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Master in Chemical Engineering

Environmental Protection Technologies

Oxidative Leaching of metals from electronic waste with solutions based on quaternary ammonium salts

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Para Pai e Mãe

“One can pay back the loan of gold, but one dies forever in debt to those who are kind”

Malayan Proverb

Acknowledgements

I could not end this Project without saying my thanks... This was a remarkable experience that I believe has made me grown deeply. I must say that I return home, although with the same values, changed... knowing that there's still so much more to learn.

First of all, I've to say thanks to my father and for all his support. Without him, all of this would have been impossible to achieve. A big "thank you" to my mother and sister that have given me the strength to carry on.

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Abstract

The treatment of electric and electronic waste (WEEE) is a problem which receives ever more attention. An inadequate treatment results in harmful products ending up in the environment.

This project intends to investigate the possibilities of an alternative route for recycling of metals from printed circuit boards (PCBs) obtained from rejected computers. The process is based on aqueous solutions composed of an etchant, either 0.2 M $CuCl_2.2H_2O$ or 0.2 M $FeCl_3.6H_2O$, and a quaternary ammonium salt (quat) such as choline chloride or chlormequat. These solutions are reminiscent of deep eutectic solvents (DES) based on quats. DES are quite similar to ionic liquids (ILs) and are used as well as alternative solvents with a great diversity of physical properties, making them attractive for replacement of hazardous, volatile solvents (e.g. VOCs).

A remarkable difference between genuine DES and ILs with the solutions used in this project is the addition of rather large quantities of water. It is shown the presence of water has a lot of advantages on the leaching of metals, while the properties typical for DES still remain.

The oxidizing capacities of Cu(II) stem from the existence of a stable Cu(I) component in quat based DES and thus the leaching stems from the activity of the Cu(II)/Cu(I) redox couple. The advantage of Fe(III) in combination with DES is the fact that the Fe(III)/Fe(II) redox couple becomes reversible, which is not true in pure water. This opens perspectives for regeneration of the etching solution.

In this project the leaching of copper was studied as a function of gradual increasing water content from 0 - 100w% with the same concentration of copper chloride or iron(III) chloride at room temperature and 80ºC. The solutions were also tested on real PCBs. At room temperature a maximum leaching effect for copper was obtained with 30w% choline chloride with 0.2 M $CuCl_2.2H_2O$. The leaching effect is still stronger at 80℃, but of course these solutions are more energy consuming. For aluminium, tin, zinc and lead, the leaching was faster at 80ºC. Iron and nickel dissolved easily at room temperature. The solutions were not able to dissolve gold, silver, rhodium and platinum.

Keywords: printed circuit board, PCB, metal recycling, ionic liquids, deep eutectic solvents, leaching.

Resumo

O tratamento de resíduos electrónicos é um tema que requer cada vez mais, a nossa atenção, pois um tratamento não adequado leva a consequências prejudiciais para o meio ambiente.

Este projecto tem como objectivo a investigação de novas alternativas de reciclagem de metais que constituem as placas de circuito impresso (PCIs) obtidas de computadores já não utilizáveis. O processo é baseado em soluções aquosas compostas por 0.2M $CuCl_2.2H_2O$ ou 0.2M $FeCl_3.6H_2O$ e um sal de amónio quaternário como o cloreto de colina. Estas soluções são designadas de solventes eutéticos e são baseados em sais quaternários. Os sais eutéticos são similares aos líquidos iónicos (LI´s) e são usados como solventes alternativos. A sua elevada diversidade de propriedades físicas torna-os atractivos para a substituição de solventes voláteis (ex. COV´s).

Uma notável diferença entre solventes eutéticos e líquidos iónicos puros é a adição de determinadas quantidades de água. A presença de água tem inúmeras vantagens na dissolução de metais, mantendo-se ao mesmo tempo as propriedades dos solventes eutéticos.

As capacidades oxidativas do Cu(II) provêm da existência de Cu(I) estável, presente em quaternários baseados em solventes eutéticos. Assim, a dissolução tem origem na actividade do par redox Cu(II)/Cu(I). A vantagem do Fe(II) combinado com solventes eutéticos é o facto de o par redox Fe(III)/Fe(II), tornar reversível mas não na presença de água. Isto abre perspectivas para a regeneração da solução lixiviante.

Neste projecto foi estudada a dissolução do cobre em função do crescimento gradual do teor de água, desde 0-100w%, mantendo a mesma concentração de cloreto de cobre(II) e cloreto de ferro(III), à temperatura ambiente e 80ºC. As soluções foram também testadas em PCI´s. À temperatura ambiente a máxima lixiviação para o cobre foi obtida com 30w% de cloreto de colina e 0.2M $CuCl_2.2H_2O$. A dissolução do cobre foi mais eficaz a 80ºC, no entanto nestas condições há um maior gasto energético. Para o alumínio, estanho, zinco e chumbo verificou-se uma rápida dissolução a 80ºC. Ao contrário do ferro e níquel, a dissolução foi mais rápida à temperatura ambiente

As soluções usadas não foram capazes de dissolver ouro, prata, ródio e platina.

Palavras – Chave: placa de circuito impresso, PCI, reciclagem de metais, líquidos iónicos, solventes eutéticos, lixiviação.

