A Rigorous Calculation Method for Determining Potential-pH Diagrams in Metal-ammonia-water Systems

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The main aim of this research work is to determine optimal leaching conditions: Eh, pH and total ammonia concentrations, for recovery of copper and nickel from electroplating hydroxide sludges containing iron, chrome, copper and nickel hydroxides. This has been preceded by a theoretical approach and numerical and computer calculation. By maintaining total dissolved metal and total ammonia constant, all equilibriums are taken into consideration simultaneously. The diagrams then show stable domains for the solution and solids. Solubility curves and potential-pH diagrams for the copper-water-ammonia and nickel-water-ammonia systems at different total metal and different total ammonia concentrations have been presented. This analysis has practical value in interpreting the process conditions required to conduct hydrometallurgical processes.

Key Words: Copper, Nickel, Eh-pH diagram, leaching, ammoniacal leaching, hydroxide sludges and industrial waste.

INTRODUCTION

There are several potential applications for complexing agents in mineral and metallurgical processing operations. In some cases these agents may provide excellent lixiviant action, while being environmentally benign. Several studies have investigated the potential of ammonia as lixiviant. These include the leaching of copper and nickel from electroplating hydroxide sludges[1,2], metal finishers, treatment of acid mine drainage, and industrial wastewater in general[3], roast reduced deep-sea manganese nodules[4]. Jeffrey[5] used ammonia-thiosulfate solutions as lixiviants for gold and silver. Kazinczy *et al.*[6] studied the ammoniacal leaching of zinc from sludges containing iron and zinc hydroxides. Philip and coworkers[7] have suggested the use of ammoniacal thiosulfate and sodium cyanide as lixiviants for preg-robbing Goldstrike ore carbonaceous matter. Shawn *et al.*[8]

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have developed the ammoniacal lixiviants for the *in-situ* leaching of chalcopyrite. Feng *et al.*[9] have developed the ammoniacal thiosulphate leaching for gold-host sulphides such as chalcopyrite, pyrite, arsenopyrite and pyrrhotite. Babu and coworkers[10] studied the recovery of zinc from sphalerite concentrate by direct oxidative leaching with ammonium, sodium and potassium persulphates. Aylmore and Muir[11] carried out the thermodynamic analysis of gold leaching by ammoniacal thiosulfate using Eh/pH and speciation diagrams.

The construction of Eh-pH diagrams is a useful way to summarize redox properties and chemical speciation. This diagram shows the Eh-pH domains for a number of aqueous systems. The most well known of such stability or predominance area diagrams is the Eh-pH diagram introduced by the work of Pourbaix[12]. Eh-pH diagrams enable us to see at a glance the range of stability of aqueous species and solid compounds under specified conditions of Eh (or redox potential) and pH.

Apart from Eh-pH diagrams, other predominance area diagrams of interest include log [M]-pH and log [NH$_3$]-pH diagrams. In this work the thermodynamic basis and the mathematical formalism underlying the construction of predominance area diagrams are developed. These thermodynamic and mathematical concepts are then applied to complex systems such as those of the type metal-NH$_3$-H$_2$O.

All calculations have used all thermodynamic equilibrium constants and mass balance equation for metal and for ammonia, and a combination between the two, for determining the three following functions:

A. The total concentration of metal ions as a function of pH at various values of total ammonia.

B. The total concentration of metal ions as a function of total ammonia at various values of pH.

C. The redox potential as a function of pH at various values of total concentration of metal and ammonia.

Theoretical

In metal finishing hydroxide sludges, the metals are usually present as hydroxides: M(OH)$_n$. The solubilities of M(OH)$_n$ in water are principally based on the expression for the solubility product K$_s$. However, the solubility of the precipitated forms is often substantially influenced by various side reactions, namely by complexation with the ammonia and by various protolytic reactions in which H$^+$ and/or OH$^-$ participate. The solubility affected by side reactions can be calculated by means of total concentration of metal ions as a function of pH at various values of total ammonia; total concentration of metal ions as a function of total ammonia at various values of pH and redox potential can be calculated as a function of pH at various values of total concentration of metal and of ammonia.

