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Treball Final de Grau

Leaching of nickel and copper from electroplating sludges containing Ni-Fe and Ni-Cu-Cr.
Lixiviació de níquel i coure a partir de fangs galvanoplàstics que contenen Ni-Fe i Ni-Cu-Cr.

Nil Marquès Palomeras

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UNIVERSITAT DE
BARCELONA

Perdonaré que no encertin però no que no s'esforcin...

Pep guardiola

Només donar les gràcies a tothom que ha tingut un simple minut per mi o m'ha ajudat d'alguna forma o altre.

Gràcies també a tota la gent d' IVALORE per donar-me l'oportunitat de fer el projecte en un àmbit professional però proper i a l'Alejandro per fer de professor, company i jefe alhora.

Finalment però no menys important agrair a companys, amics i sobretot a la meva família que m'hagin acompanyat durant aquests anys que no han sigut fàcils.

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SUMMARY

Electroplating sludges are produced by wastewater and spend baths treatment of the metal finishing and electrochemical industries. Due to their high heavy metal (Fe, Cr, Ni, Cu, Co…) content this type of sludge is considered as hazardous for the environment. For many years disposal in especial landfills has been the option to deal with sludges but not the solution to the problem. Since the sludge still contains significant amounts of valuable metals a process to recover them can be an interesting option. Recovering these metals reduces the disposal problem while providing new metal resources.

Hydrometallurgy offers the chance to extract almost any metal by using aqueous chemistry. Ammonia salts can form complexes with nickel and copper while their cost and toxicity is low. That allows the leaching of these target metals with ammonia as the first stage inside an hydrometallurgical rout that also engloves solvent extraction and electrowining or crystalitzation.

In this paper leaching behaviour of two different sludges with ammonium sulphate is studied. Also an alternative acidic leaching will be carried on to compare both leaching methods.

The sludges studied are mainly composed of Ni-Fe (sludge 1) and Ni-Cu-Cr (sludge 2). Effect on the leaching of diferent parameters like solid to liquid ratio, initial pH or number of consecutive leachings is studied with the aim to define suitablest leaching conditions.

In both sludges S/L ratio and number of consecutive leachings are the parameters that seems to affect greater leaching rates. Highest leaching rates obtained for sludge 1 and sludge 2 are 13% with 5 leachings and 36% with 4 leachings respectively. High iron and chromium seems to be the main cause of the low leaching rates obtained.

In sulphurical acid leaching lower initial pH benefits leaching effectivenes while too much stirring speed seems to decrease leaching rates. For sludge 2 initial pH of 0,5 and stirring speed of 1625 are the suitablest conditions achieving an extraction of 100% in 70 minutes. Sludge 1 presents leaching problems beacose of the high pH demand of iron and his leaching rates with the same conditions arent acceptable.

An hydrometallurgical process to recover nickel and copper involving acidic leaching at a constant pH of 0,5 its proposed since this conditions achieved better leaching behaviours for both sludges.

Following the leaching with the precipitation of chromium and iron using ammonia allows the rute to return to the first explained ammonia leaching route where the leached obtained it’s the complex between ammonia and Ni/Cu.

Keywords: Hydrometallurgy, Sludge, Leaching, Nickel, Copper, Chromium, Iron, Ammonia, Sulphuric acid

RESUM

Els fangs galvanoplàstica són produïts a través del tractament d'aigües residuals i banys esgotats provinents de l'industria dels acabats metàl·lics. A causa del seu alt contingut en metalls pesants (Fe, Cr, Ni, Cu, Co ...), aquest tipus de fang es considera perillós per al medi ambient. Durant molts anys, la disposició en abocadors especials ha estat l'opció per fer front als fangs, però no una solució al problema. Com que el fang encara conté quantitats significatives de metall, un procés per recuperar-los pot ser una opció interessant. La recuperació d'aquests metalls redueix el problema d'acumulació de fangs en abocadors mentre crea una nova font d'obtenció d'aquests metalls.

LA hidrometal·lúrgia ofereix la possibilitat d'extreure gairebé qualsevol metall mitjançant l'ús de la química aquosa. Les sals d'amoníac poden formar complexos amb níquel i coure, mentre que el seu cost i la seva toxicitat no son elevades. Això permet que la lixiviació d'aquests metalls amb amoníac sigui la primera etapa dins d'un procés hidrometal·lúrgia que també consta de l'extracció amb dissolvents i la electrodeposició o cristal·lització de las solucions obtingudes.

En aquest treball s'estudia el comportament de la dissolució de dos fangs amb sulfat amònic. També es realitzarà una lixiviació amb àcid per comparar els dos mètodes de lixiviació.

Els fangs estudiats estan formats principalment per Ni-Fe (fang 1) i Ni-Cu-Cr (fang 2). S'estudia l'efecte sobre la dissolució de diferents paràmetres com la relació sòlid a líquid, el pH inicial o el nombre de lixiviacions consecutives amb l'objectiu de definir les condicions de lixiviació més adequades per a cada fang.

En els dos casos, la relació S / L i el nombre de lixiviacions són els paràmetres que semblen afectar més a la de lixiviació. Els percentatges de lixiviació més alts obtinguts per als fangs 1 i 2 són 13% amb 5 etapes i 36% amb 4 etapes respectivament. L'elevat contingut en ferro i crom sembla ser la principal causa de les baixes taxes de lixiviació obtingudes.

En la dissolució amb àcid sulfúric, com més baix és el pH inicial, obtenim un millor comportament de la dissolució mentre que altes velocitats d'agitació disminueixen el contingut de níquel i coure obtinguts. Per al fang 2, un pH inicial de 0,5 i una velocitat d'agitació de 1625 són les condicions més adequades, amb aquestes condicions s'aconsegueix una extracció del 100%

en 70 minuts. El fang 1 presenta problemes de lixiviació a causa de l’alt consum de pH del ferro al dissoldre per això el percentatge de metall dissolt no és acceptable.

Es proposa un procés hidrometal·lúrgia per recuperar el níquel i el coure que implica la dissolució àcida a un pH constant de 0,5 ja que aquestes condicions han aconseguir els millors resultats ens els dos casos.

Després de la lixiviació, una precipitació amb amoníac del crom i el ferro, ens permet tornar a la primera ruta d'amoníac explicada on el producte de la dissolució és complex d’amoni i metall.

Paraules clau: Hidrometal·lúrgia, Fang, Lixiviació, Níquel, Coure, Crom, Ferro, Amoníac, Àcid sulfúric

1. STATE OF ART

For many years, world's industry has been increasing since the product demand gets higher and higher due to the consumer economy that we have these days. This economical-social background involves problems like increasing amount of hazardous wastes or the depletion of some raw materials that industry must deal with. In this project we will try to deal with some of these problems and reduce their impact while taking profit from it.

Metallurgy industries and in particular, electroplating industries, have to deal with both problems. This industry produces lots of hazardous wastes in form of sludge. Electroplating galvanic sludge (EPS) comes from the treatment of waste water streams and spend electrolytes baths. Usually, these heavy metals containing solutions are co-precipitated to reduce the metals and species content until it reach the local legislation limits, so they can throw these waters to the public water system. [2]

However, these sludges are still identified as a serious environmental threat due to their content of toxic high-density metals like copper, chromium, nickel or iron on their hydroxide form. Every sludge its different according to the nature of the plant producing it. Apart from the plating metals, sludges can contain different species depending on precipitation methods used (like $CaSO_4$ if its precipitated with lime) or another type of compounds related to the sludge formation or the galvanizing bath conditions. Even thought, the main part of the sludges its water. High water content makes them a difficult waste to transport and storage.

Considered as hazardous wastes, galvanic sludges are usually disposed on specific landfills. It takes an extra economical cost and involves the danger of water/soil pollution by metal mobilization. That's why sludge treatments have such importance. Every treatment aims to reduce the toxicity to transform the sludge into an eco-friendlier waste. [1][2]

1.1. SLUGE TREATMENTS

To reduce EPS's eco-toxicity there are different ways to treat hazardous sludges. Some pre-disposal. But there's also the need to decrease the amount of industrial wastes, that's why today, most treatments are focused on neutralizing the heavy metals from the EPS to reduce the environmental effect researches are focused on a clear and firm strategy of re-use or re-valuate these different metals (like nickel or copper) that can be used as raw materials for other processes on detriment of disposal the EPS in special landfills.

1.1.1. Stabilization/Solidification (S/S)

These treatments are basically focused on reducing the mobility of the heavy metals building a strongly bonded matrix to lower the leaching rate to the environment.

Almost every stabilization/solidification method use different inorganic additives to immobilize the sludge. Applied immobilization methods include mostly physico-chemical processes like: ion exchange, adsorption, encapsulation, complexation, and cementation.

Another usual stabilization treatment is pyrometallurgy. This method aims to transform the hydroxide sludge into its metallic state, ashes, and different alloys depending on the distribution of the sludge using thermal treatments for a future re-use.