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Abbreviations and Symbols

Abbreviations/Symbols	**Designation**	**Units**
A	Area	cm^2
Abs	Absorvance	
C	concentration	mol/L; ppm
E	Potencial	
m	mass	g; mg
M	Molecular weight	g/mol
n	Number of moles	mol
t	time	h;min
V	Volume	L; mL
v	Scan rate	mV/s
v_L	Leaching rate	$g/m^2.h$
CC	Choline Chloride (cloreto de colina)	
CCC	Chloormequat (cloromequato)	
DES	Deep eutectic solvents (solventes eutéticos)	
diss	dissolved	
df	Diluation factor	
DSA	Dimensionally stable anodes (ânodos dimensionalmente estáveis)	
EEE	Electrical and electronic equipments (equipamento eléctrico e electrónico)	
exp	expected	
i	initial	
ILs (LIs)	Ionic liquids (líquidos iónicos)	
QACs	Quaternary ammonium compounds (compostos de amónio quaternário)	
RDE	Rotating disk electrode (eléctrodo de disco rotativo)	
RTIL’s	Room temperature ionic liquids (líquidos iónicos à temperatura ambiente)	
PCB (PCI)	Pinted circut board (Placa de circuito impresso)	
vf	Volumetric flasks	
VOC’s (COV´s)	Volatile organic carbohydrates (compostos orgânicos voláteis)	

1. Introduction

1.1. Background

1.1.1. History of PCB´s

The concept of PCB technology dates back from 1850 and goes together with the electric evolution of several systems. Initially, metal strips were used to connect electrical compounds in wooden basis. After some time, the metal strips and wooden basis were being substituted by wires connected and a metal chassis, respectively.

In 1943, the scientist Paul Eisler, had the objective to replace all wiring of an electric circuit by only one compact board which contains all the wiring on one compact board. The most important development was in the begin of the 80´s, when the first multi layer PCB´s were created which are still at the basis of computer technology, aerospace, instrumentation and telecommunications equipment [1] [2]. Most of the electrical and electronic equipments (EEE´s) contain PCB´s and the PCB constituents can represent 30% of the total weight of some instruments.

1.1.2. Printed Circuit Board

The board of a basic PCB is made of a rigid sheet of polymer, mostly epoxy reinforced with glass fiber, but other materials such as fenolite, aramid fiber, polyester fiber, polyester film, PVC or teflon are used. The electronic components and their interconnections have a complex composition; some of it are precious metals (eg: Au, Ag, Pt) and hazardous metals (eg: Pb and Cd), but they also contain less valuable metals such as Al, Fe, Cu, Sn, Zn and Ni.

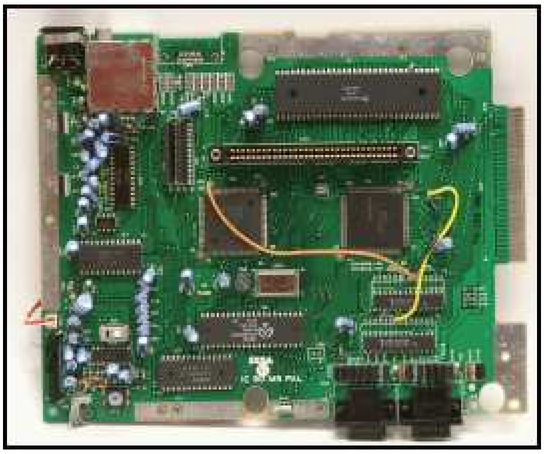


Figure 1.1-Printed Circuit Board[3]

The presence of metals, especially hazardous metals, demands treatment of rejected PCB´s as to prevent contamination of soil, water and air and consequently to reduce health risks. For example, a long exposition with Cd can cause bone and kidney injuries and lead is harmful for kidneys and the reproductive system; a low level of exposition can affect the mental development of children. Sometimes this kind of waste is deposited in a landfill or is transported to developing countries where adequate treatment is far from existing. Besides environmental aspects, the presence of valuable materials such as copper and precious metals is a stimulus to recycle these materials. Pyromettalurgical recycling processes exist where the boards or the complete electronic equipment is brought in a melt oven; the molten mixtures are then separated in several fractions and finally, the metals are won in their pure form. Pyromettalurgical recycling processes have some disadvantages: the incineration is energy-consuming and can produce highly toxic dioxins, for example when PVC is combusted.

Hydrometallurgical processes exist as well. Typically, they make use of aggressive solutions based on strong acids and strong oxidizing agents.

1.1.3. Ionic Liquids

Ionic liquids can be described as salts that are liquid at a temperature < 100 ℃. When they are liquid at room temperature they are termed ‘room temperature ionic liquids’ (RTIL’s). They are composed of a cation and an anion. Often organic anions and cations are used. In figure 1.2 some commonly used cations and anions are represented.