Equilibrium data

For each system, the mathematical consequences are expressed in terms of equilibrium constants, a mass balance equation. Each thermodynamic equilibrium constant can be rigorously written in terms of activity, and the mass balance equation can be rigorously written in terms of concentration. In dilute solution, activity coefficients depend only on the ionic strength of the solution and the charge on the ion. The theoretical prediction of activity coefficient is fairly accurate at ion concentrations below 0.1 mol/L; in more concentrated solution the activity coefficient becomes dependent upon the nature of the ion in solution and a simple formulation is note feasible. The validity of the original and of the different extended forms of the Debye-Hückel equation is fairly limited. Butler indicated that, at concentration above 1 M, the errors involved in estimating activity coefficients are usually of the order of magnitude of the activity coefficients themselves. Therefore, it is just as accurate, and also much simpler, in this situation to assume that the concentration constant (usually measured in 1–4 M $NaClO_4$, if available) is independent of ionic strength. Results obtained with this approximation are usually not in error by more than a factor of 2, if all equilibriums have been taken into account[13]. In hydrometallurgical systems, when a concentrated solution is considered, it is preferable to use concentration constants rather than activity constants[14]. In our calculation, the concentration constants at ionic strengths of 2.0 mol/L are assumed. The concentration constants of metal ions and their complexes measured at constant ionic strength are extracted from the literature[12, 15, 16]. High temperature equilibrium constants can be extrapolated from low temperature values using the correspondence Principle[17].

Equilibriums and Equations

Copper: Ammonia exists in aqueous solutions in two different forms, namely NH_4^+ (ammonium) and NH_3 (ammonia). Ammonia forms soluble complexes with both cupric and cuprous ions. Species present in solution and minerals to be considered: Cu^{2+}, Cu^+, $Cu(OH)^+$, $Cu(OH)_2$, $Cu(OH)_3^-$, $Cu(OH)_4^{2-}$, $Cu(NH_3)^+$, $Cu(NH_3)^{2+}$, $Cu(NH_3)_2^{2+}$, $Cu(NH_3)_3^{2+}$ and $Cu(NH_3)_4^{2+}$. The principal copper solid species are: Cu, CuO and Cu_2O. The thermodynamic data for Cu^{2+}-NH_3-H_2O system are represented in Table-1.

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TABLE-1

THERMODYNAMIC DATA FOR Cu – NH₃ – H₂O SYSTEM AT 25°C[12, 15–16]

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Reaction	Property at 25°C	
$2H^+ + 2e = H_2$	Eh°	0
$\frac{1}{2}O_2 + 2H^+ + 2e = H_2O$	Eh°	1.229
$Cu^{2+} + e = Cu^+$	Eh°	0.15
$Cu^+ + e = Cu$	Eh°	0.69
$Cu^{2+} + 2e = Cu$	Eh°	0.337
$H_2O = H^+ + OH^-$	log K_w	13.96
$NH_3 + H^+ = NH_4^+$	log K_N	9.5
$Cu^{2+} + H_2O = Cu(OH)^+ + H^+$	log K_1	6
$Cu^{2+} + 2H_2O = Cu(OH)_2 + 2H^+$	log K_2	10.6
$Cu^{2+} + 3H_2O = Cu(OH)_3^- + 3H^+$	log K_3	14.1
$Cu^{2+} + 4H_2O = Cu(OH)_4^{2-} + 4H^+$	log K_4	16.3
$Cu^+ + NH_3 = Cu(NH_3)^+$	log β_1	5.90
$Cu^+ + 2NH_3 = Cu(NH_3)_2^+$	log β_2	4.9
$Cu^{2+} + NH_3 = Cu(NH_3)^{2+}$	log β_3	4.24
$Cu^{2+} + 2NH_3 = Cu(NH_3)_2^{2+}$	log β_4	7.83
$Cu^{2+} + 3NH_3 = Cu(NH_3)_3^{2+}$	log β_5	10.83
$Cu^{2+} + 4NH_3 = Cu(NH_3)_4^{2+}$	log β_6	12.43
$Cu_2O(s) = Cu^+ + OH^-$	log Ksp_1	14.84
$Cu(OH)_2(s) = Cu^{2+} + 2OH^-$	log Ksp_2	19.32

Eh° = the standard reduction potential for the reaction indicated with respect to the standard hydrogen electrode; Kw = the concentration constant for the dissociation of water; K_N = the concentration constant for the formation of ammonium ion; Ksp denotes solubility product of the metal hydroxide and the β values are the concentration constant for the association reactions indicated for the progressive amines of metal.