The high amount of energy consumption to melt the hydroxides and his associated cost together with the need of gas collectors and cleaning systems are remarkable disadvantages of pyrometallurgical methods as the non-reutilizing of any source of the EPS it's the main problem of the other S/S methods. [3][4]

1.1.2. Hydrometallurgy

Hydrometallurgical processes have been applied in metal science for many years. And for this sector, hydrometallurgical techniques are becoming more attractive since they have no high energy requirements and they offer the possibility to obtain the heavy metals as distinct types of products that later on, can be used as raw materials. In global, hydrometallurgy is eco-friendlier than S/S methods.

Hydrometallurgical processes to treat and recover EPS has different steps, but the first one is the more critical. This step is the leaching or dissolution of the target metals. Leaching is the step that dictates the overall recovery of the valuable metals and its difficulty of separation from the undesirables.

We can assimilate the hydrometallurgical process to treat EPS to the one that mining industry it's based on. Mining industries obtain the main metals from a hydrometallurgical process that involves ores (sulphides, carbonates, silicates, oxides…) instead of hydroxides.

Every metal has some specific solvents that allows to obtain a reasonable leaching efficiency but in the case of nickel and copper the main leachans are ammonia and sulphuric acid. [5]

1.2. NICKEL – COPPER HYDROMETALLURGICAL PROCESS

As said, the first and crucial step of the process is leaching. Dissolution is the first process that allows to discard non-valuable metals or other impurities (like $CaSO_4$). But there are more steps until the metal its fully recovered and converted as a new raw material. In this process copper and nickel are co-extracted, separated by striping and then passed through an electrowinning step to obtain pure metal. That allows the recycling of the leach solution, the solvent and the stripping solution.

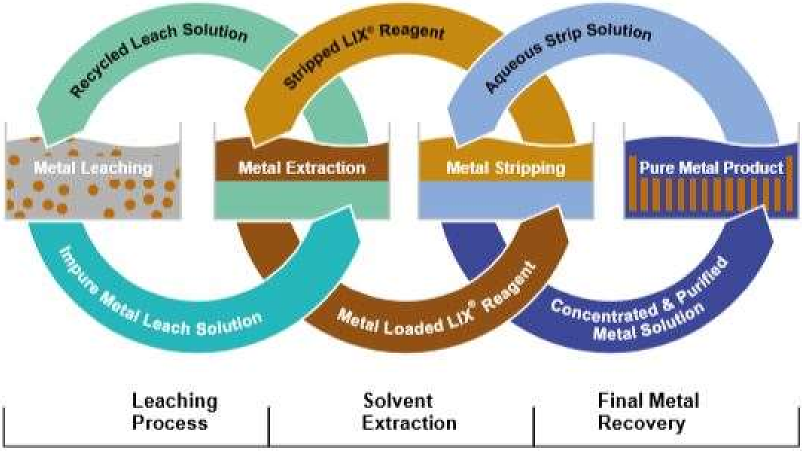


Figure 1. Metal recovery cycle (Basf Redbook, Mining solutions)

1.2.1. Nickel – Copper leaching

Normally, choosing the lixiviant is a compromise between selectivity, efficiency and economy. That's why both, ammonia and sulphuric acid are the ones usually used in this process.

1.2.1.1. Sulphurical leaching

Solubility of metal hydroxides is high on acidic pH (Figure 1), that's why sulphuric acid allows to obtain reasonable dissolution ratios while being the cheapest. However, dissolution of unwanted metals like Fe/Cr cause excess acid consumption. Also, these impurities leached in the solution with nickel and copper can cause some problems during the hole recovery process. That's why, usually, when there's the need to use sulphuric or some kind of acid as leachant, there's an extra step to separate impurities from the leached solution. [5]

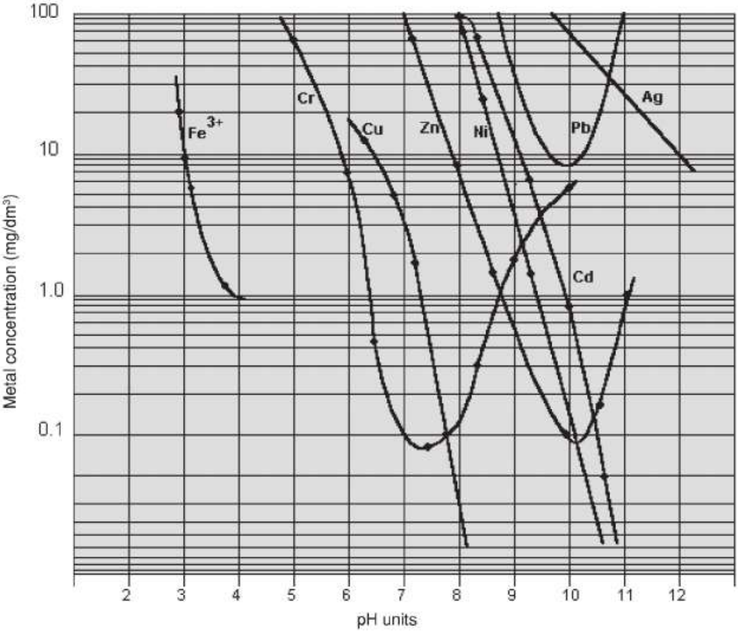


Figure 2. Metal hydroxides solubility as function of their concentration and pH

(Ensuring permeable reactive barrier efficacyand longevity, Tomasz Suponic, 2010)

We assume that the overall reactions of dissolution with sulphuric acid are of the type:

$Me(OH)_2 + H_2SO_4 \rightarrow MeSO_4 + 2H_2O$ (Equation 1)

$2Me(OH)_3 + 3H_2SO_4 \rightarrow Me_2(SO_4)_3 + 6H_2O$ (Equation 2)

1.2.1.2. *Ammonia leaching*

On the other hand, ammonia leaching has been applied to metal extraction for a long time and the application of this technology is gradually expanding. Ammonia has shown to be a good solvent to extract nickel-copper sludges, not only for its mild alkaline character but also for the high selectivity that shows with both metals. This selectivity is achieved thanks to the increased solubility of copper and nickel hydroxides in low alkaline regions. [6]

This solubility change is the result of the formation of a complex between ammonia and the metals. The complex formation mechanism can be described as the following:

$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O$ (Equation 3)

$Me^{2+} + nNH_3 \leftrightarrow Me(NH_3)_n^{2+}$ (Equation 4)

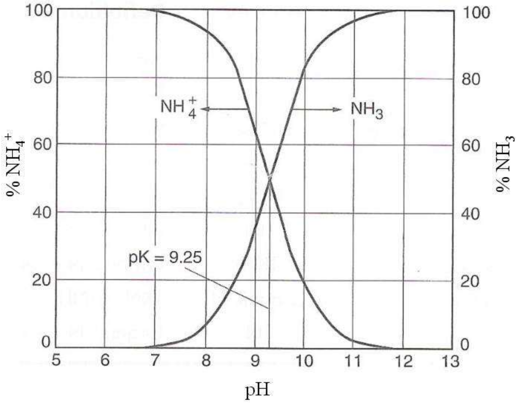


Figure 3. Ammonia ammonium equilibrium as function of pH.

It is evident that alkaline pH favors free ammonia in solution and, as we can see from the reaction, the complex is formed through free ammonia reacting with the metal cation. *Figure 3* represents the equilibrium between ammonium and ammonia as function of pH.

Although there exist many species in solution like [$Ni(NH_3)_3^{2+}$], [$Ni(NH_3)_4^{2+}$], [$Ni(NH_3)_6^{2+}$], [$Cu(NH_3)_3^{2+}$], [$Cu(NH_3)_4^{2+}$], the mainly complexes, which are the ones responsible of the solubility increase are [$Ni(NH_3)_6^{2+}$] for nickel and [$Cu(NH_3)_4^{2+}$] for copper. We can define the final expressions as:

$Ni^{2+} + 6NH_3 \leftrightarrow Me(NH_3)_6^{2+}$ (Equation 5)

$Cu^{2+} + 4NH_3 \leftrightarrow Me(NH_3)_4^{2+}$ (Equation 6)

Advantages:

- It enables the operation with another type of ores which cannot be used in acidic media due to the high consumption of acid (like carbonates).

- There's no associated problems with equipment corrosion due to acid.

- Ammonia has an specific selectivity, and metals such iron or chromium aren't soluble in ammonia conditions. That's why ammonia leaching is popular when the sludge or ore is a non-ferrous type.

-Characteristics such as low toxicity, low cost, easy recyclability, and economic gain are the main factors explaining the increased use of ammonia in hydrometallurgical processes particularly leaching.[7]

Disadvantages:

- Lower capacity of leaching.

- Ammonia is highly volatile, this leads to ammonia loses during the extraction process via evaporation. Hence, if the process needs high temperatures, it would require a closed system to prevent the ammonia concentration to fall due to evaporation.

- As said, ammonia leaching selectivity don't include Fe, Cr, Mg… That can cause huge problems when the ore or the sludge has high amounts of this metal. Alloys, non-soluble oxides layers or even double layered hydroxides (LDH) can inhibit the reaction and reduce the leaching rate. [7]

1.2.2. Metal extraction

After the leaching process the pregnant leach solution must pass through an extraction step to separate the metals in order to recover them in its metal or salt form.