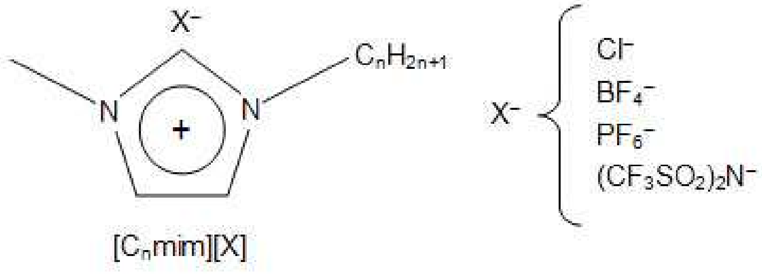


Figure 1.2 - Typical alkyl methylimidazolium-type ionic liquids [4]

Table 1.1– Some examples of cations and anions which form ionic liquids [4]

Cations	Anions
imidazolium	Cl^- (chloride)
pyridinium	BF_4^-(tetrafluoroborate)
ammonium	PF_6^-(hexafluorophosphate)
	$(CF_3SO_2)_2N$ [bis(trifluoromethanesulfonyl)amide]

They can be considered as a new class of solvents and as such they have been developed in the last decades to reduce the use of volatile organic carbohydrates (VOC’s) or other hazardous compounds. In some cases they can even replace the classical solvent completely. More and more applications on an industrial scale are reported. Because of their numerous advantages and the property they can be designed for a specific task, has lead to an enormous increase of reports on this subject.

Table 1.2 summarizes some properties of modern ionic liquids.

Table 1.2 – Properties of modern ionic liquids [5]

A salt	Cation/anion quite large
Freezing point	Preferably below 100ºC
Liquids range	Often> 200ºC
Thermal stability	Usually hight
Viscosity	Normally < 100cP, workale
Dielectric constante	Implied $\leq$ 30
Polarity	Moderate
Specific conductivity	Usually < 10 mS/cm (good)
Molar conductivity	<10 Scm^2/mol
Electrochemical window	>2V, even 4.5V
Solvent and/or catalyst	Excellent for many organic reactions
Vapour pressure	Usually negligible

In this project solutions were used based on choline chloride and chlormequat.

Choline chloride in dry conditions is a white crystalline solid in aqueous solution. At room temperature CC becomes a colourless liquid. On a laboratory scale it can result from methylation of dimethylethanolamine with methyl chloride. One of the most important applications of CC is its use as a food supplement in animal nutrition.

Chlormequat choline has the same structure as CC; the only difference between them is CC has a hydroxyl group and Chlormequat has a chloride group. CCC can be used in crop protection; it protects wheat, rye and oats on plantations against wind and rain.

Figures 1.3 and 1.4 show the structure of CC and CCC.

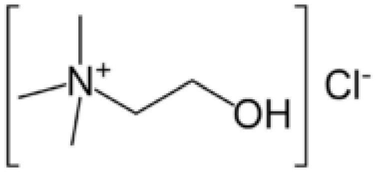


Figure 1.3 – Choline Chloride (CC) [6]

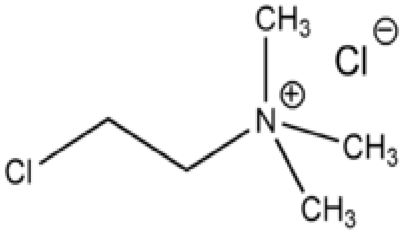


Figure 1.4 - Chlormequat Chloride (CCC) [7]

Both choline chloride [(2-hydroxyethyl)trimethylammonium chloride] and chlormequat [(2-chloro-ethyl)trimethylammonium chloride] are quaternary ammonium compounds (QACs), which are readily available on a large scale. They can be used as a constituent of true ionic liquids. For example, a mixture of $CuCl_2$ and choline chloride, both solids, results in a liquid. Here the resulting cation is choline$^+$ and the anion is $CuCl_3^-$. It can be used as well to produce a range of 'ionic liquid analogues' called 'deep eutectic solvents' (DES). These are produced by mixing choline chloride with a hydrogen bond donor such as urea, malic acid or ethylene glycol. It can be argued the H-bond donor forms some kind of anion complex with Cl^-, but in general DES are not considered as constituted of true ions and are thus not regarded as 'ionic' liquids. Besides the separate terminology, ILs and DES behave very much in a similar manner and they have parallel properties. An important distinction between ILs and DES based on QACs, is the fact that most DES are not expensive. This is in clear contrast with ionic liquids.

A popular DES that is used throughout this project is Ethaline200. It is formed by mixing ethylene glycol and CC in a molar ratio 2/1. Ethaline400 is a mixture in a ratio 4/1 etc..

Ethaline200 is very easy to prepare, cheap and featured by a low viscosity. The latter is often a problem with similar DES.

1.1.4. Recycling Processes

The recycling of electronic equipment is important from both an economical and an environmental viewpoint. The existence of big quantities of hazardous residues demands for an adequate treatment whereby valuable materials are regained. The life cycle of electronic equipment is composed of several steps: raw material, production, commercialization, consumption and management of the rejected parts.

The treatment of this kind of residue includes chemical, mechanical and thermal processes. Mechanical processes involve separation steps of the different parts a PBC is composed of. The separation is based on differences of weight, size of the parts, magnetic and electric properties.[3] Thermal processes can be incineration, fusion and pyrolysis. In first instance the metal fraction is separated here from the polymer fraction and the heat released is used to fuel the process, at least partly. Hydrometallurgical processes make use of specific solutions to dissolve metals and to separate them in this way from the other constituents of the PCB. Then, the metals are separated in their pure form. The solutions most commonly used in industry for this purpose are mixtures of acids such as: H_2SO_4; H_2SO_4+H_2O_2; HNO_3 + HCl (aqua regia). The latter being the most efficient. In this project it is shown how ionic liquids can be used as well in the recycling of metals from electronic waste.