A. Cu₂O solubility

The mass balance of ammonia ($[NH_3]_T$) is given by:

$$[NH_3]_T = [NH_3]_L + [NH_4^+] + [Cu(NH_3)^+] + 2[Cu(NH_3)_2^+] \tag{1}$$

$$[NH_3]_T = \alpha + [Cu^+]_L \cdot \gamma_1 = \alpha + 10^{pK_w - pK_s - pH} \cdot \gamma_1 = f(pH, [NH_3]_L) \tag{2}$$

$$\alpha = [NH_3]_L + [NH_4^+] = 10^{pNH_3} \cdot (1 + 10^{pK_w - pH}) \tag{3}$$

$$\gamma_1 = 1 + 10^{\log \beta_1 - pNH_3} + 2.10^{\log \beta_2 - 2pNH_3} \tag{4}$$

The mass balance of Cu($[Cu^+]_T$) is given by:

$$[Cu^+]_T = [Cu^+]_L + [Cu(NH_3)^+] + [Cu(NH_3)_2^+] \tag{5}$$

$$[Cu^+]_T = [Cu^+]_L \cdot \lambda_1 + 10^{\log K_w - pK_{sp_1} - pH} \cdot \lambda_1 \tag{6}$$

where $\qquad \lambda_1 = 1 + 10^{\log \beta_1 - pNH_3} + 10^{\log \beta_2 - 2pNH_3} \tag{7}$

B. CuO solubility

The mass balance of ammonia ($[NH_3]_T$) is given by:

$$[NH_3]_T = [NH_3]_L + [NH_4^+] + [Cu(NH_3)^{2+}] + 2[Cu(NH_3)_2^{2+}] + 3[Cu(NH_3)_3^{2+}]$$
$$+ 4[Cu(NH_3)_4^{2+}] + 5[Cu(NH_3)_5^{2+}] \tag{8}$$

$$[NH_3]_T = \alpha + [Cu^{2+}]_L \cdot \gamma_2 = \alpha + 10^{2pK_w - pK_{sp_1} - 2pH} \cdot \gamma_2 = f(pH, [NH_3]_L) \tag{9}$$

$$\alpha = [NH_3]_L + [NH_4^+] = 10^{pNH_3} \cdot (1 + 10^{pK_w - pH}) \tag{10}$$

$$\gamma_2 = 1 + 10^{\log \beta_1 - pNH_3} + 2 \cdot 10^{\log \beta_2 - 2pNH_3} + 3 \cdot 10^{\log \beta_3 - 3pNH_3} + 4 \cdot 10^{\log \beta_4 - 4pNH_3}$$
$$\tag{11}$$

The mass balance of $Cu([Cu^{2+}]_T)$ is given by:

$$[Cu^{2+}]_T = [Cu^{2+}]_L + [Cu(NH_3)^{2+}] + [Cu(NH_3)_2^{2+}] + [Cu(NH_3)_3^{2+}] + [Cu(NH_3)_4^{2+}]$$
$$+ [Cu(NH_3)_5^{2+}] + [Cu(OH)^+] + [Cu(OH)_2] + [Cu(OH)_3^-] + [Cu(OH)_4^{2-}]$$
$$\tag{12}$$

$$[Cu^{2+}]_T = [Cu^{2+}]_L \cdot \lambda_2 = 10^{2pK_w - pK_{sp_1} - 2pH} \cdot \lambda_2 \tag{13}$$

where

$$\lambda_2 = 1 + 10^{\log \beta_1 - pNH_3} + 10^{\log \beta_2 - 2pNH_3} + 10^{\log \beta_3 - 3pNH_3} + 10^{\log \beta_4 - 4pNH_3}$$
$$+ 10^{pH - \log K_1} + 10^{2pH - \log K_1} + 10^{3pH - \log K_1} + 10^{4pH - \log K_2} \tag{14}$$

and in solution of mixture, Cu^+ and Cu^{2+},

$$[NH_3]_T = \alpha + [Cu^+]_L \cdot \gamma_1 + [Cu^{2+}]_L \cdot \gamma_2 \tag{15}$$

$[NH_3]_T$ is the concentration of total ammonia in solution of mixture: Copper(I) and Copper(II) ions.

Nickel

Ammonia exists in aqueous solutions in two different forms, namely NH_4^+ (ammonium) and NH_3 (ammonia). Ammonia forms soluble complexes with nickel ions. Species present in solution and minerals to be considered: Ni^{2+}, $Ni(OH)^+$, $Ni(OH)_2$, $Ni(OH)_3^-$, $Ni(NH_3)^{2+}$, $Ni(NH_3)_2^{2+}$, $Ni(NH_3)_3^{2+}$, $Ni(NH_3)_4^{2+}$, $Ni(NH_3)_5^{2+}$ and $Ni(NH_3)_6^{2+}$. The principal nickel solid species are: Ni, $Ni(OH)_2$, Ni_3O_4, Ni_2O_3 and NiO_2. The thermodynamic data for Ni^{2+}-NH_3-H_2O system are represented in Table-2.

