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INDUSTRIAL MATERIALS RECYCLING DEPARTMENT

Evaluation of the separation technology in
a pilot plant.

Project work - TFG
Chemical Engineering

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Summary

Lithium-ion batteries are conformed by different materials, some of them in a critical situation, for example cobalt. As the consumption of REEs is increasing dramatically in the last decades, the recycling of ion-lithium batteries is constantly developed and the processes involved in the step of hydrometallurgy continuously investigated. Especially, the recycling of cobalt which is an important element in recycling of lithium-ion batteries by hydrometallurgy.

Two solvents used in the process, Cyanex 272 and versatic acid, were studied with an experimental design by trying different organic/aqueous (O/A) ratios in a separation funnel. After the experiments, McCabe-Thiele diagrams should be used to calculate the number of stages required in separation system. Unfortunately, none results obtained were adequate for the development of the diagram.

Then, experiments were carried out in a mixer settler setup at different Organic/Aqueous (O/A) ratios for both extractants. The extractant with a better behavior was used for the further analysis of the mixer settler system. Thus, the main purpose of this part of the project was to investigate the influence of the stirring ratio and O/A ratio in the extraction.

The Cyanex 272 used in this project does not work adequately. Thus, proper results were obtained and analyzed only for versatic acid. Maximum extraction was obtained for 1:1 O/A ratio at 1000rpm. An increment of the stirring ratio decreases the extraction due to the geometry of the mixing chamber as well as to the increase of O/A ratio.

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1 Introduction.

Over the 20th Century the use of different metals in new developed energy production and storage technologies has increased as the necessities have changed and evolved to a much more demanding society. Therefore, the exploitation of resources has suffered a large increment during this time and the consumption of metals has increased significantly. Among these metals, there are the so called rare earth elements (REEs) which are used for instance in magnets, electronic devices, catalysts and batteries and which primary resources and primary producers are a few. The natural resources of some REEs face a high risk of being depleted if the consumption continues. In addition to the rare earth metals (REMs), other important metals are cobalt, tungsten, indium which are in a critical resource situation and lithium, nickel or zinc which are in danger to become critical materials too.

The fabrication of batteries requires of a lot of critical materials. For instance, battery productions involves 40% of the total consumption of lithium and 60% of cobalt, which are predicted to suffer an increment.

Figure 1 , shows how the situation of some materials is today referring to the economic importance of the material itself and the risk they are facing to become critical materials, or if they are, how far the situation has gone. The materials within the upper right quarter of Figure 1 are critical materials with high economic importance and with high risk of depleting. Among critical materials, beryllium(Be), germanium(Ge) or cobalt(Co) are found. Materials close to the dashed red horizontal line are materials with a high risk to become critical materials although they are not yet. Close to the dashed lines, lithium (Li) and tin (Sn) are found and they are therefore in the risk zone.

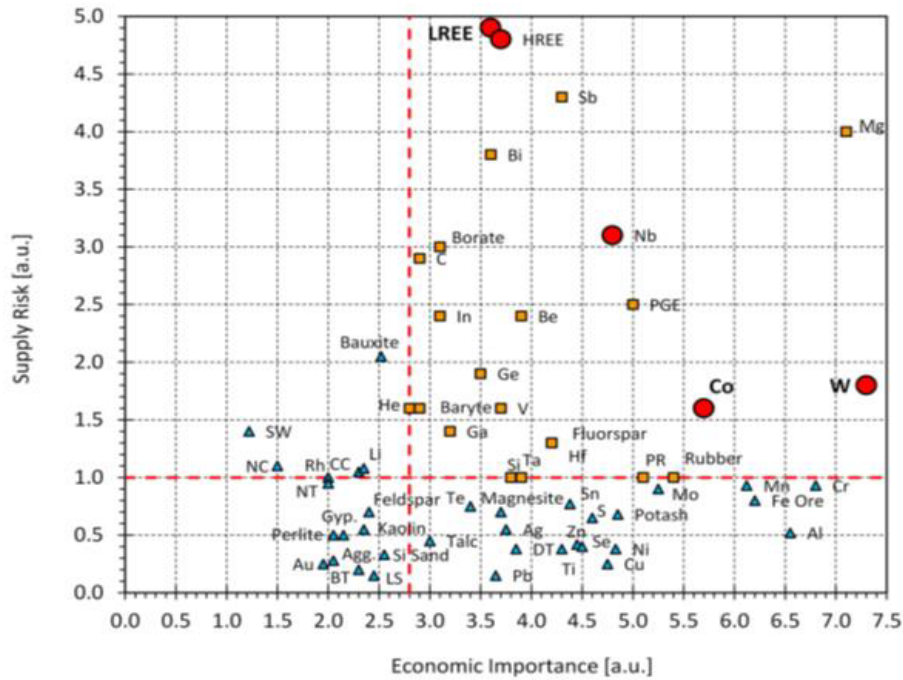


Figure 1: Critical materials and metals[1].

Concretely the production of Li-ion batteries is increasing as the production of portable electronic devices increases and due to the development and promotion of electric cars. As a result, and in order to decrease the mining of ore and the primary production of some of these metals, recycling of rare metals has become essential from the second half of 20th Century . Regarding recycling of batteries, and specially Li-ion batteries, there are two main processes: pyrometallurgy and hydrometallurgy.

Pyrometallurgy is basically smelting of the crushed materials burning the plastics first and then reducing the required metals. Electrolysis from the molten salts takes place to produce metals using current. However, in the slag produced by the pyrometallurgical process there are some metals like lithium that are not recovered or recycled by this method and hydrometallurgy must be applied if such metals need to be recovered.

Hydrometallurgy is increasingly used due to the higher capacity of recovery of metals and due to its lower energy consumption. It consists of a first leaching process

to dissolve the metals using an aqueous phase . Then different methods can be applied, separately or combined, for recovering and separation of the dissolved metals: precipitation, ion-exchange, electrowinning or solvent extraction. Some pretreatments like discharging, crushing and milling or mechanical separation are usually required prior to the process.

Solvent extraction, also referred to as liquid-liquid extraction, is generally applied to the leachate that contains the metal ions. It consists of putting in contact two phases: the leachate and the solvent phase containing an extractant suitable for the metals to be recovered, usually called aqueous phase and organic phase respectively, so the metal ions are transferred to the solvent solution. There are different compounds that can be use as extractant, for example versatic acid(neodecanoic acid), but the most common for recycling of metals (mainly cobalt) in spent Li-ion batteries are Cyanex 272 or D2EHPA.

As the use of Cyanex 272 is significant and it has a big importance in this industry, this project aimed to compare Cyanex 272 with another extractant, versatic acid, in several experiments as solvents for cobalt recovery from an aqueous solution and then the one with the best behavior would be applied in a mixer settler system. Cyanex 272 was diluted in kerosene and versatic acid in ISOPAR L in order to get concentrations 1M for both cases. The extracted cobalt would then stripped with sulfuric acid and the organic solvent be returned to the system repeatedly to investigate if there was some change in the extraction performance, i.e. the durability of selected solvent.

2 Theoretical study. Bibliographic study.

2.1 Introduction

A lot of studies have been made about metal recovery and solvent extraction as well as about recycling of different metals from lithium-ion batteries(LiBs). They allow us to understand better this process and it brings us to go further with it and to continue improving the process for industrial applications and metals recovery.

Therefore, different steps that take place during the recycling of LiBs are defined and solvent extraction is well known but is still in develop. This also happens with the different factors involved in this process like solvents (e.g. Cyanex 272 or versatic acid) or equipment (e.g mixer settlers).

2.2 Lithium ion Batteries (LiBs)

The use of LiBs has had a large increment in the last years and it is supposed to continue increasing in the next years basically due to the higher demand of portable devices and electric vehicles. This, obviously, involves the increase of the demand for the materials that are used for the production of the batteries components(anode,cathode,electrolyte,case, etc.). The chemical composition of a LiB is more or less Al (15-25%), Cu foil(5-15%), LiCoO_2 (25-45%), LiPF_6 (1-5%), graphite(10-30%) and steel, nickel, inert polymers and electrolyte.[2]

In the Figure 2 the demand of cobalt, lithium or graphite for the production of LiBs, which are rare or critical materials, and the expected consumption of these compounds are shown. It is appreciated how it is rising more and more.

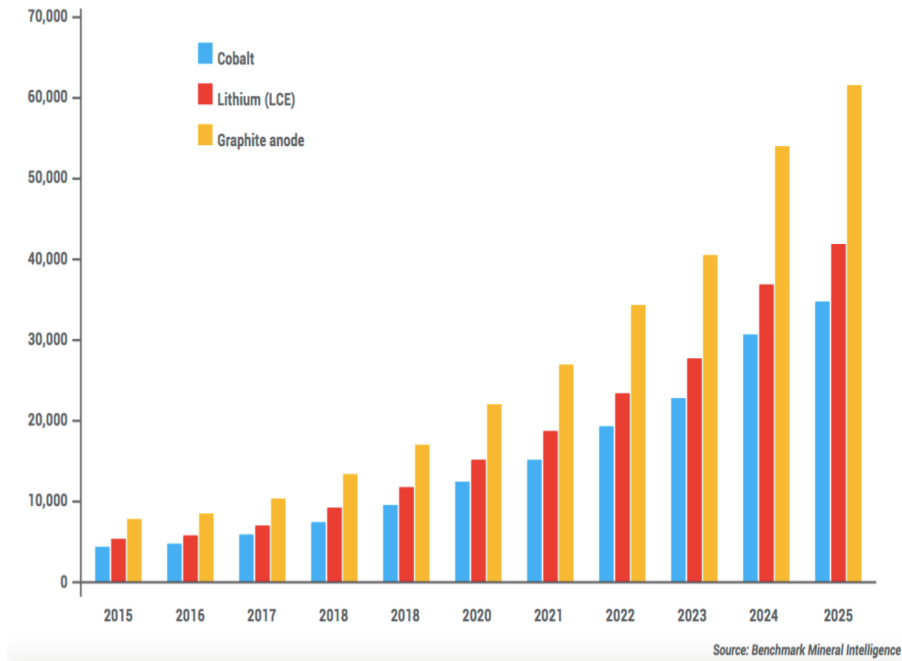


Figure 2: Demand of valuable materials in LIBs [2]

This consumption combined with the high quantity of valuable materials in the components of LiBs and the low number of producers, makes of the recycling of spent batteries a convenient and necessary way to reduce the mining in those countries richer in ore and a sustainable way to produce the batteries.

2.3 Recycling of LiBs

Generally, there are four types of recycling technologies for LIBs: mechanical treatment, hydrometallurgical treatment, combination of thermal pre-treatment and hydrometallurgical methods and pyrometallurgical treatment[3].

Despite the type of the method, some pre-treatment is always required to sort, mill or simplify the main process. The first step in the pre-treatment is the collection and sorting of batteries. There are different methods of collection but it depends mainly on the behavior of the consumer, and the main problem is that as the portable

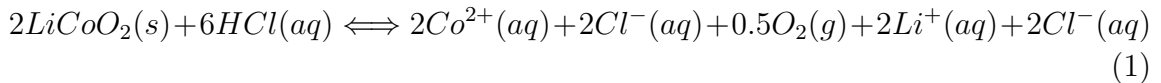
batteries are small and people tend to keep them in at home [4] and usually there is a lack of devoted collection. Once they have been collected, they must be sorted principally according to their chemistries to avoid cross contamination by using a moving belt and human manpower. Sometimes the process is performed using a combination of manual separation and automated procedures applying cameras for optical separation or X-rays for material detection[5]. Once they have been sorted and in order to prevent a spontaneous combustion or short circuiting, LIBs are discharged before dismantling [6].

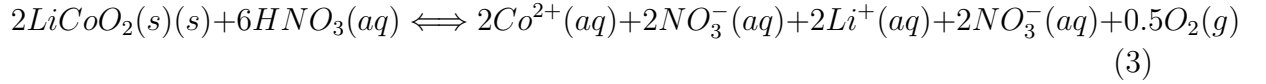
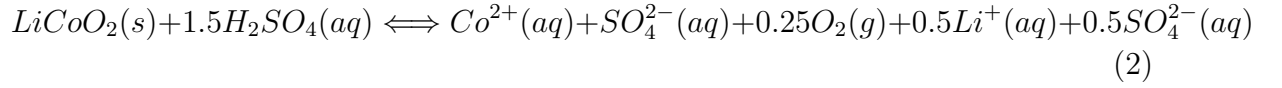
Car batteries need to be handled by dedicated dismantlers and manual dismantling to battery cells is necessary while portable batteries usually do not require this step[3].

Once LIBs have been dismantled, in order to convert the battery packs composed by cables, cooling units, printed circuit boards into a product flow that can be processed and transported, they are crushed in most cases, and this process can take place in both wet atmosphere and inert atmosphere[7].

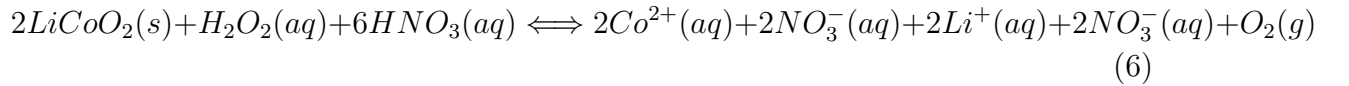
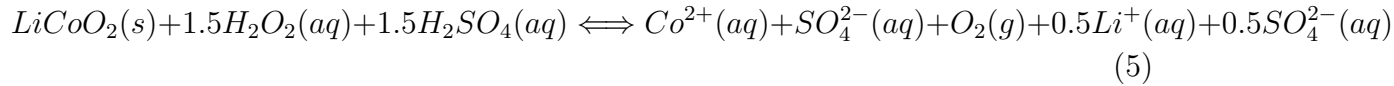
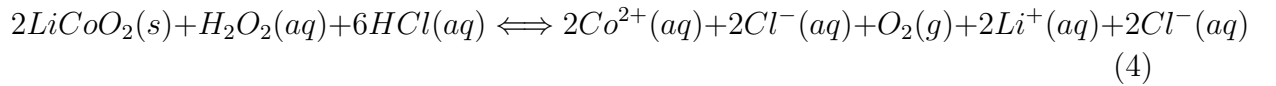
After crushing, sorting and sieving are usually applied to separate the different components. Ferromagnetic parts can be separated by magnets, and this can be complemented by air separation methods like cross-flow classification or zigzag sifting for light fractions[7].An inert atmosphere is used during the crushing process. The black mass mixed with aluminum and copper foil is transported to the hydrometallurgical or pyrometallurgical plant, where metals can be recycled[2].

