Thermodynamic properties of minerals and fluids

Bublikova T.M.[1], Setkova T.V.[1] Thermodynamic modeling of atacamite [$Cu_2Cl(OH)_3$] solubility in ammonia solutions. *UDC 549.472.226:546.171.1*

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Abstract. Atacamite (Ata), [$Cu_2Cl(OH)_3$], is a characteristic mineral of the supergene zone and is widely distributed in regions with an arid climate. As a typical mineral of the oxidation zone, it forms paragenetic associations with malachite and azurite. Atacamite, like basic copper carbonates, is among the minerals important for the industrial production of copper. To determine the composition of copper ore leaching solutions, the behavior of atacamite during interaction with ammonium hydroxide was studied. Thermodynamic modeling was applied to calculate the copper concentration during the dissolution of atacamite in 1, 2, and 3 *m* NH_3 solutions. The calculation parameters corresponded to the conditions of hydrometallurgical ammonia leaching processes: T = 25–100 °C, P = 0.1 MPa. It was established that atacamite dissolves incongruently in ammonia solutions with the formation of tenorite, the precipitation of which is the rate-limiting step of the leaching process. The concentration of dissolved copper increases with an increase in the ammonia solution concentration and decreases with increasing temperature.

Keywords: *hydrometallurgy, ammonia leaching, atacamite, tenorite, malachite, azurite, ammonia solutions, thermodynamic modeling*

Introduction. Atacamite (Ata), [$Cu_2Cl(OH)_3$], is a characteristic mineral of the supergene zone and is widely distributed in regions with an arid climate. It is also known to occur in fumaroles on volcanic slopes and in deep-sea hydrothermal vents. In the oxidation zone of copper deposits, atacamite develops as a secondary product of primary copper sulfide oxidation, being mainly characteristic of the middle stages of its formation. Upper horizons of cupriferous sandstones are frequently enriched with this mineral. Atacamite occurs in association with brochantite, malachite, azurite, tenorite, chrysocolla, and several other minerals; it is present in all copper-bearing ore bodies, often forming relatively large monomineralic segregations. Large volumes of atacamite are known to be located in the oxide zones of ore deposits in the Atacama Desert (Chile), and at the Mount Gunson copper mine (South Australia), it is the primary copper ore mineral (Cameron et al., 2007; Reich et al., 2008; Le Roux et al., 2016). Although atacamite is considered a rare collector's mineral, when forming large accumulations, it represents a high-grade copper ore and is among the 15 copper-bearing minerals of major industrial significance.

In hydrometallurgical processes, copper is obtained by chemical ore leaching. Acid leaching frequently utilizes acid solutions (Bingöl & Canbazoğlu, 2004). The dissolution kinetics of atacamite in dilute sulfuric acid, as well as the effects of temperature, interaction time, and solution concentration on the practical copper yield, have been studied in previous works (Quast, 2000; Javanshir et al., 2024). However, with a high content of carbonates or oxides in the ore, acid consumption increases to a level that renders this approach economically unviable. Alkaline leaching serves as an alternative to the acid method. The use of ammonia solutions enhances dissolution selectivity and reduces the corrosive impact of the solvent. The influence of technological process parameters (solution composition, temperature, stirring speed, solid-to-liquid ratio, and kinetic characteristics) on the percentage yield of copper has been addressed in a large number of publications (Arzutug & Kocakerim, 2004; Aracena et al., 2015, 2020; Velásquez-Yévenes & Ram, 2022). Malachite, azurite, tenorite, chrysocolla, cuprite, and both natural and synthetic ores served as model objects in those studies. The leaching of atacamite has been studied much less extensively. Data on the interaction of atacamite with ammonia solutions are very scarce, and a quantitative evaluation of atacamite solubility in ammonium hydroxide is completely lacking. Nevertheless, copper ore typically has a complex composition, and atacamite is frequently one of its components.

The aim of this study was to evaluate the feasibility of using ammonia solutions for atacamite leaching. The main objectives of the research were to study the interaction reaction between atacamite and ammonium hydroxide and to calculate the copper concentration in the solution resulting from the atacamite leaching process. To accomplish these tasks, the method of thermodynamic modeling was applied. The calculations were performed using the HCh geochemical modeling software package (Shvarov & Bastrakov, 1999) and a previously compiled database of thermodynamic properties of substances (Bublikova et al., 2025). The calculation parameters corresponded to the conditions of hydrometallurgical ammonia leaching processes: ammonium hydroxide concentration of 1, 2, and 3 *m* NH_3; T = 20–100 °C; P = 0.1 MPa (Panayotova & Panayotov, 2017).