TABLE-2

THERMODYNAMIC DATA FOR Ni-NH₃-H₂O SYSTEM AT 25°C[12, 15, 16]

Reaction	Property at 25°C	
$Ni^{2+} + 2e = Ni$	Eh°	-0.25
$Ni_3O_4 + 8H^+ + 2e = 3Ni^{2+} + 4H_2O$	Eh°	1.977
$Ni_2O_3 + 6H^+ + 2e = 2Ni^{2+} + 3H_2O$	Eh°	1.753
$Ni_3O_4 + 2H^+ + 2e = 3NiO + H_2O$	Eh°	0.897
$3Ni_2O_3 + 2H^+ + 2e = 2Ni_3O_4 + H_2O$	Eh°	1.305
$2NiO_2 + 2H^+ + 2e = Ni_2O_3 + H_2O$	Eh°	1.434
$Ni_2O_3 + 2H^+ + 2e = 2NiO + H_2O$	Eh°	1.032
$NiO_2 + 2H^+ + 2e = NiO + H_2O$	Eh°	1.593
$Ni^{2+} + H_2O = Ni(OH)^+ + H^+$	$\log K_1$	10.7
$Ni^{2+} + 2H_2O = Ni(OH)_2 + 2H^+$	$\log K_2$	7.2
$Ni^{2+} + 3H_2O = Ni(OH)_3^- + 3H^+$	$\log K_3$	11.2
$Ni^{2+} + NH_3 = Ni(NH_3)^{2+}$	$\log \beta_1$	2.79
$Ni^{2+} + 2NH_3 = Ni(NH_3)_2^{2+}$	$\log \beta_2$	5.03
$Ni^{2+} + 3NH_3 = Ni(NH_3)_3^{2+}$	$\log \beta_3$	6.76
$Ni^{2+} + 4NH_3 = Ni(NH_3)_4^{2+}$	$\log \beta_4$	7.95
$Ni^{2+} + 5NH_3 = Ni(NH_3)_5^{2+}$	$\log \beta_5$	8.70
$Ni^{2+} + 6NH_3 = Ni(NH_3)_6^{2+}$	$\log \beta_6$	8.73
$Ni(OH)_2(s) = Ni^{2+} + 2OH^-$	$\log K_{sp}$	17

The mass balance of ammonia $([NH_3]_T)$ is given by:

$$[NH_3]_T = [NH_3]_L + [NH_4^+] + [Ni(NH_3)^{2+}] + 2[Ni(NH_3)_2^{2+}] + 3[Ni(NH_3)_3^{2+}]$$
$$+ 4[Ni(NH_3)_4^{2+}] + 5[Ni(NH_3)_5^{2+}] + 6[Ni(NH_3)_6^{2+}] \qquad (16)$$

$$[NH_3]_T = \alpha + [Ni^{2+}]_L \cdot \gamma_3 = \alpha + 10^{2pK_w - pK_{sp} - 2pH} \cdot \gamma_3 = f(pH, [NH_3]_L) \qquad (17)$$

$$\alpha = [NH_3]_L + [NH_4^+] = 10^{pNH_3} \cdot (1 + 10^{pK_w - pH}) \qquad (18)$$

$$\gamma_3 = 1 + 10^{\log \beta_1 - pNH_3} + 2 \cdot 10^{\log \beta_1 - 2pNH_3} + 3 \cdot 10^{\log \beta_1 - 3pNH_3} + 4 \cdot 10^{\log \beta_2 - 4pNH_3}$$
$$+ 5 \cdot 10^{\log \beta_3 - 5pNH_3} 6 \cdot 10^{\log \beta_4 - 6pNH_3} \qquad (19)$$

The mass balance of $Ni([Ni^{2+}]_T)$ is given by:

$$[Ni^{2+}]_T = [Ni^{2+}]_L + [Ni(NH_3)^{2+}] + [Ni(NH_3)_2^{2+}] + [Ni(NH_3)_3^{2+}] + [Ni(NH_3)_4^{2+}]$$

$$+ [Ni(NH_3)_5^{2+}] + [Ni(NH_3)_6^{2+}] + [Ni(OH)^+] + [Ni(OH)_2] + [Ni(OH)_3^-]$$

$$\tag{20}$$

$$[Ni^{2+}]_T = [Ni^{2+}]_L \cdot \lambda_3 = 10^{2pK_w - K_{sp} - 2pH} \cdot \lambda_3 \tag{21}$$

where

$$\lambda_3 = 1 + 10^{\log \beta_1 - pNH_3} + 10^{\log \beta_1 - 2pNH_3} + 10^{\log \beta_1 - 3pNH_3} + 10^{\log \beta_2 - 4pNH_3}$$

$$+ 10^{\log \beta_3 - 5pNH_3} + 10^{\log \beta_4\, 0\, 6pNH_3} + 10^{pH - \log K_1} + 10^{2pH - \log K_1} + 10^{3pH - \log K_1}$$

$$\tag{22}$$

Constructions of Diagrams

This section summarizes the principles used to construct the solubility curves and potential-pH diagrams; we present our rigorous method.