Leaching is applied to dissolve the metallic fraction from the solid milled materials. Typical leaching agents used in the leaching process are inorganic acids such as H_2SO_4 , HCl , or HNO_3 Hydrochloric acid (HCl) is preferred for economic reasons, although it will involve special equipment to face chlorine (Cl_2) [8]. However, nitric acid (HNO_3) and sulfuric acid (H_2SO_4) are the most common for spent LIBs. $LiCoO_2$ can be considered the most common active material and its cobalt is going to be the subject of study of this project. For this material, the reactions that take place with some acids are given by the following equations[3]:





Sometimes it is difficult to leach the $LiCoO_2$, so H_2O_2 is used to reduce the cobalt raising the extraction rate, over 99%, but with efficiency of 75% for Co and 40% for Li as Lee and Rhee proved [9]. And for these cases, the reactions that would take place are the following:



By this way, cobalt and lithium chlorides, sulphates or nitrates are obtained in the solution. Usually, also aluminum, copper, manganese and nickel appear in the leachate and some of them, for example, aluminum and copper must be removed in order to avoid problems in the next step: the solvent extraction.

2.3.1 Solvent extraction (SX)

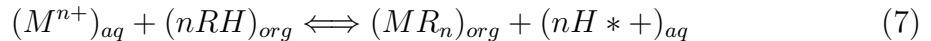
Solvent extraction, also referred to as liquid-liquid extraction, is defined by Vladimir S.Kislik[10] as "one of the favored separation techniques because of its simplicity,

speed, and wide scope. By utilizing relatively simple equipment and requiring a limited time to perform, extraction procedures offer much to the chemists and engineers. Frequently it appears to be the ideal method of separating trace constituents from large amounts of other substances.” It is an important step in the recycling of Li-ion batteries and in the recovery of valuable metals. In this process two liquids, the extractant (or solvent) and the leachate which contains the dissolved metals, are put in contact in order to recover metal ions usually in a separation column or by mixer settlers. Some organic extractants, like bis(2,2,2-trimethylpentyl)phosphinic acid (Cyanex 272), di-(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC 88A), neodecanoic acid (versatic acid) have been used to separate and recover metal ions[3]. Rarely, extractants are used in their pure form in industry. They are usually diluted by other organic components like kerosene in order to improve physical properties such as the viscosity of the organic phase, even though this may influence the extracting power of entire organic phase.

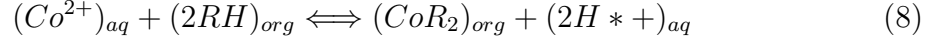
When it comes to cobalt separation or recovery, Cyanex 272 is the most commercially used due to its selectivity. The acidic form of this extractant exist as dimers, while the neutral forms exist as monomers. Both forms take part in the extraction[3]. Comparing this extractant with others in the market, some reason for Cyanex 272 to be the preferred choice for extraction of cobalt is that it is more stable than its analogues Cyanex 302 and Cyanex 301, and that it offers much higher separation factor than both D2EHPA or PC-88A or that it is the weakest acid of all the organophosphorus acids which means that it is easier to strip[11].

As Versatic 10 is also a common extractant for the recovery of metals, for example, Co and Ni [12], it was also studied and compared with Cyanex272.

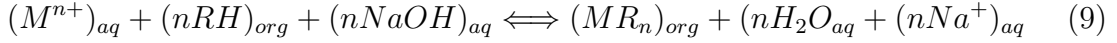
The reaction that takes between the metal extracted and the solvent and that applies for Cyanex 272 is the reaction 7 [13].



where M^{n+} is an n-valent metal cation, RH is a hydrocarbon (solvent) and aq makes reference to aqueous phase and org to organic phase. Specifically, for the extraction of Cobalt by using C272, the reaction 8 takes place.



By studying the reaction 8, it can be appreciated how the pH will drop as the hydrogen atoms are released and the cobalt is captured by the extractant. And as the pH affects the extraction, the process will be affected. Therefore, some OH^- are added to the system during its operation to prevent the excess H^+ formation and to achieve the pH required. the reaction that will take place in this case is the reaction 9 [14].



After the extraction step, usually stripping is applied to recover the metal and clean the organic. A scheme of the system is shown in the Figure 3. H_2SO_4 or HCl are the acids commonly used in this step of the process. It is basically the inverse process of extraction and the general principles for extraction apply to stripping. Stripping can equally be done in single stage, cross-flow or counter-current[15].

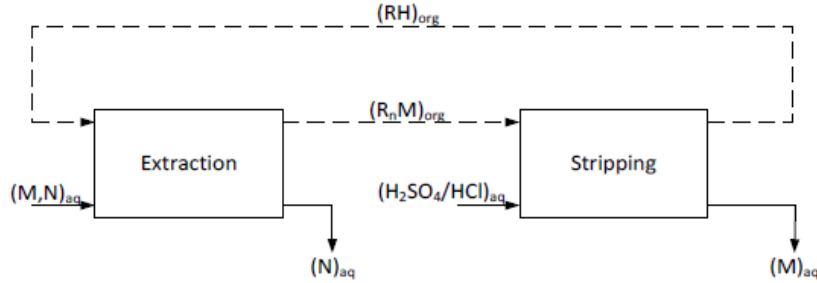


Figure 3: Scheme of the solvent extraction process with stripping[11].

The stripped extractant often still contains traces of the desired component, so it will normally be recycled to the extraction stages, but it will reduce the efficiency in the first stage. When it comes to industrial practice, this process is commonly used

as it is more economic to lose a little of the desired component than to have to dilute a strip raffinate by seeking a total strip[15].

Thus, Cyanex 272 and versatic acid, as every solvent, have a limited lifetime and can be reused a limited number of times, which is directly related with the economics of the process. As it has been commented before, one of the advantages that solvent extraction offers is the lower costs due to the possible recovery of the solvents. So, if the losses are too large or the extractant does not have a determined lifetime, it will not be profitable. Moreover, by stripping and recovery of the extractant, the chemical reaction can destroy the functional groups and therefore, it degrades in the process[16]. This is due to an undesired component that sometimes stays in the organic and accumulates there until it interferes seriously with the extraction. In this case, a stronger stripping is applied to the solvent to regenerate it and remove the contaminant[15].

Solubility in the acids of stripping or where the feed is dissolved can also cause some degradation and must be considered when study durability of a solvent.

Furthermore, another significant problem found in solvent extraction is the formation of a third phase due to solubility facts in the organic phase[11]. Usually, what occurs is that a third phase appears between the aqueous and the organic phase during the phase separation stage (settling). For example, temperature is a factor that affects a third phase formation; increasing the temperature usually helps the process to avoid the formation of this third phase as the O/A solubility decreases. Moreover, overloading of the extractant can also involve third phase formation and suspended solids can result in phase separation problems too. The type of diluent will affect directly the possible formation of a third phase; for example, aliphatic diluents commonly carry to separation problems[17].

On the other hand, the addition of a phase modifier can help to avoid the formation of a third phase. Some typical phase modifiers are isodecanol, 2-ethylhexanol, p-nonyl phenol or tributylphosphate (TBT)[18].

Liquid-liquid separation is usually coupled with the precipitation in order to get a better extraction or because some metals can affect negatively the process for others.

2.3.2 Mixer Settlers

When it comes to liquid-liquid extraction, both separation columns and mixer settlers can be used. For the recycling or recovering of valuable metals from LiBs, usually mixer settlers are preferred because of reliability, high processing capacities and flexibility.

Mixer settlers consist of a mixing vessel for phase dispersion that is followed by a settling vessel for phase separation under gravity [19] as the Figure 4 shows. This phase dispersion can be achieved by mechanical stirring, air agitation or pump circulation. High intensity of agitation in the dispersion vessel, normally, leads to high rates of mass transfer and close approach to equilibrium (i.e. maximum extraction), but this will involve a proper and careful design of the settling vessel in order to have enough time for the phases to separate before leaving the chamber. The first stage raffinate is pumped to the second stage, where it will be mixed again and this system will be repeat for each stage. Then, the fully loaded extract overflows an upper weir and passes to the stripping[15].

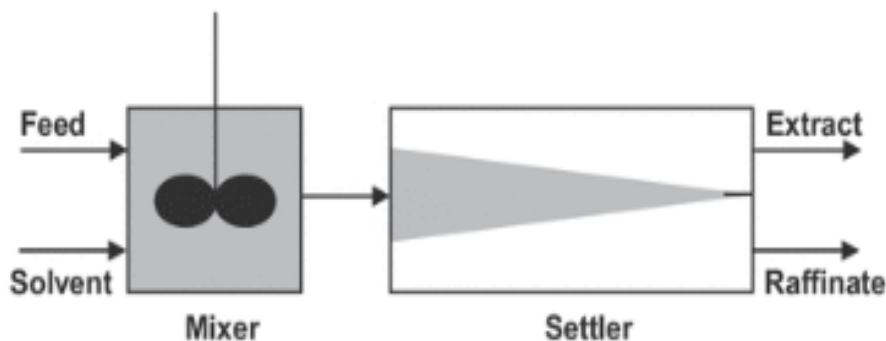


Figure 4: Scheme of a mixer settler work[19].

The principal disadvantage of the mixer settlers is the requirement of a large inventory of material introduced in the vessels and high capital cost per stage. As an approximation, in industrial units, the settlers usually represent at least the 75% of the total volume[19].

Another problem or difficulty is the scale-up to industrial systems. Usually

experiments take place and are proven in pilot plants which are commonly much smaller than large-scale industrial equipment. Here it is when the engineer has to make a careful analysis of the data obtained in laboratory and pilot experiments and supply some preliminary calculations by the large-scale experiments as the following[15]: determination of the solubility in a triangular diagram and their dependencies on pH, temperature or salt content of the raffinate, measuring the separation time to evaluate the coalescence behavior, determination of the ratio of solvent to raffinate flow rate and measurement of the physical properties of the feed and product phases.

B. Grinbaum and S.A. Angel [20] proposed a steady-state simulator for industrial-scale processes that performed well during development, design and optimization. However there were some problems due to the degradation of the solvent, assumption of ideal stages and total mass transfer and back mixing caused by entrainment.

3 Procedures and experiments.

In this project the extraction of Co by using two different organic extractants is studied at two different scales: experimental scale and pilot plant scale.

3.1 Experimental scale.

First, the extraction is performed using a separation funnel where different organic/aqueous (O/A) ratios are applied. The ratios studied are 0,05:1, 0,5:1, 1:1, 2:1, 3:1, 5:1 and 10:1. So, for each ratio three experiments will be carried out to obtain higher accuracy. The experiments consist basically in introducing volumes of organic and aqueous phases according to the studied ratio in a separation funnel and shake it in order to mix the phases. After a specific time of shaking, NaOH is added to increase the pH of the solution and favor the extraction. NaOH is added in this way until the pH required is achieved, i.e. the extraction has taken place.

For each experiment, one sample is taken and the concentration of Co is measured by ICP-OES technology. The results allow to construct a McCabe-Thiele diagram that will allow to calculate the number of extraction stages required for the mixer settlers system (at pilot plant scale).

3.1.1 Analysis of results.

Cobalt content in the organic phase was determined via mass balance calculation after measuring cobalt content in the aqueous samples. The mass balance developed is shown in the Equation 10

$$x_f \cdot V_{aq} + y_o \cdot V_{org} = x_R \cdot V_{aq} + y_E \cdot V_{org} \quad (10)$$

where x_f is the concentration of Co in the feed, y_o is the initial concentration in the organic, x_R is the concentration in the raffinate and y_E is the final concentration in the organic. V_{aq} is the volume of aqueous phase used and V_{org} is the volume organic.

As the initial concentration of Co in the solvent is null, $y_o=0$ and the Equation 10 can be reformulated as the Equation 11 in order to obtain the value of the concentration of Co in the organic phase after the extraction.

$$y_E = (x_f - x_R) \cdot \frac{V_{aq}}{V_{org}} \quad (11)$$

3.1.2 McCabe-Thiele diagram.

The McCabe-Thiele diagram is a graphical construction of an extraction isotherm, an operating line for the process and the stepwise evaluation of the number of stages. A vertical line will represent the concentration of the metal in the feed solution on the x-axis while the slope of the operating line represents the phase ratio (A/O) as it is shown in the example of the Figure 5.

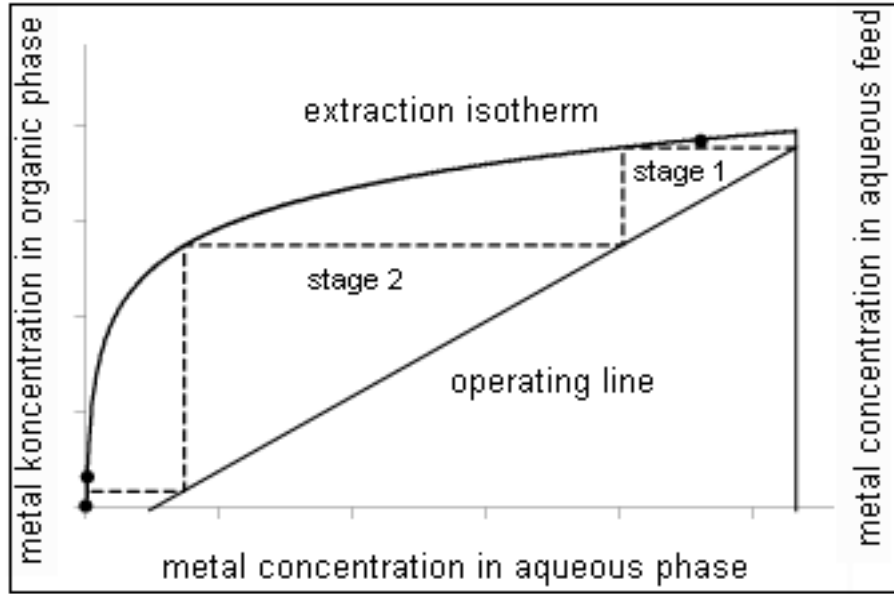


Figure 5: Standard McCabe Thiele Diagram for an extraction process.