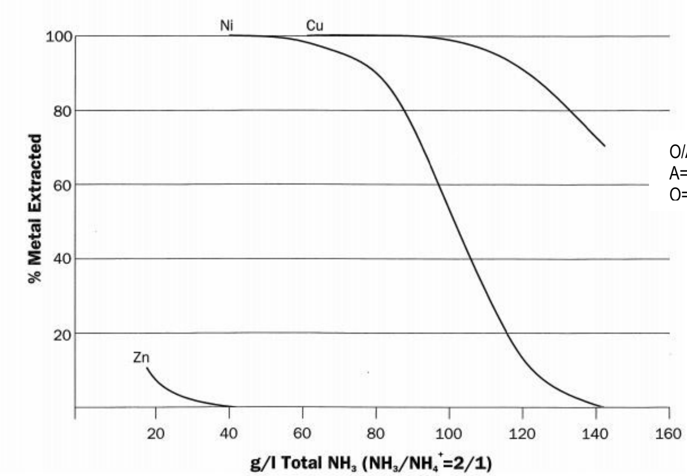
Nickel and copper are extracted from ammoniacal systems using oximes (Usually commercially called as LIX). Oximes create a new complex with the metal and ammonia ligands are pushed out. Hence, metals pass to the organic phase creating a new chelate with hydroxyoxime. This process can be written as:

$$Me(NH_3)_4^{2+}{}_{(A)} + 2Oxi_{(O)} \leftrightarrow MeOxi_{2(O)} + 2NH_{3(A)} + 2NH_4^{+}{}_{(A)} \qquad \text{(Equation 7)}$$

As we can see in *Equation 7* this reaction is reversible. Hence, it should be expected that with increasing free ammonia or ammonium concentration, the extraction rate would be reduced.

Also, high free ammonia concentrations lead to ammonia evaporation which represents a problem related with strong smells.

Figure 4 shows nickel, copper and zinc isotherms for an oxime extraction system. [8]



O/A= 1
A= 0.038 molar in sulphate
O= 0.1 molar

Figure 4. NH_3 Isotherms for 84. [8]

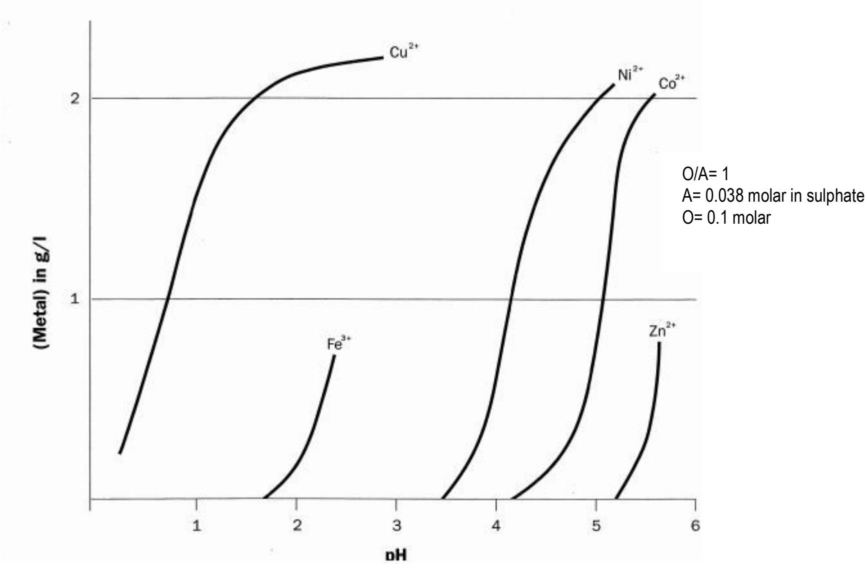
Ammoniacal leach solution, now free of metals, can be lead again to the leaching process to recycle it.

1.2.3. Stripping

With the organic phase loaded with both metals, it is necessary to strip them to an aqueous phase. Stripping can therefore be achieved by reversing the equilibrium using sulphuric acid:

$$MeOxi_{2(O)} + 2H^{+}_{(A)} \leftrightarrow 2HOxi_{(O)} + Me^{2+}_{(A)} \qquad \text{(Equation 8)}$$

In this process both metals are co-extracted using H_2SO_4. Using different concentrations of acid what mean different pH's, metals can be separated into two different solutions. While nickel can be stripped at pH=3, copper needs a higher acid concentration to be separated from the solvent. *Figure 5* shows the pH range which allow to separate nickel and copper. [8]



O/A= 1
A= 0.038 molar in sulphate
O= 0.1 molar

Figure 5. pH extraction-stripping isotherms for LIX 84. [8]

The stripped organic phase is then recirculated to continue extracting more nickel and copper. Both pure solutions ($NiSO_{4(l)}$ and $CuSO_{4(l)}$), can be crystalized to obtain a metal salt or can be subjected to an electrowinning stage where they are transformed into their metallic form.

1.3. KINETICS AND KEY PARAMETERS

There are some key parameters that can change the evolution of the reaction. It it important to define which parameters can improve the kinetics of the reaction to achieve better leaching ratios. Based on recent similar studies:

1.3.1. Key parameters effect

-Effect of ammonia concentration

Ammonia concentration influences greatly in leaching behavior. Higher ammonia differentials between the solid and the liquid phases, improves the transfer between them. However, work at high ammonia concentrations is inefficient due to the limitation of the solvent extraction step. It limits the ammonia concentration near 50 g/L (*Figure 5)*. [9]

-Effect of the pH

As *Figure 3* shows, free ammonia increases as pH does. That favors leaching velocities. But, in the other hand, higher free ammonia concentration means higher ammonia losses by evaporation.

-Effect of solid/liquid ratio

Lower solid/liquid ratios means that the concentration of the metals in solution will be lower. That changes the concentration differential thus improving the transference between both phases. [3]

-Effect of particle size

It is expected to get higher leaching rates when the particle diameter its reduced. The smaller the particle size the higher the surface area to react with. [10]

-Effect of temperature

Leaching temperature is really a key parameter on Ni/Cu leaching rate. Following *Arrhenius* equation, higher temperatures improves the reaction rate due particle collisions. Even though temperature favors reaction kinetics, it can be a problem when the solution is basically ammonia, which it's a volatile compound. [11]

-Leaching time

Leaching time, it's the most important parameter, but, after the main leachable part has been separated, leaching time loses his effect on the rate. Metal recovery increases very slowly after leaching time has been passed. [9]

1.3.2. Kinetic model

Leaching is described as the extraction of soluble constituents from a solid by mean of a solvent (liquid). Solid-liquid reactions are heterogeneous reactions, which are characterized by the reaction happening on the interphase.

There are two basic models that can represent reaction behavior:

-Shrinking particle: A un-porous particle its first attacked on the outer surface thus reducing its size until all the particle has reacted.

-Shrinking core model (un-reacted core): A porous particle reacts over time but its size results constant due to inert impurities or reaction products that forms an outer ash layer (shell).

Since our sludges contains impurities like Fe, Cr or $CaSO_4$ we will assume that the particle size is going to remain constant and the reaction takes place thanks to the particle porosity, thereby, the model that better fits into this reaction is the *unreacted shrinking core model.* [12]

1.3.2.1. Shrinking core model

This kinetic model is defined to have different consecutive stages during the hole reaction time that can be described as [12]:

1. Diffusion of the leachant from bulk phase to the shell surface.
2. Diffusion of the leachant from the shell to the core surface.
3. Reaction on the core surface to form the product (ammonia complex) and the ash layer.
4. Diffusion of the product from the core surface to the shell surface.
5. Diffusion of the product from the shell surface to the liquid bulk.

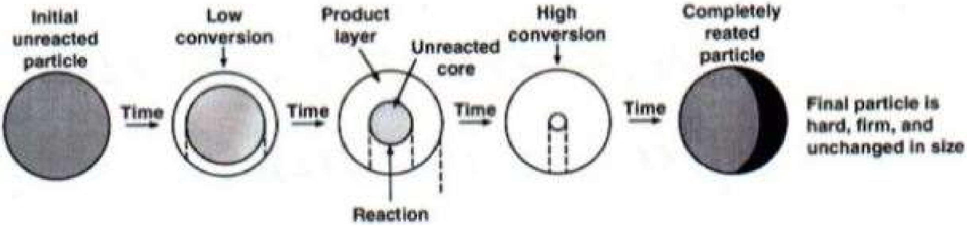


Figure 6. Shriking core model reaction evolution

Its assumed that stages 2 and 4 are similar as 1 and 5. Some studies about the kinetics of plating sludges and ores have shown that the rate limiting stage in this type of solids is the diffusion of the leachant through the inert layer (2-4). [13][14]

Therefore, we will analyze leaching results on this guess.