The system Metal-H_2O-Ligand is described by our system of equations.

If there is formation of precipitates Cu_2O, CuO or $Ni(OH)_2$, the free concentration of dissolved metal can be rigorously written:

$$[M^{n+}]_L = 10^{n(pK_w - pH) \cdot pK_w} \tag{23}$$

If there is not formation of precipitates Cu_2O, CuO or $Ni(OH)_2$, the free concentration of dissolved metal can be rigorously written:

$$[M^{n+}]_L = \frac{[M^{n+}]_T}{\gamma} \tag{24}$$

The principal influence of pH and ammonia on the solubility of copper and nickel from their hydroxides as a result of ammonia complexation is shown in the following theoretical diagrams:
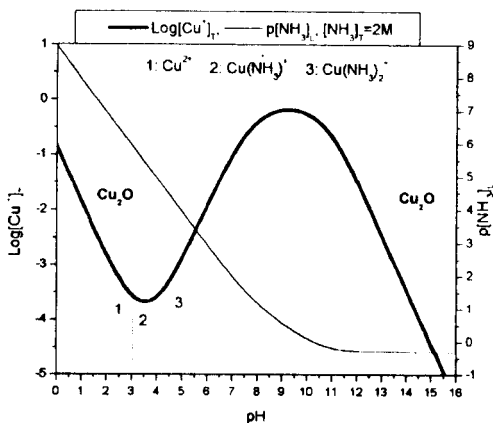
Fig. 1.   Solubility of Cu_2O *vs.* pH at $[NH_3]_T = 2M$ and distribution of species
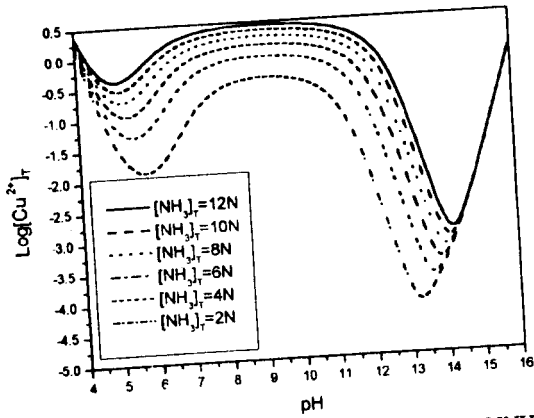
Fig. 2. Solubility of CuO *vs.* pH at various values of $[NH_3]_T$
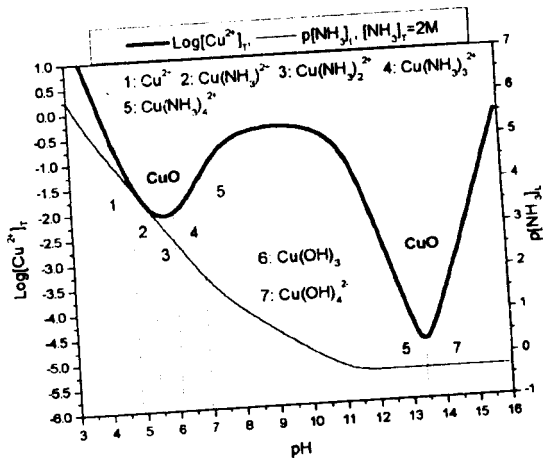

Fig. 3. Solubility of CuO *vs.* pH at $[NH_3]_T = 2M$ and distribution of species
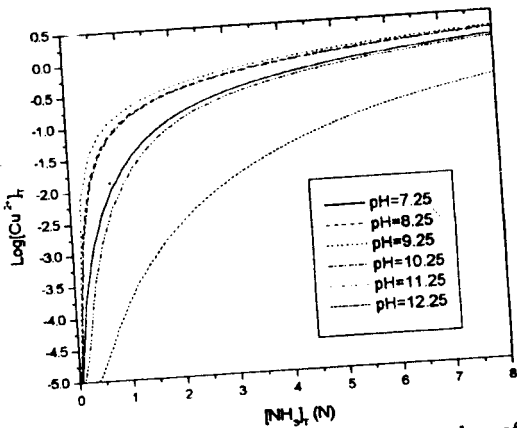

