



CHALMERS

Recycling of steel swarf via hydrometallurgy

Purification of iron chloride solution via solvent extraction, cementation, and ion exchange – a comparative study

Bachelor Thesis in Chemical Engineering

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Abstract

Several methods for purification and recovery of metals present in a swarf solution obtained from steel production and manufacturing waste are being tested in this study. The valuable elements originally present in the waste are Fe, Mn, Ni, and a small amount of Cr. The purification methods include solvent extraction with acidic and solvating extractants, cementation with an iron plate and ion exchange with the chelating resin Dowex M-4195. The extractants Cyanex 272 and D2EHPA extracted the highest amounts of Fe in comparison to the other acidic extractants. Both Cyanex 272 and D2EHPA reached 45% of Fe extraction at pH=3. Coextraction of Mn and Ni did occur in both cases indicating that solvent extraction is not the best approach for purification of the swarf. The solvating extractants TBP, Cyanex 923 and Aliquat 336 were tested at the same conditions, without adjusting the pH. Cyanex 923 extracted mostly Fe that reached 14% with less than 1% co-extraction of Mn and Ni. TBP and Aliquat 336 were inefficient in this case. A cementation technique with a piece of iron plate did not give any significant difference in metal concentration before and after the experiments. The best results are obtained from the ion exchange experiments with Dowex M-4195 at 25°C, 40°C and 60°C, shaking speed at 150 rpm for a total of 4h. Increasing amounts of Ni adsorption were observed at higher temperatures and longer shaking time. More than 95% of Ni got adsorbed by the resin at 60°C after 4h, the absorption reached 96% at room temperature after 48h. Co-extraction of the other metals decreased with increasing temperature concluding that ion exchange at temperatures above 40°C is the best method for purification of the swarf in comparison to solvent extraction and cementation.

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1. INTRODUCTION

When steel is being produced and steel products manufactured a waste called “swarf” is generated. This waste contains valuable metals which could be reused. Depending on the type of steel and additives that are included these dusts differ and may contain the elements Fe, Cr, Mo, Mn, Ni, W and Nb. While valuable amounts of these elements go to waste, they also increase the cost of disposal and make it more difficult. Landfills that accept the disposal of the waste charge more due to the content of heavy metals in the dusts. Additional costs come from the pre-treatment of the dust before disposal [1]. If this waste is disposed incorrectly, it might be harmful to the environment [2]. Being able to recover the elements from the swarf will benefit steel production, making it more effective and reducing the cost of wasteful materials. In Sweden, the production of 6 million tonnes of steel results in 2 million tonnes of waste each year [3].

1.1 PURPOSE

The aim of this project is to identify the metals present in the swarf and study if it is possible to purify iron chloride product obtained after leaching with HCl from metal ion impurities such as: Cr, Mn and Ni using selective extraction/purification method. Three different methods: solvent extraction, cementation and ion exchange were tested and compared. Different extractants and their effectiveness were tested. The cementation and ion exchange experiments were done at different conditions, varying the temperature and time in order to see which are the optimal conditions.

The purified iron chloride solution will therefore be used for production of flocculants used in the water purification, ferrous-3-chloride.

1.2 BACKGROUND

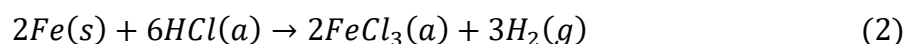
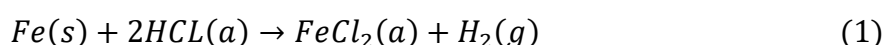
Hydrometallurgy is the technique where metals are being extracted and separated using aqueous chemistry. Previous studies about recovering metals from dusts claim that hydrometallurgical methods are the best approach to treat the dusts due to their advantages over pyrometallurgical processes. The advantages are that they require less energy and are able to handle dusts with small amounts of the desired elements in a more efficient way [3]. These methods are also considered to be more environmentally friendly because they have lower air pollution potential

as well as lower costs [4]. Due to these advantages this project will be carried out using hydrometallurgical techniques.

The stainless steel dusts obtained from the production and manufacturing processes must first be treated before the metals can be recovered. This involves a dissolution process which is usually an addition of a leaching agent [5]. High Pressure Acid Leach (HPAL) and Atmospheric Acid Leach (AAL) where sulfuric acid is used are examples of leaching techniques [6]. The leaching media helps the solid metals in the dust form metal ions soluble in water. Depending on the metals present in the swarf, different pH values affect the dissolution process differently when acids or bases are used as leaching media [7].

Mineral acids like sulphuric-, nitric- or hydrochloric acid can be used in the leaching process. These have been studied previously and proven that sulphuric acid has poor selectivity over Fe. Another alternative is to leach with an alkaline solvent e.g., NaOH which has shown some advantages separating Zn from Fe with a successful recovery. These types of solvents can be applied in Mo leaching and experimenting with different solid to liquid ratios, temperatures, and concentrations of NaOH [8].

Leaching will not be done in this project since the leachate was previously prepared and provided from another project. The provided feed solution for this project had been leached with HCL at 60°C with pH 4 and S:L= 1:20. This gave a 99% pure FeCl₂. When hydrochloric acid is used ferrous- (FeCl₂) and ferric chloride (FeCl₃) as well as hydrogen gas (H₂) are formed [7]. The irreversible reactions can be seen in the formulas below:



The leaching is followed by a purification process and a separation process. This step recovers the desired metals from the leachate and can be achieved through different methods. Separation processes that can be applied are solvent extraction, cementation, and ion exchange.

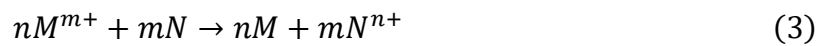
2. THEORY

2.1 CEMENTATION PRINCIPLE

Cementation is a hydrometallurgical method that can be used for purification of the swarf. This method allows the recovery of valuable metals where electrochemical precipitation of the less electro-negative metal occurs, caused by the more electro-negative metal. The precipitant causing the reaction is another metal or metal powder which is being submerged into the leachate solution. Various metals such as Zn, Fe or Al can be used depending on the metals present in the leachate. For example, Zn is more effective for Cu cementation compared to Al and Fe due to its low oxidation potential, hence why Zn is used in leachates containing Cu [9].

Cementation is also called contact reduction meaning that when metal ions come in contact with each other, electron exchange occurs. The electrons from the metal in the leachate solution with the lower nobility are transferred to the solid metal or powder with higher nobility. This happens through diffusion or electrostatic forces [10].

The overall cementation reaction which is a combination of the reduction reaction of the more noble metal and the oxidation reaction of the less noble precipitant can be described by Equation (3) below where (M) represents the more noble metal and (N) is the less noble precipitant [11].



There are many studies focusing on Cu cementation and less on cementation of other metals such as Ni. This study will test cementation of Ni in the swarf solution using an iron plate as a precipitant. The reaction should follow the formula below (Equation 4)[12]:



2.2 ION EXCHANGE PRINCIPLE

Ion exchange is a solid-liquid separation technique where the liquid is the leachate solution containing the valuable metals and the solid is a type of resin. This is a process where ions are exchanged between the leachate which acts as an electrolyte solution and the resin which is the solid phase.

There are different types of ion exchange resins with different functional groups which determine their properties. Cationic resins exchange their cation in their functional group with the cation in the leachate solution, while anionic resins exchange anions instead. Depending on their functional groups, resins can be acidic, basic, or chelating. The four main groups of resins are strongly acidic, strongly basic, weakly acidic and weakly basic [5].

Chelating resins also referred as ligand exchange resins are another subgroup. These types of resins are very effective in solutions containing many different metals, and are selective for Cu(II), Ni(II), Co(II), and Zn(II) [5]. The functional groups in these resins usually contain the atoms nitrogen, sulfur and oxygen, which are able to donate electron pairs. The functional groups usually form bonds between their central ion and the donor ions in the solution. Chelating complexes may be formed and are related to the pH. Botelho *et.al* mentions that the efficiency of metal recovery increases with increasing pH, this is due to the decreased competition of H⁺ ions [6].

The chelating resin Dowex M-4195 has a weakly basic chelating bispicolyl amine (bis(2-pyridylmethyl) amine) functional group and can be seen in Figure 1 [13].

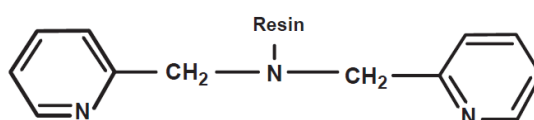


Figure 1. The weakly basic chelating bispicolyl amine (bis(2-pyridylmethyl) amine) functional group of Dowex M-4195

Previous articles focusing on ion exchange with the resin Dowex M-4195 have analysed how the pH, time, metal concentration and temperature affect the Ni(II) adsorption. According to Botelho *et.al* [6] higher temperatures and pH are preferred for Ni(II) adsorption which reaches equilibrium after 4h. However higher pH values are not suitable in solutions containing large amounts of Fe. This is due to the possibility of Fe precipitating with other metals such as Co and Cu in solutions with pH above 2 [6].

2.3 SOLVENT EXTRACTION PRINCIPLE

Solvent extraction is applied to separate compounds from each other using two solvents which are immiscible with each other and result in two layers. One of the layers in solvent extraction should have the properties to dissolve the desired compound while the impurities should be insoluble in the same solvent. The second layer must have the reversed properties which are to solve the impurities and not the desired compound. These properties cause the compounds to travel between the two layers making it possible to separate them. To get a better and a purer result, the extraction can be repeated several times in order to extract as much of the desired element as possible.[14][15]

Having a polar aqueous phase and a non-polar organic phase as solvents, results in two layers because these phases are immiscible with each other. The aqueous solution in this process consists of the valuable metals, free acid, and impurities dissolved in water. The extractant and modifier are dissolved in a diluent or a carrier and present in the organic solution. Commonly used diluents are kerosene and Isopar. The extractant makes it possible for the metals to travel from the aqueous phase to the organic, while the modifier improves the solubility of the metal and minimizes the formation of a third phase between the two layers [14][15].

