction stoichiometry was observed:

$$\text{CuFe}_2\text{S}_3 + 3\text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{CuSO}_4 + 8\text{FeSO}_4 + 3\text{S}$$

Over the temperature range 45$^\circ$ to 90$^\circ$C, the reaction displayed linear kinetics that were interpreted as indicating rate control by some reaction occurring at the surface of the cubanite. The apparent activation energy for the dissolution process is 11.6 ± 0.7 kcal per mole. The dissolution rate increases steadily with increasing ferric concentration, but decreases with increasing strengths of either H$_2$SO$_4$ or FeSO$_4$. The addition of either NaCl or HCl to the leaching solutions substantially catalyzes the rate of cubanite dissolution. Natural cubanite appears to dissolve like the synthetic material.

A new experimentally large fraction of the world's copper production comes from low-grade deposits in which copper sulfide minerals are finely disseminated throughout the host rock. The open-pit mining methods usually associated with the exploitation of such ore bodies generate large tonnages of waste rock. Although the copper content of the waste is very low (e.g., <0.3 ptc Cu), the large amount produced makes it a potentially important source of copper. Currently several producers recover significant quantities of copper from such waste rock by dump leaching.$^2$ In dump leaching practice, the active dissolution agent is generally ferric sulfate formed in situ by the action of air and acid on various iron minerals present in the dump. The acid-ferric sulfate solution oxidizes and dissolves the copper sulfides. The copper-bearing solutions are then collected at the bottom of the dump for conventional processing to recover the copper.

Although copper dump leaching has been practised for many years, it is only recently that the important chemical reactions underlying this process have been studied. Recent papers from this laboratory$^3,^4$ have suggested possible mechanisms by which chalcopyrite (CuFeS$_2$) and bornite (Cu$_2$FeS$_4$) are solubilized in acidified ferric sulfate solutions. Cubanite (CuFe$_2$S$_3$) is a copper mineral which is occasionally of economic importance, especially in the Sudbury basin.$^5,^6$ The reactions of this common Fe-Cu sulfide with acidified ferric sulfate solutions have yet to be studied. For these reasons the chemistry of cubanite dissolution in acidified ferric sulfate solutions is important for the understanding of the reactions which occur during the dump leaching of copper sulfide ores.

In the present study, pure cubanite was synthesized and then leached under controlled conditions to elucidate the primary variables that govern the rate of cubanite dissolution.

EXPERIMENTAL

The cubanite used in this investigation was prepared by reaction-sintering pellets of CuS and FeS (CuFe$_2$S$_3$ = CuS.2FeS). The synthesis of CuS and FeS was described previously.$^7$ The two simple sulfides were ground to minus 150 mesh, weighed, mixed thoroughly, and then pressed into pellets at 80,000 psi. The pellets were vacuum-sealed in Pyrex ampoules, and sintered for 4 days at 550°C after an initial period at 450°C for 1 day. The pellets were cooled, crushed to minus 150 mesh, and then pressed into disks at 80,000 psi. No binder was used for any of the pressing operations. The second sintering was done in vacuum-sealed silica tubes at 825°C for 2 hr, and then the disks were slowly cooled to room temperature. They were polished through 3/0 emery paper, rinsed with acetone, and stored for future use.

The finished disks were about 2 mm thick and 26 mm in diam; the apparent surface area was about 5.2 sq cm and they had about 85 pct of the theoretical cubanite density. The synthesized sulfide had the pale brass-yellow color usually associated with cubanite. X-ray diffraction analysis confirmed that the sulfide was cubanite. Microscopic examination of polished surfaces revealed small inclusions of pyrrhotite (less than 0.5 vol pct) as the only impurity present in the fine-grained cubanite. Electron microprobe analysis confirmed that the matrix was homogeneous cubanite and that the inclusions were pyrrhotite. At the sintering temperatures, the cubanite field does not contain the composition CuFe$_2$S$_3$. Apparently some of the FeS rejected at high temperatures does not react even on fairly slow furnace-cooling, but is retained as widely scattered inclusions in the cubanite grains. The presence of small amounts of iron sulfide will not alter the amount of dissolved copper but will, obviously, affect the ferrous ion concentration of the solution to a slight degree. Microscopic examination of a leached disk revealed that the pyrrhotite was not preferentially attacked; only those grains at the surface were dissolved. Hence, the effect of small quantities of pyrrhotite would appear to be slight. There was no evidence to indicate that the pre-
sence of small amounts of the second phase interfered with the dissolution process.