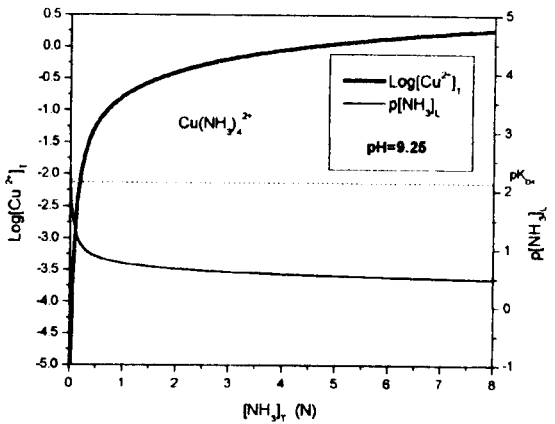Fig. 4. Solubility of CuO *vs.* $[NH_3]_T$ at various values of pH

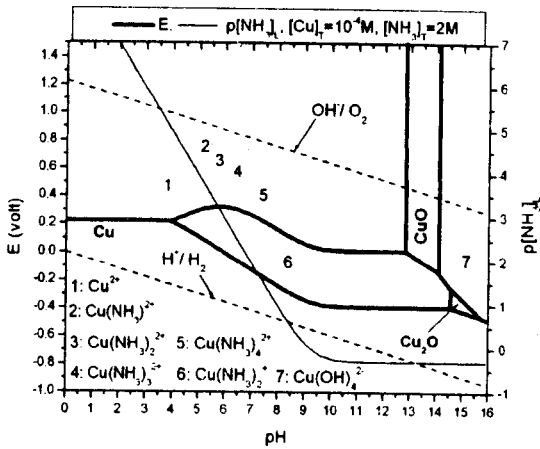Fig. 5. Solubility of CuO $vs.$ $[NH_3]_T$ at pH = 9.25 and distribution of species

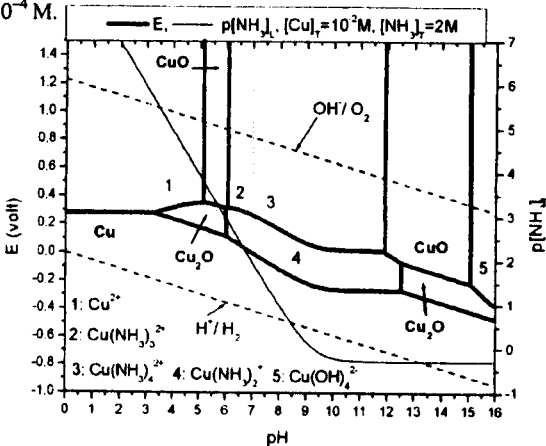Fig. 6. Eh-pH diagram for the Cu-NH$_3$-H$_2$O system at 25°C. Conditions: $[NH_3]_T = 2$ M, $[Cu]_T = 10^{-4}$ M.

Fig. 7. Eh-pH diagram for the Cu-NH$_3$-H$_2$O system at 25°C. Conditions: $[NH_3]_T = 2$ M, $[Cu]_T = 10^{-2}$ M.
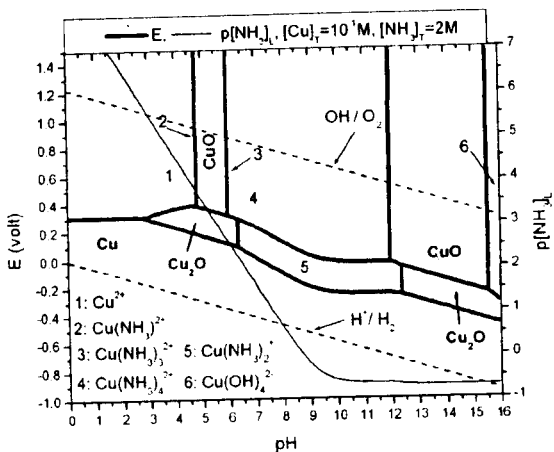
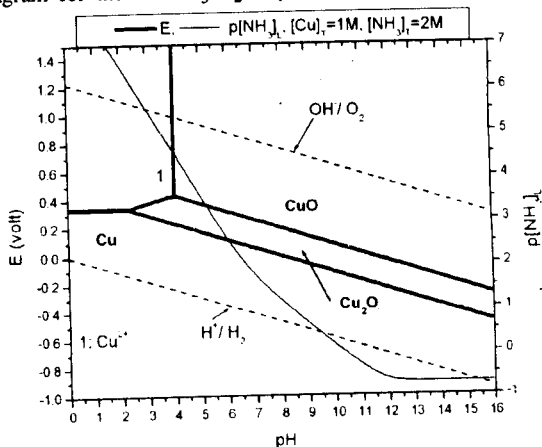Fig. 8. Eh-pH diagram for the Cu-NH₃-H₂O system at 25°C. Conditions: $[NH_3]_T = 2$ M,