After studying the number of stages, if the results are correct, the process can be applied the mixer settlers system.

3.2 Pilot plant scale: Mixer settlers

In this case, the system of mixer settlers is built with 2 extraction stages and 2 stripping stages as shown in the scheme of the Figures 6 and 7 respectively.

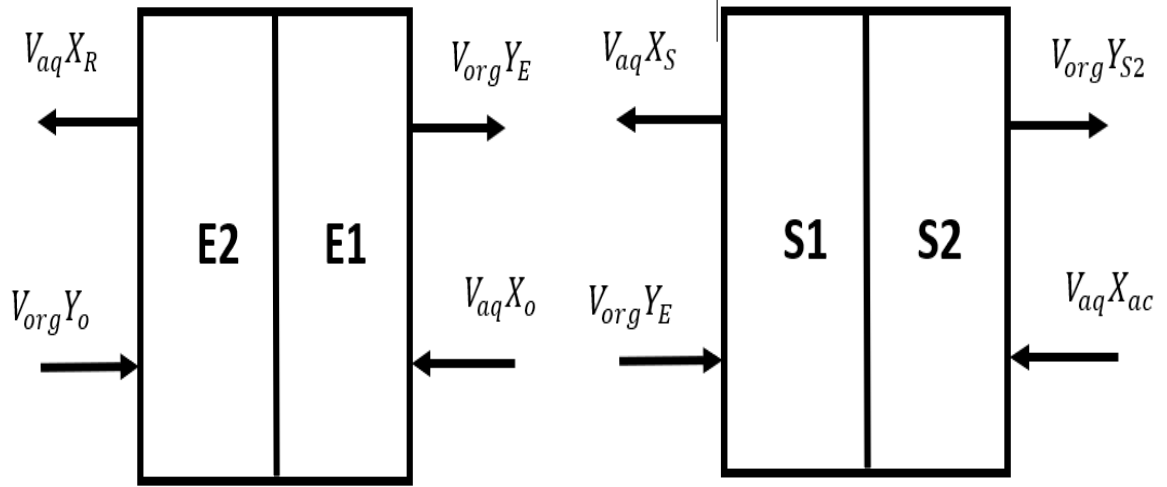


Figure 6: Scheme of the extraction stages in the MX system.

Figure 7: Scheme of the stripping stages in the MX system

NaOH is added to the extraction stages in order to increase the pH of the solution and achieve the pH required. The concentration of the NaOH solution and flow will change depending on the O/A ratio.

In this case O/A ratio of 0.5:1, 1:1 (at two different agitation speed), 2:1 and 5:1 are studied. The ratio is applied for both extraction and stripping phases. The equilibrium between organic and aqueous phase should be achieved after some time.

Samples from stages E2 and S1 have been analyzed by ICP-OES technology, where the concentration of Co has been measured. This concentration, feed concentrations and volume flows introduced in the system, allows to calculate the concentration of Co in the organic phase and, therefore, the fraction extracted. Equations 10 and

11 work for the extraction step, while equations 12 and 13 work for the stripping steps.

$$x_F \cdot V_A + y_E \cdot V_{org} = x_{S1} \cdot V_A + y_{S2} \cdot V_{org} \quad (12)$$

$$y_{S2} = y_E - x_{S1} \cdot \frac{V_A}{V_{org}} \quad (13)$$

Notation is followed as explained above in the text and as the Figures 6 and 7 show. y_{S2} is the concentration of Co in the organic at the outlet and x_{S1} is the concentration of Co stripped, i.e. in the acid after stripping.

D value is another useful tool to see how good the extraction is. It is the distribution ratio and it is calculated as the Co in the organic phase over the Co in the aqueous phase at the outlet. Equations 14 and 15 show these calculations for the extraction and stripping steps respectively.

$$D = \frac{y_E}{x_R} \quad (14)$$

$$D = \frac{y_{S2}}{x_{S1}} \quad (15)$$

4 Results and discussion.

4.1 Extractant 1: Cyanex 272

The first extractant to be studied was Cyanex 272 (C272). It has been diluted in kerosene to a 1M solution. Solutions with different concentrations of NaOH and CoSO_4/L has been used. CoSO_4 solution was prepared based on a cobalt sulphate heptahydrate salt.

Some problem with a third phase or with a milky organic or aqueous phase were found, so several attempts of avoiding it has been tried.

First, the concentration of the NaOH used to increase the pH of the aqueous phase along the process was decreased to avoid drastic increments of the pH and possible precipitation. Also, the concentration of the aqueous phase (initially 5g CoSO_4/L) was decreased. The problem persisted, so some organic phase modifiers were tried: decyl alcohol(A), tributyl phosphate (B) and tridodecylamin(C). It was found out that C did not help but affected negatively the process, so it was discarded immediately. A and B did not have a significant effect, so they were not applied either finally.

A 2M solution of C272 with NaOH was prepared and tried to reduce its posterior addition. As no advantage was observed, the use of this solvent solution was discarded.

The last attempt was to clean the extractant C272 1M with H_2SO_4 0,1M in a batch reactor before it was used for both separation funnel and mixer settlers. This organic solution was used in further experiments.

The final concentration of CoSO_4 solution was 0.5g/L and it is the one used for the McCabe-Thiele diagram development. The pH of this solution was over 4, so it was decreased adding H_2SO_4 3M to the solution. Finally, in order to avoid this addition, the solution was directly prepared with a 0.5M H_2SO_4 solution. Thus, the pH was very low initially and it could be increased slowly.

Sodium hydroxide (NaOH) was used to increase the pH until a value close to 5 was obtained. Solutions of 250g/L, 200g/L 100g/L or 25g/L have been used along this

study. For the extraction in the separation funnel, only 100g/L solution was used after 250g/L solution was observed to be too strong.

Summing up, finally a solution of 0.5 g/L of cobalt sulphate in 0.5M H_2SO_4 was used as feed and C272 1M in kerosene cleaned with H_2SO_4 0.1M was used as solvent. NaOH 100g/L was used in the separation funnel while for the mixer settlers several were used.

Even though this study was done to avoid the bad behavior of the system, the transparency of the solvents was not right as it shown in the Figure 8. They should be clear and transparent, and they were milky, what was an indication of the improper state of one of the compounds used there, which finally would be both C272 and kerosene.

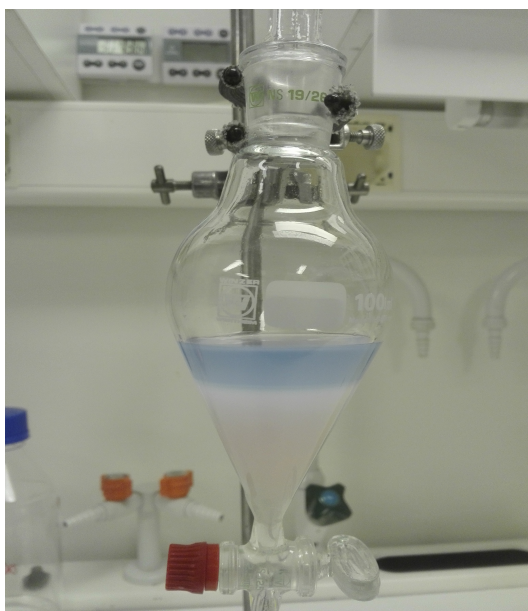


Figure 8: Separation funnel with C272 and feed after shaking. Milky organic and aqueous phases.

4.1.1 Lab scale experiments

The results of the analysis for these experiments are collected in the Table 1. There, m_{aq} makes reference to the concentration of Co in the aqueous phase after the

extraction and m_{org} to the concentration of Co in the organic phase. V_{aq} and V_{org} are the volumes introduced in the separation funnel.

The value for the feed in the ICP-OES analysis is 135.4 mg/L.

In the second part of the table there are the values for the process when phase modifiers have been added to the organic extractant. The ones with letter c refers to organic phase cleaned with sulfuric acid before the extraction in addition to the addition of a phase modifier. Here, we see how the extracted Co is lower for these combinations that for the C272 without modifiers.

Table 1: ICP-OES results for C272.

Ratio	m_{aq} (mg/L)	m_{org} (mg/L)	V_{org} (mL)	V_{aq} (mL)	D
0.05:1	32.2	2064.7	1.75	35	64.2
0.5:1	9.3	252.2	10	20	27.2
1:1	8.1	127.2	20	20	15.6
2:1	7.5	63.9	30	15	8.5
3:1	7.44	42.6	45	15	5.7
5:1	6.7	25.7	50	10	3.8
10:1	6.3	12.9	50	5	2.1
1:1 with A	13.3	122.1	20	20	9.2
1:1 with A c	12.4	122.9	20	20	9.9
1:1 with B	8.5	126.9	20	20	14.9
1:1 with B c	11.9	123.4	20	20	10.3

Unfortunately, the results were not correct enough to develop a proper McCabe-Thiele diagram as shown in the Figure 9, so it will be studied when using versatic acid in the second phase of this project. It was found that the organic constituents C272 and kerosene were contaminated before the experimental part and thus difficulties occurred which were not results of wrong experimental design.

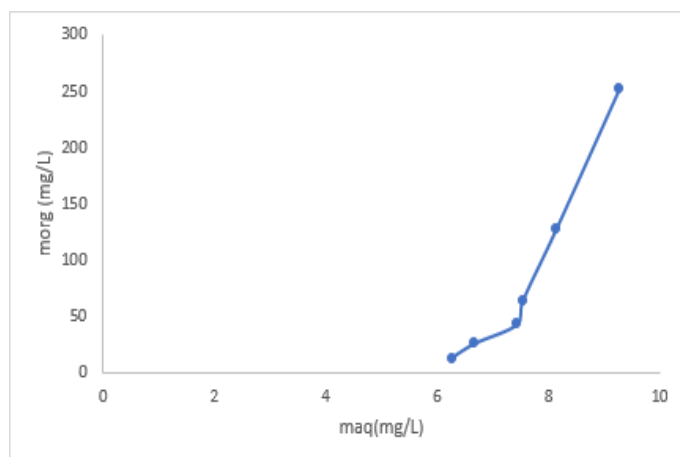


Figure 9: Co extracted vs Co remaining in the aqueous phase.

4.1.2 Mixer settler experiments.

The system of mixer settlers is built by the assumption of a proper behavior with 2 stages of extraction and other 2 stages for stripping as it is shown in the Figure 10, that shows the real system used in the lab.

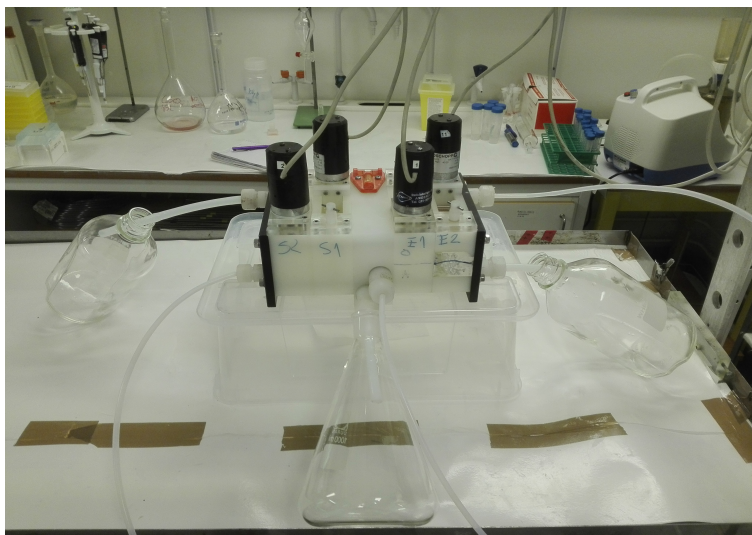


Figure 10: Mixer settlers system with 2 extraction and 2 stripping stages.

The two stages on the right are the extraction stages. Here organic and feed are introduced and Co is extracted. Then the aqueous phase leaves the system while the organic phase enters the two stages on the left, where stripping takes place. There, H_2SO_4 0.1M is introduced to clean the organic, which can be reused if the system works correctly.

Every pump was adjusted before being connected to the system to 5mL/min. These pumps are the ones in the Figure 11.

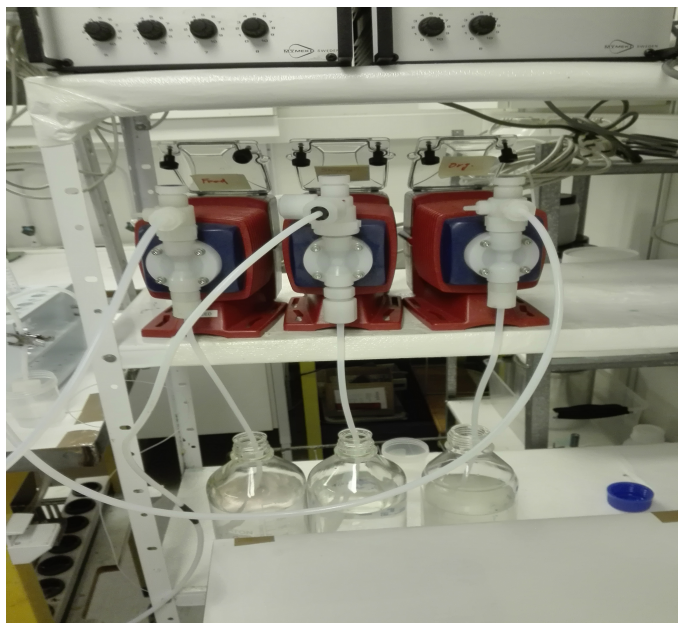


Figure 11: Pumps for feed, solvent and stripping acid.