There are various extractants that can be applied depending on the metal ions which need to be separated since the solvents have different selectivity for each ion. When extracting with aqueous and organic phases there are some factors that affect the extraction process and need to be studied. These factors are the pH of the aqueous phase and the organic to aqueous ratio (O/A). Testing different O/A ratios until equilibrium is achieved will provide an isotherm curve, where the solute concentrations in the organic and aqueous phase are related at constant conditions. The relation between the concentrations is expressed by Equation (5):

$$[M_{(o)}] = f [M_{(a)}] \quad (5)$$

The extraction stage is followed by scrubbing (aka. washing), and stripping. Scrubbing is performed to get a purer metal and is accomplished by using water, dilute acid, or base solution. This stage removes the unwanted ions from the organic solution. To recover the valuable metal collected in the organic solution it must first be stripped from it. Concentrated acid, alkaline, or salt are able to attract the metal from the organic solution and therefore make it possible to recover the final product [14][15].

2.3.1 DISTRIBUTION RATIO AND EXTRACTION PERCENTAGE

During the distribution process of the solutes between the two layers of organic and aqueous phase, they will at some point reach equilibrium. In thermodynamic equilibrium the temperature, pressure and chemical potential in the system are all constant. In that state Nernst's distribution law (Equation (6)) can be used for further calculations, where K_d represents the distribution constant, $[M_{(A)}]$ and $[M_{(B)}]$ represent the concentration of the solute M in each solvent A and B (organic and aqueous phase).

$$K_d = \frac{[M_{(A)}]}{[M_{(B)}]} \quad (6)$$

However, Nernst's law is not ideal and can lead to errors because the conditions in the system cannot be perfect and constant at all time. Thus is the distribution ratio (D) useful when the conditions in a system are not constant [16]. The distribution ratio is calculated using Equation (7), where the total solute concentrations of the organic and the aqueous phase are divided. It should be noted that solution acidity, temperature, flow rate, free ligand, impurities, and other factors affect the distribution ratio.

$$D = \frac{\sum [M_{(org)}]}{\sum [M_{(aq)}]} \quad (7)$$

When the extraction process is complete and the distribution ratio (D) has been calculated, it can be used to evaluate the extraction percentage (% E) shown in Equation (8).

$$\%E = \frac{D}{1 + D} \times 100 \quad (8)$$

Knowing the distribution ratios D for two solutes A and B, the separation factor (SF) can be determined using Equation (9) [15].

$$SF_{\frac{A}{B}} = \frac{D_A}{D_B} \quad (9)$$

With the help of these equations, we are able to perform calculations on the extraction process and therefore construct different diagrams and graphs. These graphs make it easier for us to see how effective the extraction was. Knowing the distribution ratio, extraction percentage and the separation factor we are able to compare the different extractants and parameters to see which one is the most effective one.

2.3.2 EXTRACTING AGENTS

Extracting agents have the property to form a lipophilic complex with the desired metal in the aqueous solution. This means that they turn the metal into a complex that has the ability to dissolve in the organic phase and later be separated [17]. Different extractants and their effectiveness will be tested in this project, these are: Cyanex 600, Cyanex 923, Cyanex 272, D2EHPA, Aliquat 336, Versatic acid and TBP. They all have various properties and selectivity for different elements. The extractants Cyanex 272, Versatic acid, D2EHPA and Cyanex 600 are acidic while TBP, Cyanex 923 and Aliquat 336 are solvating extractants.

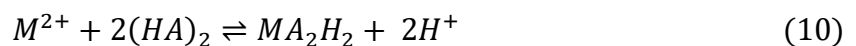
It is important for an extractant to have high selectivity, meaning that the distribution ratio (D) and separation factor (SF) is high, and the valuable metal is being transferred between the phases effectively. However, the metal ion – extractant complex must not be too strong. Being able to regenerate the extractant is a benefit. Stable temperature and thermodynamics are also preferred in the extractant-diluent mixture as well as non-toxicity and non-corrosivity [13].

Extracting with acidic extractants the pH value is of a big importance and should be observed and adjusted during the experiment. The adjustment can be done with concentrated NaOH solution.

2.3.2.1 ACIDIC EXTRACTANTS

Extractant Cyanex 923 is a mixture of four trialkylphosphine oxides and is a transparent mobile liquid. When Cyanex 923 is applied in metal extraction, the liquid works as a solvating extractant. Due to some impurity acids in the extractant, metal reduction may occur [17].

Adding an extracting agent to an aqueous solution is going to cause a decrease in pH which is a result of hydrogen protons being released from the extractant. In the case where D2EHPA (di-(2-ethylhexyl) phosphoric acid) is being used, the extraction mechanism can be written as shown in Equation (10):



The metal is denoted as M while the extractant D2EHPA in the organic phase is HA and MA_2H_2 in the metal-organic complex [14]. This extracting agent is known to be efficient for Fe(III) separation from highly acidic solutions and has shown good results in previous studies. D2EHPA is however not beneficial for separation of Cr(III) due to slow phase separation and small loading capacity. This extractant is often diluted in kerosene [18].

The optimal conditions for Mn extraction with D2EHPA are O:A of 1.25:1, pH 3.25, and 0.5 M D2EHPA which results in 70% of Mn extraction [19].

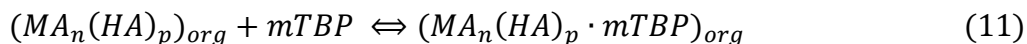
In a study from Hong-Rui Ma it is found that a complete removal of Fe(III) can be achieved with 5 vol% D2EHPA in kerosene and pH of 2.2 [18].

Versatic acids are carboxylic acids and the most commonly used one is called Versatic 10. The extraction mechanism for this type is primarily cation-exchange [16]. This extracting agent is mostly used for Ni recovery.

Cyanex 272 is an effective extractant for Co and Ni separation in solutions containing low amounts of nitrate and no Fe or Mg at all. Equilibrium is reached at pH 5, 1:1 ratio and a temperature of 25°C [20].

2.3.2.2 SOLVATING EXTRACTANTS

TBP (Tributyl phosphate) has shown to be a more effective when mixed with a modifier which can include another extractants. TBP contains a lone electron pair which allows it to be mixed with D2EHPA resulting the extraction mechanism seen in Equation (11). For the reason that D2EHPA is an acidic extractant and TBP has that lone electron pair, mixing them together allows them to form an adduct complex in the organic phase [18]. This mixture has showed to be efficient of Cr(VI) extraction [21].



TBP can also be used along with Versatic acid to improve separation. In those cases, TBP acts as a modifying agent to Versatic acid [15].

Previous studies show that Aliquat 336 has a higher selectivity for Cr(VI) extraction than for Fe(II). This extracting agent is called a basic extractant and for that reason it can only extract anion forms of Cr(VI) and does not work for cation forms of Fe(II). It is also proven that higher concentrations of Aliquat 336 result in higher extraction percentages (%E) [18]. Aliquat 336 is also used for Mo extraction and in a study of Sami Virolainen it is reported that the best selectivity for Mo/Cr is observed in the pH ranges 0.7–2.2 and achieved at the lowest pH [3].

There are no found studies where Cyanex 600 is used as an extracting agent and will be tested in this study.

3. MATERIALS AND METHODS

3.1 PREPARATION OF THE FEED

The dust samples for this project are provided by STENA RECYCLING INTERNATIONAL AB. The preparation of the aqueous solution consists of a leaching process. Leaching the dusts results in an inorganic solution where the metals are dissolved, this solution is later used for the extraction process.

However, leaching will not be performed in this project. The swarf solution was previously prepared as a part of another project and later used as the feed in this project. The dust samples containing 69% Fe, 0.09% Ni, 0.56% Mn and 1.35% Cr had been leached with 5M hydrochloric acid (HCl) for 4 h at 60°C, pH 4 and S:L=1:20 [7]. The composition of the leachate can be seen in Table 1.

Table 1 Composition of the swarf solution used as a feed for the experiments.

Element	Concentration (g/l)
Fe	21.78
Mn	0.15
Ni	0.012

3.2 SOLVENT EXTRACTION TECHNIQUE

Solvent extraction was tested with acidic and solvating extractants to see which technique is more efficient. All organic extractants were first diluted in Isopar L to a desired concentration of 0.5 M or 2M.

Extraction was performed in a small funnel where 4 ml of the organic and aqueous solution respectively were added and mixed for 60 seconds. The pH of the feed was adjusted with sodium hydroxide (5M) and samples were taken from the aqueous phase for different pH values for the acidic extractants, keeping the contact time and temperature the same.

Once the extraction was done, the aqueous solution was studied and analysed in an ICP-OES equipment. The distributed amount of the metals in the organic phase was determined by mass balance calculations and the information gained from the ICP-OES.

