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Recovery of nickel and copper from metal finishing hydroxide sludge by kinetic acid leaching

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Abstract:

The aim of the present work was the recovery of nickel and copper from metal finishing hydroxide sludge by kinetic acid leaching. The study was divided into two main parts: First, a kinetic model of precipitate leaching with the presence of acid was developed and subjected to theoretical approach so as to determine optimal leaching conditions (pH and time). Next, the study was conducted experimentally on pure metals hydroxides and then on electroplating sludges. The leaching operation was performed at atmospheric pressure with constant stirring. pH and solubility versus time at different temperature values and different amounts of sludge were carried out. The resulting filtrate was found to contain more than 99% of nickel and copper.

Keywords: *Acid leaching, Copper, Nickel, Electroplating sludge, Metal recovery*

Introduction

The electroplating waste waters are generally detoxified (oxidation of cyanide and reduction of chromium) and then neutralized to precipitate metal hydroxides [1-3].. In the present work, the electroplating sludges are subjected to precipitation so as to get rid of hazardous metals. Many studies reported that the sludges may present a great danger to the environment. The economic considerations are also worth considering because of the appreciable loss of metals. Since the eighties, the environment protection, the waste minimization and the metals recovery became a social and political issue in the U.S.A.[4-7] where the volume of sludges is so important owing to the large electroplating industries To combat this problem some solutions can be convenient to be implemented such as:

- The clean technologies (membranes processes): The rinsing wastewaters are directly treated by electrodialysis, ultrafiltration, and solvent extraction. The metals are concentrated and reused in the electrodeposition bath. The water is also recycled. [8-20]. However some economic, technical and psychological considerations hindered a rapid progress of this approach.
- The metal recovery from electroplating sludges: This solution is extremely necessary to treat, at least, the existing sludges. The American government through the EPA encouraged this solution and research projects were supported.

The economical recovery of metals with a sufficient purity is quite intricate and needs a big effort and hard research based on two main aspects:

- First, it is necessary to develop simple and economical analysis methods to define the sludges composition. The simultaneous precipitation of many metals is always accompanied by secondary processes such as: co-precipitation, occlusion adsorption etc. The precipitate aging is also a problem.

- Secondly it is required to choose of a qualitative method of selective dissolution (acidic, ammoniacal, etc) depending on the sludge composition and the leaching agent (recyclable or not) . This step needs a deep knowledge of chemical equilibrium, the mutual influences (E-pH), solubility complex, etc). [21-39]

Theory

Kinetic and Thermodynamic Theory of Acid - Basic Leaching

Kinetic Aspect

The leaching of industrial waste is generally nonreactive. The reactions are most often carried out at high temperature or pressure and administrated by heterogeneous kinetic characteristics. In most cases, the rate of the overall reaction is characterized by diffusion of reactant and is therefore proportional to its concentration. Furthermore the overall rate increases with stirring owing to the slow diffusion in the electrolyte. In some cases, the overall dissolution rate may be affected by the transfer of the charged particles making up the initial crystal through a solid-electrolyte interface [40].

The most extensive study performed up to date on the leaching behavior of metal hydroxides and metal sulfide sludge may be the study reported by Hohman who developed a kinetic model of precipitate leaching [41]. The leaching process was based upon an area-dependent mass transfer controlled process. The driving force for the leaching process was assumed to be proportional to the difference between the concentration of metal in solution (C) and the saturation concentration (Cs) predicted from precipitate equilibria consideration. The basic differential equation describing the leaching process is as follows [48, 49]:

$$\frac{dc}{dt} = K.A(C_S - C) \qquad (1)$$

Where:

Cs: saturation concentration of metal (moles/L)

C: metal concentration in solution at time t (moles/L)

A: area available for mass transfer, (cm^2)

K: mass transfer coefficient ($cm^2.min^{-1}$)

t: leaching time (min).

and the fraction leached (α) of dissolved sludge depends on:

r_0: initial radius of precipitate particle (cm).

Ksp: metal hydroxide solubility product ($moles^n/L^n$).

WT: total weight of precipitate (g).

ρ: molar density of the precipitate particles ($moles/cm^3$).

ρ_M: mass density of the precipitate (g/cm^3).

Vs: volume of solution (L).