In figure 1.5 a general process to recycle televisions and monitors is shown.

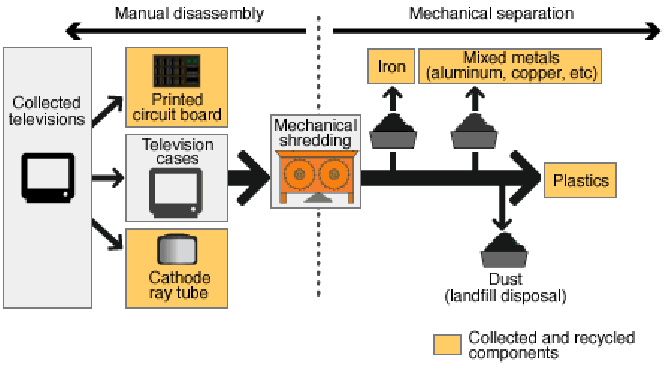


Figure 1.5 - Recycle process of television and monitors [8]

This process involves several steps:

- storage;
- disassembly of equipment with separation in several materials;
- grinding of different materials in several phases;
- separation of materials in non-ferrous and plastic fractions;
- evacuation and elimination of dust

1.2. Analytical determinations

1.2.1. Atomic Absorption Spectrometry

Atomic absorption Spectrometry is based on the absorption of radiant energy by neutral atoms, vaporized to the gas state. The spectrum absorbed in the flame is composed of resonance bands, which approach the absorption bands of pure atoms very close. In this method a lamp is used which contains a filament coated with the element to be determined. When the lamp is switched on, the filament glows, emitting radiation with the characteristic wavelength of the element.

In atomic absorption spectroscopy the sample to determine is lead via a nebulizer into a flame, which is fuelled with an acetylene/oxygen mixture or alternatively with an acetylene/N_2O mixture. The flame actually serves as a cuvette. The absorption of one specific wavelength is proportional with the concentration of the element in the flame and thus, indirectly with the concentration of the element in the sample. For each element there exists a specific range where the absorption is linearly related with the concentration according to the Lambert-Beer law: $A = \varepsilon\ b\ c$.

With:

A - Absorbance

ε – molar absorptivity (constant characteristic of the species absorbing)

b – optical path length (cm)

c – molar concentration of solution (mol/L)

Figure 1.6 represents the atomic absorption spectrophotometer (Consult appendix A.1.) used to determine the concentration of some metals.

Figure 1.6 - Atomic absorption spectrophotometry

1.2.2. UV-Vis Spectometry

In qualitative analysis, molecular absorption spectometry is very useful in the UV-Vis region. This technique identifies components by the absorption peaks present in the spectrum scanned in the visible and UV-region.

UV-Vis spectrometry is often limited because of intensive absorption bands of the solvent, especially in the UV-region. Absorption in the UV-Vis region involves electronic transitions; this means that electrons are excited to higher energy levels. Molecular absorptions can involve either electronic transitions or variations in vibrational and rotational states.

Transparent cuvettes are used to hold the sample. When absorption in the UV-region is to be recorded quartz cuvette are used. Cuvettes are treated with special care: scratches on the cuvettes or grease must be avoided and typically special cuvette cleaning paper is used.

This technique allows characterization and analytical determinations of the concentration of chemical species that show a distinct absorption in the UV-Vis region.

Figure 1.7 represents UV-Vis spectometry (Consult appendix A.1.) used to quantify copper and iron.

Figure 1.7 – Uv-Vis spectrometry

1.2.3. Cyclic Voltammetry

Cyclic voltammetry is an electrochemical technique where the potential is swept linearly between two potential intervals followed by a reversal of the potential; typically, the end potential is identical to the start potential, but other scanning profiles are possible as well. The measurement is run in a three-electrode cell:

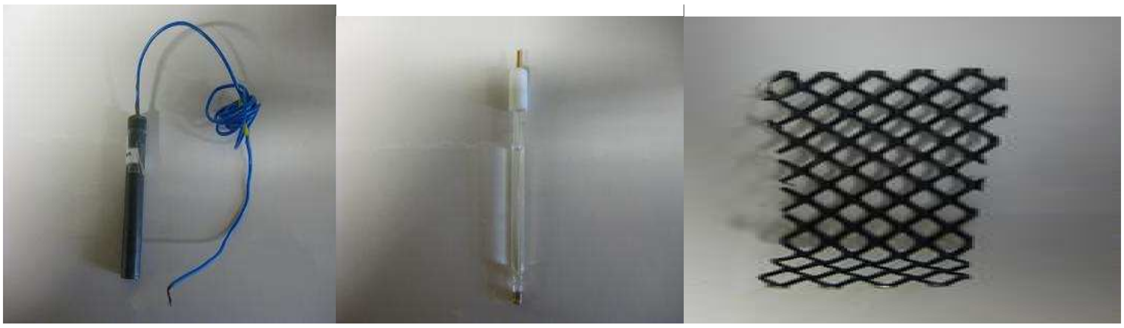
-Working electrode (substrate), where the reactions under study occurs.