Calculation Results and Discussion. Figure 1 shows the calculated isotherm-concentration curves representing the dissolved copper content as a function of temperature in the range of 20–100 °C at

fixed initial ammonia concentrations of 1, 2, and 3 *m* NH_3. The obtained results allowed for the following conclusions to be drawn. An increase in the NH_3 concentration exerts a determining effect on atacamite solubility. At a temperature of 20 °C, increasing the ammonia content from 1 to 3 *m* leads to more than a 12-fold increase in the copper concentration in the solution (from 0.04 to 0.51 mol/kg), which indicates the intensive occurrence of complexation processes with the formation of dominant copper ammine complexes (Wang et al., 2009; Bublikova et al., 2025). The nature of the temperature dependence in the studied interval indicates the exothermic nature of the dissolution process; with an increase in temperature from 20 to 100 °C, the mineral solubility decreases. However, the dynamics of this decrease significantly depend on the excess of the reagent. While a sharp drop in copper concentration is observed in 1 m and 2 *m* NH_3 solutions, the system demonstrates high thermal stability under 3 *m* NH_3 conditions. In this case, the decrease in solubility has a nearly linear character, and the copper content at 100 °C remains at a high technological level of approximately 0.41 mol/kg. The degree of copper concentration reduction varies: from 20% for 3 *m* NH_3 to an order of magnitude difference in 1 *m* NH_3 solutions.

The dissolution of atacamite in ammonia solutions occurs incongruently with the formation of tenorite. Figure 2a shows the calculated ratio of solid phases in thermodynamic equilibrium with a 1 *m* NH_3 mother liquor in the temperature range of 20–100 °C. The simultaneous presence of residual amounts of atacamite (62% at 20 °C) and newly formed tenorite (38%) in the equilibrium precipitate confirms the incongruent nature of the mineral dissolution in an ammonia medium. An increase in temperature across the entire studied range leads to a slight increase in the tenorite fraction (from 38% at 20 °C to 42% at 100 °C). Upon transitioning to a more concentrated ammonia solution (2 *m* NH_3), the character of the heterogeneous equilibrium changes significantly (Fig. 2b). Even at the base temperature of 20 °C, the fraction of secondary tenorite in the equilibrium precipitate becomes dominant and amounts to 68%, while the residual atacamite accounts for only about 32%. Heating the system monotonically intensifies the process of incongruent transformation across the entire investigated temperature interval. At 100 °C, the replacement of the initial phase by copper oxide reaches its maximum: the tenorite content in the solid residue increases to 92%, and the residual amount of atacamite drops to a minimum of 8%. The maximum concentration of the reagent (3 *m* NH_3) leads to the complete completion of the incongruent transformation of the initial mineral. Across the entire investigated temperature range (20–100 °C), atacamite is absent from the equilibrium solid phase, and 100% tenorite is the only stable crystalline phase of the residue. Such dynamics of the phase ratios are in strict causal relationship with the temperature behavior of the liquid phase. The intensive increase in the tenorite mass upon heating is driven by the destruction of copper-ammonia complexes and hydrolysis, accompanied by the directed redistribution of dissolved copper into the thermodynamically stable copper oxide (CuO) phase, which is recorded at the macro-level as a sharp drop in the total solubility of the mineral.

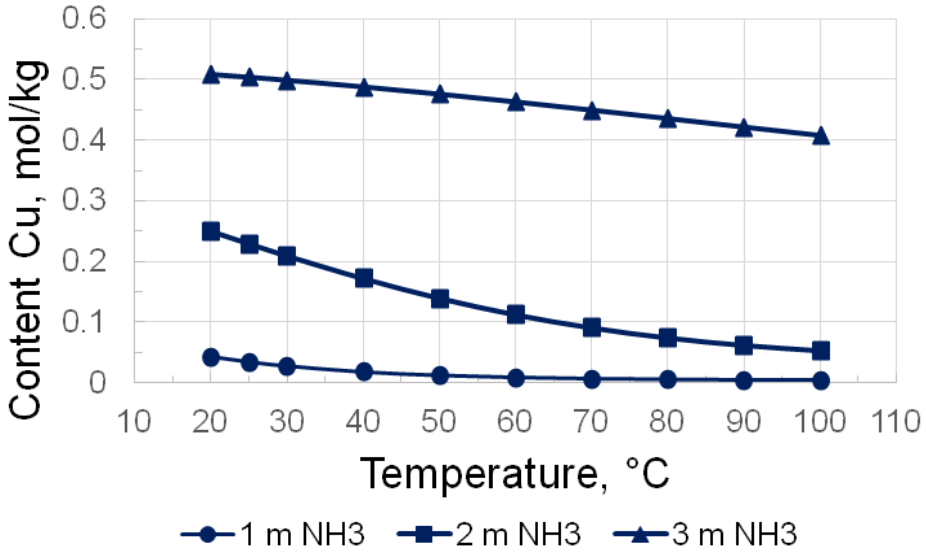

Fig. 1. Copper concentration in solution as a function of temperature during atacamite leaching with 1, 2, and 3 *m* NH_3 solutions. P = 0.1 MPa.