2. OBJECTIVES

- Study the lixiviation behavior in ammoniacal medium of two different electroplating sludges (EPS) which contains Ni-Fe and Ni-Cu-Cr respectively.
- Analyze the effect of various parameters such solid to liquid ratio, initial pH or stirring speed which can affect the leaching rate in both cases.
- Relate the effect of the high content of non-soluble compounds with the leaching rates.
- Analyze the obtained results to determinate if ammonia leaching it's a viable industrial process to recover nickel and copper from sludges with a high content of insoluble compounds.
- If ammonia leaching doesn't show reasonable results, find other ways to leach both metals.
- Study the new proposed method behavior.
- Analyze the effect of various parameters.
- Analyze the results to be able to compare both leaching types and which one obtains better leaching rate results.
- Propose a high efficiency process to recover nickel and copper from both EPS.

3. MATERIAL AND METHODS

3.1 ELECTROPLATING SLUDGE

All the sludges used on this project comes from sewage plants that treat wastewater from galvanizing industries. EPS is formed during the neutralization of this wastewaters.

To reduce wastewaters metal content industries usually precipitate these metals with lime (limestone is used also to reduce wastewater sulfate content). This process lets to the formation of an amorphous sludge composed mainly of water (around 75%), metal hydroxides and $CaSO_4$.

All the samples were collected from IVALORE plant. There, wet sludges are pre-treated with an air-drier between 120-200ºC and grinded to reduce its particle size up to 100 µm. The result is a dry fine powder.

Both samples have been analyzed via ICP (inductively coupled plasma).

	Content [wt.%]				
Metals	Ni	Cu	Cr	Fe	Ca
Sludge 1	28,3	-	-	19,8	12,7
Sludge 2	6,5	4,85	14,67	-	3,92

Table 1. Sludge composition in dry basis.

Table 1 shows the composition in dry base of the two sludges which are studied in this project. Other minority components like salts that come from water (Cl^-, F^-…) or metals with less than 0,1% dry mass were neglected and not evaluated further in this study.

Sludge 1 mainly contains: $Ni(OH)_2$, $Fe(OH)_3$ and $CaSO_4$.

Sludge 2 it's a mix of: $Ni(OH)_2$, $Cu(OH)_2$, $Cr(OH)_3$ and $CaSO_4$.

One special characteristic of sludges is their color that is given by their metal content. Thanks to that, a sludge can be identified for its own color. *Figure 7* shows sludge 1 and sludge 2, where the difference in color its noticeable. Iron content on sludge 1 gives a light brown color, while the mixture of Cr, Ni (green) and Cu (blue), gives to sludge 2 the following blue-green color.

Figure 7. Sludge 1 and sludge 2

3.2 LEACHING EXPERIMENTS

Several experiments were carried out to study the leaching of both sludges. Experiments were carried out at room temperature using a 2000 ml beaker and a mechanical stirrer. After the leaching, to recover the non-reacted solid, the slurry was passed through a vacuum filter to obtain the solid. To study the lixiviation evolution, 10ml samples were withdrawn to test tube at regular time intervals to be analyzed.

3.2.1 Procedure

Two different types of experiments were made due to development of the results. Leaching in alkaline and in acidic medium.

3.2.1.1 Alkaline medium

Solid to liquid ratio and pH (free ammonia content) were employed as experimental variables to study the leaching. As exposed above, these variables can affect the leaching rate. Other parameters were maintained constant during all experiments as *Table 2* shows.

Variable	Values
(NH4)2SO4 concentration [g/L]	183,5
Total ammonia [g/L]	50
Temperature [ºC]	20
pH range	0 - 14
Particle size [µm]	≤ 100
Stirring speed [rpm]	1650
Leaching time [min]	90
Solid to liquid ratio [Cu+Ni g/L]	5 - 10

Table 2. Leaching parameters

To prepare the leaching experiment the following steps where followed:

1- Preparation of 1000 ml of ammonia sulfate solution.

2- Adjusting of the initial pH with caustic soda and H_2SO_4.

3- Addition of the necessary amount of sludge to form the slurry.

3.2.1.2 Acidic medium

The procedure on the acidic leaching was the same as in alkaline medium but excluding the step 1. The studied parameters were also the initial pH and the S/L ratio.

3.2.1.2 Successive stages

In this type of test, the sludge slurry was filtrated, cleaned and dried after every leaching done to be prepared for another leach.

3.2.2 Sample Analysis

In every sample, copper and nickel were analyzed by iodometric titration and complexometric EDTA titration respectively. Some samples were sent to an external laboratory to be analyzed via ICP. All reagents used were of analytical grade type.

All calculations were made to find the percentages of Cu+Ni leached.

4. RESULTS AND DISCUSSION

This chapter focuses on presenting and analyzing the results of the leaching experiments. Results will be compared between both sludges and between different parameters. Also, to go deeper, the results will be compared with another study where the sludge doesn't contain either Fe or Cr.

4.1 AMMONIA LEACHING OF SLUDGE 1

This section shows the results of the leaching of sludge 1, which only contains iron and nickel. Parameters such S/L, initial pH and number of leaching stages have been studied to achieve the highest leaching ratio. Other parameters haven't been changed due to technical limitations or by the assumption of their effect based on other studies.

4.1.1 Effect of the solid/liquid ratio

Experiments relating to the effect of solid/liquid ratio were carried out at 5 and 10 [g/L]. Other parameters like ammonium sulphate concentration pH, particle size, stirring speed, and temperature were kept constant at 183.5 g/L, 8.5, ≤100, T amb, respectively.

Figure 8 lustrates the effect of the solid/liquid ratio on the leaching rate. There, we can see that exists a difference between both experiments. Leaching rate seems to increase when the S/L ratio decreases. Also, we can see that the maximum leaching time its low since, in both cases, with 10 minutes the leaching rate stops increasing and remains almost constant during the remaining leaching time.

After 90 minutes of leaching, 7,7% of metal is extracted for 5 g/L and a 5% for 10 g/L. The low leaching ratios can be because of the high iron content of this sludge. In the other hand, the difference between S/L ratios can be explained as the free ammonia decreases with the amount of metal extracted.

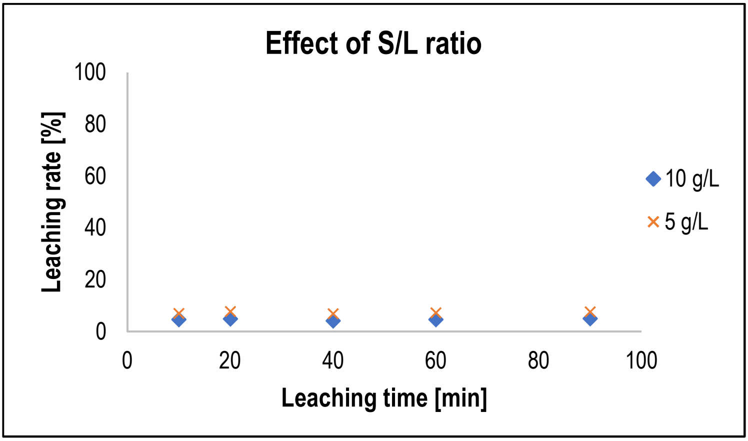


Figure 8. Effect of the S/L ratio in the lixiviation of Ni.

(stirring speed: 1650, T: 20 ºC, particle size ≤100, total ammonia: 50 g/L, pH:8.5)

4.1.2 Effect of the pH

As explained with *equation 3,4* (page 17) the leaching reaction happens between the metal and the free ammonia. To evaluate the effects of initial pH to the leaching, three experiments have been carried at 8.5, 9, 9.5 pH values while ammonium sulfate concentration, stirring speed, S/L ratio, temperature and particle size were remained constant. *Figure 9* shows the effect of pH on the lixiviation of Ni.

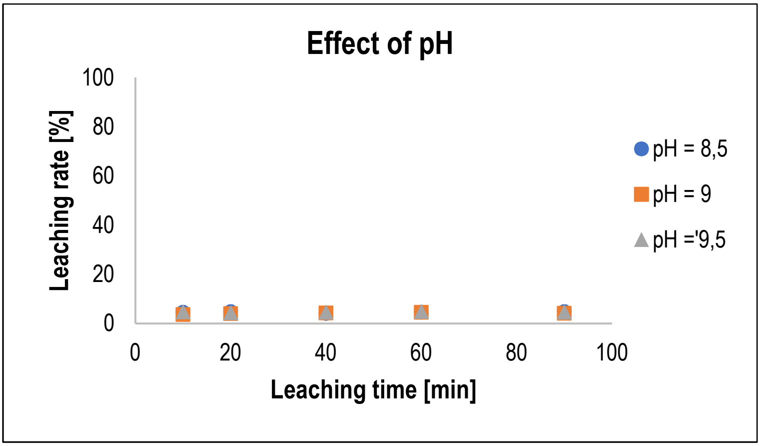


Figure 9. Effect of the pH in the lixiviation of Ni
(Stirring speed: 1650, T: 20 ºC, particle size ≤100, total ammonia: 50 g/L, S/L: 10 g/L)

Results from the *Figure 9* shows that the pH for a 10 g/L solution almost don't affect the reaction since the rates for these different pH's are 5 %, 4,7%, 4,9%. Leaching rates keep being very low and almost no Ni is dissolved.