Equation (12) expresses the mass balance which was used to determine the amount of the metals in the organic phase expressed by $[M]_{org, out}$.

$$[M]_{aq,in} \times V_{aq,in} + [M]_{org,in} \times V_{org,in} = [M]_{aq,out} \times V_{aq,out} + [M]_{org,out} \times V_{org,out} \quad (12)$$

The concentration of the metal entering the system through the aqueous phase is $[M]_{aq,in}$ and the concentration exiting is $[M]_{aq,out}$. V_{org} and V_{aq} are the volumes of the organic and aqueous phase respectively entering and exiting the system. Finally the $[M]_{org,in}$ stands for the concentration of the metal entering the system through the organic phase, which in this case is 0, because the metals are only present in the aqueous phase when entering the system. The distribution ratio (D) and extraction percentage (%E) were calculated using equations 7 and 8 in chapter 2.3.1.

3.2.1 SOLVENT EXTRACTION WITH ACIDIC EXTRACTANTS

Different pH values were tested for each acidic extractant Versatic acid, D2EHPA, Cyanex 600 and Cyanex 272. Experiments were carried out in room temperature with contact time of 60 seconds and O:A ratio 1:1. The experiments were performed in a separating funnel where 4 ml of aqueous solution was added with a 5000 μ L micropipette and 4 ml of the organic solution was added using a 4 ml glass volumetric pipette. The organic solution containing the extractant was diluted in Isopar L to a concentration of 2M or 0.5M. The first samples were taken after 60 seconds of shaking without any NaOH addition. Shaking was done by hand in a fume hood. Then the pH was increased adding 5 M NaOH with a 200 μ L micropipette and the amount of each addition was noted. The pH was measured with a pH meter after each addition of NaOH and noted. Samples were taken from the aqueous phase and diluted in HNO₃ 100 and 1000 times in 15 ml tubes for the ICP-OES analysis.

3.2.2 SOLVENT EXTRACTION WITH SOLVATING EXTRACTANTS

The solvating extractants TBP, Cyanex 923 and Aliquat 336 were also diluted in Isopar L to a concentration of 2M and only tested in room temperature and contact time of 60 seconds. Parameters were not adjusted, and the experiments were carried out in a similar way to the solvent extraction with the acidic extractants. The same equipment, volumes and leachate solution were used. The pH values were only measured for the leachate feed solution to see if it has changed over time and new samples of the leachate were taken. A sample of the aqueous phase was taken for each extractant and diluted in HNO₃ for the analysis.

3.3 CEMENTATION TECHNIQUE

A thin iron plate was cut into smaller pieces to fit into small glass vials for the cementation experiments. A piece of the plate was previously dissolved in aqua regia and diluted samples were prepared for ICP-OES analysis to see if the plate is pure iron. The analysis did not show any traces of Ni or other metals which meant that the plates were suitable for the cementation experiments.

Each small piece of iron was weighed on a very precise scale before starting the experiment. The plate and 2 ml of the leachate solution were then added into glass vials as seen in Figure C.1 (Appendix) and sealed. The tubes were loaded into a shaking machine (IKA Vibrax VXR basic) with a temperature adjustment. Cementation was done in triplicates for each temperature where the tested temperatures were 25°C, 40°C, 60°C and the shaking speed was set to 300 rpm. After 3h of shaking the tubes were taken out of the shaking machine and 100µl samples were diluted in 9.90 ml HNO₃. The tubes were then sealed again and returned back into the machine for another 3h and taken out again as seen in Figure C.2 (Appendix). When the experiment was complete after a total of 6h, samples were taken again and the iron plates were taken out of the vials with tweezers, dried gently with some tissue paper and weighed again, the difference between the iron plate before and after the experiments can be seen in Figure C.3 (Appendix). The weights before and after the experiments were noted and are presented in Table C.1 (Appendix).

3.4 ION EXCHANGE TECHNIQUE

The resin used for the ion exchange experiments was Dowex M-4195. Before starting the experiment, the resin was prepared as instructed by a study of Silva [22] by washing and drying in order to remove any traces of other metals. The washing was done by first adjusting the pH of the distilled water to 4. The adjustment was done by adding HCl to the water and monitoring the pH with a pH meter until it was as close to 4 as possible. The resin was transferred into three glass centrifuge vials with volumes 40 ml, and weighed to 2g in a fume hood. 10 ml of the distilled water was added to the vials using a 5 ml micropipette. The vials were sealed and placed into a shaking machine to shake for 5h at 150 rpm and 25°C. Figure D.1 in the appendix shows the vials with resin after being washed. The vials were then opened in a fume hood and the water in the vials was drained as much as possible using a funnel and a filter paper. The resin was then left to dry in the fume hood for at least 48h.

The experiments were carried out in triplicates using 40 ml glass vials. Dry resin (0.25 g) was first let to swell for 1 h by adding 1ml of the previously prepared distilled water. The water was then sucked out with a micropipette without getting any resin in. Filtering the water resulted in a loss of resin because small amounts of resin got stuck to the filter paper, which is why filter paper was not used. When the resin was ready to use 2.5 ml leachate was added into the vials containing the swelled resin and sealed and let to shake in the shaking machine for a total of 4h. Figure D.2 in appendix shows the sealed vials ready to be loaded into the shaking machine. Samples were taken each hour and the procedure was repeated at 25°C, 40°C and 60°C. The vials from the 25°C experiments were left in the fume hood for a total of 48 hours and samples were taken after 24h and 48h. Samples were then prepared for the ICP-OES analysis preparing 1:50, 1:100 and 1:1000 dilutions.

The percentage of ion adsorption was calculated with Equation (13) where the concentration of the specific metal ion at $t=0$ (C_0) is the concentration of the metal in the feed and (C_t) is the concentration after a certain time [6].

$$\%S = \frac{C_0 - C_t}{C_0} \times 100\% \quad (13)$$

When the adsorption experiments were done, the resin was separated from the leachate and washed with distilled water. The washing stage was followed by a stripping stage where 1 ml of 2M sulphuric acid was added to the resin and mixed in a shaking machine at 25°C for 6 hours.

4. RESULTS AND DISCUSSION

4.1 SOLVENT EXTRACTION

All extractants for the solvent extraction experiments were first tested and analysed to see how efficient they are. Depending on the first testing results some extractants that performed better were tested again while others were excluded from further experiments. Due to the feed solution changing its colour and iron oxides forming, a new feed with a different composition and pH was used for the last experiments. The composition of the first feed which was used for the acidic extractants can be seen in Table 1.

4.1.1 ACIDIC EXTRACTANTS

The first extractant to be tested was D2EHPA (0.5M) where the pH was increased up to 2.4 before a third phase and precipitation occurred. Precipitation occurred at pH=2.4 when Cyanex 600 (0.5M) was tested as well.

In order to get better results and more samples for the ICP-OES analysis, the extractant concentration was increased to 2 M for all acidic extractants (Cyanex 600, Versatic acid, Cyanex 272 and D2EHPA). The procedure for the experiments was the same keeping the contact time at 60 seconds in room temperature and increasing the pH with 5M NaOH. A third phase occurred again when extracting with Versatic acid and adding NaOH to increase the pH. A sample was taken from the aqueous phase with a pH close to 2.

The starting pH of the feed after the addition of D2EHPA without the addition of NaOH was 0.5. The pH was then increased, and samples were taken for pH $\approx$ 1, 2 and 3. Samples were taken around those pH values for each extractant and analysed with ICP-OES, the results were investigated, and new tests were performed with the extractants that gave better results.

The different acidic extractants had varying efficiency on the different metal ions. Because the acidic extractants had high pH sensitivity and the leachate had a low pH value, some of the extractants were not suitable. Cyanex 600 did not allow any pH changes without any precipitation or third phase forming resulting in only one sample at pH $\approx$ 2. Versatic acid did allow some pH adjustments, but metals were only extracted at pH $\approx$ 4. The results for these two extractants can be observed in Figure 2:

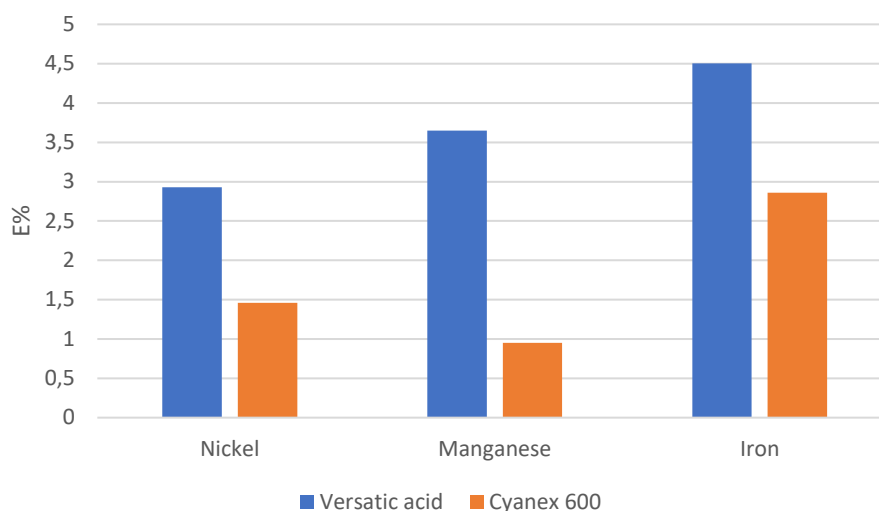


Figure 2 Extraction percentage for each metal in the feed after extracting with Versatic acid 2M at pH=3.8 and Cyanex 600 0.5M at pH= 1.9. Conditions: room temperature, 60 s of shaking time.