The polished cubanite disks were cemented to lucite rods in such a way that only the polished face was exposed to the leaching solution, and the disks were then leached by an established method. This technique consists of rotating the disk at a fixed speed in an acidified ferric sulfate solution and periodically sampling and analyzing the solution for dissolved copper with a Technicon AutoAnalyzer. Liquid removed from the vessel by sampling or evaporation was replenished by a return feed of barren solution or of water, respectively.

RESULTS AND DISCUSSION

As mentioned previously, there are no published data on the dissolution of cubanite in acidified ferric sulfate solutions. In view of this deficiency, the first step in this study was to determine the reactions by which cubanite is dissolved. To this end, pellets of cubanite were reacted for various times at several temperatures, broken in half, and then examined by a variety of means to identify the solid reaction products. Fig. 1 shows a photomicrograph of a typical pellet that had been leached for 172 hr at 80°C in 0.1 M Fe⁺³ and 0.1 M H₂SO₄ solution. In the photograph, the white material is unreacted CuFe₂S₄, the black material is either reaction product or void space, and the light-grey band at the top of the picture is petrographic mounting resin. The reaction product was shown by X-ray diffraction analysis to consist of a mixture of elementary sulfur and unreacted cubanite; no other reaction products could be detected. The same reaction products were obtained under all experimental conditions investigated. Microprobe traces across the unreacted islands showed no new phases, even at the junction of the cubanite and the reaction product. In addition, microprobe analysis did not detect any appreciable stoichiometry variations in the unreacted cubanite. The sensitivity of this instrument was about ±0.5 pct of the Fe or Cu present in CuFe₂S₄.

The only soluble reaction products detectable were Fe⁺² and Cu⁺²; sulfate ion could not be detected accurately against the high sulfate background. The observed reaction products suggest that the dissolution of cubanite proceeds according to the following reaction:

\[ \text{CuFe}_2\text{S}_4 + 3\text{Fe}^2(\text{SO}_4)_2 = \text{CuSO}_4 + 8\text{FeSO}_4 + 3\text{S} \]  

This equation predicts a ferrous-ion-to-dissolved-copper ratio equal to 8. In the current tests, this ratio would rise slowly from about 2 to 8 as the total dissolved copper approached about 25 mg. This indicates a very slight initial preferential dissolution of copper from the cubanite; such small variations in stoichiometry were beyond the sensitivity of the microprobe. Once the total dissolved copper exceeded about 25 mg (or about 2 pct of the copper present in the pellet), the Fe⁺²/Cu⁺² ratio increased above 8, often as high as 10. Reaction [1] also predicts an elemental sulfur to dissolved copper ratio of 3. In our studies, this ratio was found to be between 2.6 and 2.8. These ratios appear to indicate that some of the finely divided sulfur produced by Reaction [1] is subsequently oxidized to sulfate; thus:

\[ \text{S}^0 + 6\text{Fe}^3+ + 4\text{H}_2\text{O} = \text{SO}_4^2- + 8\text{H}^+ + 6\text{Fe}^2+ \]  

This small amount of sulfate is difficult to detect against the high background of sulfate in the leaching solutions. Reaction [2] would explain both the high Fe⁺³/Cu⁺² ratios and the low S/Cu⁺² ratios. It appears that Reaction [1] accounts for the primary dissolution of the cubanite, while Reaction [2] simply consumes part of the elemental sulfur produced by the primary reaction.

Fig. 2 shows the type of curve obtained when synthetic cubanite was leached at temperatures between 45° and 90°C. The dissolution curves are linear, and this linearity persisted for several days. Positive deviations from linearity were observed in some tests when substantial amounts of copper were dissolved. This is