Agitator motors are introduced in the mixing chamber of each stage at 1000rpm and the O/A ratio is controlled also in each stage by manual plastic screws.

NaOH is pumped by a peristaltic pump with two different tubes, so each stage can be supplied by different NaOH solutions. The second stage will require much less concentrated NaOH than the first one.

Once everything is connected and the ratios adjusted to 1:1, NaOH can be pumped and the change of color of the organic in the extraction phase is appreciated as in the Figure 12.



Figure 12: Mixer settlers system with 2 extraction and 2 stripping stages with NaOH added.

Here it is also observed that the stripping stages did not work correctly as in the second stage of the stripping (left part) is still blue and the organic leaving the system is completely blue and milky as in the Figure 13. Even when increasing the flow of the acid in the stripping part or decreasing the flow of solvent in the system, this color continues at the outlet of the system, so it is not working correctly. Also, some precipitation occurred in the second stage of the extraction part when added NaOH and increase too much the pH.

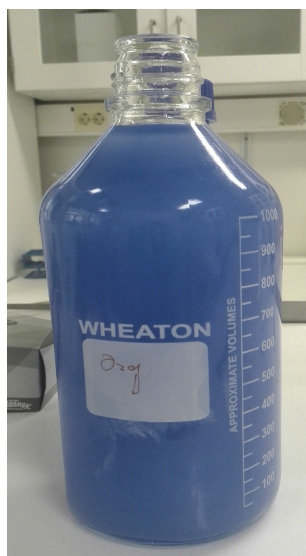


Figure 13: Organic after stripping in phase 1.

Then it was confirmed that something was wrong with this Cyanex 272 and this kerosene used in the process and no more study has been done about the mixer settler system with C272.

4.2 Extractant 2: Versatic Acid.

Once Cyanex 272 and kerosene were concluded to be contaminated, versatic acid(neodecanoic acid 10) diluted in ISOPAR L was chosen as an alternative for the process.

Versatic acid 1M has been prepared and used for the study of the extraction of cobalt in mixer settlers too.

In this case, a feed consisting of a solution of 1g of Co per liter was used, which means a solution of 4.77g $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ per liter of solution. It was dissolved in water this time and some H_2SO_4 was added to adjust the pH 4 (3.86).

NaOH of 200g/L, 100g/L and 25g/L are used during the process to increase the pH and achieve a proper extraction.

The process is the same as with C272: first it has been studied in a separation funnel for different ratios O/A and then it will be moved to mixer settlers. O/A ratios studied in this case were also: 0.05:1, 0.5:1, 1:1, 2:1, 3:1, 5:1, 10:1.

4.2.1 Lab scale experiments.

In this case, the colors observed at pH very close to 6 when the extraction has taken place are very clear and transparent, so the solvent is working correctly. The O/A ratios studied are the same as before with C272 and the calculations for the concentration of cobalt in the organic phase are the same too, with the Equation 11.

It has been observed a little milky aqueous phase at pH around 5 that disappears when increasing the pH to 6 and with longer mixing, so the separation takes place correctly. Approximately, with pH values over 6.5, there is precipitation of a Co compound. The Figures 14 and 15 show the colors of the phases in the separation funnel before and after the extraction.

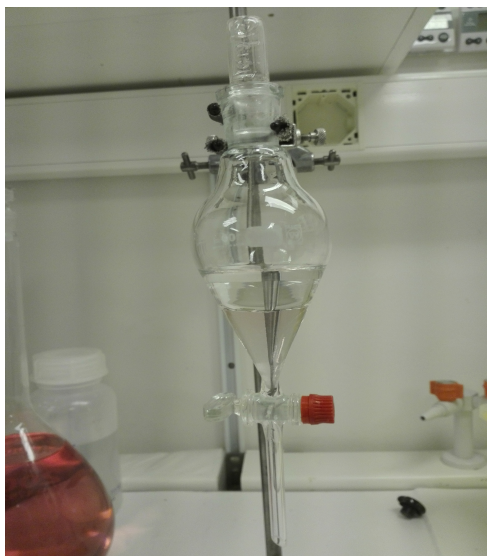


Figure 14: Phases in separation funnel before extraction.

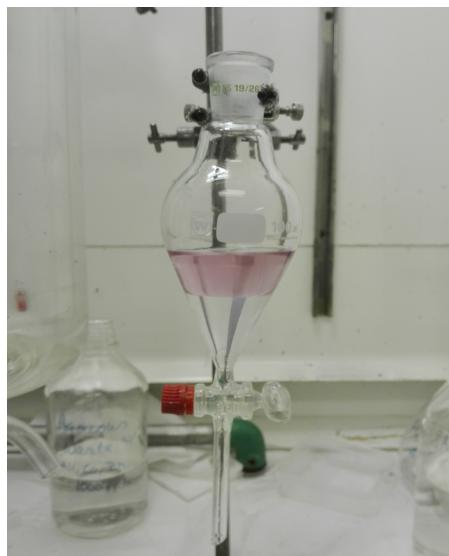


Figure 15: Phases in separation funnel after extraction.

The results of the ICP-OES analysis are collected in the Table 2. The concentration of Co in the feed is 1030.7 mg/L.

Table 2: ICP-OES results for Versatic Acid.

Ratio	maq(mg/L)	morg(mg/L)	Vorg(mL)	Vaq(mL)	D
0,05:1	232.9	16046.3	1.75	35.2	68.9
0.5:1	155.3	1768.2	10	20.2	11.4
1:01	225.6	815.8	15	15.2	3.6
2:01	232.4	404.5	30	15.2	1.7
3:01	158.9	294.9	30	10.15	1.9
5:01	136.2	181.6	50	10.15	1.6
10:01	95.3	94.8	50	5.07	1.0

In the Figure 16, the results of the analysis are collected with their respective standard deviation. Here, the concentration of Co in the organic phase is plotted against the concentration of Co in the aqueous phase. By increasing the O/A ratio, the concentration of Co in the aqueous phase decreases. Then some values are omitted to develop a possible McCabe-Thiele diagram as shown in the Figure 17.

Unluckily, a proper McCabe-Thiele diagram cannot be developed, so as in the previous study, 2 stages for the extraction set and 2 stages for the stripping set are used for the mixer settlers experiments.

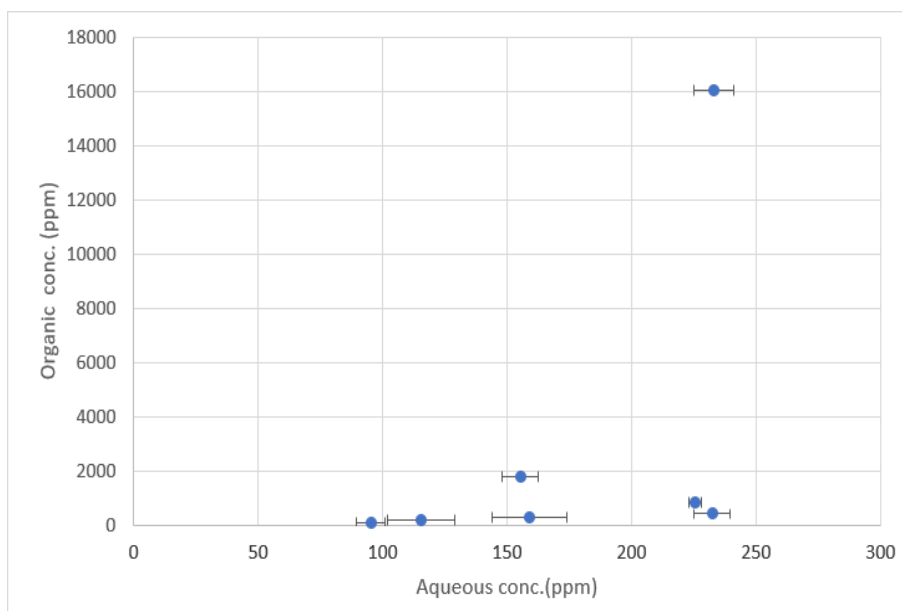


Figure 16: Results of concentration of Co in organic phase(versatic acid) vs. aqueous phase.

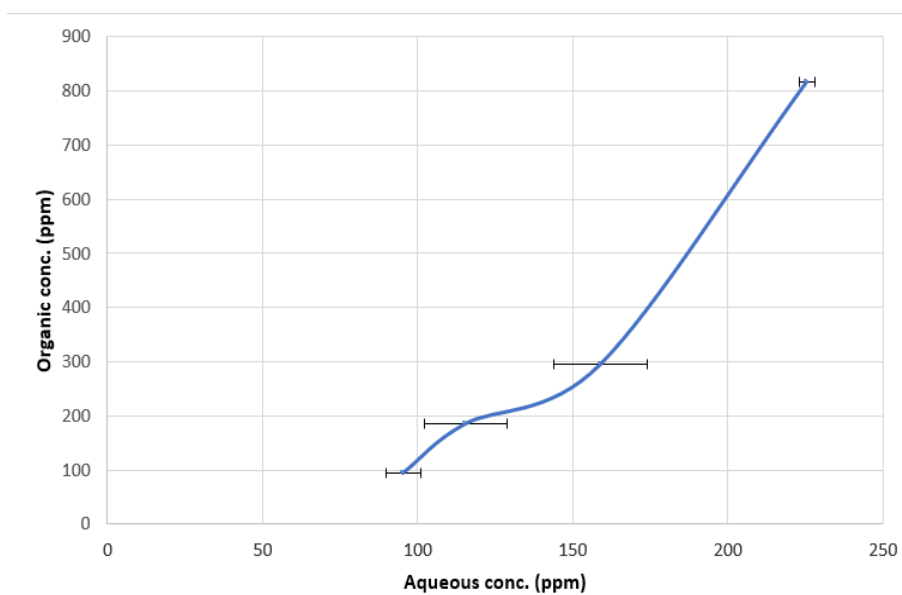


Figure 17: Concentration of Co in organic phase(versatic acid) vs. aqueous phase. Selected values for O/A ratios 10:1, 5:1, 3:1 and 1:1.

4.2.2 Mixer settlers experiments.

In this case, first, the system has been run at O/A ratio 1:1 and 1000rpm. NaOH is added also to the system but with different concentrations as before as the feed is not diluted in H₂SO₄ this time. NaOH 25g/L is the only one used in the system and it is always pumped to the stage E1 of extraction but not always to the E2 as it could overpass the pH required and cause precipitation.

In the Figure 18, it is shown how the organic phase in the Extraction stages (2 on the right part) is pink as it has extracted some cobalt and how the second stage is a bit less pink than the first as the pH is lower and the extraction has not been so strong as in the first one. In the stripping part (2 stages on the left part) we can see that in the first stage there is a bit of pink in the organic phase but the second one is completely transparent as the cobalt has been stripped.

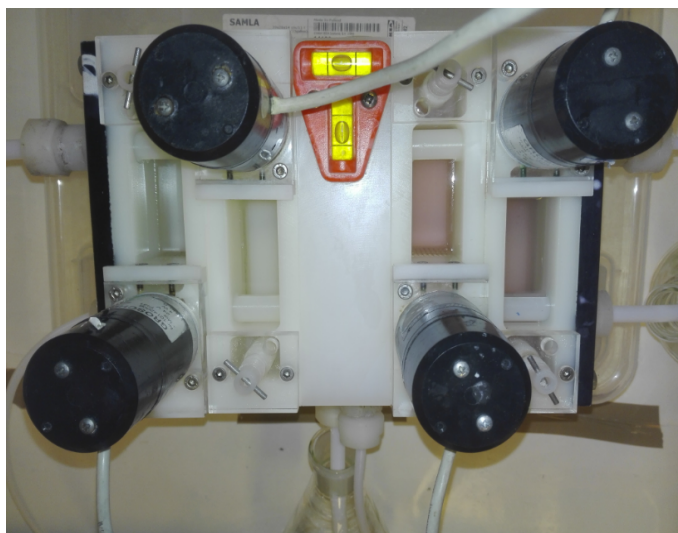


Figure 18: Mixer settler system for VA from above.

Then, the agitators were set at 2000rpm and O/A ratios of 1:1, 2:1, 5:1 and 0.5:1 have been considered.

The equilibrium between organic and aqueous phase should be achieved after some time. So, samples are taken each 30/45 min to measure the pH and check the system's stability. After several samples, a proper equilibrium is only obtained for ratio 5:1.

For the rest of the experiments, values close to the equilibrium are considered for the study.

The values obtained for the extraction process and for the stripping process at different O/A ratios are shown in the Figures 19 and 20.

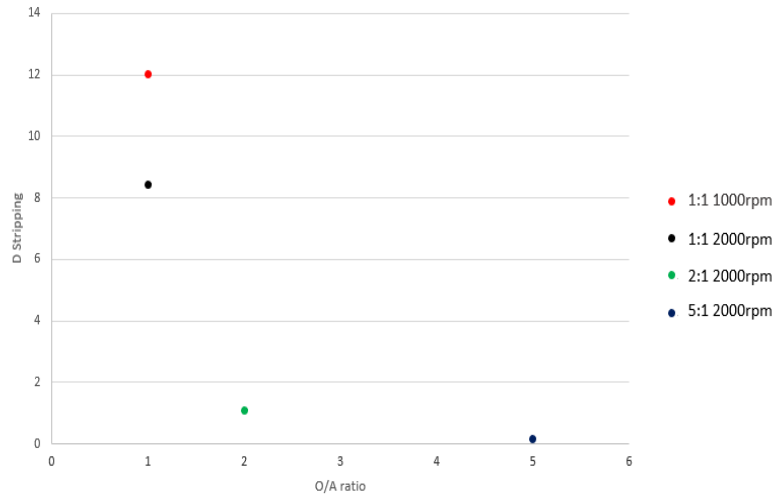


Figure 19: D values for the extraction step at different ratios.