Both Versatic acid and Cyanex 600 resulted in low Fe extraction and coextraction of Ni and Mn. Versatic acid extracted the highest amounts of Fe at 4,5%, but it also co-extracted the highest amounts of Ni and Mn at ~3,5% and ~3% respectively (Figure 2). Previous study suggests that successful Ni, Co or Fe(II) separation can be achieved at pH= 7.0 using 20% Versatic 10 along with the modifier TBP (5%). It was found that higher %E are reached at pH above 5 and increasing the temperature to 40°C prevents the formation of a third phase [23]. All solvent extraction experiments in this project were performed in room temperature without any modifiers which explains the formation of a third phase and precipitation when extracting with Versatic acid.

Increasing the pH did however cause the organic phase to turn a darker colour after each NaOH addition, Figure B.1 in appendix shows the colour transition of the organic phase. Samples were taken from pH 2 to 4 for ICP-OES analysis, which showed that metals were only extracted at pH= 3.3 and 3.8. Lower pH values showed no signs of extraction. This indicates that Versatic acid is not suitable for the feed solution due to its low pH value, since it can't be increased above 4 without precipitation occurring. Further tests were therefore not carried out with Versatic acid.

Smaller percentages of coextraction were observed when Cyanex 600 was tested with a concentration of 0.5M which resulted ~3% Fe extraction and 1.5% Ni and 1% Mn extraction. Due to the low extraction percentages and high amounts of co-extraction as well as the difficulties varying the pH no further tests were carried out with Cyanex 600.

Better results were achieved by Cyanex 272 and D2EHPA where the extraction percentage for Fe reached 45% (Figure 3 c)). Several tests were carried out using these two extracting agents at different pH values. The extraction percentages were determined after mass balance calculations for the organic phase. The best results obtained from these experiments for each metal are summarized in Figures 3 a)-c) which demonstrate the correlation between the pH and %E. The vertical error bars in the graphs represent the standard deviation from different tests with D2EHPA. Extraction could not be achieved at identical pH values for both extractants which is why the average pH was plotted in the graph where the horizontal error bars represent the standard deviation.

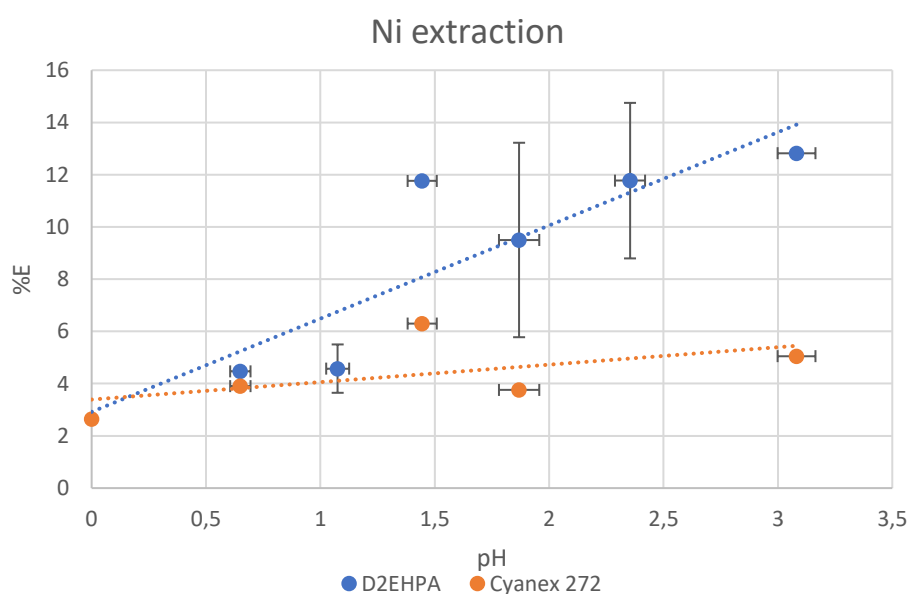


Figure 3 a) Extraction percentage (%E) for Ni using Cyanex 272 and D2EHPA with a concentration of 2M at different pH and shaking time of 60s at room temperature. Data from Table B.2 and B.3 (Appendix).

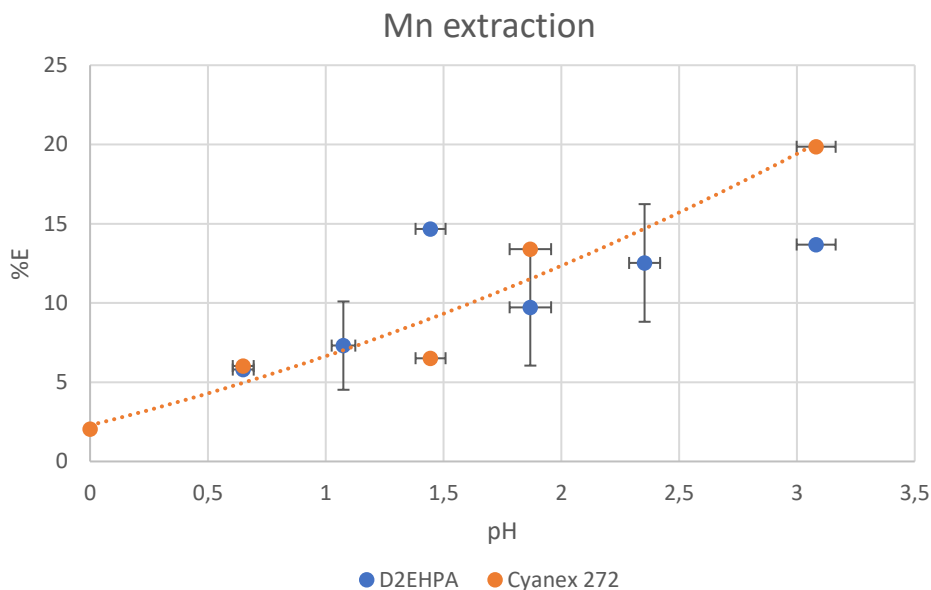


Figure 3 b) Extraction percentage (%E) for Mn using Cyanex 272 and D2EHPA with a concentration of 2M at different pH and shaking time of 60s at room temperature. Data from Table B.2 and B.3 (Appendix).

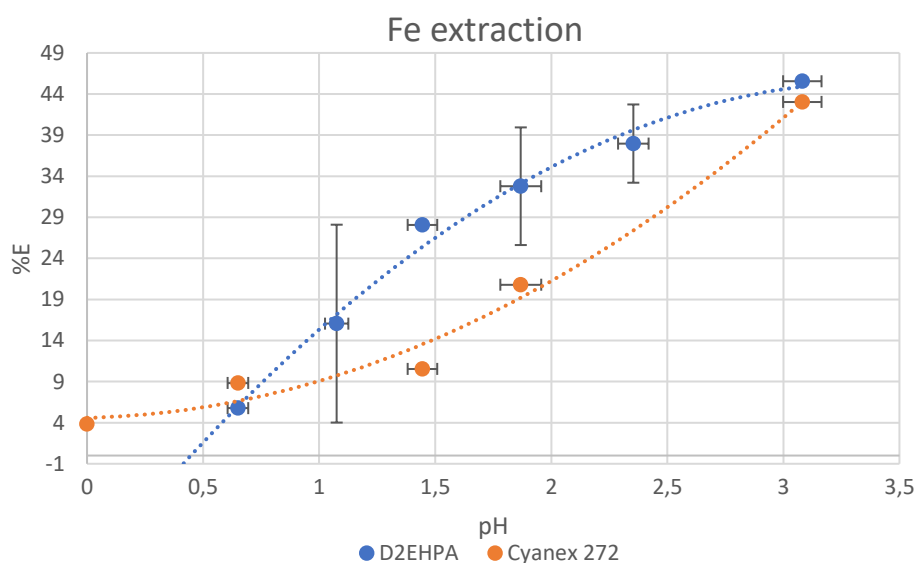


Figure 3 c) Extraction percentage (%E) for Fe using Cyanex 272 and D2EHPA with a concentration of 2M at different pH and shaking time of 60s at room temperature. Data from Table B.2 and B.3 (Appendix).

The extraction pattern for Fe and Mn obtained from D2EHPA and Cyanex 272 in Figures 3 b) and c) is seen to be very similar. It was found that the %E for Fe and Mn increases almost linearly when the pH is increased. The extraction of Ni seems to be increasing significantly with the pH (Figure 3 a)) when D2EHPA is used, the increase is however insignificant when Cyanex 272 is used instead. The extracted amount of Ni stays between 2.5 and 6% for Cyanex

272 while it reaches ~13% when D2EHPA is used. Comparing figures 3a) – c) it can be concluded that Cyanex 272 is more selective and extracts more Fe and Mn leaving most of the Ni behind.

Most Fe was extracted with D2EHPA which was expected since previous studies and Ma *et.al* [18] had mentioned that this extracting agent is known to be efficient for Fe(III) separation from highly acidic solutions.

4.1.2 SOLVATING EXTRACTANTS

The experiments with the solvating extractants were performed with the new feed solution due to the old one changing its colour and composition. The pH of the new feed is 0.5 and its composition is presented in Table 2.

Table 2 Composition of the feed solution used in the experiments with the solvating extractants.

Element	Concentration (g/l)
Fe	21.33
Mn	0.16
Ni	0.014

The solvating extractant Aliquat 336 did not extract any of the metals and was therefore not tested again. A study from Ma *et. al* [18] had stated that Aliquat 336 is an inefficient extractant for cation forms of Fe(II).

The extracting agent TBP did not perform good and almost only 0% of the metals were extracted which can be seen in Figure 4. The cause of this is the lone electron pair that TBP has which allows it to be mixed with other acidic extractants. Previous study from Zhang *et al* [15] mentions that mixing TBP with D2EHPA or Versatic acid improves separation and acts as a modifying agent. Because the extractant was used on its own, extraction did not occur.