-Reference electrode with a fixed potential.

-Counter or auxiliary electrode.

Figure 1.8 represents the electrodes that were used.

The potential is controlled between the working and the reference electrode, while the current flows between the working and the counter electrode.



(a) (b) (c)

Figure 1.8 – Electrodes used in Cyclic Voltammetry: (a) work electrode; (b) reference electrode; (c) count electrode

In figure 1.9 the equipment for Cyclic Voltammetry is shown (Consult appendix A.1)

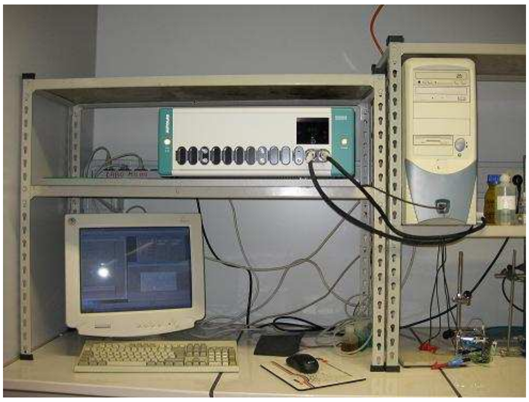


Figure 1.9 – Cyclic Voltammetry

Application of a programmed and controlled potential results in a current response. As the potential is changed, the reaction rate increases exponentially, thereby consuming material close to the electrode. This current reaches a maximum value because of the mass transport towards the electrode becomes the limiting factor i.e. the rate the product is transported to the electrode is the slowest step in the overall reaction. When the potential sweep is reversed, the products formed at the surface of the electrode can drive the reaction in the opposite direction. However, this is not always observed. In any way the behaviour of the current in the cyclic voltammogram gives a clue about the mechanisms behind the investigated reaction.

1.2.4. Karl Fischer

This method gives the quantity of water present in solutions and is based on the oxidation of SO_2 with I_2 in presence of water. The reagent is prepared by reaction of iodine in a mixture of anhydrous pyridine dissolved in anhydrous methanol. The reaction shows that each iodine molecule reacts with one water molecule.

$I_2 + SO_2 + 2H_2O \rightarrow 2\,HI + H_2SO_4$

The final point can be detected visually as the colour turns from yellow to brown when the titrant is present in excess. A potentiometric detection is possible as well as the potential increases sharply when the titrant is present in excess. The Karl Fisher reagent should be standardized at least once a day to avoid methanol in excess which causes some instability.

2. Methods

2.1. Preliminary Work

2.1.1. Metal dissolution in a solution with 0.2M $CuCl_2.2H_2O$ / 50w% CC

In this preliminary work the dissolution of metals that are typically found on a PCB in an aqueous solution of 0.2M $CuCl_2.2H_2O$ with 50w% of choline chloride. The tested metals were aluminium, iron, copper, tin, silver, platinum, zinc, nickel, lead and gold.

In each test a sample of pure metal was added in 40 mL of solution; the weight of the metal was registered in intervals of 10, 30 or 60 minutes, depending on the leaching rate of the metal. For example, in the experiment with aluminium the metal dissolves immediately after the solution was added; then, for this metal the weight was registered in intervals of ten minutes. Tests were done at room temperature and at 80ºC in order to investigate the temperature effect on the metal dissolution as well. The experiment was stopped when the dissolved mass had reached the expected maximum value and when it was observed the weight of the substrate remained indeed more or less constant.

2.1.2. Study of the influence of the CC concentration in copper dissolution at room temperature and 80ºC

The objective of this preliminary work was to study the influence of the choline chloride concentration on the dissolution of copper, i.e. to determine the optimal concentration and leaching rate of copper. Therefore, aqueous solutions were prepared with 0.2M $CuCl_2.2H_2O$ in 0w%, 10w%, 20w%, 30w%, 50w%, 70w%, 90w% choline chloride at room temperature and at 80ºC. In some tests 0.1M HCl was added to solutions of 10w% and 20w% choline chloride as to see if the leaching rate could be improved in this way. In another experiment a solution of 0.2M $CuCl_2.2H_2O$/50w% CC was prepared and the extraction tested with simultaneous air agitation.

The possibility to leach gold was tested too with a solution of 90w% CC. In an earlier experiment it was observed that with lower concentrations of choline chloride, gold did not dissolve at all. However, with 90w% choline chloride there was no dissolution neither.

2.2. Copper Leaching

2.2.1. Copper(II) recovery by oxidizing agents

In this work copper recovery by comproportionation with Cu(II) was studied, i.e. copper is etched by the reaction:

$$Cu + Cu^{2+} \leftrightharpoons 2\,Cu^{+}$$

Other oxidizing agents that can be used with the objective to recover Cu(II) are H_2O_2, NaOCl etc.. When complexing agents such as NH_3 are added oxidation with air (O_2) is possible.

2.2.2. Copper leaching by electrochemical cell

In this work an electrochemical cell was used with:

Cathode – brass, an alloy of copper and zinc
Anode – DSA’s, titanium coated with a mixture of RuO_2/IrO_2
Solution: 250 mL of 0.2M $CuCl_2.2H_2O$ and 20w% choline chloride with 250mL of 0.1M HCl

This experiment was run for one hour. Solution samples were taken initially every 20 minutes and later every hour with the objective to determine the quantity of recovered copper.

