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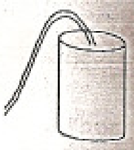

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SELECTIVE RECOVERY OF METAL VALUES FROM ELECTROPLATING SLUDGES : A NUMERICAL AND MODELING APPROACH

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Calculations and computations are applied to find the optimal conditions (pH, [NH3], ...) of a selective recovery of metal values from the electroplating sludges .
This study compares a classical and approximate method, based on the superposition of solubility-pH-complex diagrams, and our rigorous approach. The studied example is the selective recovery of Ni++ and Cu++ from their hydroxide sludges by an ammoniacal leaching .
We introduce also a direct relation between the solubility and the total concentration of NH3, $[NH3]_T$.

INTRODUCTION

The electroplating waste waters are generaly detoxicated (oxydation of CN- and reduction of Cr(VI)) and then neutralised to precipitate metal hydroxides. This precipitate constitutes the electroplating sludge .

Many studies have shown that the sludges may become a danger to the environment .

The economic considerations are also important because the loss of metals is not negligible .

During the eighties, the protection of environment, the waste minimization and the metals recovery become a social and political problem in the U.S.A. In this country the volume of sludges is enormous because electroplating industries are very developped .

Among the proposed solutions we cite :

- The clean technologies (membranes processes, ...) : The rinsing waste waters are directly treated by electrodialysis, ultrafiltration, solvent extraction, ... The metals are concentrated and reused in the electrodeposition bath; The water is also recycled. This is an elegant solution. However some economical, technical and psychological considerations don't permit a rapid progress of this technology .
- The metal recovery from the electroplating sludges : This solution is absolutely necessary to treat, at less, the existing sludges. The american government through the EPA, encouraged this solution. Research projects were supported .

The recovery of metals with a sufficient purity and economicaly is not an easy problem. It needs a serious effort of research .

Firstly, it is necessary to develop simple and economical methods of analysis to define the sludges composition. Also many organic (additives) and inorganic impurities (Ca++, PO4---, ...) are present. The simultaneous precipitation of many metals is always accompanied by abnormal phenomena : coprecipitation, occlusion adsorption ... The precipitate aging is also a problem .

Secondly we choice a qualitative method of selective dissolution (acidic, ammoniacal, ...) which depends on the sludges composition and the leaching agent (recyclable or no). This step needs a deep knowledge of chemical equilibrium and their mutual influences (E-pH, solubility complexe, etc ...) .

The third step consists to find the optimal conditions of a selective recovery of metal values from the electroplating sludges. A direct experimental study is not economical and too long. This step needs calculations and computations because the number of metals, parameters (pH-E, concentration, ...) and of dissolved species is important. This step is the main aim of our study. This paper is limited to the selective dissolution of Cu++ and Ni++ by NH3 from an hydroxide mixture .

Classical studies of selective dissolution of metals are generaly based on the superposition of the respective solubility-pH, solubility-complexe or solubility-E diagrams .

This study, applied to an ammoniacal leaching shows the advantage of rigorous calculations and computations .

THEORY AND BASIC EQUATIONS

Introduction

It is a classical problem of analytical chemistry to find the optimal conditions of dissolution (pH, $[NH_3]_T$...) of $Ni(OH)_2$ by complexes formation $\left[Ni(NH_3)_2^{2+}\right]...\left[Ni(NH_3)_6^{2+}\right]$. However the presence of a mixture of hydroxides ($Ni(OH)_2$ and $Cu(OH)_2$) is, generally, treated by superposition of the solubility pH diagrams (for a given concentration of NH_3). It is a classical and approximate method. In this study we present our rigorous method and we compare them.