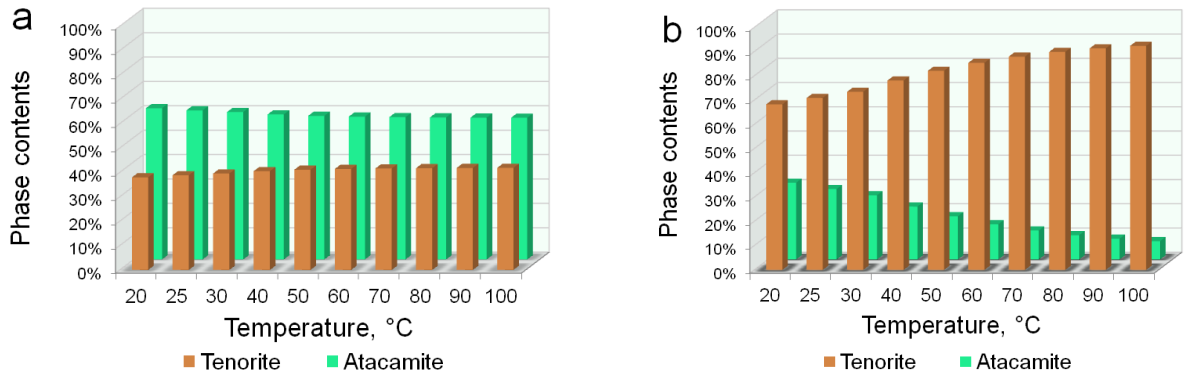

Fig. 2. Change in the ratio of solid phases as a function of temperature during the incongruent dissolution of atacamite in solutions of: a – 1 *m* NH_3; b – 2 *m* NH_3.

To evaluate the thermodynamic stability of copper-bearing minerals in an ammonia medium and to identify the factors limiting the leaching process, a comparative modeling of the solubility of malachite, azurite, atacamite, and tenorite was performed. Table 1 presents the calculated values of the equilibrium copper concentration in the liquid phase at the boundary temperatures of the studied interval (20 and 100 °C).

Table 1. Equilibrium copper concentration in solution during the leaching of copper-bearing minerals with ammonia solutions as a function of ammonia concentration and temperature (mol/kg)

Solution concentration	Temperature, °C	Malachite $[Cu_2CO_3(OH)_2]$	Azurite $[Cu_3(CO_3)_2(OH)_2]$	Tenorite [CuO]	Atacamite $[Cu_2Cl(OH)_3]$
1 *m* NH_3	20	0.1620	0.1230	0.0029	0.0423
	100	0.0567	0.0540	0.0002	0.0040
2 *m* NH_3	20	0.3810	0.3820	0.0111	0.2414
	100	0.2130	0.2200	0.0008	0.0518
3 *m* NH_3	20	0.6010	0.6130	0.0230	0.4863
	100	0.3900	0.4000	0.0020	0.3902

A comparative analysis of the obtained quantitative data allows for the following patterns to be formulated. Under the studied physicochemical conditions at temperatures of 20–100 °C and concentrations of 1–3 *m* NH_3, the equilibrium copper concentration during the dissolution of tenorite is minimal and remains within the range of 0.0002–0.0230 mol/kg. A comparison with the initial atacamite reveals that the copper concentration during tenorite dissolution is 15–20 times lower at 20 °C, and at 100 °C this difference becomes maximum, reaching two orders of magnitude (for instance, in a 1 *m* NH_3 solution). At the base temperature of 20 °C, the solubility of atacamite is of the same order of magnitude and is only slightly lower than the values for malachite and azurite investigated by us previously (Bublikova et al., 2025). In an excess of the reagent (3 *m* NH_3) at 100 °C, the solubility of atacamite practically equates to that of malachite, and the copper concentration values in the equilibrium solutions are very close. Since the thermodynamic solubility of tenorite is significantly lower than that of the initial atacamite (as well as malachite and azurite), its spontaneous formation during the incongruent dissolution of these minerals leads to the kinetic inhibition of the process. The formation of tenorite is the rate-limiting step in the atacamite leaching process.

Conclusion. The high values of the equilibrium copper concentration during atacamite leaching (up to 0.4863 mol/kg in 3 *m* NH_3) substantiate the fundamental feasibility of its processing via hydrometallurgical ammonia leaching on par with the basic copper carbonates, malachite and azurite (Welham et al., 2015). The enormous gap in solubility between atacamite and tenorite acts as the primary factor complicating the actual technological process. The physicochemical stability of tenorite indicates that, in an experimental setting, atacamite leaching will rapidly shift into a diffusion-controlled regime and halt long before the calculated copper capacity of the solution is reached. To overcome this barrier in practice, methods of intensive mechanical activation or attrition stirring can be utilized within

the technological process, aimed at the continuous destruction of the passivating oxide layer.

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