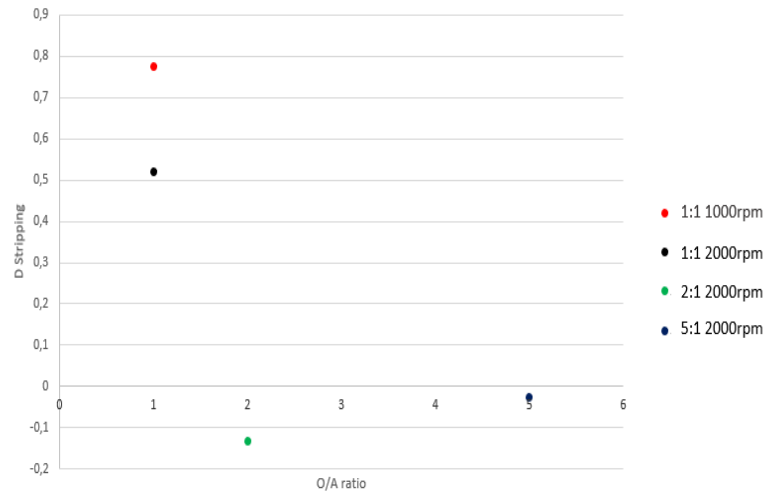


Figure 20: D values for the stripping step at different ratios.

First, we can see how the D values for the extraction are quite larger than for the stripping. Thus, there is a concordance as for the stripping, the fraction required in the organic is the lowest possible.

D value is shown for two different impeller speed, at 1000rpm and 2000rpm at O/A ratio 1:1. Here, it is appreciated how D is higher for 1000rpm than for 2000rpm. This can be due to that at high agitation speed, drop sizes are very small and population is large, so mass transfer changes and also the extraction efficiency does[21]. This fact depends on the height and diameter of the mixing chamber as well as of the ratios or flow rates.

It is also interesting to see how the percentage of Co extracted behaves when the O/A ratio decreases as Figure 21 shows. Again, the effect of an impeller speed of 1000rpm and of 2000rpm for O/A ratio 1:1 are studied.

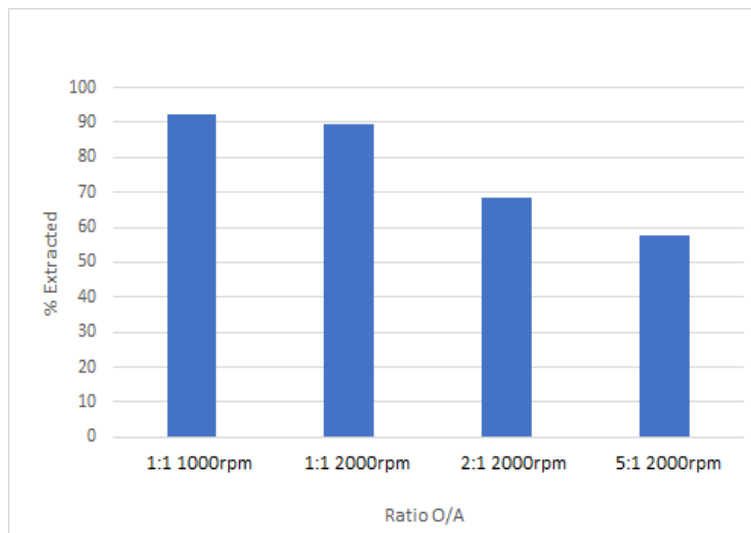


Figure 21: Percentage of Co extracted by versatic acid in the mixer settlers system.

The decrease of both D value and extraction percentage can be affected also by the durability of the solvent. Each time that 800mL of organic leaves the system, this volume is returned to the organic feed. This means that if the stripping has not been completed, this organic can contain Co that affects the rest of the extraction. This fact is confirmed by the results of the analysis for the stripping step. There, values of around 70% are obtained for ratio 1:1, being a bit lower for 2000rpm than for 1000rpm

again. When increasing the O/A ratio, the stripping percentage also increases to almost 100% for ratio 5:1. Here, maybe an error about the stability of the O/A ratio could affect the results a bit. Moreover, each time that the organic is stripped and, therefore, put in contact with sulfuric acid, the extractant get deteriorated and it can also affect the problem after several recirculations.

5 Conclusion.

Bibliographically, Cyanex 272 seems to perform an effective extraction of metals for their recycle. It is widely used in hydrometallurgy and it offers high rates of recovery. However, in this project the quality of the C272 and kerosene used is not proper and it brings us to erroneous results. Thus, a proper comparison between C272 and versatic acid has not been developed.

On the other hand, versatic acid has behaved correctly and further investigation has been possible. It can be concluded that high rates of recovery can be achieved for low O/A ratios in this mixer settler system. Agitating usually favors the extraction, but each geometry has a minimum point where the mixing is worse at high speeds. So geometry is a parameter that will influence significantly the rest of the parameters involved in the process. Also, recirculating the solvent means a decrease of material costs and in terms of "green industry" can be proper, but overtime it reduces its extraction potential and deteriorates.

Mixer settlers offer high processing capacities for extraction and recovery of rare metals like cobalt from spent Li-ion batteries and flexibility of operation. This method allows the engineer to design a proper design of extraction or adapt the configuration to specifications by varying O/A ratios, concentrations or stirring speed in the mixing chambers.

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Appendix I: Lab book

07-02-2019

Take 1L of Cyanex 272(C272).

Take NaOH and CoSO₄ from Inorganic storage room.

Prepare 1L solution C272 1M by using 315mL pure C272 and 685mL of kerosene to dilute it and put it in a bottle.

Prepare 100 mL of NaOH solution 250g/L by using 25.1295g NaOH and 100mL of H₂O in erlenmeyer and move to bottle.

Prepare 500mL CoSO₄ solution 5g/L (feed)by using 2.4987g CoSO₄ solid to 500mL of H₂O in a flask.

Return NaOH and CoSO₄.

Calibration of pH meter with buffer solutions of pH=4 and pH=7.

Feeling shoked by something that happened yesterday's evening.

Measure of pH of CoSO₄ solution. pH=5.09

Addition of 100 microL of HSO₄ 3M (could be some error).

Wait for 5 min while it is stirred.

Measure of pH=2.83.

Stop stirring.

Introduce in the same flask as before.

Lab class with Thea and Gabriele at the same time.

08-02-2019

Calibration of pH meter.

Going to start separation in separation funnel with ratio 1:1.

Introduce 20mL of aqueous solution in funnel.

Introduce 20mL of organic solution in funnel.

Shake for 5 min.

Take aqueous phase to measure pH. pH=3.17.

Return sample and add NaOH:0.2mL.

Measure pH: pH=6.35

Some particles in the solution(precipitation).

Remove liquids in their respective containers (organic or aqueous).

11-02-2019

Calibrate pH meter.

Going to start separation with separation funnel ratio 1:1.

Add 20mL of feed to separation funnel.

Add 20mL of C272 to separation funnel.

Shake 5 min.

Measure pH aqueous phase: pH=3.61.

Add 0.19 mL of NaOH to separation funnel.

Shake 5 min.

Measure pH of aqueous phase: pH=6.07.

Aqueous phase is too milkish, also organic a bit. Not working properly. Remove both phases and clean.

12-02-2019

Prepare 20mL of the solution of 250g/L to put in the reactor with C272 1M. Add heating to 50°C

Introduce C272 into the reactor.

Wait for 30 min and check temperature. T=50°C

Add NaOH very slowly. Wait 10/15 min. T=50°C

pH meter calibration.

Add 20 mL of feed to separation funnel.

Add 20 mL of C272 treated with NaOH to separation funnel.

Shake for 5 min.

Something is leaking from reactor.

There are 3 phases in the separation funnel. Something is wrong. Remove solutions and clean.

Take a big beaker to introduce the flask of the CoSO₄ 5g/L solution to raise the temperature to 50°C too as the organic phase.

There is some blue leaking from reactor, probably due to some metals that could have been before.

There is a lab class at this moment in the lab.

Once it is T=50°C, take aqueous solution in a beaker and introduce 20mL in separation funnel.

Add 20mL of C272 with NaOH to the separation funnel.

Shake for 5 min.

It is not working. Remove everything and clean.

Dilute the CoSO₄ solutions 5 times to 1g/L by taking 100mL of solution 5g/L and add 400mL H₂O in a flask. Shake it.

Heat this new solution to 50°C.

Gabriele has gone to take me some distilled water.

Cover flask of 5g/L with parafine just in case I needed it and save in fumehood.

Now let's work with solution CoSO_4 1g/L as feed

Add 20mL of feed to separation funnel

Add 20mL of C272 with NaOH to separation funnel.

Shake for 5 min.

Not working good either.

Remove everything and clean

13-02-2019

Measure 750mL of C272 1M and put it in a bottle.

Measure 237 mL C272 pure and add to the bottle. Mix it by shaking.

Clean instruments.

About to start extraction with ratio 1:1.

Add 20mL of feed to separation funnel.

Add 20mL of C272 2M with NaOH to separation funnel.

Shake for 5 min.

Again working bad.

Going to prepare solution of NaOH 100g/L by using 10.0077g of NaOH solid and add 100mL of H_2O . Shake it.

Going to prepare again solution C272 1M in kerosene by using 316mL of C272 and 684 of kerosene. Shake it.

Measure pH of feed: pH=3.44.

Let's try extraction. Add 20mL of feed to separation funnel.

Add 20mL C272 2M with to the separation funnel.

Shake 5 min and wait.

Measure pH of aqueous phase: pH=3.30.

Return sample to the separation funnel.

Add 0.07mL of NaOH to sep. funnel.

Milky phase in aqueous phase. pH=4.03

Throw it away. About to try with less NaOH.

Add 20mL of feed to separation funnel.

Add 20mL of C272 1M to separation funnel.

Shake it 5 min. Colours seems good.

Measure pH: pH=2.94.

Add 0.05 mL of NaOH. bad colour appear. Not two good clear phases. Again milky.

Throw it away every solution for feed and prepare new one with 0.5g/L by using 0.2501g of CoSO_4 and 500mL in a flask. Shake the flask.

Measure pH of new feed solution: pH=4.89

We need pH around 4 or less. Add 0.02mL of H_2SO_4 3M to solution of feed. Shake it

Measure pH: pH=3.63

Proceed to mix in separation funnel. Add 20mL of new feed to separation funnel.

Add 20mL of C272 1M to separation funnel.

Shake it for 5 min. Bad colour. Remove it.

Clean everything.

13-02-2019

Calibrate pH meter with buffer solutions of pH=4 and pH=7.

Take a sampler of 30mL of CoSO_4 0,5g/L already prepared.

Measure pH. pH=3.64

Add H_2SO_4 3M to decrease much pH. Final pH=0.64

Proceed to use the separation funnel. Add 20mL of CoSO_4 to the separation funnel.

Add 20 mL of C272 1M to separation funnel.

Shake for 5 min.

Colours are not good, very milky. Throw the mixture away. Clean everything. Clean also a flask of 100mL.

Take CoSO_4 , Kleenex and gloves.

Prepare 100mL solution of CoSO_4 0.5g/L: Prepare 100mL of H_2SO_4 by using 16,667mL of H_2SO_4 3M and completing the flask to 100mL with H_2O . Weight 0,0513g of CoSO_4 and add to the flask and shake it.

Add 20mL of solution CoSO_4 0,5g/L to the separation funnel.

Add 20mL of solution C272 1M to separation funnel.

Shake for 5 min.

Bad again, throw it away and clean instruments.

Try the same process with same results. Not proper.

Prepare acid H_2SO_4 0,1M and use to clean C272 1M. Prepare acid by using 3 mL of 3M solution of sulfuric acid and add 27mL of water.

Add 20mL of H_2SO_4 0,1M to separation funnel.

Add 20mL of Cyanex 272 1M to separation funnel.

Shake it.

Separate aqueous and organic phase. Get rid of aqueous phase. Save organic phase (C272 cleant) for separation.

Add 20mL of solution CoSO_4 0,5g/L to the separation funnel.

Add 20mL of solution C272 1M cleant to separation funnel.

Shake it and measure pH: pH=0.33

Add a total of 8.850mL of NaOH and shake.

Measure pH: pH=4.87. Colours seem to be OK. Take a vial of it: Z11.

Clean everything

15/02/2019

Take cobalt sulfate, pipete tips (5mL) and 50 mL of 3 different phase modifiers: Dceyl Alcohol 98%(A), Tributyl phosphate 97% (B) and tridodecylamin $\text{C}_{36}\text{H}_{75}$.

Clean erlenmeyers.

Prepare 100mL of solution of 5% of phase modifier(each modifier) in C272: take 5mL of A,B and C and put them respectively in different erlenmeyers. Add 95mL of C272 1M to each of the erlenmeyers.

Prepare new feed by adding 29mL of H_2SO_4 3M and 174mL of H_2O to a flask and shake. Add then 0.1013 g of CoSO_4 to the flask and shake.

Calibrate pH meter with buffer solutions of pH=4 and pH=7.

Measure pH of the feed solution : pH=0.51.

Let's try separation in separation funnel with ratio 1:1.

Add 20mL of feed to separation funnel.

Add 20mL of C272 with A to separation funnel.

Shake 2mn and measure ph: pH=0.40.

Add a total of 3.10mL ofNaOH 100g/L to separation funnel and shake.

Measure pH: pH= 4.76. Take a sample: A11. Clean everything.

Lunch break

Add 20mL of feed to separation funnel.

Add 20 mL of C272 with B to separation funnel.

Shake for 2 min. Measure pH: pH=0.44

Add a total of 7.40mL of NaOH and shake.