Because the low leaching rates obtained, a pH evolution study was made in order to check if the fast loss of pH was the cause. Two tests with an initial pH of 9,5 (the higher) were made at 5 g/L and 10 g/L.

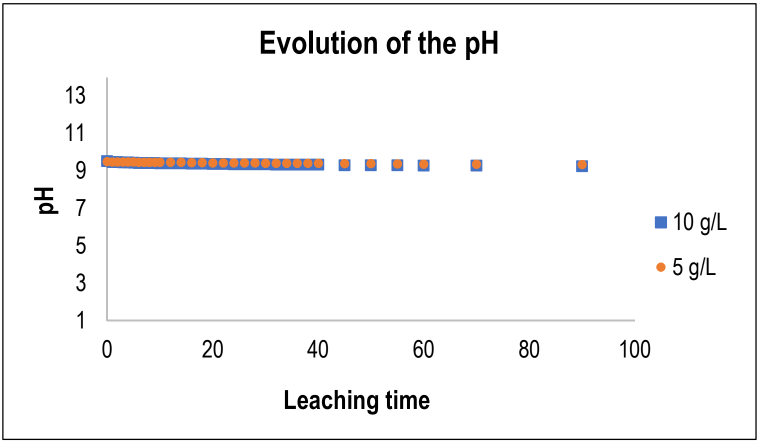


Figure 10. Evolution of the pH in the lixiviation of Ni

(stirring speed: 1650, T: 20 ºC, particle size ≤100, total ammonia: 50 g/L, pH:9,5)

We can see that almost no pH decrease is observed during all the reaction time for both S/L rates. This discards that the problem is the lack of pH force.

4.1.3 Effect of the number of stages

To find a way to improve sludge 1 leaching rates, a consecutive number of leaching stages were made under the same conditions. *Table 3* shows the results achieved with a total of 5 in series. After 5 sequential leachings, the leaching rate stops increasing arriving then to what we will consider as the total leachable nickel of the sludge.

Whit the experiments shown above, we could have said that the maximum nickel leachable was the one obtained with 5 g/L and pH = 8,5 (7,7%) and that there was a limitation due to the iron present in the particle. But, in the other hand, consecutive leaching has proved that iron isn't the only limitation when trying to achieve high rates. Nickel ammonia complex concentration within the solution can be the other reason. Equilibrium between driving forces (dc, dpH...) and resistances that iron can cause, may be occurring when the Ni concentration increases. Thus, increasing the concentration of nickel in the solution may decrease the concentration differentials of nickel between the phases which could be acting as a driving force.

STAGE	g/L	% tot
1	0,5	5
2	0,3	8
3	0,4	12
4	0,1	13
5	0,02	13,2

Table 3. Leaching rate for every stage

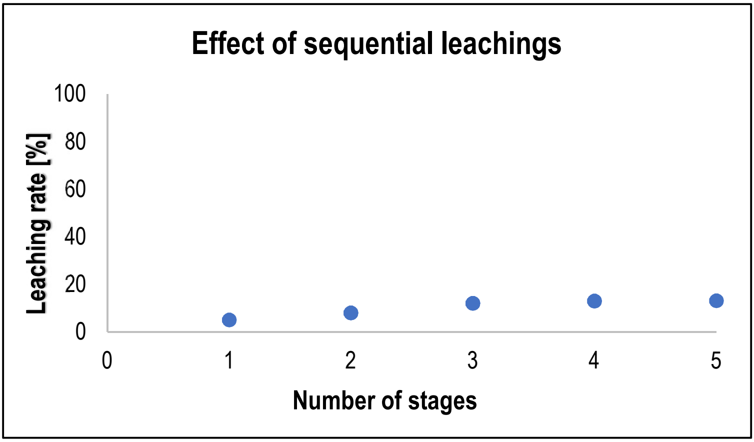


Figure 11. Sequential leaching rates in the lixiviation of Ni

(stirring speed: 1650, T: 20 ºC, particle size ≤100, total ammonia: 50 g/L, S/L: 10 g/L, pH= 9.5)

While the greatest leaching rates with one stage where 7,7% and 5% when the ratio was 5 g/L and 10g/L respectively, it can be seen that with a 10 g/L lixiviation and 5 stages a 13,2% ratio its achieved.

S/L ratio differences can be explained by the same principle, since the same nickel concentration in solution means different leaching rates. Because of that, the limiting concentration can be the same for both S/L rates, but at the end it signifies a different leaching rate.

Even though these results improves the previous ones, leaching rates are still too low to design a process whit a reasonable efficiency. Discarding ammoniacal leaching as a good way to obtain nickel from a Ni-Fe EPS (sludge 1), other processes will be proposed and analyzed

.

4.2 AMMONIA LEACHING OF SLUDGE 2

This section shows the results of the leaching of sludge 2, which contains copper, nickel and chromium (3^+). Parameters such S/L, initial pH and number of leaching stages have been studied to achieve the highest leaching ratio. Other parameters haven't been changed due to technical limitations or by the assumption of their effect based on other studies.

4.2.1 Effect of the solid/liquid ratio

Experiments relating to the effect of solid/liquid ratio were carried out at 5 and 10 g/L. Other parameters like ammonium sulphate concentration pH, particle size, stirring speed, and temperature were kept constant at: 183.5 g/L, 8.5, ≤100, T 20 ºC, respectively.

The results obtained (*Figure 12)* show the influence of S/L in the leaching. While the 5 g/L test obtains a 18,4% total leaching, the one at 10 g/L, reach a leaching rate of 9,6%.

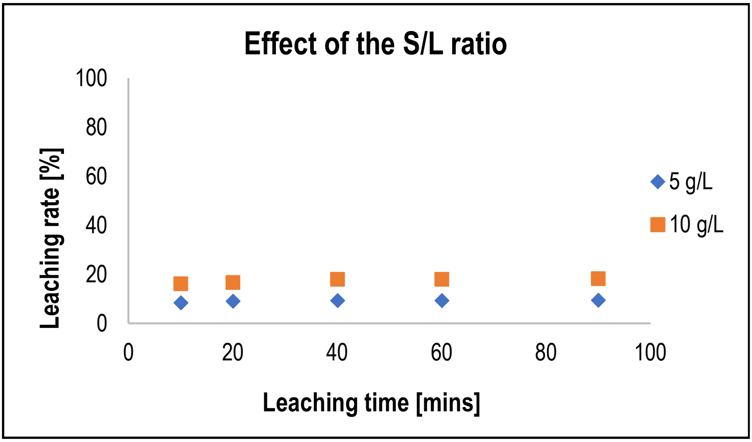


Figure 12. Effect of the S/L ratio in the lixiviation of Ni and Cu
(Stirring speed: 1650, T: 20 ºC, particle size ≤100, total ammonia: 50 g/L, pH =8.5)

Then, while decreasing the S/L ratio, the leaching rate increases. In this case, the relation between the S/L and the leaching rate its almost lineal. Hence, we could consider that as in sludge 1, exist an equilibrium limit between driving forces and resistances at a certain nickel-copper concentration.

4.2.2 Effect of the pH

As explained with *equation 3,4* (page 17) the leaching reaction happens between the metals and the free ammonia. To see how the initial pH affects to the leaching, three experiments have been carried out at 8.5, 9, 9.5 pH values while ammonium sulfate concentration, stirring speed, S/L ratio, temperature and particle size were remained constant. *Figure 13* shows the effect of pH on the lixiviation of Ni and Cu.

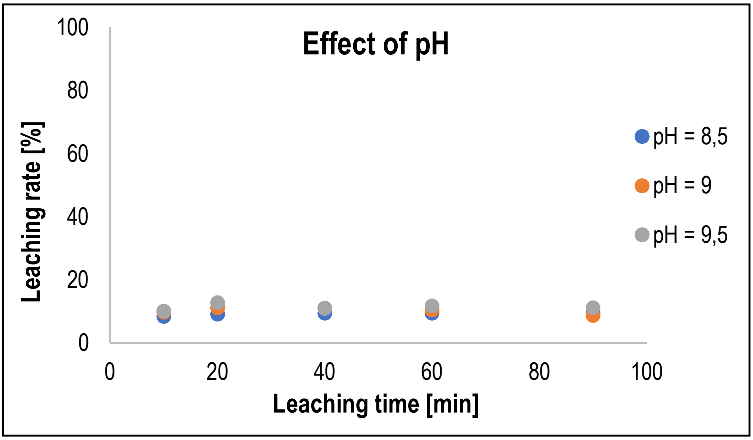


Figure 13. Effect of the pH in the lixiviation of Ni and Cu

(Stirring speed: 1650, T: 20 ºC, particle size ≤100, total ammonia: 50 g/L, S/L : 10 g/L)

It is seen that changes in the initial pH do not lead to significant variation on the copper-nickel leaching rates. The ratios achieved with pH's of 8.5, 9 and 9.5 were 9,6%, 11,2% and 12,9% respectively.