For large particles (1mm < r < 1cm) the change in particle size influences the leaching behavior. The slow concentration rise indicates that the surface area decreases quickly, causing a rapid dropping in effective mass transfer coefficient. For small particles (1μm < r < 10μm), the driving force dominates, causing a rapid rise in the heavy metal concentration until saturation. Intermediate radius values show a balance of both effects.

In the case of small molecules, it is considered that the specific surface area is constant, so the integrated equation (1) becomes:

$$\int_{C_0}^{C} \frac{dc}{C_S - C} = KA\int_0^t dt \Rightarrow \frac{C_S - C_0}{C_S - C} = e^{KAt} \qquad (2)$$

C_0: the initial consumable concentration of metal. ($C_0=0$)

and the leaching reaction is:

$$M(OH)_n + nH^+ \leftrightarrow M^{n+} + nH_2O \qquad (3)$$

So leaching concentration (mole/L) of M^{n+} requires (nC mole/L) of H^+:

The consumable concentration of H^+ is:

$$\left[H^+\right]_c = n(C - C_0) \qquad (4)$$

The remaining amount of H^+ in the solution at the time t is:

$$\left[H^+\right]_c = \left[H^+\right]_0 - n(C - C_0) \qquad (5)$$

If $C_0=0$

$$C = \frac{\left[H^+\right]_0 - \left[H^+\right]}{n} \qquad (6)$$

and

$$C = C_s\left(1 - e^{-kAt}\right) \qquad (7)$$

This relationship is represented in Fig. 1. a.

where we note that when:

$$t \to \infty$$

$$C = C_s$$

to find the variation of pH with respect to time we replaced C of the equation (6) in the equation (7) we get:

$$\left[H^+\right] = \left[H^+\right]_0 - nC_s\left(1 - e^{-kAt}\right) \qquad (8)$$

The concentration of the saturated solution is:

$$K_{sp} = \left[M^{n+}\right]\left[OH^-\right] \Rightarrow C_s = \left[M^{n+}\right] = \frac{K_{sp}}{K_w^n}\left[H^+\right]^n \qquad (9)$$

We replaced C_s of the equation (9) in the Equation (8) we got:

$$\left[H^+\right] = \left[H^+\right]_0 - n\frac{K_{sp}}{K_w^n}\left[H^+\right]^n\left(1-e^{-kAt}\right) \qquad (10)$$

$$pH = -\log\left(\left[H^+\right]_0 - n\frac{K_{sp}}{K_w^n}\left[H^+\right]^n\left(1-e^{-kAt}\right)\right) \qquad (11)$$

This relationship is shown in Fig. 1. b.

Where we note that when:

$t \rightarrow \infty$

$$pH \rightarrow pH_s = -\log\left(\left[H^+\right]_0 - n\frac{K_{sp}}{K_w^n}\left[H^+\right]_s^n\right) \qquad (12)$$

Where:

pH_s, $[H^+]_s$: pH and $[H^+]$ concentration of saturation concentration of metal (moles/L)

we replaced n=2 in equation (10) we get:

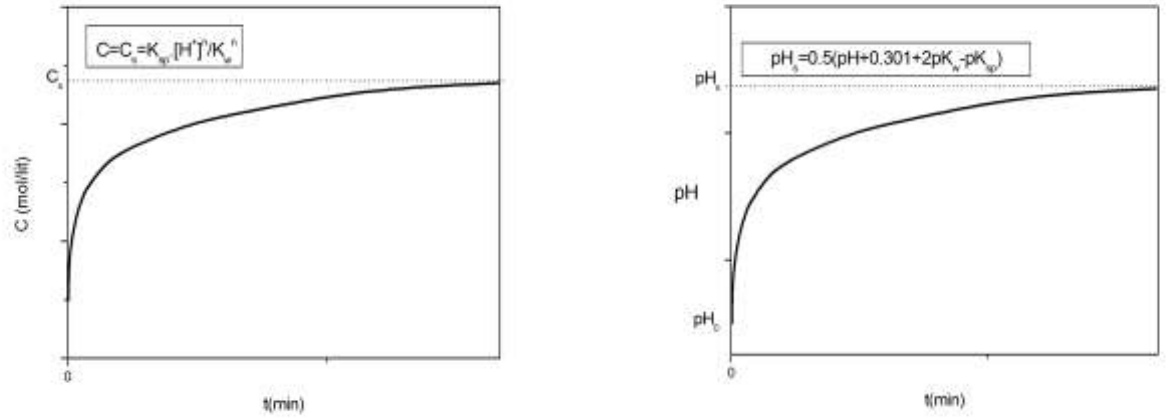
$$2\frac{K_{sp}}{K_w^2}\left[H^+\right]_s^2 + \left[H^+\right]_s - \left[H^+\right]_0 = 0 \qquad (13)$$