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Equilibriums and Equations

Solubility of Metal Hydroxides in Ammoniacal Solutions :

- Formation of hydrocomplexes :

$$M(OH)_n + H^+ \Leftrightarrow M(OH)^+_{n-1} + H_2O \qquad K_n = \frac{[M(OH)_n][H^+]}{[M(OH)^+_{n-1}]}$$

- Formation of amino complexes :

$$M(NH_3)^{n+}_{m-1} + NH_3 \Leftrightarrow M(NH_3)^{n+}_m \qquad K_{D_m} = \frac{[M(NH_3)^{n+}_{m-1}][NH_3]}{[M(NH_3)^{n+}_m]}$$

- Formation of NH_4^+ :

$$NH_3 + H^+ \Leftrightarrow NH_4^+ \qquad K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

- Formation of hydrocomplexe in basic mediums :

$$M(OH)_n + H_2O \Leftrightarrow M(OH)^-_{n+1} + H^+ \qquad K_{n+1} = \frac{[M(OH)^-_{n+1}][H^+]}{[M(OH)_n]}$$

- Formation of H_2O :

$$H^+ + OH^- \Leftrightarrow H_2O \qquad K_e = [H^+][OH^-]$$

- Formation of the precipitate $M(OH)_n \downarrow$:

$$M(OH)_n \Leftrightarrow M^{n+} + nOH^- \quad .... K_s = [M^{n+}][OH^-]^n$$

Equation of Mass Conservation

Conservation of The Total Concentration of NH_3 $[NH_3]_T$:

$$[NH_3]_T = [NH_3]_L + [NH_4^+] + [M(NH_3)^{n+}] +..+ i[M(NH_3)_i^{n+}] +..+ m[M(NH_3)_m^{n+}]$$

$$[NH_3]_T = [NH_3]_L \cdot \left[1 + \frac{[H^+]}{K_a}\right] + [M^{n+}]_l \cdot \left[\frac{[NH_3]}{K_{D_1}} +.+ \frac{i[NH_3]^i}{K_{D_1} \cdot K_{D_2} .. K_{D_i}} +.+ \frac{m[NH_3]^m}{K_{D_1} \cdot K_{D_2} .. K_{D_m}}\right]$$

$$[NH_3]_T = \alpha_0 + [M^{n+}]_L \cdot \alpha_1$$

$$\alpha_0 = [NH_3]_L \cdot \left[1 + \frac{[H^+]}{K_a}\right] = 10^{-pNH_3} \cdot \left[1 + 10^{pK_a - pH}\right]$$

$$\alpha_1 = \left[\frac{[NH_3]}{K_{D_1}} + \frac{2[NH_3]^2}{K_{D_1} K_{D_2}} +...+ \frac{i[NH_3]^i}{K_{D_1} K_{D_2} ... K_{D_i}} +...+ \frac{m[NH_3]^m}{K_{D_1} K_{D_2} ... K_{D_m}}\right]$$

Conservation of the total concentration of the dissolved metal M^{n+} $[M^{n+}]_T$

$$[M^{n+}]_T = [M^{n+}]_L + [M(OH)^{(n-1)+}] +..+ [M(OH)_i^{(n-i)+}] +..+ [M(OH)_n] +$$
$$+ [M(OH)_{n+1}^-] +..+ [M(OH)_j^{(n-j)-}] + [M(NH_3)^{n+}] +.+ [M(NH_3)_i^{n+}] +..+ [M(NH_3)_m^{n+}]$$

$$[M^{n+}]_T = [M^{n+}]_L \cdot \left[1 + \frac{K_1}{[H^+]} +..+ \frac{K_1 K_2 ... K_i}{[H^+]^i} +..+ \frac{K_1 K_2 ... K_n}{[H^+]^n} +..+ \frac{K_1 K_2 ... K_i ... K_j}{[H^+]^j}\right.$$
$$\left. + \frac{[NH_3]}{K_{D_1}} + \frac{2[NH_3]^2}{K_{D_1} K_{D_2}} +..+ \frac{i[NH_3]^i}{K_{D_1} K_{D_2} ... K_{D_i}} +...+ \frac{m[NH_3]^m}{K_{D_1} K_{D_2} .. K_{D_m}}\right]$$

