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Copper Precipitation from Sulfate Solutions with Calcium Carbonates

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Abstract—Mechanism of interaction of copper sulfate with natural calcium carbonates, responsible for low residual copper concentrations in solutions and for the behavior of open and closed systems in storage is considered.

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Natural calcium carbonates (limestone, marble, and dolomite) are used in wastewater treatment mainly as neutralizing reagents included in formulations [1, 2]. The use of calcium carbonates for acidity neutralization is widely known and has been repeatedly implemented in practice. The possibility of fixing toxic admixtures, including copper(II) ions, has been reported [2–6]. The interaction of solutions with a solid phase is usually regarded in this case as exchange of calcium and magnesium ions for ions of heavy non-ferrous metals in solution [5, 6] or as sorption of products of their hydrolysis by carbonates [3–5]. Accordingly, the sorption or exchange capacity of a precipitator should be in the range from one hundredth of a milligram to tens of milligrams per gram, which restricts the application field of natural calcium carbonates for treatment of wastewater with low concentrations of metals and complicates analysis of the resulting compounds [2, 3].

Hydrolytic purification of solutions to remove copper requires that they should be alkalized to pH 8–12 [7], whereas precipitation of copper on carbonates occurs at pH 4–7 and the pH rarely reaches a value of 7.5–8 in real flow-through systems [5, 8]. When cakes are subjected to X-ray and microscopic analyses, independent copper-containing mineral phases are occasionally identified (mostly poorly soluble basic salts) [3, 5, 8]. The capacity of a precipitator reaches 0.83 g g⁻¹ [5], which corresponds to reagent (but not sorption) precipitation methods and is close in stoichiometry to complete decomposition of the carbonate matrix.

The precipitation of basic salts of heavy metals has been studied in sufficient detail for the case of crystallization from solutions [9]. The formation of basic salts in a heterogeneous system constituted by a sulfate solution and solid calcium carbonate has virtually not been considered, despite the discovery of a number of natural associates of the corresponding composition in deposits of oxidized copper ores [10, 11]. An attempts to synthesize their artificial analogues from malachite or in the CuO–SO₃H₂O system failed [12]. It was shown in [8] that a wide range of minerals of basic copper sulfates (brochantite, posnjakite, and devilline) can be formed, depending on conditions of precipitation on natural calcium carbonates (initial concentration, temperature, and precipitator grain size).

This study is devoted to analysis of the mechanism of copper sulfate interaction with natural calcium carbonates.

EXPERIMENTAL

In the experiments, we used model solutions of copper sulfate with copper concentrations of up to 1 g l⁻¹, prepared from pure-grade reactive copper sulfate pentahydrate. To 1 l of the solution was added 1, 2, or 5 g of a precipitator. The experiments were carried out in glass beakers under static and dynamic conditions at room temperature.

The pH of the pulp was measured at regular intervals of time and 5-ml liquid-phase samples were taken.
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Fig. 1. X-ray diffraction patterns of the products of copper precipitation from sulfate solutions on (1) limestone, (2) marbled limestone, and (3) dolomite. Mineral phase: G, gypsum (CaSO$_4 \cdot 2$H$_2$O); B, brochantite [CuSO$_4 \cdot 3$Cu(OH)$_2$]; P, posnjakite [CuSO$_4 \cdot 3$Cu(OH)$_2$H$_2$O]; C, calcite (CaCO$_3$); D, devilline [CaCu$_4$(SO$_4$)$_2$(OH)$_6$H$_2$O]; and M, malachite [Cu$_2$(OH)$_2$CO$_3$].

for determining the copper content of a solution on an AAS-30 atomic absorption spectrometer (Carl Zeiss, Jena, Germany).

The X-ray phase analysis of the precipitates was carried out on a DRON-3 X-ray diffractometer (Cu$_{K\alpha}$ radiation, scanning at 0.02° intervals, accumulation time at a point 1 s). The X-ray diffraction patterns obtained were interpreted by the standard method, using the JCPDS file of reference spectra.

Compact colored precipitates (cyan to light green) readily separable from the liquid phase in settling or filtration were obtained in all the experiments. According to published data, copper precipitation upon contact with natural carbonates proceeds by an exchange reaction to give basic copper carbonates: malachite or azurite [11], in accordance with the overall equation

$$2\text{CaCO}_3 + 2\text{CuSO}_4 + 3\text{H}_2\text{O} = \text{CuCO}_3\cdot\text{Cu(OH)}_2 + 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CO}_2.$$  \(1\)

The solubility product of malachite ($1.7 \times 10^{-34}$) [13] is sufficiently low for deep purification of solutions; however, the calculation formula (2) for this open system contains equilibrium concentrations of carbonate and hydroxide ions, resulting from the solubility of poorly soluble calcium carbonate (SP = $3.8 \times 10^{-9}$) [13] and from partial hydrolysis of carbonate ions, respectively, which leads to a pronounced increase in the threshold concentration of copper precipitation.

$$\text{SP}_{\text{malachite}} < [\text{OH}^-]^2[\text{CO}_3^{2-}]a^{2+}_{\text{Cu}}.$$  \(2\)

The appearance of gypsum in the system reduces the equilibrium concentrations to an even greater extent and raises the residual copper concentrations to tens of parts per million.

In the experiments on solution purification, we obtained well-crystallized copper minerals, which can be readily identified. The X-ray diffraction patterns of typical products of copper precipitation on natural calcium carbonates are shown in Fig. 1. The key factor in copper fixation is the content and form of calcite (CaCO$_3$, JCPDS, 47-1743, $d = 3.03$ Å). Gypsum (CaSO$_4 \cdot 2$H$_2$O, JCPDS, 6-46, $d = 7.56$, 4.27, 3.79 Å) was crystallized in all the experiments, except those with the most dilute solutions. In all cases, the precipitates are a mixture of basic copper sulfates with...