$$\left[H^+\right]_s = \frac{1+\sqrt{1+8\frac{K_{sp}}{K_w^2}\left[H^+\right]_0}}{4\frac{K_{sp}}{K_w^2}} \qquad (14)$$

$$pH_s = -\log\left(\frac{1+\sqrt{1+8\frac{K_{sp}}{K_w^2}\left[H^+\right]_0}}{4\frac{K_{sp}}{K_w^2}}\right) \qquad (15)$$

$$pH_s \approx -\frac{1}{2}\log\left(\frac{\left[H^+\right]_0}{4\frac{K_{sp}}{K_w^2}}\right) \qquad (16)$$

$$pH_s \approx \frac{1}{2}\left(0.301 + pH_0 + 2pK_w - pK_{sp}\right) \qquad (17)$$



a- The variation of the concentration of dissolved ion

b- pH variation

Fig. 1: Qualitative hydroxides leaching curves

If the specific surface area A is known, the constant K can be determined by the following relationship:

$$\ln(C_s - C) = \ln(C_s - C_0) - KAt \qquad (18)$$

If we plot the curve ln (Cs - C) = f (t), we can determine the constant KA from the tangent to the curve.

From this theoretical approach, we conclude that to dissolve 1 mg of hydroxide containing N mole of hydroxyle $[OH^-]$, we need N mole of $[H^+]$ ions. If using 1 liter of acid solution with a concentration ($[H^+]_0$) we obtain a saturated solution with a concentration: Cs = N/ n (mol/L), and with a pH equal to:

$$pH_s \approx \frac{1}{2}\left(0.301 + pH_0 + 2pK_w - pK_{sp}\right) \quad (17)$$

The speed of leaching increases with the increase of the amount of $[H^+]_0$

Thermodynamic Aspect

Most dissolution reactions occur in strong acid medium such as :(HCl, HNO_3, H_2SO_4) depending on the type and composition of the material to be dissolved. These reactions are applied to metals oxides, mining and industrial wastes. In Lewis acids and bases the ion in the mineral compound is displaced by the proton in the acidic medium and fixes the O^{2-} or OH^- to give dissolved complex in the basic medium, as shown in the solubility curves represented in Fig. 2.

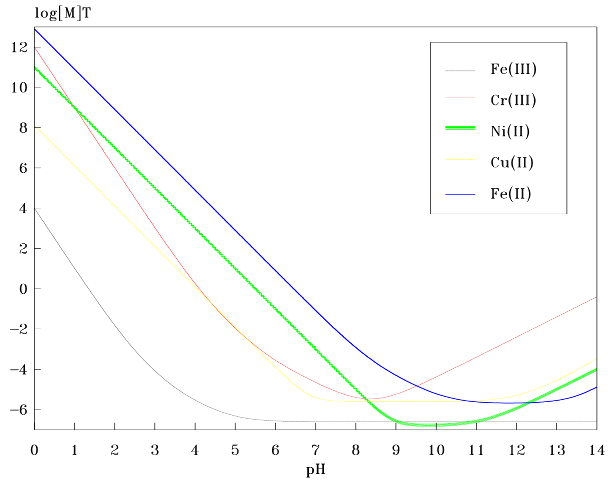


Fig. 2: The variation of the hydroxides solubility with pH

Experimental

The solubility of nickel and copper was experimentally studied using:

1- Analytical $Ni(OH)_2$, $Cu(OH)_2$, (CuO) were purchased from Aldrich

2- Sludges (mixture of $Ni(OH)_2$, $Cu(OH)_2$, $Fe(OH)_3$ and $Cr(OH)_3$ were prepared by precipitation from respective solutions of $NiSO_4$, $CuSO_4$ with NaOH before being washed with distilled water and dried at 40°C. The electroplating sludges were originated from the industrial area of 'El alma', in ALGERIA, where a galvanization plant had previously operated. These sludges are classified as F006 by the EPA [7].