2.2.3. Copper leaching with a solution of 0.2M $CuSO_4.5H_2O$ / 20w% CC

In this experiment the copper recovery was studied in absence of chloride of the metal salt i.e. the only chloride present is the chloride from CC. A solution with 0.2M $CuSO_4$ in 20w% CC was used. A piece of copper was placed in the solution and after one hour extraction the solution was analysed with cyclic voltammetry. In figure 2.1 the measuring setup is presented.

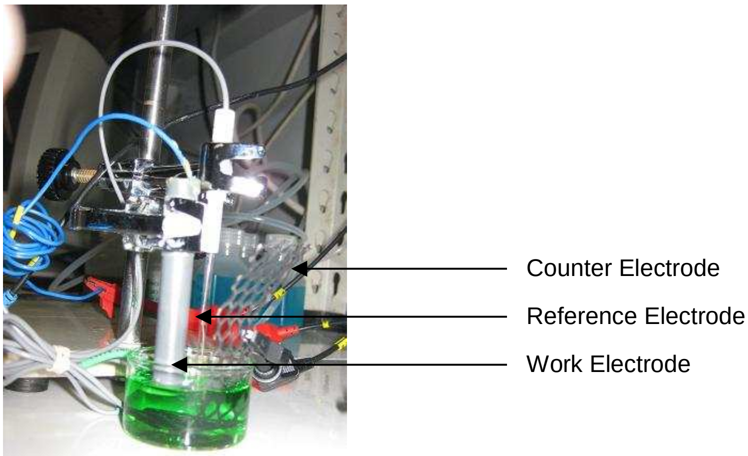


Figure 2.1 – Measuring setup

2.2.4. Copper leaching with a solution of 0.2M $FeCl_3.6H_2O$ / CC

In this experiment copper leaching was studied in solution of 0.2M $FeCl_3.6H_2O$ with CC or CCC. Different concentrations and conditions were used such as:

- 30w%CC
- 30w% CCC
- 30w% CC and air
- 30w% CC and N_2

The reactions that can occur are:

1) $2Fe^{3+}+Cu\rightarrow Cu^{2+}+2Fe^{2+}$
2) $Fe^{3+}+Cu\rightarrow Cu^{+}+Fe^{2+}$

During leaching of copper there is formation of iron precipitates and also Cu(I) or Cu(II). The dissolution of copper was made while the pH is controlled simultaneously for two hours for the 3 first conditions in order to maintain a constant pH of 1.80 value during the whole experiment. For the last 2 conditions air and N_2 were bubbled through the solution and the effect on the pH was checked.

2.3. Metal dissolution from PCB´s

This work had the objective to analyse the metal content of some metals most likely to be present in PCB's (Cu, Sn, Pb etc.) after dissolution in 500mL 0.2M $CuCl_2.2H_2O$ in 30w% CC and 0.2M $FeCl_3.6H_2O$ in 30w% CC. The experiment was run at room temperature and at 80ºC. A sample was taken every hour during 6 hours and then the metal concentration in the samples was measured in atomic absorption spectrophotometry.

2.4. Gold dissolution

2.4.1. Gold dissolution in different solutions at room temperature

In this work a mass of gold was weighted and placed in 25mL of a solution of 0.2M $CuCl_2.2H_2O$ in Ethaline200, 0.2M $FeCl_3.6H_2O$ in Ethaline200 and 15 mL of 0.2M $CuCl_2.2H_2O$ in Ethaline200 with 10mL of 45w% CCC at room temperature and 80ºC. The dissolution of gold was measured by weighing the piece after some hours depending on the capacity of the solution. The concentration of dissolved gold was determined as well by atomic absorption spectrophotometry. Detection of the gold was performed as well by recording a cyclic voltammogram after and before the dissolution of the gold.

2.4.2. Gold dissolution in Ethaline200 in presence of Cl_2/ Cl_3^- (piece of gold)

The objective of this work was to study if a solution of Cl_2/ Cl_3^- in Ethaline200 is able to dissolve gold. Cl_2 gas was produced by two methods.

<u>1st Method</u>

Cl_2 is formed in a distillation flask with three-neck bottle through addition of 38% HCl to a solution of NaOCl causing Cl_2 bubbles formation. The chemical reaction is:

$NaOCl(l) + 2\ HCl(l) \rightarrow Cl_2(g) + H_2O(l) + NaCl(l)$

After production of Cl_2, the gas was led through three consecutive solutions. The first solution was the Ethaline 200 where we wanted to achieve a solution of dissolved Cl_3^-/ Cl_2; then a NaOH washing solution was used to capture Cl_2 that passed the first solution and after this water was used to protect the pump for damage.

During the experiment air was directed from the three-neck bottle towards the water safety solution by means of an air pump over a period of 20 minutes because the formation of Cl_2 was very fast.

2nd Method

In this method an electrochemical cell was used to produce Cl_2 gas. The solution used was Ethaline 200 and current used for this process was 0.2 A. Two DSA anodes were used with a stainless steel cathode in the middle. Figure 2.2 shows an electrochemical cell used for this method.