Cyanex 923 did successfully extract 14% Fe with minimal Mn co-extraction and 0% Ni. The results obtained from these experiments are presented in Figure 4.

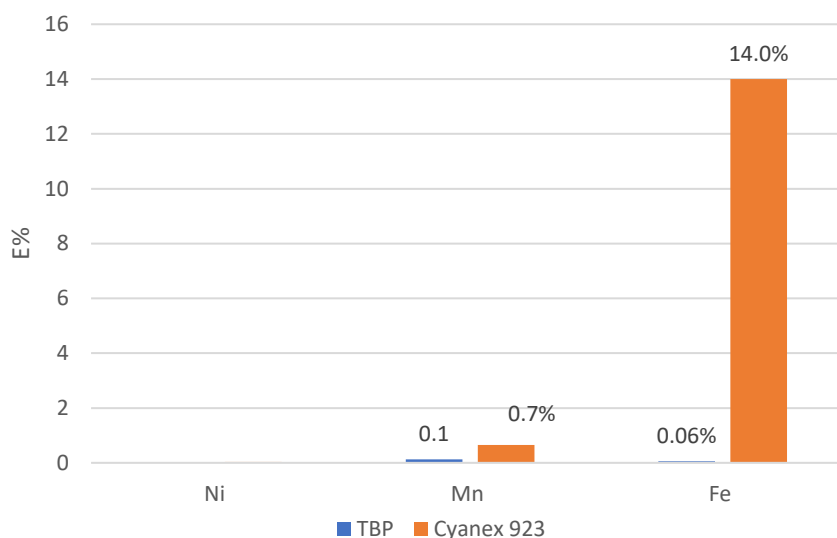


Figure 4 Solvent extraction with the solvating extractants TBP and Cyanex 923. Conditions: room temperature, contact time: 60s

The overall low extraction percentages may be a cause by the diluent Isopar L used in the experiments. Most previous studies where these extracting agents had been used and successfully extracted metals the diluent which was used was kerosene.

4.2 CEMENTATION

The use of an iron plate for cementation was an inefficient approach for purification of the swarf solution. There was no significant change in metal concentration before and after the experiments, which indicates that none of the metals reacted with the iron plate at the tested temperatures and time. However, a very small amount of Ni did get extracted from the solution at 60°C after 6h indicating that higher temperature and longer contact time may give better results. Autoclaves are known to increase the reaction temperature and reaction rate. This technique can be used to separate more nickel at temperatures above 110° C [24].

The highest extraction percentage achieved at 60 °C after 6h was $\approx 5\%$ of Ni as seen in Figure 5.

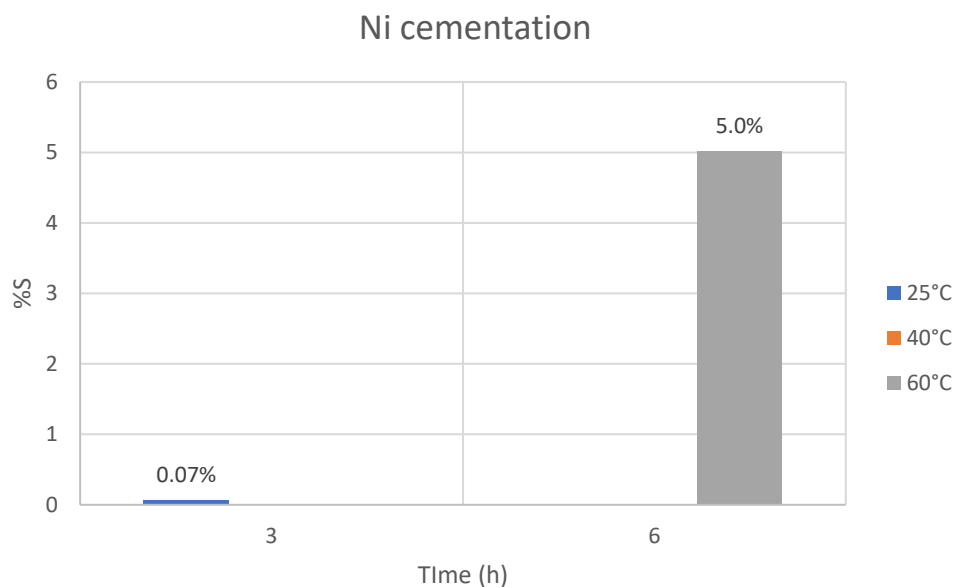


Figure 5 Cementation of Ni using an iron plate with shaking speed of 300 rpm for 3h and 6h at different temperatures.

A significant increase in Fe concentration was observed after the cementation which is an indication of the iron plate dissolving in the solution. This was confirmed by weighing the iron plate and discovering that the mass of the iron plates had decreased. The decrease of the mass and increase of the concentration had risen with the temperature and can be seen in figures 6 and 7. The error bars in the graphs represent the standard deviation of the triplicates.

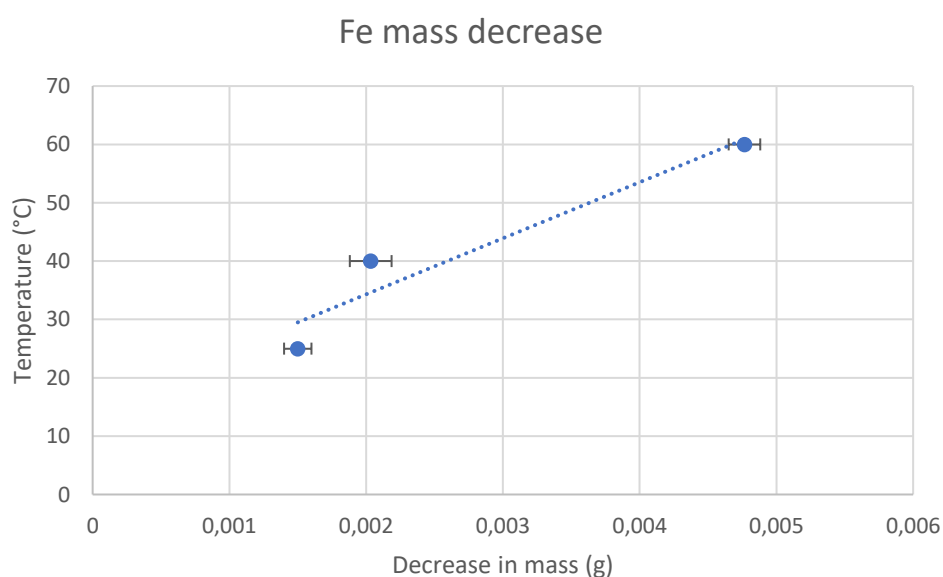


Figure 6 The mass decrease of the iron plate after the cementation in correlation to the temperature with the conditions: shaking speed of 300 rpm and shaking time 6h. Data from Table C.1 (appendix).

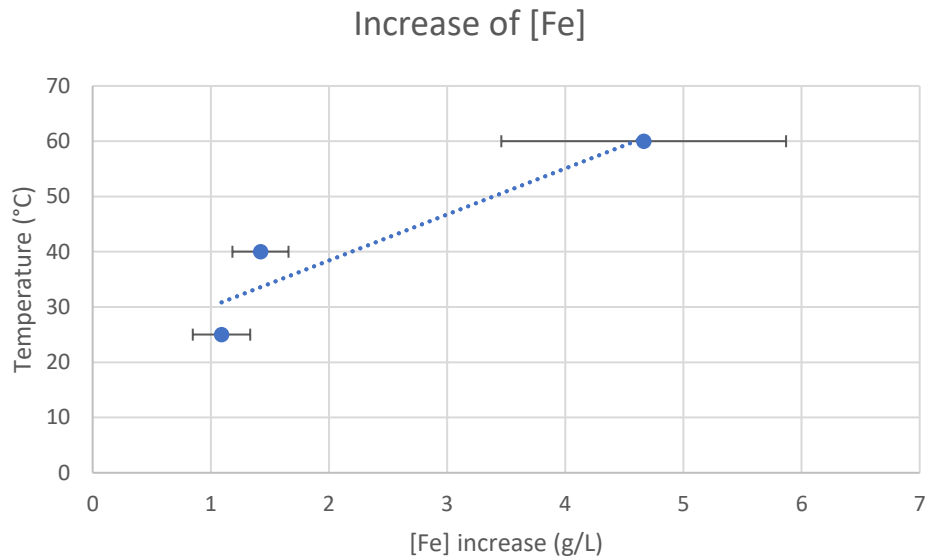


Figure 7 The increase of Fe concentration in the feed solution after the cementation experiments in correlation to the temperature. Data from Table C.1 (appendix).

It can be seen that the two graphs are very similar, and the Fe increase in Figure 6 in the solution is mainly caused by the iron plate dissolving in the acidic feed. Since the iron plate dissolves it results in a decrease in mass which is explained by Figure 7.

When the plate dissolves in the leachate it contaminates it which can be seen in Figure C.2 (Appendix) where the feed solution in the vials has turned an orange colour. The iron plate did also change in the process, Figure C.3 in appendix shows that it has lost its shine and now has rough edges.

4.3 ION EXCHANGE

Dowex M-4195 successfully adsorbed Ni from the swarf solution leaving the other metals behind. Over 85% of the Ni in the solution got adsorbed withing the first hour. Higher temperatures and longer contact times resulted in higher extraction percentages of Ni. The highest extraction percentage of 95.5% was reached after 4h of shaking at 60°C. Figure 8 shows the correlation between absorption percentage of Ni and the time.

