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Solubility prediction of malachite in aqueous ammoniacal ammonium chloride solutions at 25 °C

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ABSTRACT

The solubility of malachite in the presence of ammonia, ammonium chloride and their mixed solution is calculated by a geochemical modeling code and is measured in a series of dissolution experiments using synthetic malachite at 25 °C. The simulated results show a good agreement with the experimental data gained at 25 °C. The predicted and experimental results indicate that the precipitate CuO limits the copper solubility in aqueous ammonia and $Cu(OH)_{1.5}Cl_{0.5}$ in aqueous ammonium chloride. For a mixed solution containing ammonia and ammonium chloride, highest copper solubility can be achieved by adjusting the $[NH_3]/[NH_4Cl]$ ratio to about 2:1. The thermodynamic model presented rationalises the interactions between the different components and predicts the influence of changes in the concentration of ammonia and ammonium chloride on the copper solubility of malachite.

1. Introduction

Copper oxide minerals such as tenorite (CuO) and those containing silicate (chrysocolla, $(Cu,Al)_2H_2Si_2O_5(OH)_4\cdot nH_2O$), carbonate (malachite, $Cu_2(CO_3)(OH)_2$, azurite, $Cu_3(CO_3)_2(OH)_2$) and chloride (atacamite, $Cu_2Cl(OH)_3$) are generally treated by leaching of the crushed ore with either sulphuric acid or alkaline medium, followed by a separation step such as adsorption, precipitation, solvent extraction (SX) or/and electrowinning (EW) to produce a cathode or powder products. Sulphuric acid is the most usual leaching agent for copper oxide ores, but the acid consumption and cost may be important factors in extracting copper from low grade oxide ores containing carbonate minerals, such as limestone and dolomite. Alkaline leaching is more selective and offers less corrosion and lower reagent consumption for calcareous carbonate gangue.

Ammonia, together with ammonium salts have been tried on a commercial scale for many years. The ammonia leaching process was first used to recover copper from copper carbonate and native copper tailings at the Kennecott plant, Alaska in 1915 (Habashi, 1983; Alguacil, 1999). The oxides and carbonates of copper are quite readily soluble in ammonia but the leach solution must be kept in sealed vessels due to the perceptible volatility of the gas in aqueous solution. When the ammoniacal copper solution is boiled, black copper oxide is precipitated and the ammonia vapor is condensed in towers and recycled. However, this process has not met much encouragement, due largely to the slow leaching kinetics and low solubility of copper. In addition, ammonia-tight vessels have proved complicated and expensive to operate.

For high copper extraction and fast leaching kinetics without fine grinding, Arbiter developed an ammoniacal pressure leaching process at elevated temperatures to treat copper oxide and sulphide ores, followed by SX/EW (Kuhn et al., 1974). The process used ammonia/ammonium sulphate as a lixiviant with 34.5 kPa oxygen to extract copper from copper sulphide concentrates. After filtering the solids, copper was solvent extracted by LIX-65N, then stripped by sulphuric acid and electrowon to give metallic copper. This process was applied to Anaconda's Arbiter Plant and BHP's Coloso plant in Chile. Although they showed a high reaction rate and good yields, the two plants were shut down in late 1977 and in mid-1998, respectively, as a result of high maintenance and operating costs with this technique (Arbiter and McNulty, 1999). Numerous review articles on such applications can also be found in the literature (Arbiter and Fletcher, 1993; Meng and Han, 1996).

Malachite is the most common mineral in copper oxide ores and a considerable amount of research focuses on the leaching kinetics of malachite in ammonia/ammonium salt solutions such as $(NH_4)_2CO_3$, $(NH_4)_2SO_4$ or NH_4Cl (Bingol et al., 2005; Ekmekyapar and Oya, 2003; Künkül et al., 1994). The process chosen usually depends upon both the composition and the localization of the ore. However, the use of NH_4Cl presents certain advantages over other salts, such as: (i) many non-ferrous metals are complexed by chloride ions and are highly soluble in water; (ii) chloride is an aggressive ion which improves the kinetics of dissolution of oxides (Ek et al., 1982) and sulphides (Winand, 1991); (iii) ammonium chloride is more soluble than ammonium sulphate and lower cost in China.

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In previous work on the treatment of copper oxide minerals by ammonia leaching (Bingol et al., 2005; Ekmekyapar and Oya, 2003), emphasis was put on the effects of process conditions on copper recovery such as leaching time, solid/liquid ratio, leaching temperature, particle size, ammonia/ammonium salt concentration ratio and pH. However, many details of the chemistry of such systems were unclear and no systematic study of copper solubility under these conditions has been found.