Figure 2.2 - Electrochemical cell used to produce Cl_2/Cl_3^-

2.4.3. Gold dissolution with 0.2M $FeCl_3.6H_2O$ in Ethaline200 and 0.2M $FeCl_3.6H_2O$ in CCC

A piece of gold of 0.39 g was immersed in 25mL of 0.2M $FeCl_3$ in Ethaline200. It was made the same procedure described in 2.4.1. The piece of gold was preferred because the gold powder was difficult to handle: powder is lost easily during weighing and thus it is difficult to obtain a precise result. After 17h immersion and stirring the weight of the piece of gold had not changed. Then, the same piece of gold was put in contact with 25mL of 0.2M $FeCl_3.6H_2O$ with 20w% CCC.

The use of this solution was based on the experimental work made by Vanhoecke[9], who performed a study on the optimum composition (w% CCC in water) of a 0.2M $FeCl_3.6H_2O$ etching solution.

2.5. Platinum dissolution

In this experiment the same solution to dissolve gold as in 2nd Method of 2.4.3 was used. A piece of 0.14 g of platinum was immersed and stirred for 17 hours in the solution, but the weight remained the same. It is concluded platinum did not dissolve at all.

2.6. Rhodium dissolution

In this work the objective was to test the capability of different solutions to dissolve rhodium. A solution of 0.2M $FeCl_3.6H_2O$ in Ethaline200 and a solution of 0.2M $CuCl_2.2H_2O$ in Ethaline200 were tested as well as the solution used to dissolve gold described in 3.4.3. second method. Figure 2.3 presents the pieces of rhodium used in different solutions.

(a) (b) (c)

Figure 2.3 - Rhodium in different solutions: (a) 0.2M $FeCl_3.6H_2O$ in Ethaline200; (b) 0.2M $CuCl_2.2H_2O$ in Ethaline200; (c) Ethaline200 with Cl_2/Cl_3^-

2.7. Analytical methods to quantify Fe(III) and Fe(II) in solutions

2.7.1. Study of Nernst Equation on solutions containing Fe(III) and Fe(II)

In this experiment was made several mixes with two solutions containing cations Fe(III) and Fe(II) to obtain different proportions of each cation. Then, the potential of each solution was measured in a system with two electrodes:

Indicator electrode: platinum wire

Reference electrode: Ag/AgCl in 3M KCl.

Nernst equation is one quantity relation which allows calculating the electromotive force and is represented by:

$$E = E^0 + \frac{RT}{nF} \ln \frac{|Fe^{3+}|}{|Fe^{2+}|} \quad (2.1)$$

where :

E – electromotive force

Eº - standard cell potential

R – universal gas constant

T – absolute temperature

n - number of electrons transferred

F – Faraday constant

$|Fe^{3+}|/|Fe^{2+}|$ - concentration ratio

A linear relation is expected between potential (E) and the ln of the ratio Fe(III)/Fe(II).

2.7.2. Identification and quantification of Fe(III) and Fe(II) in different concentrations

In this experiment several solutions with different concentrations of $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ in 50w% CC were analysed with the aim to find a reliable procedure to determine both Fe(II) and Fe(III) simultaneously. The solutions were analysed voltammetrically with a rotating disk electrode (RDE) in order to find the potential where the oxidation of Fe(II) or the reduction of Fe(III) occurs. The electrodes used were:

Working electrode: platinum rotating electrode working at (a constant voltage of 7.5 V is applied to the motor that rotates the disk; this corresponds to an applied current of 1A). This electrode was used in order to create a constant hydrodynamic layer in the neighbourhood of the electrode; in this way a diffusion layer is created: the concentration outside this layer is equal to the bulk concentration of Fe(III) and Fe(II) at all time, while a concentration gradient exists inside this layer.

Reference electrode: Ag/AgCl in 3M KCl

Counter electrode: RuO_2/IrO_2 DSA

Figure 2.4 represents experimental setting-up for analysing solutions in cyclic voltammetry.

Figure 2.4 – Experimental setting-up for analysing solutions of Fe(III) and Fe(II) in cyclic voltammetry

3. Results and Discussion

3.1. Metal dissolution in a solution of 0.2M $CuCl_2.2H_2O$ / 50w% CC

Figures 3.1 and 3.2 show the piece of aluminium used during the experiment and the result of its dissolution, respectively.

- Aluminium

Figure 3.1 – Piece of aluminium

Figure 3.2 – Dissolution of aluminium

Figure 3.3 shows the comparison between room temperature and 80ºC in aluminium dissolution.