$$\alpha_2 = \left[1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2} + \ldots + \frac{K_1K_2\ldots K_i}{[H^+]^i} + \ldots + \frac{K_1K_2\ldots K_n}{[H^+]^n} + \ldots + \frac{K_1K_2\ldots K_i\ldots K_j}{[H^+]^j} + \frac{[NH_3]}{K_{D_1}} + \frac{2[NH_3]^2}{K_{D_1}K_{D_2}} + \ldots + \frac{i[NH_3]^i}{K_{D_1}K_{D_2}\ldots K_{D_i}} + \ldots + \frac{m[NH_3]^m}{K_{D_1}K_{D_2}\ldots K_{D_m}}\right]$$

$$[M^{n+}]_T = [M^{n+}]_L \cdot \alpha_2$$

<u>The Resulting Equations</u> :

The combination of equilibrium and mass balance equations applied to $Ni(OH)_2$ gives :

$$[NH_3]_T^{Ni} = \alpha_0 + 10^{11\text{-}2pH} \cdot \alpha_1^{Ni}$$

$$[Ni^{2+}]_T = 10^{11\text{-}2pH} \cdot \alpha_2^{Ni}$$

It is evident that the simplest system $Ni(OH)_2$ /NH_3 gives the previous equations which are not easy to solve and needs a numerical and computation approach to obtain the solubility - pH and the solubility - $[NH3]_T$ diagrams .

Similar equations describe the system $Cu(OH)_2$ /NH_3.

Generally the solubility ratio between Cu and Ni is obtained by the superposition of the solubility - pH diagram of each hydroxide: it is an approximate method .

We present our rigorous method; the mixture of $Ni(OH)_2$ and $Cu(OH)_2$ in an ammoniacal solution is described by an other system of equation :

$$[NH_3]_T = \alpha_0 + 10^{11\text{-}2pH} \cdot \alpha_1^{Ni} + 10^{8.1\text{-}2pH} \cdot \alpha_1^{Cu}$$

$$[Ni^{2+}]_T = 10^{11\text{-}2pH} \cdot \alpha_2^{Ni}$$

$$[Cu^{2+}]_T = 10^{8.1\text{-}2pH} \cdot \alpha_2^{Cu}$$

The solution of this system gives the actual ratio of solubility between Cu and Ni (37.8). This result is completly different compared to the superposition method.

NUMERICAL CALCULATIONS AND COMPUTATIONS

The results of calculations and computations are presented in the figures 1, 2, 3 and 4.

The solubility diagrams are presented versus wellknown parameters : pH and $[NH3]_T$.

The figures 1 and 2 present the superposition method; the selective leaching is not possible :

$$\frac{[Cu^{2+}]_T}{[Ni^{2+}]_T} = 1.48$$

Our rigorous calculation method permits a selective dissolution :

$$\frac{[Cu^{2+}]_T}{[Ni^{2+}]_T} = 37.8$$

REFERENCES

- R. Salhi Master Thesis, University of Constantine (Algeria), Oct. 1995

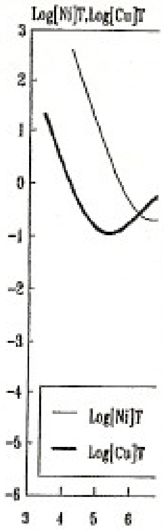

Fig. 1

Fig. 3

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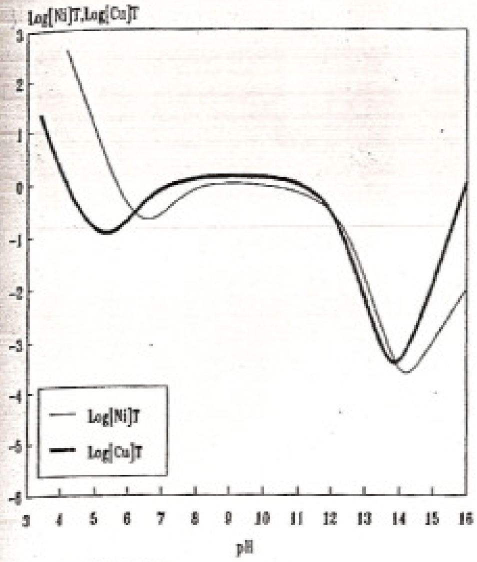