Table 1 : Compositions of four electroplating sludges, g kg^{-1}

	Sludge number			
Metal	1	2	3	4
Ni	139.8	134.3	124.2	85.9
Fe	67.4	98.4	55.6	50.3
Cu	39.9	11.25	32.6	14
Cr	0.72	0.083	0.39	0.028

The compositions of four hydroxide sludges are shown in Table 1 and purities of the dried hydroxides were higher than 99%. The sludges and hydroxides were dissolved in sulfuric acid and after filtration. The metal concentrations in the filtrate were determined by atomic absorption spectroscopy.

Kinetic Aspect

Solubility Experiments for Pure Hydroxides and Electroplating Sludges

Kinetic Leaching Behavior of Metal Hydroxides:

A mass m (in g) of $Ni(OH)_2$, $Cu(OH)_2$ and electroplating sludges respectively, was put into a 50 mL using a screw-cap glass bottle with known initial conditions (temperature, pH, specific conductivity), The bottle was shaken continuously, and the pH and specific conductivity were measured as function of time. At different times, small volumes (1 mL) of solution were taken and filtered immediately. The metal concentrations in the filtrate were measured by atomic absorption spectroscopy.

Thermodynamic Aspect

different amounts of $Ni(OH)_2$, $Cu(OH)_2$ and electroplating sludges were put into a 50 mL screw cap glass bottle to which 25 mL of a solution ranging from 1 to 0.01 mol/L of acidic solution was subsequently added. The pH of the bottled solutions was adjusted by adding a predetermined amount of NaOH, H_2SO_4 and H_2O, in such a way that the volume in the bottle was not substantially changed. The bottles were shaken for 8 h at $25^{\circ}C$, after which the pH was measured and the solution was filtered immediately. The metal concentrations in the filtrate were measured by atomic absorption spectroscopy.

Dissolution Kinetics

A- Effect of Temperature on the Dissolution Rates:

Figure 3 illustrates the difference between the leaching process when the initial pH is 0.5, 1 and 1.5, Figs. 4. 5. 6. show the temperature effect with respect to the starting pH value.

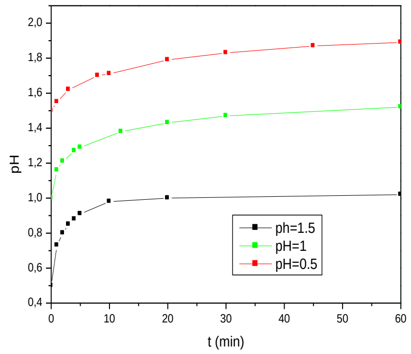


Fig. 3: The difference between the leaching of hydroxidesludge when the initial pH is 0.5, 1 and 1.5.

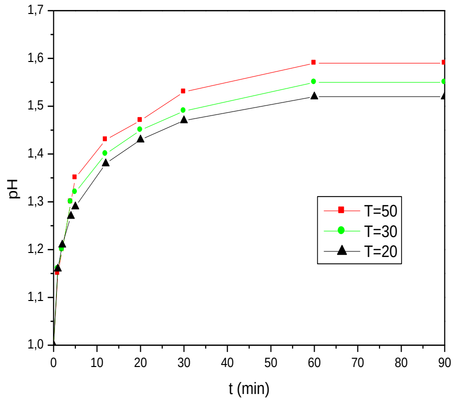


Fig. 5: The temperature effect on leaching of hydroxide sludge when the initial pH is 1

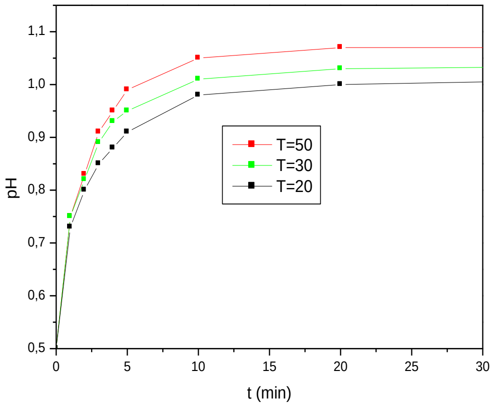


Fig. 4: The temperature effect on leaching of hydroxide sludge when the initial pH is 0.5