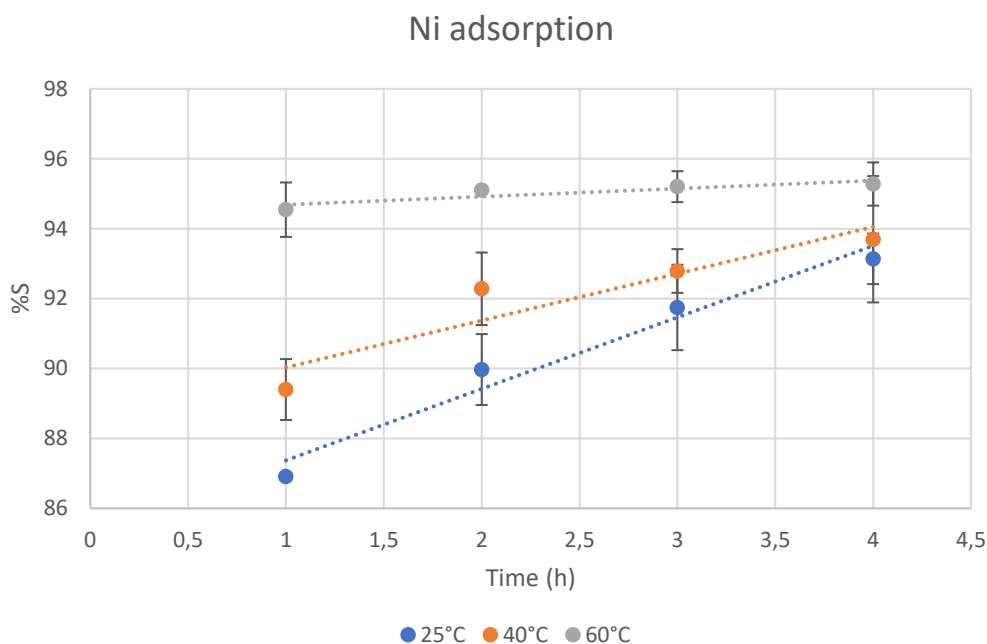


Figure 8 Correlation between time and adsorbed amount of Ni at different temperatures. Data from Table D.1 (appendix).

The graph (Figure 8) shows very clearly that higher temperatures remove more Ni and equilibrium is reached almost immediately at 60°C. The adsorption rate is faster at lower temperatures, however >93% adsorption percentages are reached after 4h at all temperatures. Even at the lowest temperature of 25°C, 87% of the Ni is adsorbed within the first hour of the experiment indicating that the resin is very effective for Ni separation from the leachate.

It was noted that the samples which were left in the fume hood for 48h at room temperature resulted in even higher Ni adsorption, indicating that the extraction percentage increases potentially with the time as seen in Figure 9 where the maximum of 96.6 % is reached after 48h. Almost the same amount is separated after 4h at 60°C.

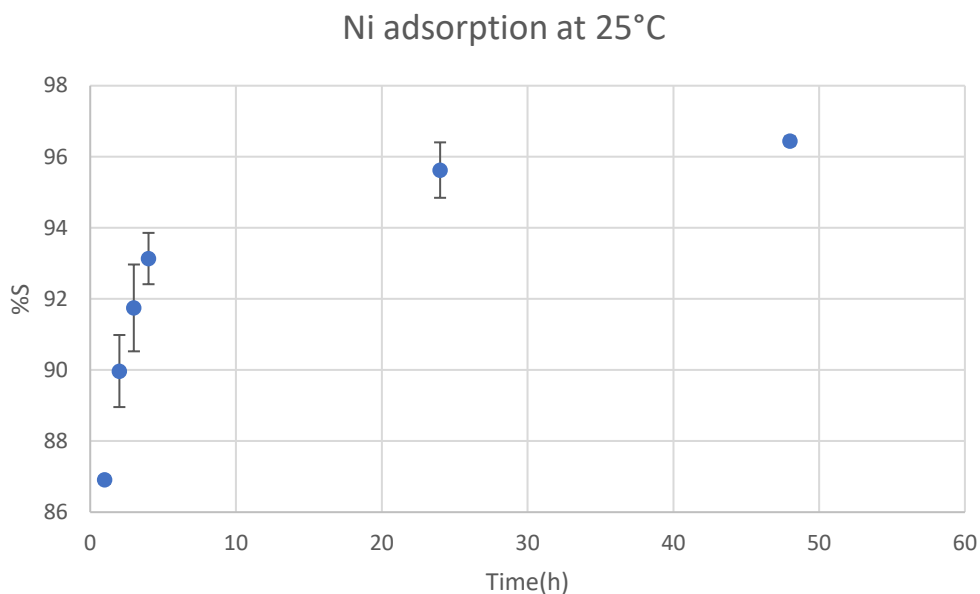


Figure 9 Ni adsorption at room temperature for a total of 48h.

Between 11% and 14.4 % of Mn did also get adsorbed of the resin at room temperature, at 40°C and at 60°C the amount was significantly lower barely reaching 2%.

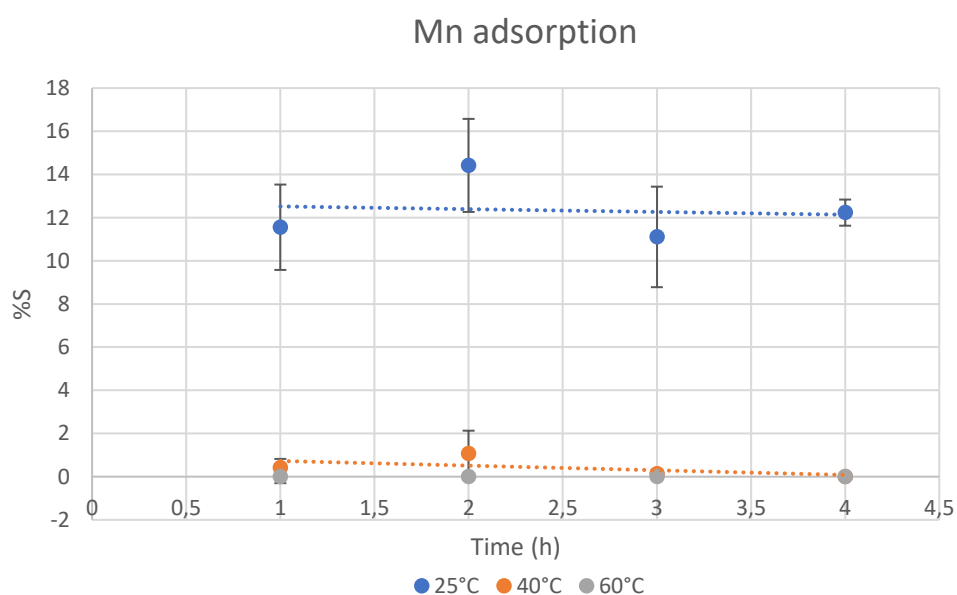


Figure 10 Mn adsorption at different temperatures and time with the constant shaking speed of 300 rpm. Data from Table D.2 (appendix).

Figure 10 shows that higher temperatures decreased the adsorption of Mn into the resin resulting in a successful Mn/Ni separation. Temperatures above 40°C are preferred for the separation of Ni in the swarf solution. Similar statements were mentioned by Botelho [5] where Dowex M-

4195 shows its selectivity for Ni(II) adsorption with the optimal parameters of pH below 2 and high temperatures, equilibrium is reached after 4h.

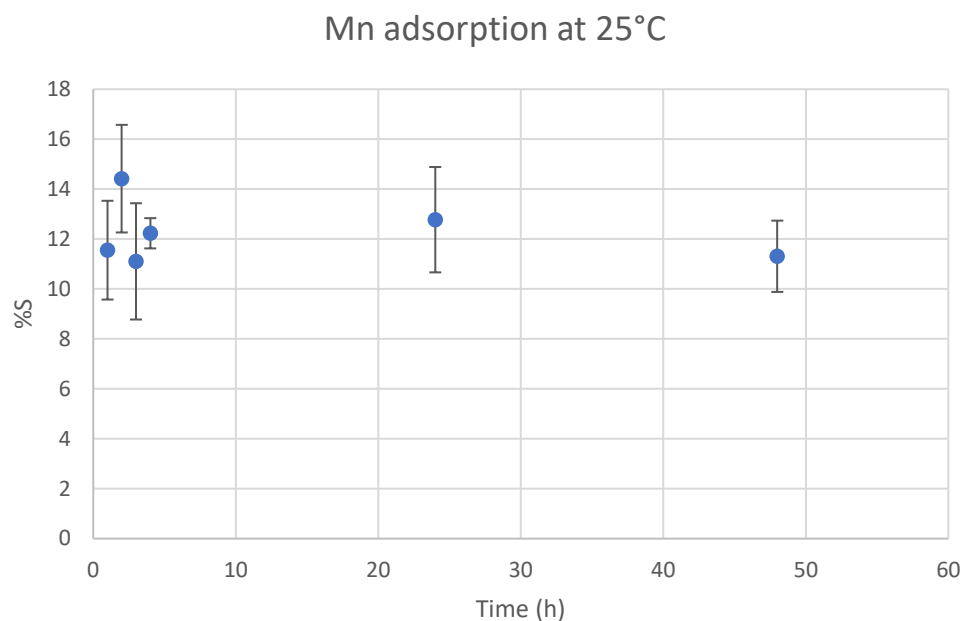


Figure 11 Mn adsorption after 48h in room temperature. Data from Table D.2 (appendix).

The absorption of Mn from the feed to the resin did not exceed 14.4 % at room temperature, which is shown in Figure 11 where the error bars represent the standard deviation of the triplicates. The adsorbed amount after 48h is seen to be slightly lower than at 24h, which could indicate desorption of Mn.