Like with sludge 1, the pH evolution (*Figure 14)* was followed to see if the cause of low leaching rates was the lack of free ammonia (that can be traduced to lack of pH).

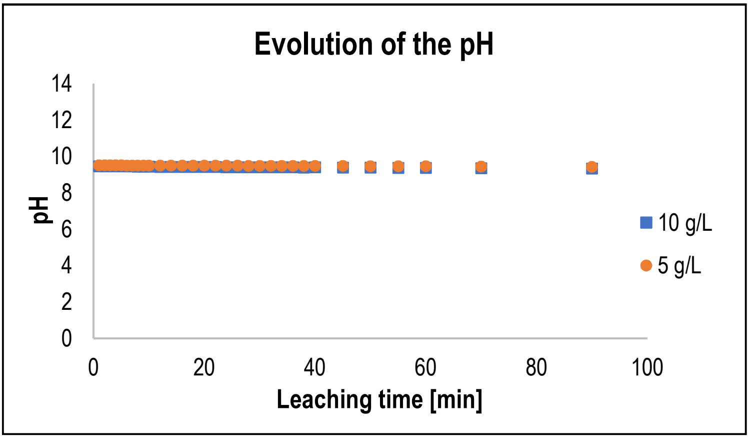


Figure 14. Evolution of the pH in the lixiviation of Ni and Cu

(stirring speed: 1650, T: 20 ºC, particle size ≤100, total ammonia: 50 g/L, pH: 9.5)

PH evolution shows that almost no pH is consumed, which means that the reaction isn't stopping because lacking on alkaline pH. Therefore, leaving aside the pH need, high chromium contain may be the reason why the leaching rates are that low.

4.2.3 Effect of the number of stages

To reduce the effect of concentration in solution equilibrium theory, as in the sludge 1, sequential dissolution with the same conditions were carried on with a S/L of 10 g/L. What are we looking forward is to reinitiate the concentration differentials to favour the reaction and hence increasing the total leaching of Ni and Cu.

STAGE	g/L	% tot
1	1,3	12,9
2	0,98	22,7
3	1,24	35,1
4	0,14	36,5

Table 4. Leaching rate for every stage

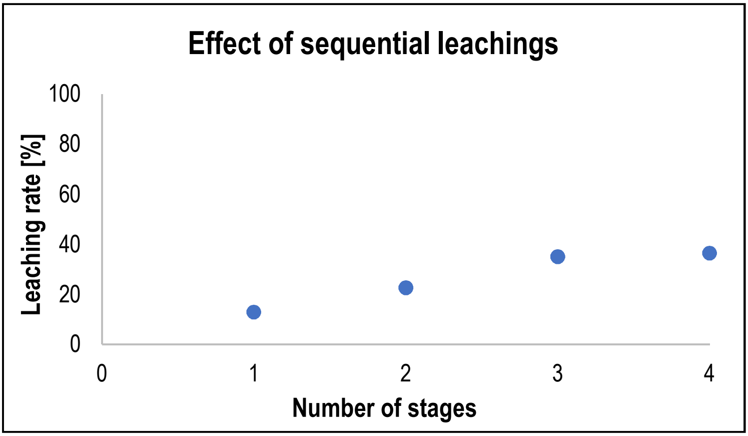


Figure 15. Sequential leaching rates in the lixiviation of Ni and Cu

(stirring speed: 1650, T: 20 ºC, particle size ≤100, total ammonia: 50 g/L, S/L: 10 g/L. pH: 9.5)

Ni-Cu are leached until stage 4, when it seems to stop reacting. As with the sludge 1, a highest leaching rate its achieved. While with only one leaching the highest rate was 18,4% at 5 g/L, with only 2 more extra stages, the separation of nickel and copper increases to the 36.5%.

4.3 SLUDGES COMPARISION

A priori, both sludges seem to present the same leaching problems, low leaching rates because high content of an insoluble trivalent metal (Cr and Fe). Iron and chromium are highly insoluble in ammoniacal media, so they difficult ammonia access to the soluble nickel/copper.

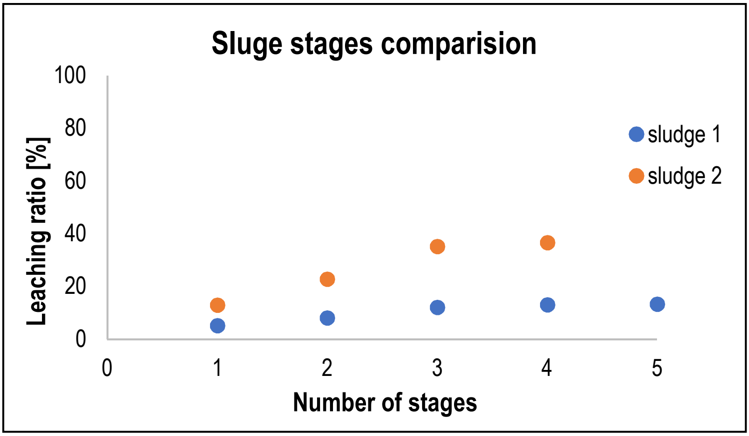


Figure 16. Stages comparison

(stirring speed: 1650, T: 20 ºC, particle size ≤100, total ammonia: 50 g/L, S/L: 10 g/L, pH: 9.5)

Sludge 2 with a total of 4 stages arrives to an 36% of Ni-Cu leaching while sludge 1 needs one more leach to only obtain a 13% rate. The difference between these results could be because of two different reasons:

1- Copper its more stable as ammonia complex than nickel, for that, is easier to leach and with the same conditions, more Ni+Cu (%) is leached in sludge 2.

2- Chromium has a better behavior allowing nickel and copper to be leached more than iron.

On the other hand, there's a possible reason to the low leaching rates which encompasses both reasons, the formation of a complex called double layered hydroxide (LDH) during the precipitation of the sludge.

To secure that the main reason of the low leaching rates are Cr and Fe, another sludge will be compared. This sludge is the one *Alejandro López* studied in 2017. [3] The leaching results obtained in his study with a sludge only formed by Ni-Cu (23,38 - 16,58%) are the following.

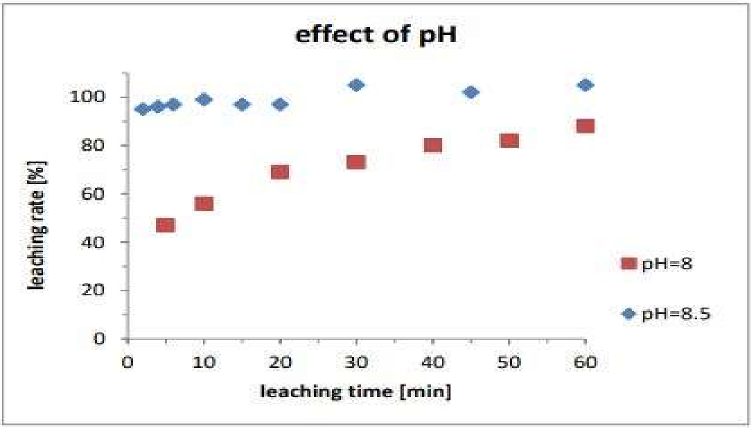


Figure 17. Effect of the pH on the leaching rate for a S/L ratio = 10 g/L

(stirring speed: 1650, T: 20 ºC, particle size ≤100, total ammonia: 50 g/L, S/L: 10 g/L)

It's evident that these leaching rates have nothing to do with the ones obtained in this study. While at higher pH's (9 – 9.5), sludge 1 and sludge 2 don't reach the 20% Ni-Cu dissolution, at pH = 8 the free Cr/Fe sludge achieves ratios greater than 80% with the all the other leaching parameters being the same. With a pH= 8,5 almost the 100% its separated while with sludge 1 and 2 only 5% and 10% of total nickel and copper is lixiviated.

4.4 DOUBLE LAYERED HYDROXIDES IN EPS

LDH or hydrotalcite-like compounds are a large family of two-dimensional (2D) anionic clay materials which can be represented by the general formula:

$$M_{1-x}^{2+}M_x^{3+}(OH)_2^{x+}[A_{x/n]}]^{n-}mH_2O$$

LDHs are composed of brucite-like layers in which the divalent metal cations ($Mg^{2+,}$ $Fe^{2+,}$ $Co^{2+,}$, **$Cu^{2+,}$**, **$Ni^{2+,}$**, or $Zn^{2+,}$) are coordinated octahedrally with the trivalent metal cations (Al^{3+}, **Cr^{3+}**, Ga^{3+}, In^{3+}, Mn^{3+} or **Fe^{3+}**). The value of x its generally between 0,2-0,33.