Measure pH: pH=5.53. A bit more milky. Save a sampler: B11.

Clean everything and try C272 with C.

Add 20mL of feed to separation funnel.

Add 20mL of C272 1M with C to separation funnel.

Shake for 2 min. Bad colours, not two different phases. Get rid of it. Not going to work with C.

Clean everything.

Let's clean C272 with A and C272 with B with H₂SO₄ 0,5M.

First, prepare 100mL of H₂SO₄ 3M by taking 16mL of H₂SO₄ 18,76M and adding water until 100mL in a flask.. Put it in a glass bottle.

Prepare 50mL of H₂SO₄ 0,5M by taking 8,33mL of H₂SO₄ 3M and water until 50mL in a flask.

Add 20mL of H₂SO₄ 0,5M to separation funnel.

Add 20mL of C272 with A to separation funnel.

Shake it for 1 min. Remove aqueous phase and save organic phase.

Clean funnel and proceed exactly in the same way but using C272 with B.

Clean everything.

18/02/2019

Calibrate pH meter with buffer solutions pH=4 and pH=7.

Let's try separation with cleant solvents (treated with H_2SO_4):

Add 20mL of feed to separation funnel.

Add 20mL of C272 with A and cleant to separation funnel.

Shake for 1 min and measure pH of aqueous phase: pH=0.49

Add a total of 7.466mL of NaOH to separation funnel and shake it. Measure pH: pH=4.65. Take a vial: A21.

Clean everything

Add 20mL of feed to separation funnel.

Add 20mL of C272 with B and cleant to separation funnel.

Shake for 1 min and measure pH of aqueous phase: pH=0.41.

Add 7.1mL a total of NaOH to separation funnel and shake it.

Measure pH of aqueous phase: pH=4.71.

At the same time there has been an accident in the corridor with pure HNO_3 and they have taken my NaOH. Need to prepare 100mL more.

Clean everything. Lunch break.

Prepare 250mL of H_2SO_4 0.5M by adding 41,667mL H_2SO_4 3M and 208,33mL of H_2O .

Add 20mL of H_2SO_4 0,5M to separation funnel.

Add 20mL of C272 1M to separation funnel.

Shake it, remove aqueous phase and save organic phase.

Add 20mL of feed to separation funnel

Add 20mL of organic cleant with H_2SO_4 .

Shake it. Measure pH: pH=0.34.

Add a total of 7.45mL of NaOH to separation funnel and shake it.

Measure pH: pH=4.72. Take a vial: Z22.

Clean funnel

Add 20mL of feed to separation funnel

Add 20mL of C272 with A to separation funnel.

Shake it for 1 min.

Add a total of 7.02mL of NaOH to the separation funnel and shake it. Final ph: pH=4.61. Take a vial: A12.

Clean funnel and samplers.

Add 20mL of feed to separation funnel.

Add 20mL of C272 with B to separation funnel.

Shake it for 1 min.

Add 8.11 mL of NaOH to separation funnel and shake it. Final pH: pH=4.67. Take a vial:B12.

Clean separation funnel and samplers.

Add 20mL of H₂SO₄ 0,5M to separation funnel.

Add 20mL of C272 with A to separation funnel.

Shake it for 1 min and remove aqueous phase. Save organic phase.

Clean separation funnel.

Add 20mL of feed to separation funnel.

Add 20 mL of C272 with A and cleant to separation funnel.

Shake it for 1 min.

Add 7.35mL of NaOH to separation funnel. Final pH: pH=4.85. Take a vial: A22.

Clean separation funnel and samplers.

Prepare more feed: solution of CoSO_4 in $0,5\text{MH}_2\text{SO}_4$. For this, weight 0.0517 g of CoSO_4 and put in a flask. Fill the flask with H_2SO_4 until 100mL .

Shake.

Add 20mL of H_2SO_4 0.5M to separation funnel.

Add 20mL of Cyanex 272 with B to separation funnel to clean it.

Shake it for 2 mins.

Separate aqueous and organic and get rid of aqueous. Clean separation funnel.

Add 20mL of feed to separation funnel.

Add 20mL of Cyanex 272 with B clean to separation funnel.

Shake it for 1 min.

Add a total of 7.565 mL of NaOH . Final ph: $\text{pH}=4.73$. Take a sample: B22.

Clean everything and finish.

19/02/2019

Proceed to try different ratios O/A.

First proceed to clean C272 with H_2SO_4 0.5M .

Add 30mL of acid to separation funnel.

Add 30mL of C272.

Shake for 2 min.

Separate aqueous and organic phase. Get rid of aqueous phase. Save organic phase.

Going to try ratio 2:1

Add 15mL of feed to separation funnel.

Add 30mL of organic clean to separation funnel.

Shake for a minute.

Calibrate pH meter.

Measure pH: pH=0.44.

Return sample. Add a total of 6.1mL to a final pH of 5.89, so it is not valid.

Let's clean 170mL of C272 1M as described previously with separation funnel and ratio 2:1. Save the organic together. Remove aqueous phase.

Add 15mL of feed to separation funnel.

Add 30mL of C272 to separation funnel.

Shake it for 1 min.

Add a total of 5.7mL of NaOH to a pH of 4.72. Take a vial: Z21.

Remove and clean everything.

Add 15mL of feed to separation funnel.

Add 30mL of C272 cleant to separation funnel.

Shake for 1 min.

Add a total of 5.725 mL of NaOH to final pH 4.77.

Take a vial: Z22.

Remove everything and clean all instruments.

20/02/219

Prepare 100mL of H_2SO_4 3M by taking 16,67mL of H_2SO_4 concentrated in a volumetric flask of 100mL and add distilled wáter until 100mL. Shake it.

Prepare 0,5L H_2SO_4 0,5M by taking 81.667mL of H_2SO_4 3M in a volumetric flask and add distilled wáter until 500mL, Shake it.

Prepare 100mL of solution 100g/L NaOH by weighting 10g of NaOH solid and put them into a flask. Add then distilled wáter to 100mL.

Prepare 250mL of solution 0,5g/L CoSO_4 in H_2SO_4 0,5M by adding 0.125g of CoSO_4 to a flask and add H_2SO_4 0,5M until 250mL. Shake it.

Let's clean C272 with H_2SO_4 0,5M in the separation funnel:

Add 90mL of H_2SO_4 0,5M to separation funnel.

Add 90mL of C272 1M to separation funnel.

Shake it for 2 min. Remove aqueous phase and save organic phase.

Let's try ratio 3:1.

Add 15mL of feed to separation funnel.

Add 45mL of C272 clean to separation funnel.

Shake it for 1 minute.

Add a total of 5.6mL of NaOH until pH=4,70. Take a sample:Z31.

Clean everything and remove liquids.

Add 15mL of feed to separation funnel.

Add 45mL of C272 clean to separation funnel.

Shake it for 1 minute.

Add a total of 5.7mL of NaOH until pH=4,90. Take a sample:Z32.

Remove every liquid and clean everything.

Lunch break.

Let's try ratio 0,5:1

Add 20mL of feed to separation funnel.

Add 10mL of C272 clean to separation funnel.

Shake it.

Add a total of 7.3mL of NaOH to a pH over 5.5, so remove it and try again.

Add 20mL of feed to separation funnel.

Add 10mL of C272 clean to separation funnel.

Shake it.

Add a total of 7.84mL of NaOH to a final pH=4.87. Take a vial:Z61.

Add 20mL of feed to separation funnel.

Add 10mL of C272 cleant to separation funnel.

Shake it.

Add a total of 7.65mL of NaOH to a final pH=4.72. Take a vial:Z62.

Remove the resto of the liquids and clean. Go to take more pipete tips of 5mL

FIKA TIME

Let's try ratio 0.05:1.

Add 35mL of feed to separation funnel.

Add 1,75mL of C272 cleant to separation funnel.

Shake for 2 min.

Add a total of 13.75mL of NaOH to a final pH=4.87. Take a vial: Z71.

Remove liquid and clean everything.

Add 35mL of feed to separation funnel.

Add 1,75mL of C272 cleant to separation funnel.

Shake for 2 min.

Add a total of 13.5mL of NaOH to a final pH=6. There is precipitation, so it is wrong. Get rid of everything and try again.

Add 35mL of feed to separation funnel.

Add 1,75mL of C272 cleant to separation funnel.

Shake for 2 min.

Add a total o 12mL. The pipete tip has dropped into the separation funnel, remove everything and clean everything.

21/02/2019

Prepare 2L of C272 cleant 1M.

Put in the reactor 2L of H_2SO_4 0,1M

Put 2L of C272 in the reactor.

I forgot to dilute the C272 before in kerosene, so I must empty the reactor separating acid and C272. There has been some leak when emptying it.

Take 631,37mL of C272 and put it in the reactor. Add 1368,6mL of kerosene.

Prepare 2L of CoSO_4 0,5g/L in 0,5M H_2SO_4 by taking 55,55mL of H_2SO_4 18M (concentrated) and put them in a flask of 2L. Fill the flask with distilled water until 2L. Then add 0.9998g of CoSO_4 .

Shake it.

Going to set the mixer settlers with Martina. Two stages for stripping and two stages for separation. Take long screws for motors and short for structure.

Measure volumes flow for organic, feed and acid and fix 5mL/min by using the cell phone timer and a vial of 15mL.

22/02/2019

Let's try the second solution of ratio 0,05:1.

Add 35mL of feed to separation funnel.

Add 1,75mL of C272 cleant to separation funnel.

Shake it for a minute.

Calibrate pH meter.

Add a total of 14.42 mL of NaOH to a final pH=4.73. Take sample: Z72

Remove liquids and clean everything.

Let's try ratio 5:1.

Add 10mL of feed to separation funnel.

Add 50mL of C272 cleant to separation funnel.

Shake for 1 min.

Add a total of 4.2mL of NaOH to the separation funnel shaking to a pH=4.60. Take a sample:Z41

Remove liquids and clean everything.

Fika Break.

Add 10mL of feed to separation funnel.

Add 50mL of C272 to separation funnel.

Shake it for 1 min.

Add a total of 4.015mL of NaOH to a pH=4.72. Take a sample: Z42.

Remove everything and clean.

There is no more C272 prepared for this. I will take the one for the mixer settlers.

Let's try ratio 10:1:

Add 5mL of feed to separation funnel.

Add 50mL of C272 cleant to separation funnel.

Shake for 1 min.

Add a total of 1.845mL of NaOH to separation funnel to a pH=4.63. Take a sample: Z51.

Remove everything and clean.

Add 5mL of feed to separation funnel.

Add 50mL of C272 cleant to separation funnel.

Shake it.

Add 1.985mL of NaOH to a pH=4.59. Take a vial:Z52.

Remove everything and clean.

Lunch break.

Prepare 100mL of NaOH 100g/L by taking 10,1210g of NaOH and put them in a flask with 100mL of H₂O and shake. Put it in a plastic bottle.

Prepare 1L of HNO₃ 0,5M by taking 35mL of HNO₃ concentrated 65% and put it in a 1L flask. Add H₂O until 1L.

Now let's prepare the vials for ICPOES. First dilute the sample 100 times by taking 0,1mL of the sample and add 9,9 of HNO₃ 0,5M into a 15mL vial and shake. Repeat this for every vial.

Now dilute it 10 times more (so it will be diluted 1000 times) by taking 1mL of the vial 100 times diluted and add 9mL of HNO₃ 0,5M. Shake it. Repeat it for each vial.

Save them.

Calibration of the pump for stripping (with H₂SO₄) 0,1M by using a vial and cell phone timer.

There is a lab class running at the same time.

25/02/2019

Prepare estándar solutions of 20ppm, 10ppm, 5ppm and 0ppm of Co for the ICPOES.

For that, take 1mL of pure Co in HNO₃ and dilute it with 49 mL of HNO₃ 0,5M in a 50mL vial so I obtain 20ppm. By taking 20mL of this 20ppm solution and mix them with 20mL of HNO₃ 0,5M, I obtain 10ppm solution. By taking 15mL of this 10ppm solution and add 15mL of HNO₃ 0,5M, I obtain 5ppm solution. For the 0ppm solution just add 50mL of HNO₃ 0,5M.

Let's calibrate the volumen Flow of the pumps again for the mixer settlers.

Connect tubes to the mixer settlers.

Put 80 mL of feed in each mixing chamber of the extraction part. And add 80mL of H_2SO_4 to each mixing chamber in the stripping part.

Activate the pumps of C272 cleant 1M until it fill the hole system. Turn then off the pump

Turn on the pumps again. There is one bad connection. Stop every pump and change the connection to the correct one.

Run again the system. It works correctly.

C272 at the out has a good colour.

Stop every pump and stirrers.

26/02/2019

Going to start to repeat every ratio once more to have a third repetition.

Add 20mL of feed to separation funnel.

Add 20mL of C272 1M cleant to separation funnel.

Shake it.

Add a total of 8mL of NaOH to pH very high. Remove it and try again.

Clean everything.

Add 20mL of feed to separation funnel.

Add 20mL of C272 1M cleant to separation funnel.

Shake it.

Add a total of 7mL of NaOH to pH=5.80. Take a vial: Z13. Remove and clean everything.

Add 15mL of feed to separation funnel.

Add 30mL of C272 1M cleant to separation funnel.

Shake it.

Add a total of 6.48mL of NaOH to pH=4.67. Take a vial: Z23. Remove and clean everything.

FIKA BREAK

Add 15mL of feed to separation funnel.

Add 45mL of C272 1M cleant to separation funnel.

Shake it.

Add a total of 6.380mL of NaOH to pH=4.60. Take a vial: Z33. Remove and clean everything.

Add 5mL of feed to separation funnel.

Add 50mL of C272 1M cleant to separation funnel.

Shake it.

Add a total of 1.5mLof NaOH to pH=5.27. Take a vial: Z53. Remove and clean everything.

27/02/2019

Calibrate pH meter with buffer solution pH=4 and pH=7.

Add 10mL of feed to separation funnel.