Fig. 9. Eh-pH diagram for the Cu-NH₃-H₂O system at 25°C Conditions: $[NH_3]_T = 2$ M, $[Cu]_T = 1$ M
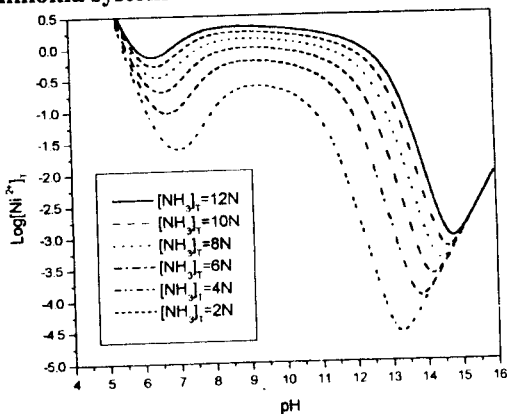
Nickel-water-ammonia system

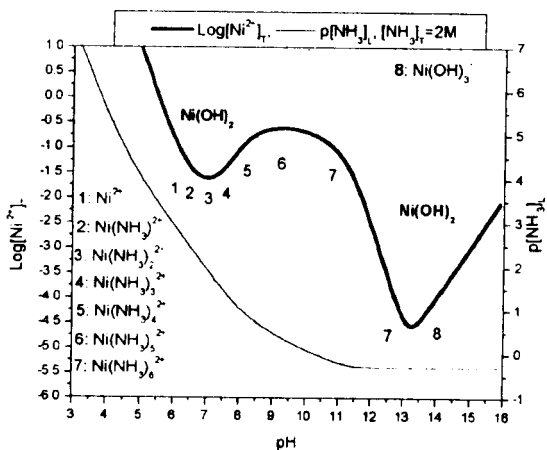Fig. 10. Solubility of Ni(OH)₂ *vs.* pH at various values of $[NH_3]_T$

Fig. 11. Solubility of $Ni(OH)_2$ *vs.* pH at $[NH_3]_T = 2N$ and distribution of species

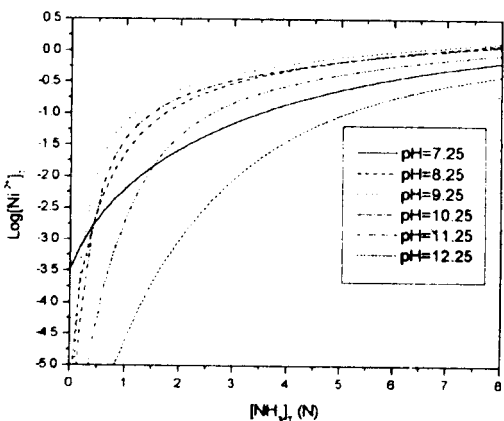Fig. 12. Solubility of $Ni(OH)_2$ *vs.* $[NH_3]_T$ pH at various values of pH
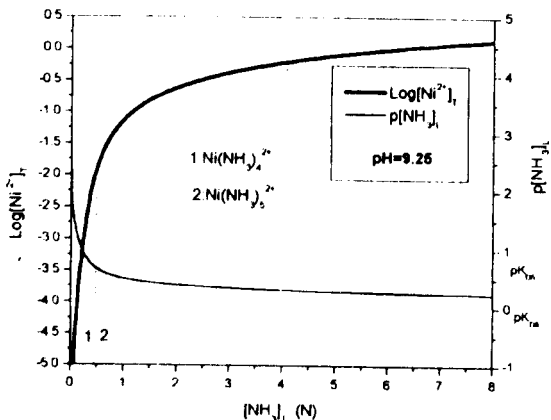