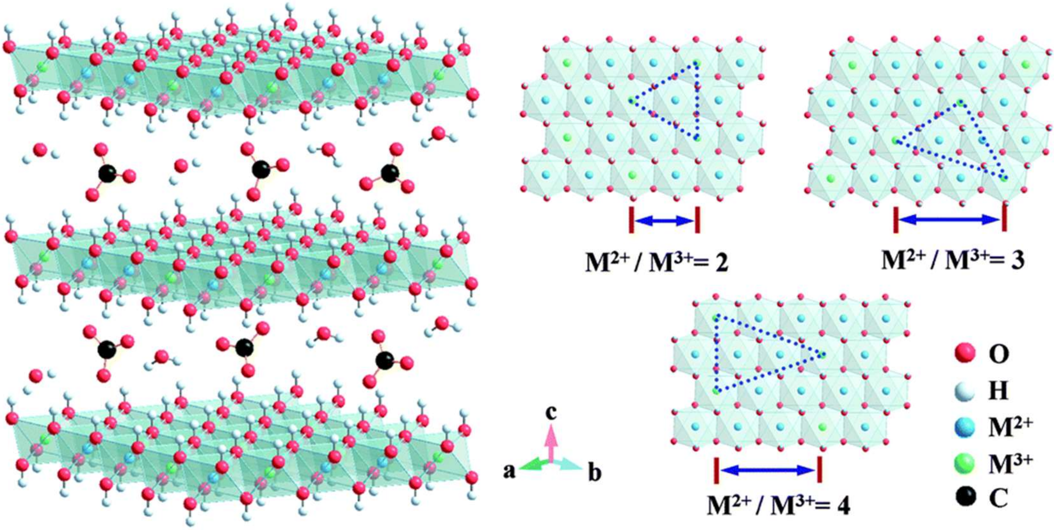


Figure 18.
LDH structure (via ResearchGate, Transition metal based double hydroxides tailored for energy conversion and storage. 2015)

Typically, LDH are synthetized by coprecipitation at a very high grades of base dosing and followed by aging at moderate temperatures. This description fits perfectly into our sludge formation. To neutralize wastewaters, lime is added to coprecipitate the metals. After, the sludge is dried with hot air where, with temperatures between 120-200 ºC the LDH is formed. [15]

LDH	pH Range Low Limit	 High Limit
$[Zn_{1-x}Cr_x(OH)_2](Cl^-)_{x/n}$	4.5	10.0
$[Ni_{1-x}Al_x(OH)_2](CO_3^{2-})_{x/n}$	5.0	10.0
$[Ni_{1-x}Cr_x(OH)_2](Cl^-)_{x/n}$	5.5	11.5
$[Zn_{1-x}Al_x(OH)_2](Cl^-)_{x/n}$	6.0	10.0
$[Co_{1-x}Fe_x(OH)_2](Cl^-)_{x/n}$	7.5	10.5
$[Mg_{1-x}Al_x(OH)_2](Cl^-)_{x/n}$	8.0	10.5

*Table 5. LDH pH range. (*Review of the synthesis of layered double hydroxides. Juan J. Brabo et al.)

Table 5, shows the pH range where some LDH may exist. It can be seen that some of this LDH's are equal or similar to the ones we may have. Can be appreciated that pH's are in our range of work, which means that these double hydroxides are stable in this medium.

Since some nickel and copper its able to be leached, we assume that no all the sludge is in this LDH form. For this reason, it is difficult to find a correlation between the sludge composition and the metal leached. Every sludge has been precipitated differently, that's why LDH percentage in sludges don't has to be the same.

4.4.1 Effect of LDH on sludge 2

Sludge 2 has 1,65% less copper than nickel, however, in leaching tests, copper leaching results way higher than nickel.

	10 g/L Ni+Cu content [%]	Leached Cu+Ni [%]
Ni	57	17
Cu	43	83

Table 6. Comparison between Ni and Cu leaching

This may be because the stability of NiCr double layered hydroxides its larger than that of CuCr. We can't obtain a final LDH formula associated with every sludge since the results obtained, don't express a clear M2+-M3+ relation like theory says (0,2≤ x ≤ 0.33).

In mining industry, some complex ores have a reductive pre-treatment that allows them to reduce the amount M^{3+} metals that could have a negative influence on the leaching rates.

4.5 ACIDIC LEACHING OF SLUDGE 2

Having this leaching issues, the need to find other ways to recover nickel and copper was evident. Lixiviation with acidic media is proposed to try to improve the previous results.

4.5.1 Effect of the initial pH

To study if the acidic leaching it's an efficient way to separate Ni/Cu, a study of the pH evolution has been done to find the better conditions. To create a comparison between acidic and ammoniacal medium, worse parameters in with ammonia leaching have been chosen for these tests.

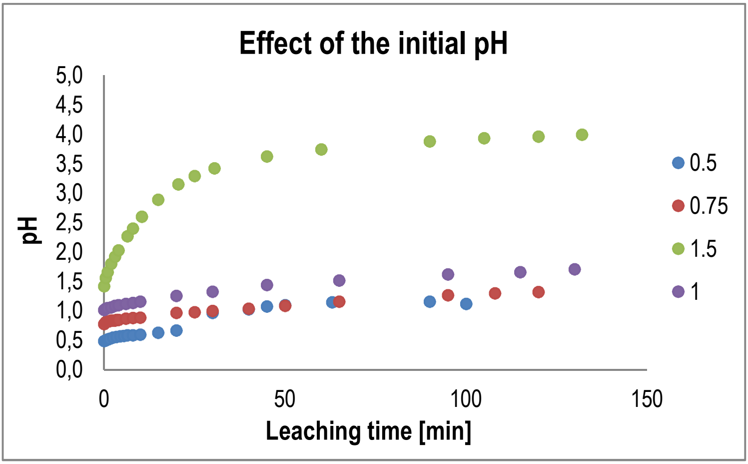


Figure 19. Effect of the initial pH in pH evolution

(*stirring speed: 1650, T: 20 °C, S/L: 10g/L, sulphurical medium.)*

Initial pH	Leaching time [min]	Leaching rate [%]
0,5	70	100
0,75	90	97
1	120	87
1,5	130	33

Table 7. Leaching time and leaching rates with diferent initial pH

Figure 19 shows the differences between the initial pH in sulfuric lixiviation. With pH= 0,5 and 0,75 all the Ni/Cu is extracted which means that the pH is low enough to lixiviate all the metals. For pH's higher than 0.75, it seems that there is a lack of pH which is transformed in an incomplete dissolution. In leaching time terms, it is seen that the lowest the pH is the leaching time needed. The lowest leaching time its for pH 0,5 (70 mins) while the highest at pH 1,5 (130).

4.5.2 Effect of stirring speed

To add another parameter and check the assumptions made from recent studies, stirring speed variations have been done.

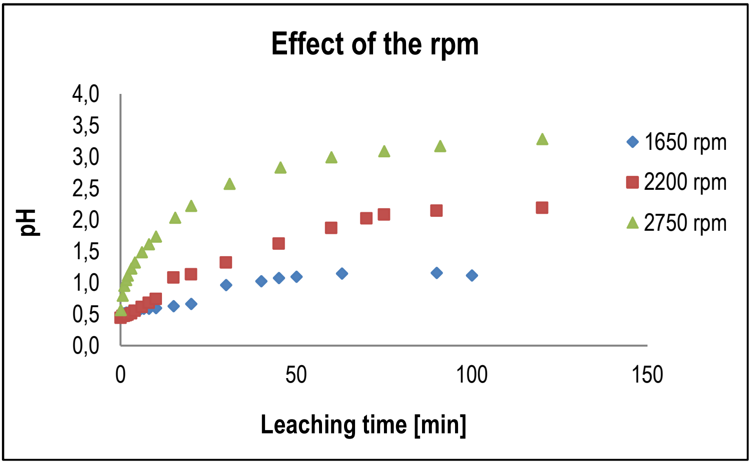


Figure 20. Effect of rpm in the pH evolution

(initial pH= 0.5, T: 20 ºC, S/L: 10g/L, sulphurical medium.)

rpm	Leaching time [min]	Leaching rate [%]
1650	70	100
2200	80	70
2750	110	42

Table 8. Leaching time and leaching rates with rpm variation

The results show that by increasing the stirring speed, leaching loses efficiency. It seems that the increase of rpm is traduced into a faster pH consumption but also decreasing his leaching efficiency. Because of that, with a speed of 1650 rpm the leaching time it's the lowest and the leach its completed, 70 mins and 100% Cu+Ni leached.

Because of the difficulties to form preferential ways into the particle when there's a high stirring speed, the particle, which will be rotating with the solution, may react like a shrinking particle. This could explain the higher consumption of pH with lower leaching rates. More pH potential its used to leach chromium. [16]

4.6 ACIDIC LEACHING OF SLUDGE 1

Equally as sludge 2, the high content of iron in the EPS, seems to inhibit the total leaching of nickel in ammonia medium. An acidic lixiviation with sulfuric acid is studied since iron is also soluble at low pH's.

4.6.1 Effect of the initial pH

To find the optimal conditions to leach iron and nickel when working with sulphurical medium pH evolution has been studied changing the initial pH.