Add 50mL of C272 1M cleant to separation funnel.

Shake it.

Add a total of 5mL of NaOH to pH=4.74. Take vial:Z43. Remove everything and clean.

Add 20mL of feed to separation funnel.

Add 10mL of C272 to separation funnel.

Shake it.

Add a total of 7.6 NaOH to the separation funnel, to pH=5.01. Take vial:Z63. Remove everything and clean.

I have broken a volumetric cylinder while cleaning. Take another one.

Fika Break.

Add 35mL of feed to separation funnel.

Add 1,75 of C272 to separation funnel.

Shake it.

Add 13mL of NaOH to separation funnel to pH=4,97. Take a vial:Z73. Clean everything.

Prepare vials 15mL for diluting for the ICPOES.

Prepare 1L of HNO₃ 0,5M by adding 35mL of concentrated acid nitric to a flask and add H₂O until 1L.

Then take 0,1mL of one vial and put them into another vial of 15mL adding 9,9 mL of HNO₃ 0,5M to dilute it 100 times. Shake it. Repeat it with every vial.

Take 1mL of this 100 times diluted vials and put in another vial of 15mL adding 9mL of HNO₃ 0,5M to dilute it 10 times more (1000 times in total). Repeat for every vial.

Clean samplers and glasses.

01/03/2019

Start by taking out the liquids in the pumps that is from the lab class of yesterday. Do it by starting the pumps with my solutions.

There is some leaking, principally in the organic, so change the tubes of the pumps and run it again.

Configure the pumps with the new tubes to volume flow of 5mL/min.

Connect the tubes to the mixer settlers set that was already configured from last days. There has been some leaking from the stripping and the extraction part (more in the stripping). So put 40mL of acid in the last stage of the stripping and some

organic(around 20mL). put some feed in the second stage of the extraction and some organic too.

Start to pump the liquids. No leaking.

Play with the system until the ratio is 1:1. It took some time as the leaks has change a bit the system.

There is no extraction appreciated, and it makes sense as the pH of the feed is very low(close to 0,5). So the feed (not raffinated) can be returned to the pump as well as the stripping acid.

04/03/2019

Prepare 1L NaOH 100g/L with 100,0264g NaOH and 1L of H₂O.

Run mixer settlers and take samples each 30 min approx with the names: E1,E2,S1 and S2 and the number of sample before each case. It is working at 1000rpm and $V_{NaOH}=0,5\text{mL}/\text{min}$.

Take 1E1,1E2,2S2 and 2S2 with pH: 0.54,0.44,1.06 and 0.97 respectively.

After 20min take 2E1,2E2,2S1,2S2 with pH: 1.33,3.45,1.08 and 0.96 respectively.

Prepare 500mL solution 50g/L of NaOH with 50,0433g NaOH and 500mL of H₂O.

pH very high in E2 (over 7) so introduce NaOH 50g/L to E2 and 100g/L in E1. Still pH over 7.

Decrease V_{NaOH} to 0.15mL/min and increase pump of acid as stripping is not working correctly. Organic is leaving blue (without being stripped).

Change again NaOH solution and add 25g/L NaOH to E2 and 100g/L to E1.

V_{NaOH} increased again to 0,5mL/min and increase again pump of acid of stripping.

It seems to be to low 25g/L so prepare 0,5L solution 200g/L adding 99,9865g of NaOH to 500mL and connect it to E1 and 100g/L to E2 at 0,2mL/min.

Prepare 1L C272 1M and add 50mL of TBP (5%).

Change E2 to 25g/L and increase V_{NaOH} to 0,5mL/min. Take samples 3E1,3E2,3S1 and 3S2 with pH 2.86, 2.61, 1.76 and 1.17 respectively.

Increase V_{NaOH} to 0,57mL/min. But there is precipitation. Stop everything.

Remove liquids in solvent extraction chambers with acid and ethanol.

Fill mixing chambers again with 80mL with feed and some organic. Pump organic until it is full.

Prepare 1L H_2SO_4 0,1M by taking 5,56mL of H_2SO_4 concentrated and water until 1L flask.

Stop everything.

05/03/2019

Fill the feed and acid bottles. Start strirrers. Start pumps and check ratio 1:1 inside the mixer settlers. Then start to pump NaOH 0,15mL/min, 100g/L to E2 and 200g/L to E1.

Take samples 4E1,4E2,4S1 and 4S2 with pH 0.58, 0.54, 1.06 and 0.97.

Increase V_{NaOH} to 0.4mL/min.

Prepare 2L $CoSO_4$ 0,5g/L in 0,5M H_2SO_4 by taking 55.55mL of H_2SO_4 concentrated in a volume flask of 2L. Add H_2O until 2L. Then add 1.0023 g of $CoSO_4$. Shake.

Control ratios 1:1. $V_{NaOH}=325mL/min$.

Take samples 5E1,5E2,5S1 and 5S2 with pH 1.17, 1.89, 1.18 and 0.99.

V_{NaOH} to 0.49 mL/min.

Prepare 800mL of C272 1M with 5% TBP by add 250mL of C272 pure to a bottle. Add 545mL kerosene adnd 35mL TBP to the bottle. Shake.

Take samples 6E1,6E2,6S1,6S2 with pH 2.13, 2.79, 1.56 and 1.15.

Up to 0.522 mL/min. There is something wrong in the E1 stage. Take out pump, add NaOH 100g/L. Change V_{C272} to 3mL/min. Connect again NaOH: 200g/L to E1 and 100g/L to E2.

Decrease V_{NaOH} 0.320mL/min. Change E2 to 25g/L.

V_{NaOH} =0.36mL/min. Change ratio O/A to 1:2.

Some precipitation in E2, bad colours again and it is not working correctly. Not more pumping of NaOH in E2. Stop everything.

Martina tested feed and different organics. C272 and Kerosene are not correct.

Prepare solutions 100x and 1000x for ICP-OES. Prepare 1L HNO_3 0,5M by adding 35mL of concentrated acid to a flask and up to 1L with water.

06/03/2019

Prepare standard solutions for ICP-OES: 0ppm,1ppm,5ppm,10ppm and 20ppm with solution of Co 1000ppm by adding 1mL to 50mL vial and 49 mL of HNO_3 obtaining 20ppm and then dilute to 1ppm.

Test 10mL of C272 1M in ISOPAR L with 10mL $CoSO_4$ 0,5g/L. At same time, test 10mL of versatic acid 1M in ISOPAR L with 10mL of $CoSO_4$ 0,5g/L.

For C272: take 3,15 mL C272 pure and dilute it in 6,85mL ISOPAR L. For versatic acid take 1,87mL of versatic acid pure and dilute it with 8.13 mL ISOPAR L.

Much better results and colours for versatic acid, but colour is pink, not blue. So let's try ratios again with separation funnel but with versatic aci 1M.

Prepare 1L 1M versatic acid in ISOPAR L by 187 mL pure versatic acid and add 813mL ISOPAR L.

Try ratio 1:1. Add 15mL of feed and 15mL of versatic acid. Shake it.

Add NaOH: 3mL+3mL+3mL+2mL to pH over 7 and much NaOH added. Throw away.

Run ICP-OES with 100x solutions instead of 1000x.

Don't continue with this feed solution. Remove it.

07/03/2019

Prepare 2L solution 1g/L of Co by adding 0.541g $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ to a volumetric flask and fill it with H_2O until 2L. Shake it. Obtained 1g/L Co solution.

Measure pH of this new feed solution: pH= 4.28

Add 0.1mL of H_2SO_4 3M to the feed to a pH=3.86.

08/03/2019

Calibrate pH meter.

Start ratio 1:1.

Add 15mL of feed and 15mL of versatic acid to separation funnel. Shake for 2 min.

Add NaOH 100g/L: 0.25 mL to a pH=6.29. Take sample X11.

FIKA BREAK

Clean everything and repeat.

Add 15mL of feed and 15mL of versatic acid to separation funnel. Shake for 2 min.

Add NaOH 100g/L: 0.25 mL to a pH=6.27. Take sample X12.

There is some milky phase when pH around 5 but when added a bit more of NaOH and shake it disappears.

Clean everything and repeat.

Add 15mL of feed and 15mL of versatic acid to separation funnel. Shake for 2 min.

Add NaOH 100g/L: 0.2 mL to a pH=6.19. Take sample X13.

Clean everything and try ratio 2:1.

Add 15mL of feed and 30mL of versatic acid to separation funnel. Shake for 2 min.

Add NaOH 100g/L: 0.2 mL to a pH=6.08. Take sample X21.

Clean everything and repeat.

Add 15mL of feed and 30mL of versatic acid to separation funnel. Shake for 2 min.

Add NaOH 100g/L: 0.2 mL to a pH=6.09. Take sample X22.

Clean everything and repeat. Colours are perfect. Take photo.

Add 15mL of feed and 30mL of versatic acid to separation funnel. Shake for 2 min.

Add NaOH 100g/L: 0.2 mL to a pH=6.12. Take sample X23.

Clean everything and try ratio 3:1.

Add 10mL of feed and 30mL of versatic acid to separation funnel. Shake for 2 min.

Add NaOH 100g/L: 0.15 mL to a pH=6.21. Take sample X31.

Clean everything and repeat.

Add 10mL of feed and 30mL of versatic acid to separation funnel. Shake for 2 min.

Add NaOH 100g/L: 0.15 mL to a pH=6.24. Take sample X32.

Clean everything and repeat.

Add 10mL of feed and 30mL of versatic acid to separation funnel. Shake for 2 min.

Add NaOH 100g/L: 0.15 mL to a pH=6.14. Take sample X33.

Clean everything and try ratio 5:1.

Add 10mL of feed and 50mL of versatic acid to separation funnel. Shake for 2 min.

Add NaOH 100g/L: 0.14 mL to a pH=6.06. Take sample X41.

Clean everything and repeat.

Add 10mL of feed and 50mL of versatic acid to separation funnel. Shake for 2 min.

Add NaOH 100g/L: 0.14 mL to a pH=6.03. Take sample X42.

Clean everything and repeat.

Add 10mL of feed and 50mL of versatic acid to separation funnel. Shake for 2 min.

Add NaOH 100g/L: 0.14 mL to a pH=6.05. Take sample X43.

Clean everything and try ratio 10:1.

Add 5mL of feed and 50mL of versatic acid to separation funnel. Shake for 2 min.

Add NaOH 100g/L: 0.07 mL to a pH=5.95. Take sample X51.

Clean everything and repeat.

Add 5mL of feed and 50mL of versatic acid to separation funnel. Shake for 2 min.

Add NaOH 100g/L: 0.07 mL to a pH=5.96. Take sample X52.

Clean everything and repeat.

Add 5mL of feed and 50mL of versatic acid to separation funnel. Shake for 2 min.

Add NaOH 100g/L: 0.07 mL to a pH=5.93. Take sample X53.

Clean everything. Put some KCl in pH meter. Go home.

11/03/2019

Calibrate pH meter.

Prepare 1L HNO₃ 0.5M in a volumetric flask by adding 35 mL of concentrated HNO₃ and H₂ until 1L.

Prepare vials for ICP-OES : take 0.1mL of each sample and add 9.9mL of HNO₃ 0,5M to dilute them 100 times in different vials.

Run ICP-OES with imported calibration from last analysis.

Start ratio 0.5:1.

Add 20mL of feed to separation funnel. Add 10mL of versatic acid(VA) 1M to separation funnel. Shake for 2 min.

Add 0.2mL of NaOH and shake 2 min. pH=6.13. Take sample X61.

Clean everything and repeat:

Add 20mL of feed to separation funnel. Add 10mL of versatic acid(VA) 1M to separation funnel. Shake for 2 min.

Add 0.195mL of NaOH and shake 2 min. pH=6.05. Take sample X62. Clean everything and repeat:

Add 20mL of feed to separation funnel. Add 10mL of versatic acid(VA) 1M to separation funnel. Shake for 2 min.

Add 0.195mL of NaOH and shake 2 min. pH=6.14. Take sample X63.

Clean everything and try ratio 0.05:1.

Add 35mL of feed to separation funnel. Add 1.75mL of VA 1M to separation funnel. Shake for 2 min.

Add 0.2mL of NaOH and shake 2 min. pH=6.43. Good colours. Take sample X71.

Clean everything and repeat.

Add 35mL of feed to separation funnel. Add 1.75mL of VA 1M to separation funnel. Shake for 2 min.

Add 0.195mL of NaOH and shake 2 min. pH=6.47. Good colours. Take sample X21.

Clean everything and repeat.

Add 35mL of feed to separation funnel. Add 1.75mL of VA 1M to separation funnel. Shake for 2 min.

Add 0.19mL of NaOH and shake 2 min. pH=6.31. Good colours. Take sample X73.

Clean everything .

12/03/2019

Bad results for ratios 1:1 and 3:1 in ICP-OES so repeat those.

Calibrate pH meter with buffer solution pH=7 and pH=4.

Try again ratio 1:1

Add 15mL of feed to separation funnel. Add 15mL of VA 1M to separation funnel. Shake for 2 min.

Add 0.2mL of NaOH and shake 2 min. pH=6.25. Good colours. Take sample X11₂.

Clean everything and repeat.

Add 15mL of feed to separation funnel. Add 15mL of VA 1M to separation funnel. Shake for 2 min.

Add 0.2mL of NaOH and shake 2 min. pH=6.21. Good colours. Take sample X12₂.

Clean everything and repeat.

Add 15mL of feed to separation funnel. Add 15mL of VA 1M to separation funnel. Shake for 2 min.

Add 0.2mL of NaOH and shake 2 min. pH=6.30. Good colours. Take sample X13₂.

Clean everything and try ratio 3:1.

Add 10mL of feed to separation funnel. Add 30mL of VA 1M to separation funnel. Shake for 2 min.

Add 0.15mL of NaOH and shake 2 min. pH=6.21. Good colours. Take sample X31₂.

Clean everything and repeat.

Add 10mL of feed to separation funnel. Add 30mL of VA 1M to separation funnel. Shake for 2 min.