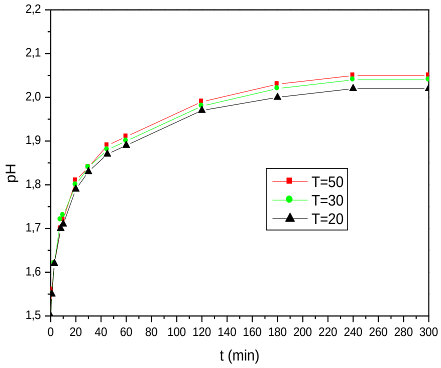


Fig. 6: The temperature effect on leaching of Hydroxide sludge when the initial pH is 1.5

B- Effect of the Mass of Sludge on the Dissolution Rates

Under the same conditions of initial leaching, pH, temperature and volume are kept constant; only the mass of sludge is varied. The impact of the increase in the sludge mass is highlighted by the increase of the consumption of the acid, and then leading to an increase in pH value which in role leads to a precipitate of trivalent cations such as iron and chromium. Then the pH leveled up at about 6 for the remaining time. Figs. 7. 8. show the mass of hydroxide sludge effect to the starting pH value.

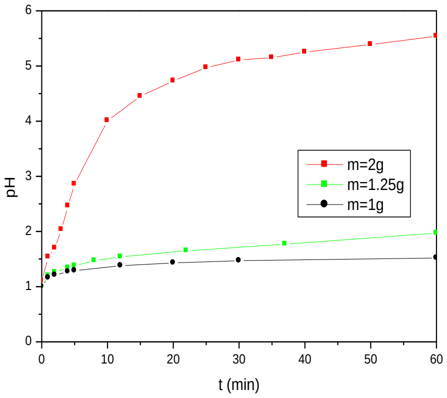


Fig. 7: The mass of hydroxide sludge effect on leaching of hydroxide sludge when the initial pH is 1

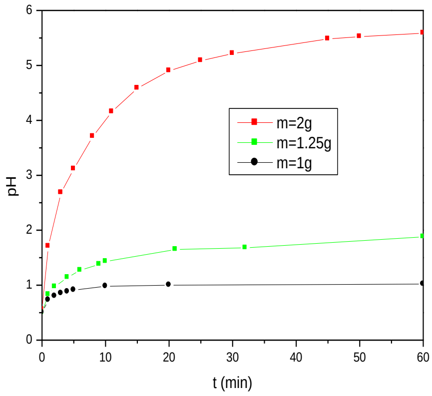


Fig. 8: The mass of hydroxide sludge effect on leaching of hydroxide sludge when the initial pH is 0.5

Results and Discussion

According to the dissolution kinetic curves of the hydroxides, the dissolution starts when the pH is less than the values specified in theory and in particular for the trivalent hydroxides such as ($Cr(OH)_3$, Fe $(OH)_3$).

These two hydroxides begin to dissolve in theory at pH of 3.35 and 7.3 respectively. However in practice their dissolution is very slow and does not even begin at pH = 0.5 as shown in tables 2 and 3. For other hydroxides, such as (CuO, $Ni(OH)_2$), the dissolution starts quickly, even at pH of 1.5.

Table 2 : the dissolution kinetics of Iron (III) hydroxide at t=0; (v=70ml ,[HCl]=20mmol, pH_0=0.5) + 0.25g $Fe(OH)_3$

Time (min)	0	4	21	30	40	2 days
pH	0.50	049	0.50	0.51	0.52	0.50
Conductivity $.10^{3}$ (Ω^{-1} cm^{-1})	69.8	69.5	69.96	69.7	69.6	69.95

Table 3: the dissolution kinetics of chromium (III) hydroxide At t=0; (v=70ml ,[HCl]=20mmol, pH_0=0.5) + 0.25g $Cr(OH)_3$

Time (min)	0	14	15	18	43	2 days
pH	0.50	049	0.5	0.51	0.52	0.51
Conductivity $.10^{3}$ (Ω^{-1} cm^{-1})	69.98	69.55	69.96	69.7	69.9	50.70

The copper oxide dissolution rate is greater than that of nickel hydroxide although CuO is more soluble than $Ni(OH)_2$: as shown in Fig. 9 and 10, ($pKs_{Ni(OH)2}$ = 17, pKs_{CuO} = 19.9) and the basicity of CuO is low compared to that of nickel ($pKa_{(Ni2+/Ni(OH)2)}$ = 8.9; $pka_{(Cu2+/CuO)}$ = 6.85). This difference relies on the structures of these hydroxides. In fact the structure of the nickel hydroxide is crystalline whereas that of copper is colloidal. The same behavior was observed in the leaching of the mixture of two hydroxides (CuO, $Ni(OH)_2$) and three hydroxides ($Fe(OH)_3$, CuO, $Ni(OH)_2$) as shown in fig. 11 and 12, as well as the hydroxide sludge as shown in fig 13,14,15, 16 and 17, where a higher leaching copper rate was recorded compared to that of nickel even if the amount of nickel in these samples ranged from 4 to 6 times the amount of copper.