Fig. 13. Solubility of $Ni(OH)_2$ *vs.* $[NH_3]_T$ at pH = 9.25 and distribution of species
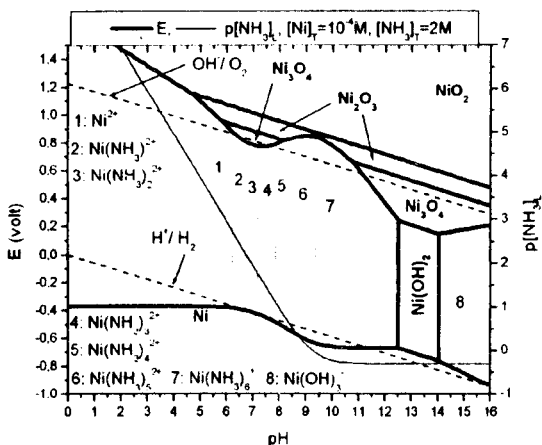
Fig. 14. Eh-pH diagram for the Ni-NH₃-H₂O system at 25°C. Conditions: $[NH_3]_T = 2$ M, $[Ni]_T = 10^{-4}$ M
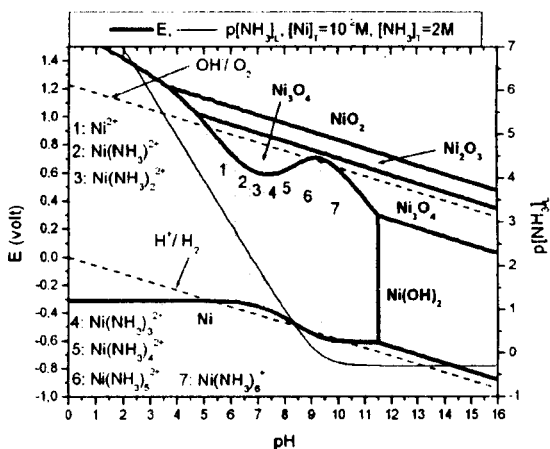

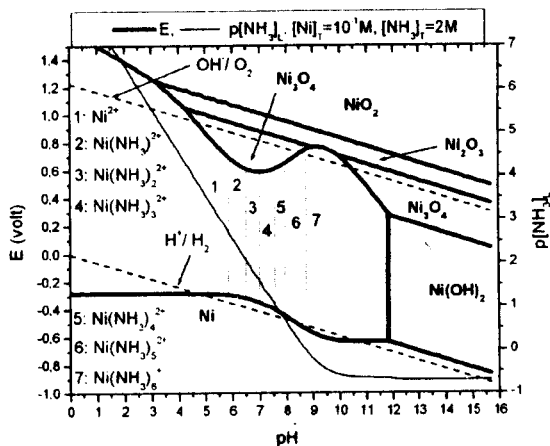Fig. 15. Eh-pH diagram for the Ni-NH₃-H₂O system at 25°C. Conditions: $[NH_3]_T = 2$ M, $[Ni]_T = 10^{-2}$ M

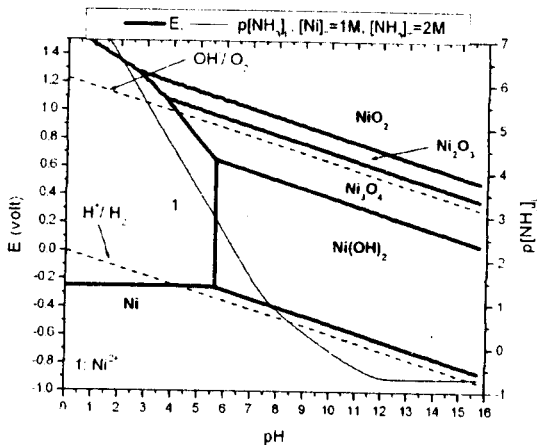Fig. 16. Eh-pH diagram for the Ni-NH₃-H₂O system at 25°C. Conditions: $[NH_3]_T = 2$ M, $[Ni]_T = 10^{-1}$ M

Fig. 17. Eh-pH diagram for the Ni-NH$_3$-H$_2$O system at 25°C. Conditions: [NH$_3$]$_T$ = 2 M, [Ni]$_T$ = 1 M

Summary

The results of calculation and computations are presented in the following figures, the used language is FORTRAN 77.

Based on mass balance for metal and for ammonia, and a combination between the two, calculations have been made, with examples, in Cu- and Ni-ammonia-water systems to express equilibrium relations between solid phases and associated aqueous phase.

Diagrams log [Cu]-pH and Eh-pH of our method is the use diagram solubility-total concentration of ligand instead of the classical diagram solubility free concentration of ligand, the total concentration of ligand is well determined (thanks to a numerical method and data processing).

Our rigorous calculation method permits to find the optimal conditions of dissolution (E, pH, [L]$_T$), and realized the Eh-pH diagrams by high speed at different given conditions.

More quantitative information on practical hydrometallurgical processes can be obtained from this calculation compared with the conventional calculation.

We point out that the traditional methods give an opposite result; the diagrams of distribution of species (E, pH, pL) and their data-processing exploitation become a powerful tool to contribute ways to solve the serious problem of environment. This calculation method can readily be applied to other metal-ammonia-water systems.

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