The Fe concentration after the ion exchange experiments had slightly increased, which could be caused by Fe(III) formation or improper wash of the resin. Two studies from Botelho *et.al* claim that a high presence of Fe(III) in the solution will cause precipitation. To avoid that Fe(III) can be reduced to Fe(II) resulting in higher adsorption percentages of the other metals [5] [6].

The last step of the purification process was stripping and the results from this step are presented in Table 3.

Table 3 Metal concentration after the stripping procedure.

Sample	[Ni] (mg/l)	[Mn] (mg/l)	[Fe] (mg/l)
25	0.137	0.016	6.00
40	0.137	0.013	7.10
60	0.117	0.037	11.73

Stripping was done by first washing the resin containing the adsorbed metals with water and then stripping it with H₂SO₄. Table 3 shows how much of each metal was desorbed from the resin. The results from the stripping steps show that some Fe did get adsorbed by the resin as well, which could not be seen by the previous results since the Fe concentration had increased. However, Fe adsorption seems to be lower at lower temperatures.

The amount of Ni which got adsorbed at the different temperatures does not differ much from the previous results, considering that all temperatures reached almost the same extraction percentages after 4h. It should be also noted that the stripping step was not done immediately after the ion exchange experiments, which may have caused the composition of the leachate in the vials to change. This may also have given the resin more time to adsorb some of the other metals as well explaining the traces of Fe.

5. CONCLUSION

After testing the three different methods: solvent extraction, cementation, and ion exchange for purification of the swarf solution, it can be concluded that the best results were obtained from the ion exchange experiments.

The resin Dowex M-4195 resulted in a successful Ni separation and extracted ~95% of the Ni in the feed leaving Fe and Mn behind. The optimal parameters for these experiments were found to be temperatures above 40°C and shaking time of 4h. Higher amounts of Ni adsorption may be reached after a longer time at temperatures above 60°C. Temperatures below 40°C are not preferred since Mn co-extraction and the time needed for the adsorption of Ni to reach its equilibrium increases. The results from the stripping stage showed that there were some traces of Fe and Mn in the resin. This should be investigated more in order to see if the Fe and Mn traces were caused by improper washing of the resin before the experiments or if they did get adsorbed from the feed.

Coextraction was a big issue for solvent extraction with the acidic extracting agents. The extractants that worked best were D2EHPA and Cyanex 272 which reached a maximum of 45.6% and 43.0% Fe extraction. However almost 14% of Ni and 15% of Mn were coextracted with D2EHPA and 6% and 20% of the same metals were co-extracted with Cyanex 272. Indicating that separation was not very successful.

The solvating extractants gave even lower %E for Fe but the results showed less co-extraction of the other metals. The highest extraction percentage was gained from Cyanex 923. This extracting agent removed 14% of the Fe from the feed and almost 0% co-extraction of Mn and Ni was observed, indicating a more successful separation of the metals.

Cementation with an iron plate was not a successful approach for purification of the swarf. The analysis showed minimal amounts of Ni cementation at 60°C. However, an increase of Fe concentration and decrease in the mass of the plate was observed, indicating that the iron plate dissolved in the leachate and increased the Fe concentration. This resulted in a contaminated feed solution and failed experiments.

Comparing all the results from the three methods it can be concluded that the best route for purification of the swarf solution is the ion exchange technique with the chelating resin Dowex M-4195.

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APPENDIX

A. SAMPLE ANALYSIS

When the experiment is complete and samples from solvent extraction and cementation are prepared, they will be analysed to see how much of the metal is present in those samples.

The analysis can then be done using equipment such as ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) and ICP-MS (Inductively Coupled Plasma Mass Spectrometry). ICP-OES equipment uses hot plasma which the liquid sample passes through where the atoms and ions emit light due to excitation. The wavelength of the emitted light is therefore captured and separated which at the end provides a spectrum. The information provided from the ICP-OES equipment can be studied to identify each element in the sample as well as their concentration and quantity. The ICP-MS equipment which operates similarly but uses a mass spectrometer instead of optical emission is known to be more precise with low concentrations [25].

Samples collected from the solvent extraction, cementation and ion exchange experiments were diluted with 0.5 M HNO_3 50, 100 and 1000 times for ICP-OES analysis with Thermo Fisher, iCAP 6000. The 1:50 dilutions were prepared by taking 100 μl sample and adding 4.9 ml 0.5 M HNO_3 with a micropipette, for the 1:100 dilutions 9.9 ml 0.5 M HNO_3 was added instead and for the 1:1000 dilutions 1ml of the 1:100 diluted samples was taken and 9 ml HNO_3 was added to it. Standard solutions containing 0 ppm, 5 ppm, 10 ppm and 20 ppm of the studied elements Fe, Cr, Ni and Mn were prepared for calibration of the ICP-OES equipment. The samples were then placed on the ICP-OES racks for the analysis starting with the lowest concentration of 1:1000 dilution to the highest 1:50 dilution. Suitable wavelengths were chosen for the analysis of each element to avoid interference. Suitable wavelengths for each element in this case were: 257.610 for Mn, 231.604 for Ni and 238.204 for Fe. All metals were measured with Aqueous-Radial-iFR. Data was collected from the analysis for each sample with the concentration of each element in ppm. The collected data was processed, and calculations were performed by only using concentrations within the calibration curve (0 ppm – 20 ppm). Microsoft excel was used for all the calculations and plots.

B. SOLVENT EXTRACTION DATA

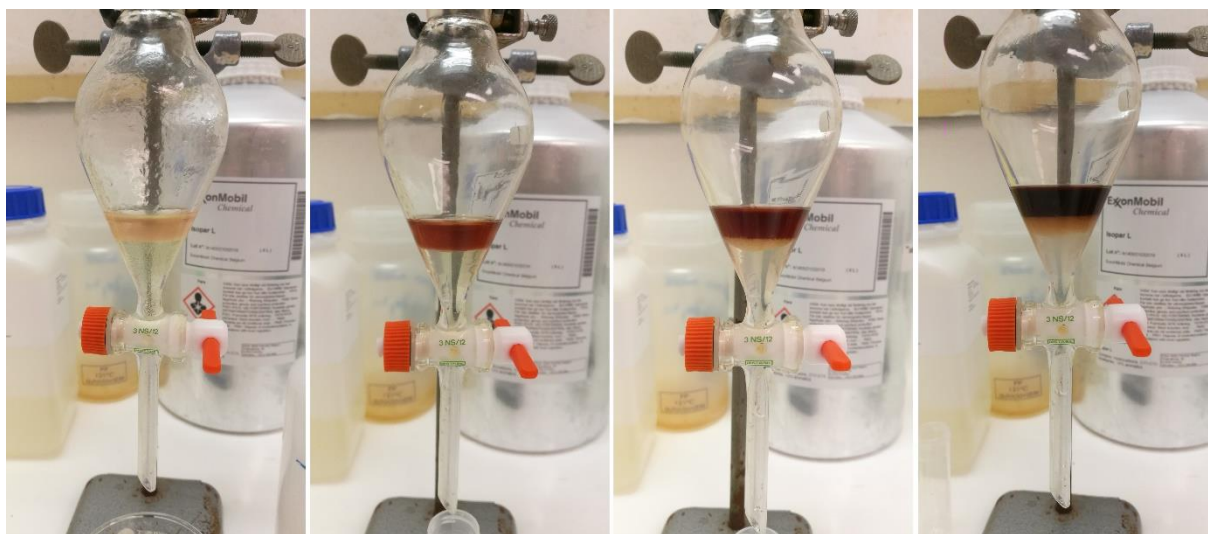


Figure B.1 Solvent extraction stages with 2M Versatic acid after each addition of NaOH.

Table B.1 Samples from all solvent extraction experiments using different acidic extracting agents and adjusting the pH, performed in room temperature with a contact time of 60 seconds. The samples were diluted to 1:100 and 1:1000 ratio in HNO_3 for the ICP-OES analysis resulting in 26 samples in total.

Extractant	Concentration (M)	pH	NaOH addition (μl)
D2EHPA	0.5	2.0	200
Cyanex 600	0.5	1.9	50
Versatic 10	2	1.8	30
D2EHPA	2	1.1	250
D2EHPA	2	2.0	325
D2EHPA	2	3.1	425
Cyanex 600	2	1.4	0
Versatic 10	2	1.9	0
Versatic 10	2	3.3	50
Versatic 10	2	3.8	70
D2EHPA	2	1.2	0
D2EHPA	2	1.8	270
D2EHPA	2	2.4	420
Cyanex 272	2	0.6	0
Cyanex 272	2	1.8	150

Cyanex 272	2	1.5	200
Cyanex 272	2	3.0	250

Table B.2 Extraction percentage (%E) for each element in the swarf solution after solvent extraction with D2EHPA with concentration of 2M at room temperature and contact time 60s.

pH avg.	%E (Ni)	%E (Mn)	%E (Fe)
0.7	4.47	5.80	5.77
STD 0.04	0	0	0
1.1	4.57	7.31	16.06
STD 0.05	0.93	2.79	12.04
1.5	11.76	14.68	28.07
STD 0.06	0	0	0
1.9	9.50	9.73	32.78
STD 0.09	3.72	3.68	7.16
2.4	11.77	12.52	37.97
STD 0.07	2.98	3.71	4.76
3.1	12.82	13.69	45.55
STD 0.08	0	0	0