On the contrary the iron hydroxide (III) does not begin to dissolve even at pH = 0.5. The lixiviation solutions of industrial sludge at pH=1.5 contain iron ions, which confirm that the sludge contains iron other than $Fe(OH)_3$.

At pH = 0.0 the leaching of all metal components of hydroxide sludge is complete. Copper and Nickel can be separated from iron and chromium starting from initial pH of 1 over a period of 90 minutes and leveling up at pH of 1.6 where almost 100% of copper and more than 70% of Nickel were dissolved, whereas the iron dissolution does not exceed 30% over that period. The separation may take place from initial pH of 0.5 over a period of 25 minutes and leveling up at 1 where 70-80% of copper and 60-70% of nickel were dissolved, however iron is dissolved only within 20-50%.

The separation may also occur by leaching from initial pH of 1.5, but over a longer period of about 240 minutes where pH levels up at 2. Under these conditions 100% of copper and 95% of nickel were dissolved while iron does not exceed 19%.

Based on the previous results we suggest the following procedure for copper and nickel dissolution from hydroxide sludge as seen in figure 18.

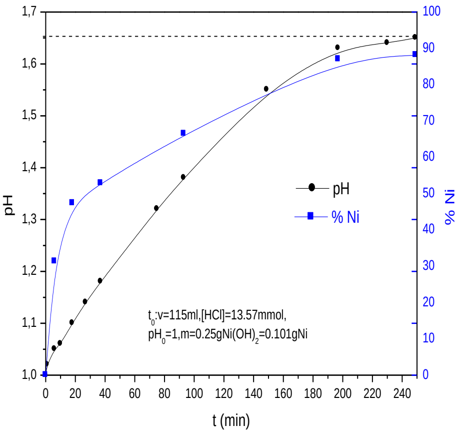


Fig 9: The variation of pH and the concentration of dissolved nickel ion from nickel hydroxide ($Ni(OH)_2$)

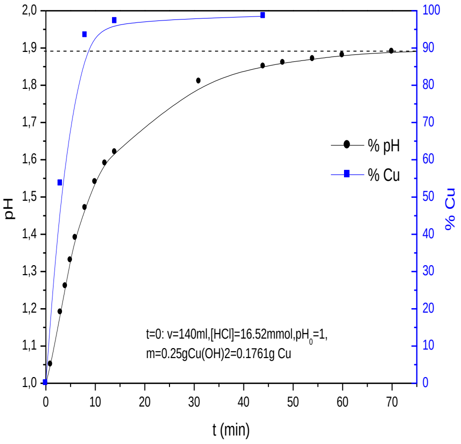


Fig 10: The variation of pH and the concentration of dissolved copper ion from copper hydroxide ($Cu(OH)_2$)

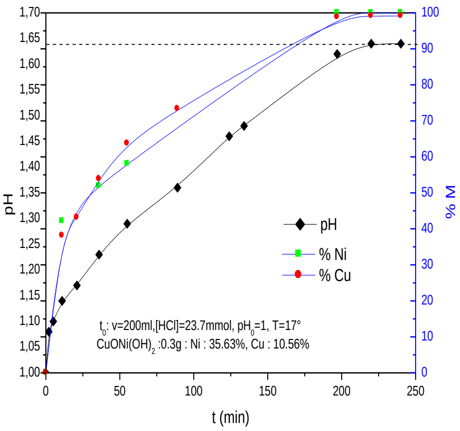


Fig 11: The variation of pH and the concentration of dissolved copper and nickel ion from mixture of hydroxides (CuONi$(OH)_2$)