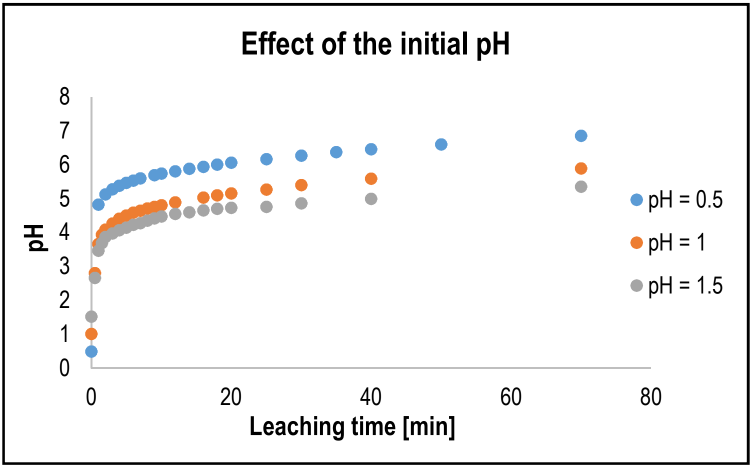


Figure 21. Effect of the initial pH in pH evolution

(*stirring speed: 1650, T: 20 °C, S/L: 10g/L, sulphurical medium.)*

Initial pH	Leaching time [min]	Leaching rate [%]
0,5	30	34
1	25	22
1,5	18	19

Table 9. Leaching time and leaching rates with diferent initial pH

Figure 21 shows how the pH increases faster than with sludge 2. That's because iron has lower solubility and needs more pH force to react. Nevertheless, faster pH consumption doesn't mean a higher leaching rate. Because of that, when pH increases that fast the solution lacks on pH to end a complete dissolution. As we can see in *Table 9* leaching stops due to the rising of pH.

4.6.2 Leaching at constant pH

To deal with the lack of pH on the lixiviation of sludge 1 a leach maintaining the pH at 0.5 has been done for both sludges to achieve higher leaching rates and lower leaching times.

	Leaching time [min]	Leaching rate [%]
Sludge 1	51	97
Sludge 2	33	100

Leaching time of sludge 1 is higher because as said before iron is harder to leach than chromium.

4.7 PROCESS PROPOSED TO LEACH AND RECOVER NI-CU

Based on the obtained results, a process to leach and recover Ni and Cu its proposed:

The first stage, which is leaching, is a sulphurical leaching at constant pH = 0,5 that allows to lixiviate all metals including iron and chromium. The slurry obtained is filtered with a belt filter to remove insoluble impurities like $CaSO_4$. Thanks to the filtration a pure metal sulphate solution is obtained.

Next step is to remove impurities like Cr or Fe, these metals are removed via precipitation with free ammonia. The agent chosen to precipitate $Cr(OH)_3$ and $Fe(OH)_3$ is ammonia because while precipitating the impurities, ammonia also forms a Ni/Cu-ammonia complex.

To obtain a pure ammonia metal solution, another filter stage is needed to remove iron and chromium hydroxides. The solution obtained is the same as if an ammonia leaching had been made.

This solution is led to extraction with solvents and then stripped with an acidic solution at different pH's to finally separate nickel and copper to obtain their sulfate forms. These sulfates can be crystallized to obtain their solid form or can be led to electrowinning to convert them into his metal state.

With this process, a high efficient Ni/Cu recover is achieved, however, it can cause extra economical costs due to the spending of NH_3 and H_2SO_4 which are obtained in form of $(NH_4)_2SO_4$.

Ammonia sulfate its obtained as a by-product in the extraction stage. Ammonia can be recovered and sent to precipitation stage which would mean that no ammonia is spent during the process. In the other hand, finding a way to commercialize ammonium sulphate can cover the NH_3 and H_2SO_4 costs.

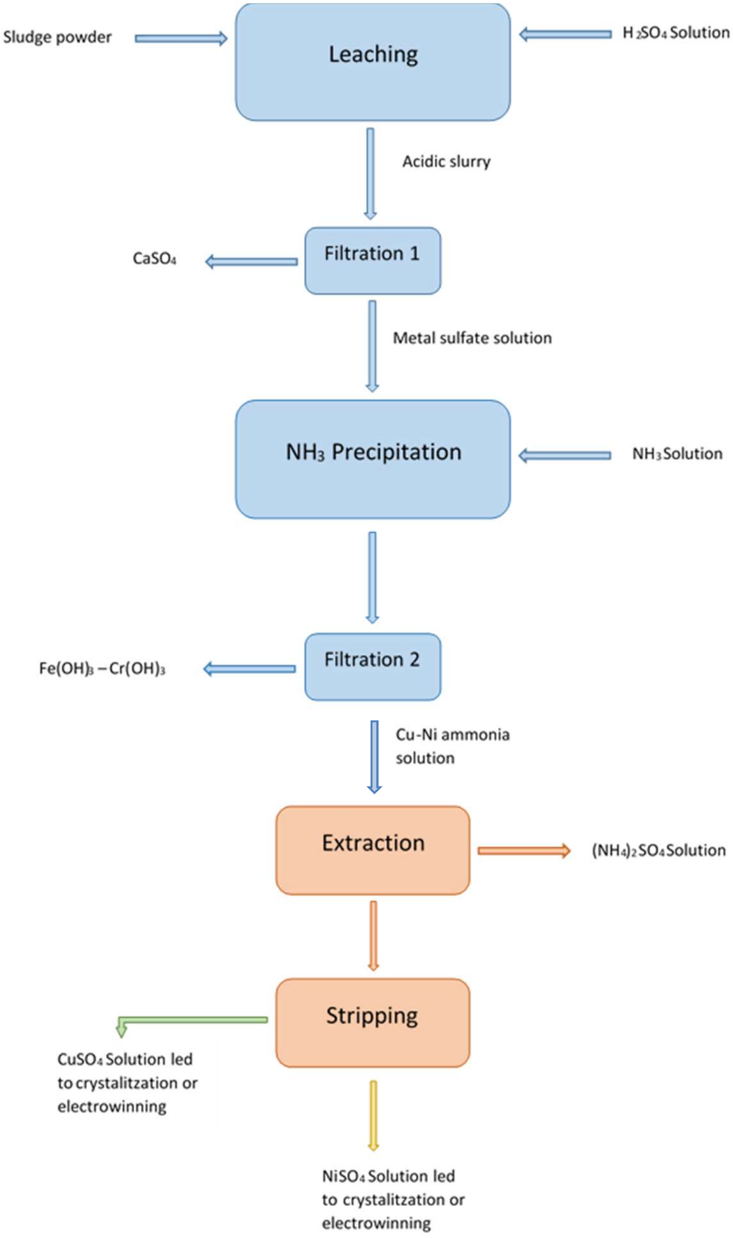


Figure 22. Nickel – Copper recover flowsheet process

5. CONCLUSIONS

Based on the analysed results of the present study it can be said:

- **Sludge 1**, which contains nickel, and a large amount of iron, shows serious leaching difficulties when the leaching is carried on ammonia medium.

Even though decreasing solid to liquid ratio seems to benefit the lixiviation allowing then to obtain better leaching rates, initial pH almost don't influence the leaching rate. Therefore, considering a S/L ratio of 5 and an initial pH of 8.5 as the better conditions for the process, leaching rate obtained was only **5%.**

In the other hand, it can be seen that by adding more leaching stages in series, the leaching rate increases. It may be cause of the metal concentration gradients in the solution. After 5 leaching steps, the rate obtained its **13%.**

Based on these results, iron present in the particle, seems to be the main reason for the low leaching results. Acting like an ash layer, iron or his double hydroxide form could be inhibiting the ammonium transfer to the internal nickel until the reaction stops.

- **Sludge 2**, which contains nickel, copper and chromium, also shows difficulties to leach both nickel and copper with ammonia sulfate as the lixiviant.

As with the sludge 1, S/L seems to be the parameter that most influences leaching rates while, initial pH, shows almost a negligible influence. Considering as the most beneficial conditions a S/L ratio of 5 and an initial pH of 9.5, the leaching rate obtained was **18,4%.**

After 4 sequential dissolutions, leaching rates also raised up to **36%** of Cu+Ni leached. With sludge 2, we assume that chromium its acting like iron in the first case. Chromium doesn't allow ammonium to reach all the nickel and copper present in the particle.

- Because of that, the presence of double hydroxides or possible M^{2+}-M^{3+} alloys and his influence in the leaching, needs a deeper study. Study the effect on the lixiviation of a reducing pre-treatment of the sludge could be an interesting project.

Ammoniacal leaching rates obtained are so low, hence, it is considered that this process is not viable as an efficient industrial process.

To improve leaching results, an acidic leaching has been studied. Sulphuric acid is proposed as reagent. After analyzing the results obtained, its seen that iron its harder to dissolve and it requires more acidic force. Still, leaching rates in acidic medium reach a 100% rate for both sludges when pH its maintained constant at 0.5. That’s why a process that unifies the treatment of both sludges its proposed:

Therefore, the leaching stage will be hold at pH = 0.5 with a stirring speed of 1625 rpm. This lets to a complete leaching time of 33 mins for sludge 2 and 51 for sludge 1.

The efficiency of the process proposed will remain on the ammonium sulphate generated after ammoniacal precipitation. It may be considered the option to recover the ammonia present on this solution to create an ammonia cycle.

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