The knowledge of copper solubility under these conditions is very important for developing a suitable hydrometallurgical process. An understanding the soluble and solid phases in solution during the leaching of copper oxide minerals, can give important insights into the chemical processes and the interactions between the liquid and solid phases. The modeling of these interactions using geochemical speciation codes is the basis for the chemical understanding of these processes and the factors influencing them. In addition, adequate thermodynamic models allow easy and fast parameter variations and make it possible to predict the response of the system to changes that may result from the dissolution of minerals.

The aim of the present study is to use geochemical speciation codes to predict the solubility of malachite and to understand the behavior of the system in the presence of ammonia, ammonium chloride and their mixed solution.

2. Experimental

The copper solubility of malachite ($Cu_2CO_3(OH)_2$) in ammonia solution, ammonium chloride and their mixed solution was studied over the concentration range of 0–3 m (mol/kg H_2O). For the mixed solution, the relative amounts of ammonia and ammonium chloride were changed while keeping the total concentration of ammonia equal to 3 m. As received synthetic malachite having similar composition and crystal structure as natural malachite was used to conduct dissolution experiments at a concentration of 10 g/kg H_2O for aqueous NH_4Cl solutions, 150 g/kg H_2O for aqueous ammonia solutions or the mixed solutions.

Table 1
Thermodynamic data of the species used to calculate ion and phase distribution of dissolution experiments at 25 °C.

Species	Log*K*	Reference
$Cu^{2+}+Cl^-=CuCl^+$	0.413	Sverjensky et al. (1997)
$Cu^{2+}+2Cl^-=CuCl_{2(ac)}$	−0.665	Sverjensky et al. (1997)
$Cu^{2+}+2Cl^-=CuCl_{2(s)}$	3.73	Ball and Nordstrom (1991)
$Cu^{2+}+3Cl^-=CuCl_3^-$	−2.252	Sverjensky et al. (1997)
$Cu^{2+}+4Cl^-=CuCl_4^{2-}$	−4.54	Sverjensky et al. (1997)
$Cu^{2+}+H_2O=CuOH^++H^+$	−7.497	Smith and Martell (1997)
$2Cu^{2+}+OH^-=Cu_2OH^{3+}$	8.05	Martell and Smith (2003)
$Cu^{2+}+2H_2O=Cu(OH)_{2(ac)}+2H^+$	−16.194	Smith and Martell (1997)
$Cu^{2+}+2H_2O=Cu(OH)_{2(s)}+2H^+$	8.67	Smith and Martell (1998)
$Cu^{2+}+3H_2O=Cu(OH)_3^-+3H^+$	−26.879	Smith and Martell (1997)
$Cu^{2+}+4H_2O=Cu(OH)_4^{2-}+4H^+$	−39.98	Smith and Martell (1997)
$2Cu^{2+}+2OH^-=Cu_2(OH)_2^{2+}$	17.5	Martell and Smith (2003)
$3Cu^{2+}+4OH^-=Cu_3(OH)_4^{2+}$	35.2	Martell and Smith (2003)
$Cu^{2+}+NH_3=Cu(NH_3)^{2+}$	4.02	Martell and Smith (2003)
$Cu^{2+}+2NH_3=Cu(NH_3)_2^{2+}$	7.40	Martell and Smith (2003)
$Cu^{2+}+3NH_3=Cu(NH_3)_3^{2+}$	10.20	Martell and Smith (2003)
$Cu^{2+}+4NH_3=Cu(NH_3)_4^{2+}$	12.30	Martell and Smith (2003)
$Cu^{2+}+5NH_3=Cu(NH_3)_5^{2+}$	12.43	Smith and Martell (1976)
$Cu^{2+}+NH_3+OH^-=CuNH_3OH^+$	11.3	Gübeli et al. (1970)
$Cu^{2+}+3NH_3+OH^-=Cu(NH_3)_3OH^+$	15	Gübeli et al. (1970)
$Cu^{2+}+2NH_3+2OH^-=Cu(NH_3)_2(OH)_{2(ac)}$	17	Gübeli et al. (1970)
$Cu^{2+}+NH_3+3Cl^-=CuNH_3Cl_3^-$	3.62	Limpo et al. (1993)
$Cu^{2+}+CO_3^{2-}=CuCO_3(aq)$	6.77	Martell and Smith (2004)
$Cu^{2+}+2CO_3^{2-}=Cu(CO_3)_2^{2-}(aq)$	10.2	Martell and Smith (2004)
$Cu^{2+}+HCO3^-=CuHCO_3^+$	1.8	Martell and Smith (2004)
$Cu_2CO_3(OH)_{2\ (s)}+2H^+=2Cu^{2+}+CO_3^{2-}+2H_2O$	−5.18	Ball and Nordstrom (1991)
$Cu^{2+}+1.5OH^-+0.5Cl^-=Cu(OH)_{1.5}Cl_{0.5(s)}$	17.3	Martell and Smith (2003)
$Cu^{2+}+2OH^-=CuO_{(s)}+H_2O$	19.5	Martell and Smith (2003)
$Cu^{2+}+CO_3^{2-}=CuCO_3(s)$	11.5	Martell and Smith (2004)