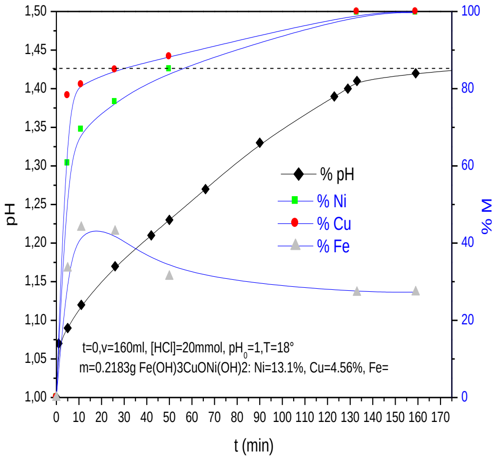


Fig 12: The variation of pH and the concentration of dissolved copper, iron and nickel ion from mixture of hydroxides $Fe(OH)_3CuONi(OH)_2$)

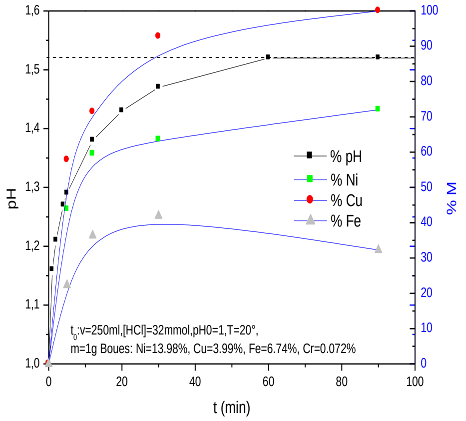


Fig 13: The variation of pH and the concentration of dissolved copper, iron and nickel ion from hydroxide sludge at pH1 (m=1g, v=250ml)

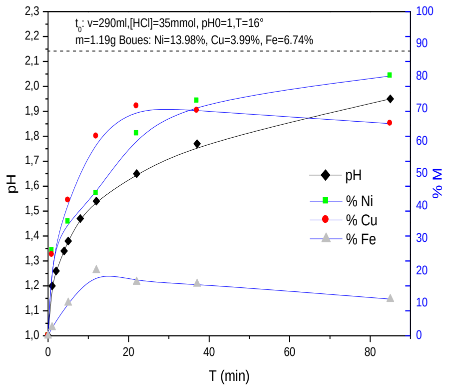


Fig 14: The variation of pH and the concentration of dissolved copper, iron and nickel ion from hydroxide sludge at pH1 (m=1.19g, v=290ml)

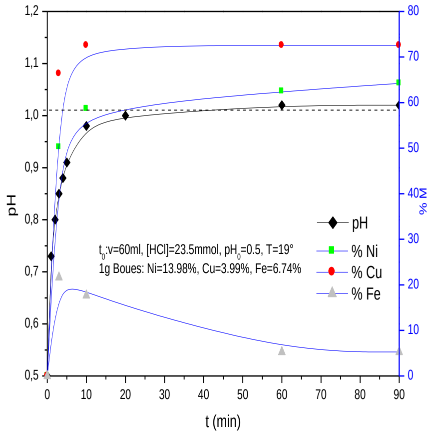


Fig 15: The variation of pH and the concentration of dissolved copper, iron and nickel ion from hydroxide sludge at pH0.5 (m=1g, v=60ml)

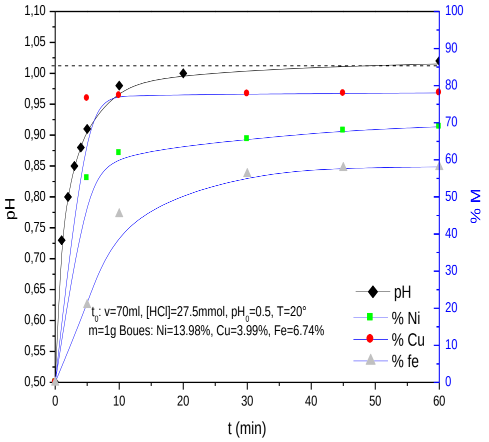


Fig 16: The variation of pH and the concentration of dissolved copper, iron and nickel ion from hydroxide sludge at pH0.5 (m=1g, v=70ml)

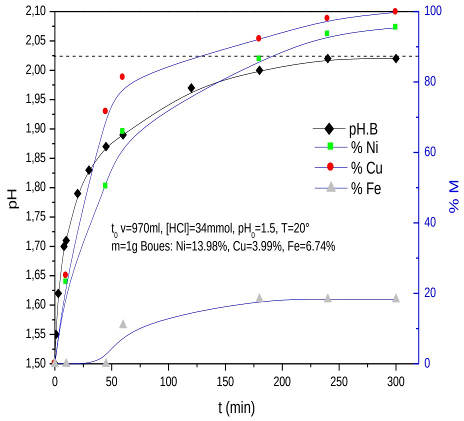


Fig 17: The variation of pH and the concentration of dissolved copper, iron and nickel ion from hydroxide sludge at pH =1.5 (m=1g, v=250ml)