Add 0.15mL of NaOH and shake 2 min. pH=6.31. Good colours. Take sample X32₂.

Clean everything and repeat.

Add 10mL of feed to separation funnel. Add 30mL of VA 1M to separation funnel. Shake for 2 min.

Add 0.15mL of NaOH and shake 2 min. pH=6.23. Good colours. Take sample X33₂.

Clean everything.

Prepare 1L versatic acid 1M in ISOPAR L with 187mL of VA and 813mL ISOPAR L.

Adjust pumps to 5mL/min for mixer settlers.

Prepare 1L H₂SO₄ 0.2M with 11.11 mL of H₂SO₄ concentrated and H₂ until 1L.

Fill E1 and E2 with the feed (80mL each) and S1 and S2 with H₂SO₄ 0.2M (each one 80mL again).

Run pump of organic until it flows out. Then stop system and finish.

13/03/2019

Start mixer settlers. First take out some bubbles from organic tuve. Run with ratio 1:1.

Prepare 1L H_2SO_4 0.2M with 11.11mL of H_2SO_4 concentrated and H_2O until 1L.

Prepare 2L of $CoSO_4$ 1gCo/L with 9.5494g of $CoSO_4$ and H_2O until 2L.

Take samples 1E1 (pH=3.42), 1E2 (pH=3.53), 1S1(pH=0.90) and 1S2(pH=0.85)

FIKA BREAK

10:25 Start to pump NaOH: 100g/L solution to E1 and 25g/L solution to E2 at velocity:5

Prepare 0.5L of VA 1M with 93.5mL of VA pure and 406.5 mL of ISOPAR L. Add them to the bottle which is being pumped.

10:45. Take samples: 2E1 (pH=6.32), 2E2 (pH=6.8), 2S1(pH=0.85) and 2S2(pH=0.87).

Disconnect NaOH in E2.

11:15. Take samples: 3E1 (pH=6.34), 3E2 (pH=6.47), 3S1(pH=0.90) and 3S2(pH=0.80).

Decrease NaOH addition to 3.5. Add feed and acid to the bottles.

LUNCH BREAK (without stopping the system).

12:15: Take samples 4E1 (pH=6.36), 4E2 (pH=6.97), 4S1(pH=0.89) and 4S2(pH=0.86)

Decrease V_{NaOH} to 2.1 because there has been some precipitation. Add H_2SO_4 0,2 M to the chamber to dissolve it. No more precipitation.

13:10: Take samples 5E1 (pH=6.21), 5E2 (pH=6.10), 5S1(pH=0.88) and 5S2(pH=0.81)

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Prepare ICP-OES vials by taking 0.1mL of each sample and put in different 15mL vials. Add 9.9mL of HNO₃ 0.5M to each vial to dilute them by 100 times.

13:55: Take samples: 6E1 (pH=6.29), 6E2 (pH=6.23), 6S1(pH=0.92) and 6S2(pH=0.82).

Return 1 bottle of VA 1M stripped to the bottle where it is being pumped.

14:45: Take samples: 7E1 (pH=6.29), 7E2 (pH=6.41), 7S1(pH=0.91) and 7S2(pH=0.85).

Increase $V_{H_2SO_4}$

FIKA BREAK

Let's try with 2000rpm in the agitating motors. Same ratio 1:1.

15:30. Take samples: 10E1 (pH=6.20), 10E2 (pH=6.26), 10S1(pH=0.84) and 10S2(pH=0.78).

Same V_{NaOH}

16:00. Take samples: 11E1 (pH=6.16), 11E2 (pH=6.01), 11S1(pH=0.94) and 11S2(pH=0.82).

16:45. Take samples: 12E1 (pH=6.02), 12E2 (pH=5.69), 12S1(pH=0.81) and 12S2(pH=0.73).

Increase V_{NaOH} but try tomorrow. Stop agitators and pumps.

14/03/2018

Run ICP-OES at 8:00h.

Start mixer-settlers with 2000rpm.

Calibrate pH meter.

09:20. Take samples: 13E1 (pH=6.19), 13E2 (pH=6.02), 13S1(pH=0.77) and 13S2(pH=0.69).

09:50. Take samples: 14E1 (pH=6.07), 14E2 (pH=6.29), 14S1(pH=0.82) and 14S2(pH=0.71).

10:40. Take samples: 15E1 (pH=6.02), 15E2 (pH=6.13), 15S1(pH=0.83) and 15S2(pH=0.78).

Return approx 800mL organic.

Prepare 1L of H₂SO₄ 0.2M with 11,1mL of H₂SO₄ concentrated and H₂O until 1L in a volumetric flask.

Prepare 2L Co 1g/L with 9.5039 g CoSO₄ · H₂O and 2 of H₂O in a volumetric flask. Add 0.1mL of H₂SO₄ 3M to a pH=3.63.

11:40. Take samples: 16E1 (pH=5.98), 16E2 (pH=6.12), 16S1(pH=0.79) and 16S2(pH=0.71).

Stop the system. Change to ratio 2:1.

For ratio 1:1: organic pump=67 and feed pump=78.

For ratio 2:1: organic pump(8mL/min)=82 and feed pump (4mL/min)=58.

Start pumps and control ratio 2:1. Start pumping NaOH at level 1.6

13:40. Take samples: 20E1 (pH=5.71), 20E2 (pH=5.75), 20S1(pH=0.76) and 20S2(pH=0.68).

14:25. Take samples: 21E1 (pH=5.90), 21E2 (pH=6.24), 21S1(pH=0.74) and 21S2(pH=0.69).

Increase V_{NaOH} to 2

Return approx 700mL organic (14:45)

15:35. Take samples: 22E1 (pH=5.74), 22E2 (pH=6.37), 22S1(pH=0.72) and 22S2(pH=0.70).

16:35. Take samples: 23E1 (pH=6.39), 23E2 (pH=7.67), 23S1(pH=0.77) and 23S2(pH=0.65).

Stop everything. Go home.

15/03/2019

8:15. Start mixer settlers. After 10 min start pumping NaOH.

08:45. Take samples: 24E1 (pH=6.15), 24E2 (pH=6.41), 24S1(pH=0.72) and 24S2(pH=0.67).

09:25. Take samples: 25E1 (pH=6.14), 25E2 (pH=7.02), 25S1(pH=0.86) and 25S2(pH=0.88).

Stop adding NaOH in E2.

Return approx. 800mL organic.

10:30. Take samples: 26E1 (pH=6.01), 26E2 (pH=6.12), 26S1(pH=0.82) and 26S2(pH=0.69).

Prepare 1L HNO₃ 0.5M with 35mL HNO₃ concentrated and H₂O until 1L in a volumetric flask.

Prepare 1L H₂SO₄ 0.2M with 11.1mL H₂SO₄ concentrated and H₂O until 1L in a volumetric flask.

Prepare ICP-OES vials and run a part of it. Continue preparing other vials for future analysis.

11:20:Take samples: 27E1 (pH=5.93), 27E2 (pH=5.86), 27S1(pH=0.77) and 27S2(pH=0.75).

Go to ratio 5:1. 2mL/min of feed and 10mL/min of VA.

For ratio 5:1: organic pump =101 and feed pump=58.

13:00 Start pumping again and increase also $V_{H_2SO_4}$. Fill bottles of H₂SO₄ and CoSO₄ for the pumps.

Prepare 2L CoSO₄ (1g/L of Co) with 9.5021g of cobalt sulfate heptahydrated and H₂O until 2L in a volumetric flask.

Start adding NaOH at 13:20 (level 4.2).

Change 25g/L to E1 at level 5 and nothing to E2.

13:40 Take samples: 30E1 (pH=6.20), 30E2 (pH=5.75), 30S1(pH=0.75) and 30S2(pH=0.75).

Return 750mL of organic.

14:25 Take samples: 31E1 (pH=6.16), 31E2 (pH=5.88), 31S1(pH=0.77) and 31S2(pH=0.73).

Increase V_{NaOH} to 4.6 level.

FIKA BREAK

15:30 Take samples: 32E1 (pH=6.23), 32E2 (pH=5.91), 32S1(pH=0.75) and 32S2(pH=0.71).

16:10 Take samples: 33E1 (pH=6.22), 33E2 (pH=5.94), 33S1(pH=0.76) and 33S2(pH=0.73).

Stop pumps and stirrers. Return 550 mL organic. Cover bottle.

Total of VA returned already: 4.5L.

18/03/2019

8:30. Run mixer settlers. Pump also NaOH 25g/L to E1.

08:35 Take samples: 34E1 (pH=6.04), 34E2 (pH=5.79), 34S1(pH=0.80) and 34S2(pH=0.73).

09:20. Take samples: 35E1 (pH=6.11), 35E2 (pH=5.83), 35S1(pH=0.78) and 35S2(pH=0.72).

Prepare 1L H_2SO_4 0.2M with 11.1mL H_2SO_4 concentrated and H_2O until 1L. Fill bottle of pumping.

FIKA BREAK.

10:25 Take samples: 36E1 (pH=6.14), 36E2 (pH=5.85), 36S1(pH=0.78) and 36S2(pH=0.78).

Prepare 500mL of Versatic 10 1M with 93.5mL of pure VA and 406.5 mL of ISOPAR L.

11:25 Take samples: 37E1 (pH=6.16), 37E2 (pH=5.86), 37S1(pH=0.80) and 37S2(pH=0.79).

Finish and stop pumping to adjust the ratio now to 0,5:1 by adding 7mL/min of feed and 3,5mL/min of solvent. Feed pump level=94 and Organic pump level=32

12:25. Start system. At 12:50 Start pumping NaOH 25g/L to E1 at level 10. Change to 100g/L at level 5.

In a separation funnel try ratio 2:1 again. Add 15mL of feed + 30mL of VA 1M. Shake for 2 min.

Add 0.19mL of NaOH 100g/L to a pH=6.02. Take sample X21₂

Repeat. Add 15mL of feed + 30mL of VA 1M. Shake for 2 min.

Add 0.195mL of NaOH 100g/L to a pH=6.08. Take sample X22₂.

The NaOH was leaked, not pumped into the mixing chamber. Change the tube and pump 100g/L NaOH at level 2.5 to E1.

Repeat experiment in separation funnel. Add 15mL of feed + 30mL VA 1M. Shake 2min.

Add 0.195mL NaOH 100g/L to a pH=6.07. Take sample X23₂

13:40. Take samples: 40E1 (pH=5.90), 40E2 (pH=5.35), 40S1(pH=0.76) and 40S2(pH=0.71).

Let's start to repeat ratio 5:1 in separation funnel. Add 10mL of feed + 50mL of VA 1M and shake for 2min.

Add 0.144mL NaOH 100g/L to pH=6.08. Take sample X41₂.

13:40. Take samples: 41E1 (pH=6.17), 41E2 (pH=5.77), 41S1(pH=0.80) and 41S2(pH=0.73).

Add 10mL of feed + 50mL of VA 1M to separation funnel. Shake for 2 min.

Add 0.146mL of NaOH 100g/L to pH=6.00, Take sample X42₂.

14:45. Take samples: 42E1 (pH=6.13), 42E2 (pH=5.78), 42S1(pH=0.81) and 42S2(pH=0.75).

Add 10mL of feed+ 50mL of VA 1M to separation funnel. Shake for 2 min.

Add 0.15mL NaOH 100g/L to pH=6.13. Take sample X43₂.

Stop pumping and stirrers. Clean and remove aqueous in the bottles.

19/03/2019

Return 500mL of VA stripped. Start pumping to the mixer settlers, also NaOH.

Let's try ratio 10:1 again in separation funnel.

Add 5mL of feed + 50mL of VA 1M to separation funnel. Shake for 2 min.

Add 0.08mL NaOH 100g/L to a pH=6.12. Take sample X52₂.

There are some problems with the mixer settlers. Pump NaOH doesn't work correctly. Some organic is leaking. pH too high.

Run it normally at 12:45.

Add 5mL of feed+ 50mL VA 1M to separation funnel. Shake for 2min.

Add 0.82mL of NaOH 100g/L to a pH=6.16. Take sample X53₂.

13:20: pump NaOH at level 1.4. 100g/L to E1 and 25g/L to E2.

13:40: Take samples: 43E1 (pH=6.21), 43E2 (pH=6.05), 43S1(pH=0.79) and 43S2(pH=0.81).

14:15. Take samples: 44E1 (pH=6.32), 44E2 (pH=6.50), 44S1(pH=0.83) and 44S2(pH=0.90).

Decrease V_{NaOH} level to 1.2

Precipitation in E1. Stop pumping. Clean chambers, removing liquids of E1 and E2.

22/03/2019

Fill settling chambers of E1 and E2 with 80mL of feed solution. Put approx 15 mL of VA1M too.

Pump organic until it flows out of the system. Then pump feed and stripping acid. Check ratio 0.5:1. Pump NaOH at level 0,6. 100g/L to E1 and 25g/L to E2.

Prepare 1L of HNO₃ 0.5M with 35mL of HNO₃ concentrated and H₂O until 1L in a volumetric flask.

Prepare vials for ICP-OES 100 times diluted.

Calibrate pH meter.

FIKA BREAK.

10:30. Take samples: 45E1 (pH=6.19), 45E2 (pH=6.49), 45S1(pH=0.74) and 45S2(pH=0.69).

11:10. Take samples: 46E1 (pH=6.06), 46E2 (pH=6.4.), 46S1(pH=0.81) and 46S2(pH=0.77).

132:10. Take samples: 47E1 (pH=6.08), 47E2 (pH=6.445), 47S1(pH=0.84) and 47S2(pH=0.81).

Stop the system. Stop pumping and agitators.

Empty NaOH tubes by pumping H₂O. Measure V_{NaOH} at level 500 :1mL/min per tube.

Dismantle mixer settlers completely, emptying chambers and cleaning with ethanol, sulphuric acid and H₂O.

Prepare more vials for ICP-OES diluted 100 times in HNO₃.