Table 2
Copper solubility data in the malachite–NH_3–NH_4Cl–H_2O system at 25 °C.

No.	Amounts of input species (mol/kg H_2O)			Solution composition at equilibrium (mol/L)			Measured pH
	Malachite	NH_4Cl	NH_3	$[Cu]_T$	$[Cl]_T$	$[NH_3]_T$	
1	0.045	0.499	–	0.0005	0.519	0.0054	6.82
2	0.045	0.995	–	0.0024	0.911	0.0089	6.72
3	0.045	1.490	–	0.0051	1.414	0.0196	6.66
4	0.045	1.993	–	0.0089	1.846	0.0275	6.54
5	0.045	2.492	–	0.0122	2.258	0.0415	6.39
6	0.045	2.988	–	0.0190	2.637	0.0576	6.33
7	0.678	–	0.513	0.0873	–	0.498	10.16
8	0.678	–	1.053	0.2222	–	1.011	10.27
9	0.678	–	1.599	0.3431	–	1.483	10.60
10	0.678	–	2.162	0.4359	–	2.085	10.99
11	0.678	–	2.396	0.4664	–	2.371	10.90
12	0.678	–	3.000	0.6071	–	2.764	10.94
14	0.678	2.490	0.512	0.2038	2.490	0.532	7.51
15	0.678	1.993	1.024	0.3859	2.004	1.193	8.06
16	0.678	1.490	1.536	0.5570	1.400	1.956	8.59
17	0.678	0.996	2.048	0.6502	0.907	2.296	9.57
18	0.678	0.498	2.560	0.5976	0.422	2.627	10.60

The reactants were stored in sealed glass-bottles, shaken at 25 ± 1 °C in a thermostat bath for 2 months and the solid and liquid phases were separated by vacuum filtration. The solid phases were characterized by X-ray diffraction (XRD) analysis using a Philips Rigaku™ DMAX 2250VB + diffractometer to determine the composition of the leach residues. The concentrations of the dissolved copper ions were analyzed using atomic absorption spectrometry (AAS) and ammonia by back titration by adding excess standardized HCl solution and titrating with standardized NaOH using methyl orange as an indicator. Chloride ion was determined by the Volhard method. The pH measurements were performed after the solutions reached equilibrium using pH-300C pH-meter. All experimental solutions were prepared from distilled water and analysis grade reagents.

3. Thermodynamic model and data

The Gibbs free energy minimization program GEMS-PSI (version 2.3.0 rc8) (Kulik, 2009) was used to calculate the presence, amount

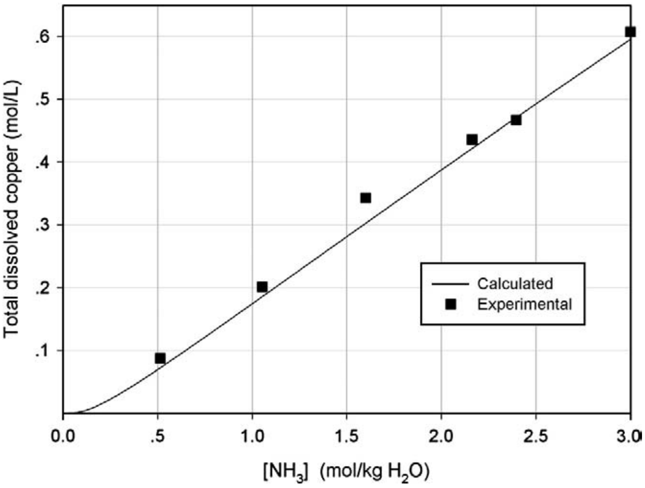

Fig. 1. Calculated and experimental copper solubility for malachite as a function of concentration of NH_3 at 25 °C.