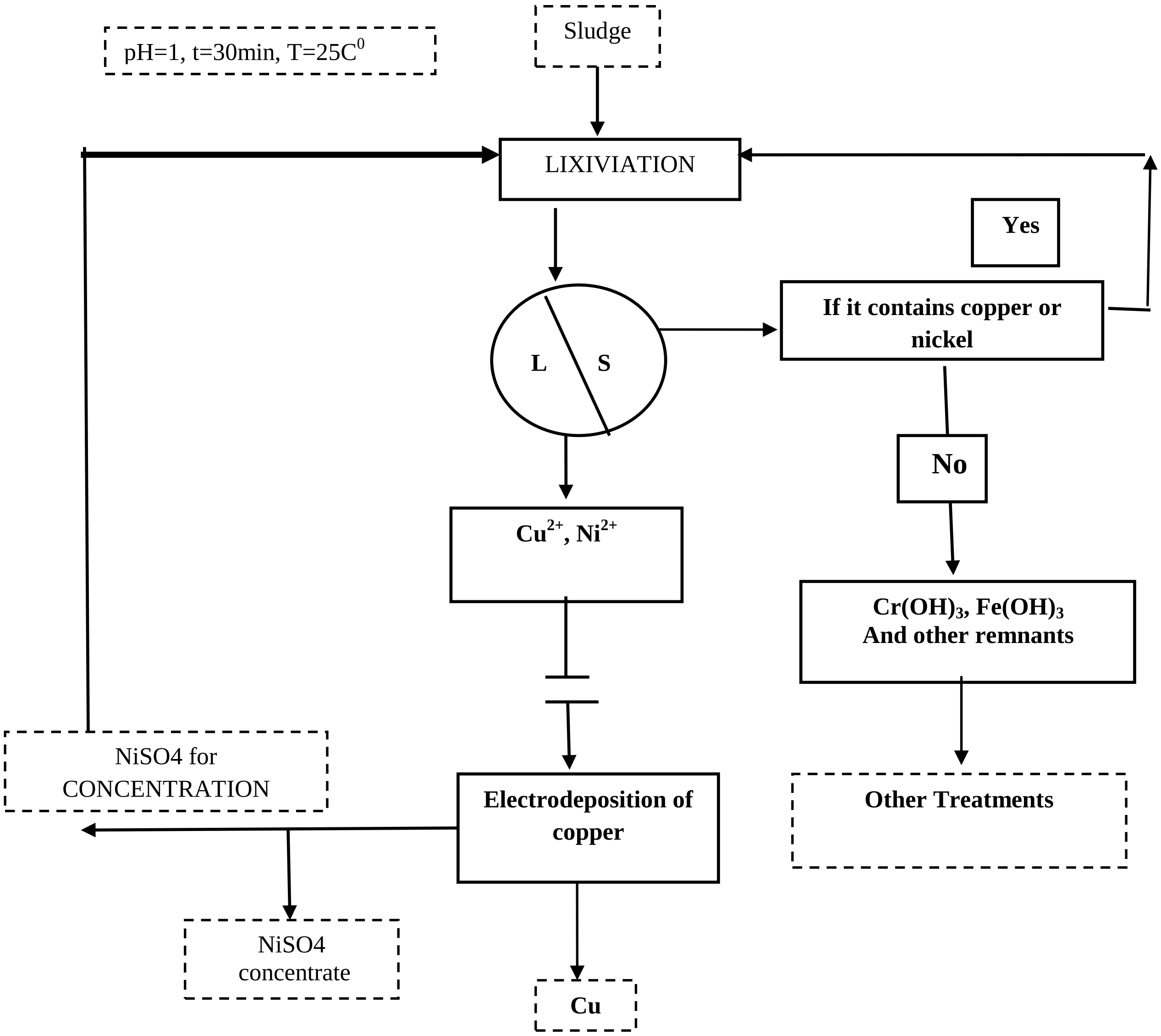


Fig 18: the various stages of the process of separation of Cu and Ni

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