Table B.3 Extraction percentage (%E) for each element in the swarf solution after solvent extraction with Cyanex 272 with concentration of 2M at room temperature and contact time 60s

pH avg.	%E (Ni)	%E (Mn)	%E (Fe)
0	2.64	2.04	3.83
0.7	3.90	6.02	8.84
1.5	6.30	6.51	10.54
1.9	3.76	13.39	20.79
3.1	5.05	19.85	43.04

C. CEMENTATION DATA

Table C.1 *Weights of the iron plates in the vials before and after the experiment and the decrease in mass and increase in Fe concentration in the feed solution.*

Sample	Temperature (°C)	Weight of plate at start (g)	Weight of plate at end (g)	[Fe] g/l after 6h	Mass decrease (g)	[Fe] increase (g/l)
1 (a)	25	0.024	0.022	22.19	0.002	1.371
1 (b)	25	0.016	0.015	21.77	0.001	0.955
1 (c)	25	0.023	0.021	21.76	0.002	0.946
2 (a)	40	0.022	0.019	22.12	0.002	1.303
2 (b)	40	0.019	0.017	22.08	0.002	1.266
2 (c)	40	0.023	0.021	22.51	0.002	1.694
3 (a)	60	0.016	0.011	24.72	0.005	3.903
3 (b)	60	0.018	0.013	24.85	0.005	4.036
3 (c)	60	0.024	0.019	26.87	0.005	6.053

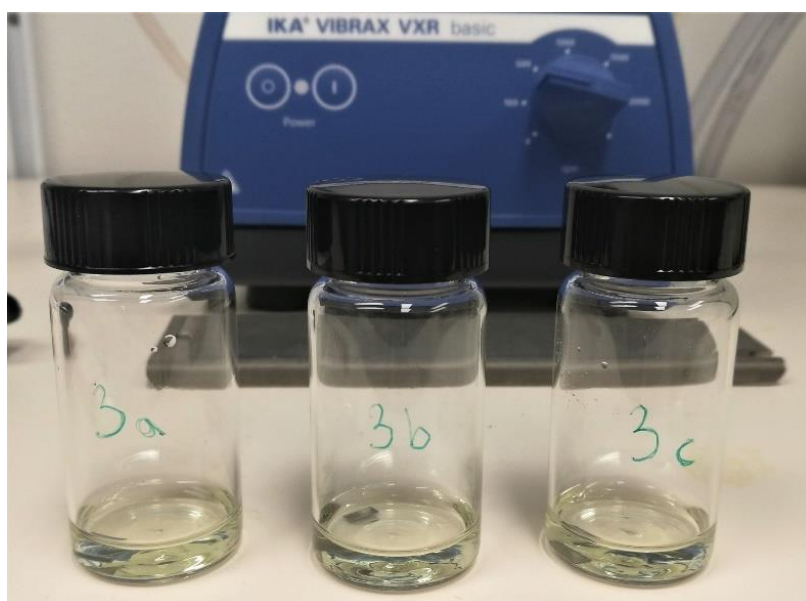


Figure C.1 Glass vials containing 2ml of the swarf solution and a piece of iron plate ready to be loaded into the shaking machine.

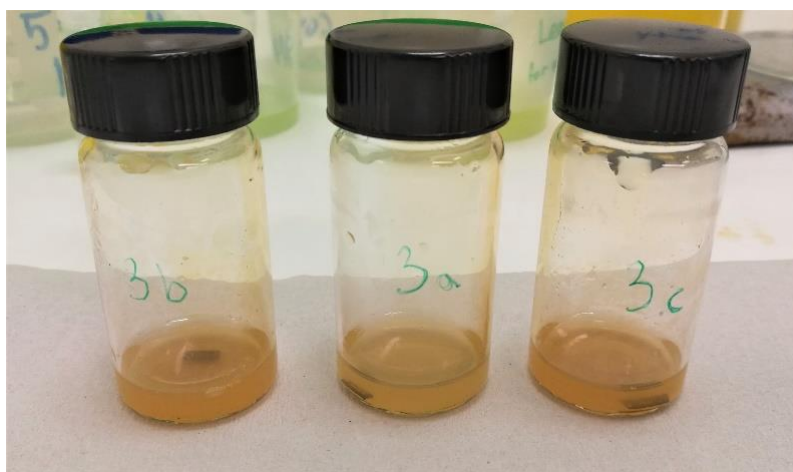


Figure C.2 The glass vials containing the iron plate and swarf solution taken out of the shaking machine after 6h at 60°C.



Figure C.3 An iron plate used in a cementation experiment before (left) and after (right) the procedure.

D. ION EXCHANGE DATA

Table D.1 Adsorption of Ni at different temperature and time

Time (h)	Ni adsorption (%)		
	25°C	40°C	60°C
1	86.91	89.40	94.54
STD ($\pm$)	0.11	0.87	0.78
2	89.97	92.28	95.10
STD ($\pm$)	1.01	1.04	0.01
3	91.75	92.79	95.20
STD ($\pm$)	1.22	0.62	0.44
4	93.14	93.70	95.28
STD ($\pm$)	0.72	1.81	0.62
24	95.63	—	—
STD ($\pm$)	0.78		
48	96.44	—	—
STD ($\pm$)	0.12		

Table D.2 Adsorption of Mn at different temperature and time

Time (h)	Mn adsorption (%)		
	25°C	40°C	60°C
1	11.55	0.41	0
STD (±)	1.98	0.71	0
2	14.42	1.07	0
STD (±)	2.16	0.98	0
3	11.11	0.14	0
STD (±)	2.33	0.24	0
4	12.23	0	0
STD (±)	0.61	0	0
24	12.78	—	—
STD (±)	2.11		
48	11.31	—	—
STD (±)	1.43		

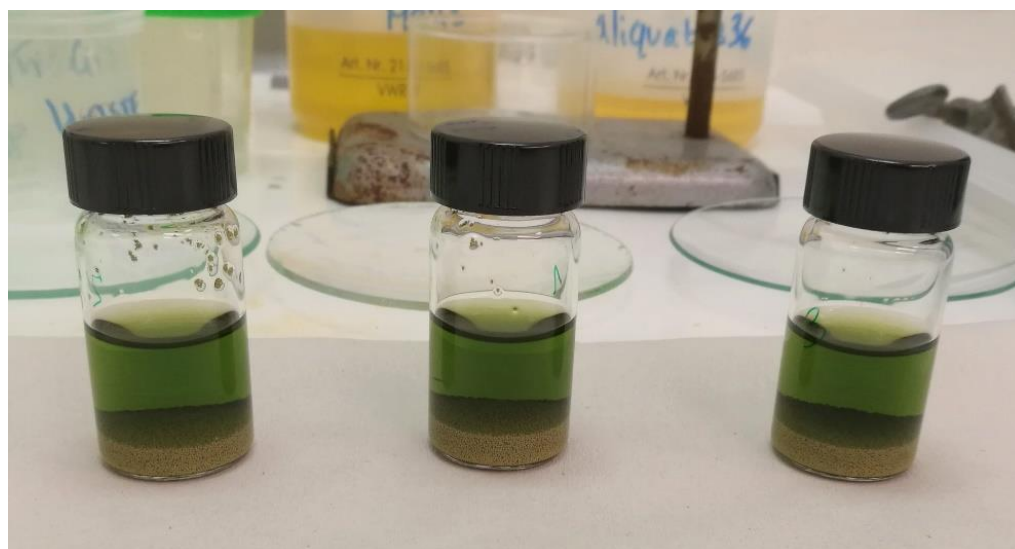


Figure D.1 The vials containing the washed resin with water, taken out of the shaking machine after the washing stage for 5h.

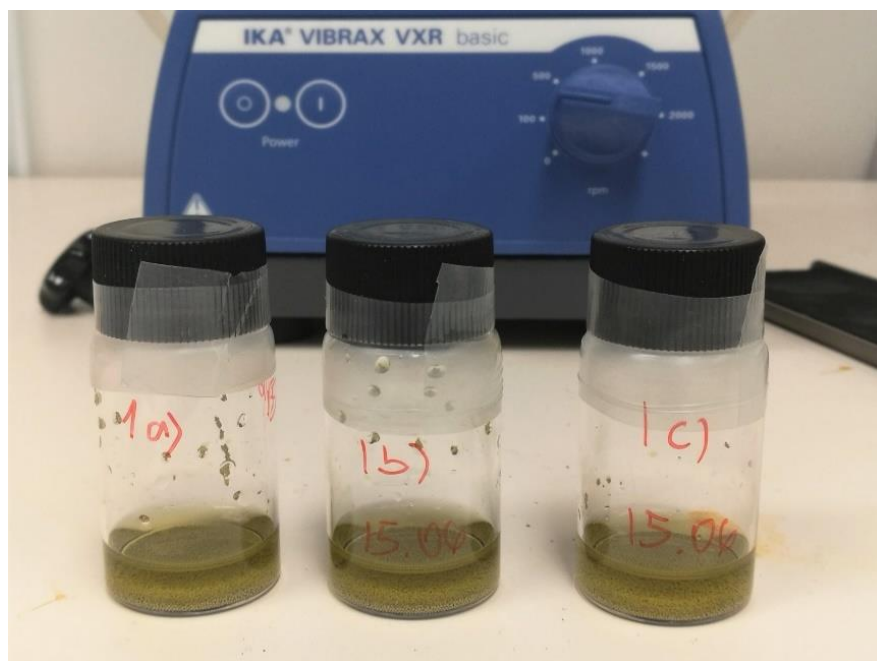


Figure D.2 Glass vials containing 2.5 ml of the swarf solution and 0.25g of washed and dried Dowex M-4195 resin, sealed ready to be loaded into the shaking machine