Fig. 1

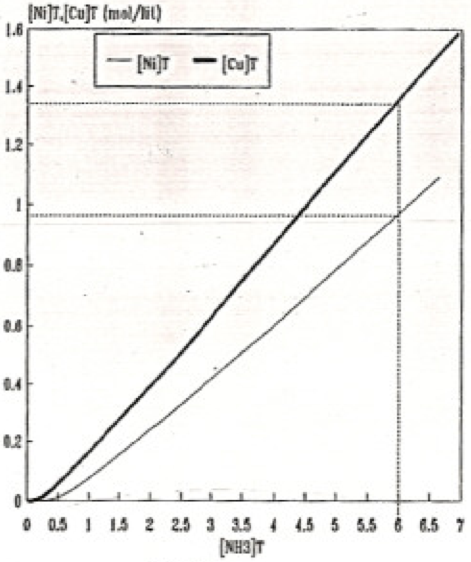

Fig. 2

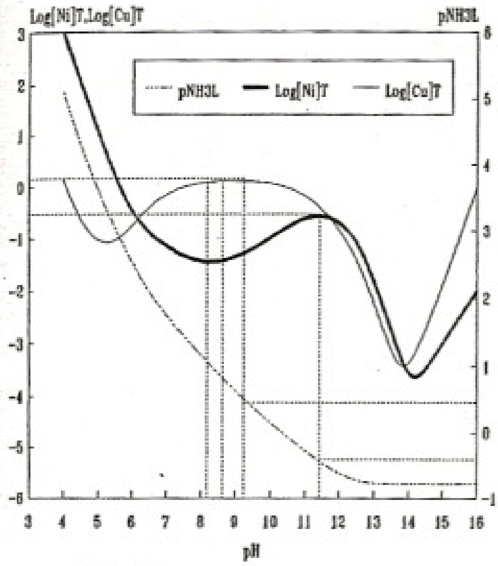

Fig. 3

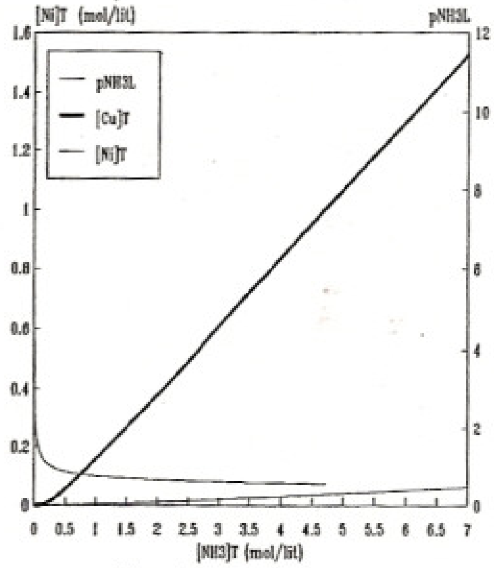

Fig. 4

Fig 1: ***SUPERPOSITION OF SOLUBILITY- pH DIAGRAMS OF*** $Ni(OH)_2$ ***AND*** $Cu(OH)_2$
Fig 2: ***SUPERPOSITION OF SOLUBILITY-***$[NH_3]_T$ ***DIAGRAMS OF*** $Ni(OH)_2$ ***AND*** $Cu(OH)_2$
Fig 3: ***SOLUBILITY- pH DIAGRAMSOF*** $Ni(OH)_2$ ***AND*** $Cu(OH)_2$***: RIGOROUS CALCULATION***
Fig 4: ***SOLUBILITY-*** $[NH_3]_T$ ***DIAGRAMSOF*** $Ni(OH)_2$ ***AND*** $Cu(OH)_2$***:RIGOROUS CALCULATION***