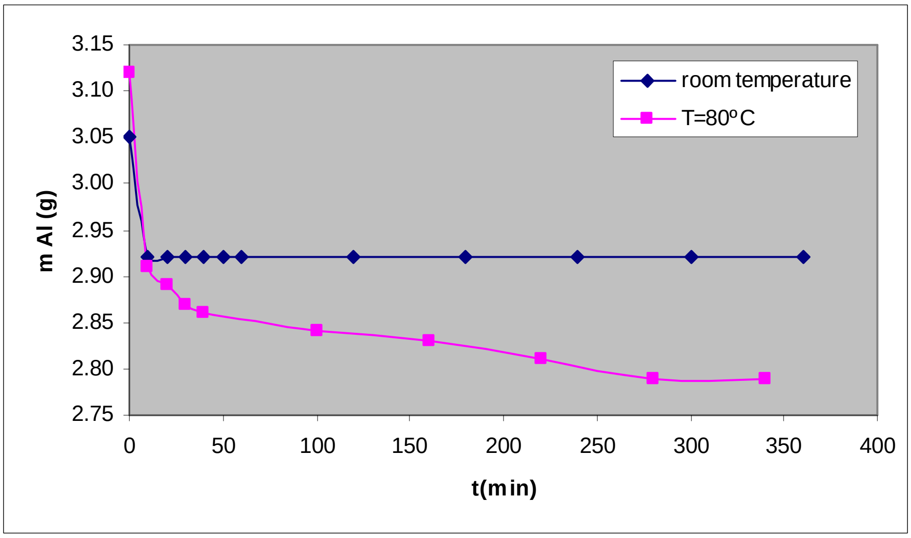


Figure 3.3 – Variation of weight of aluminium in 0.2M $CuCl_2.2H_2O$ / 50w% CC at room temperature and 80ºC

m_{Al} which is possible to dissolve = 0.14g (consult appendix 6.2.2.)
m_{Al} dissolved at room temperature = 0.13g
m_{Al} dissolved at 80ºC = 0.33g

As observed in figure 3.3 the dissolution of aluminium was faster at 80ºC than room temperature. In the first 10 minutes, dissolution was very fast for both conditions. After this time, the weight of copper piece was the same in whole experiment at room temperature.
This can be due to the formation of a protective oxide layer. At 80ºC, after 10 minutes the weight of the piece continued to decrease possibly due to attack of the protective layer.
At room temperature 0.13g of aluminium was dissolved, approximately the weight that is expected.

- Iron

Figures 3.4 and 3.5 show the pieces of iron used for the experiment and its dissolution, respectively.

Figure 3.4 – Pieces of iron

Figure 3.5 – Dissolution of iron

Figure 3.6 shows the comparison of iron leaching at room temperature and 80ºC.

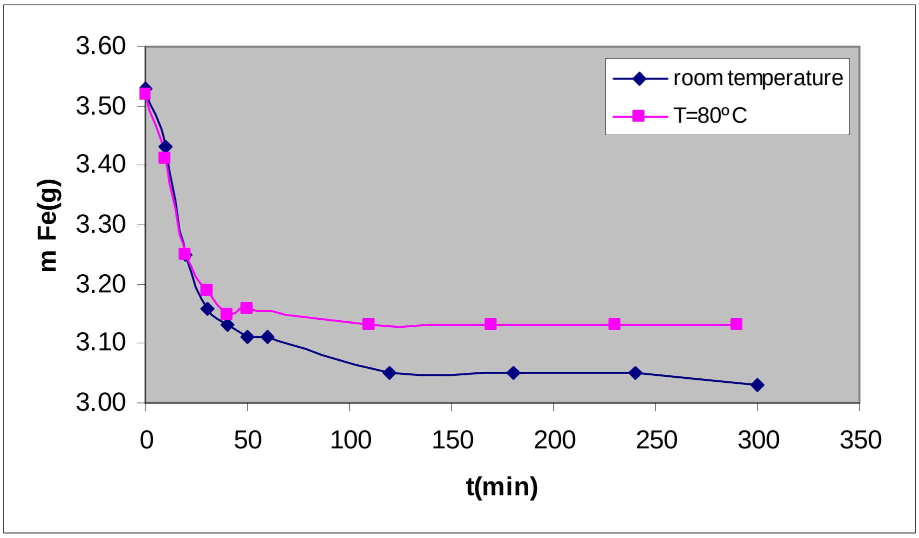


Figure 3.6 – Variation of weight of iron in 0.2M $CuCl_2.2H_2O$ / 50w% CC at room temperature

m_{Fe} which is possible to dissolve = 0.29g (consult appendix 6.2.2.)
m_{Fe} dissolved at room temperature = 0.50g
m_{Fe} dissolved at 80ºC = 0.39g

After one hour of leaching it was possible to see deposition of copper on the iron pieces. Four hours later the solution turned brown due to the presence of Fe(III) and the pieces of iron stayed black for both situations. Until 20 minutes of leaching, the variation of mass of both situations is similar. After this time, it was at room temperature that the leaching was faster, being an advantage because it does not need so much energy as the dissolution at 80ºC. In the case of iron, it was expected dissolution of 0.29g of this metal and for both situations it was dissolved more than expected.

- Copper

Figures 3.7 and 3.8 show the piece of copper used for the experiment and the result of its dissolution, respectively.

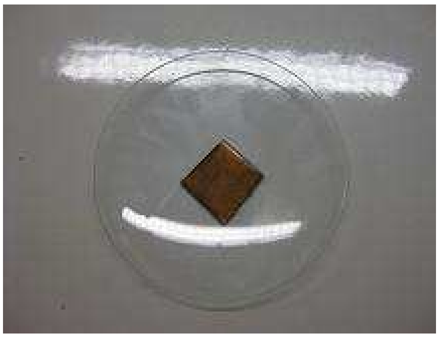


Figure 3.7 – Piece of copper

Figure 3.8 – Dissolution of copper

Figure 3.9 shows comparatively the evolution of mass of copper piece at room temperature and 80ºC during the leaching.

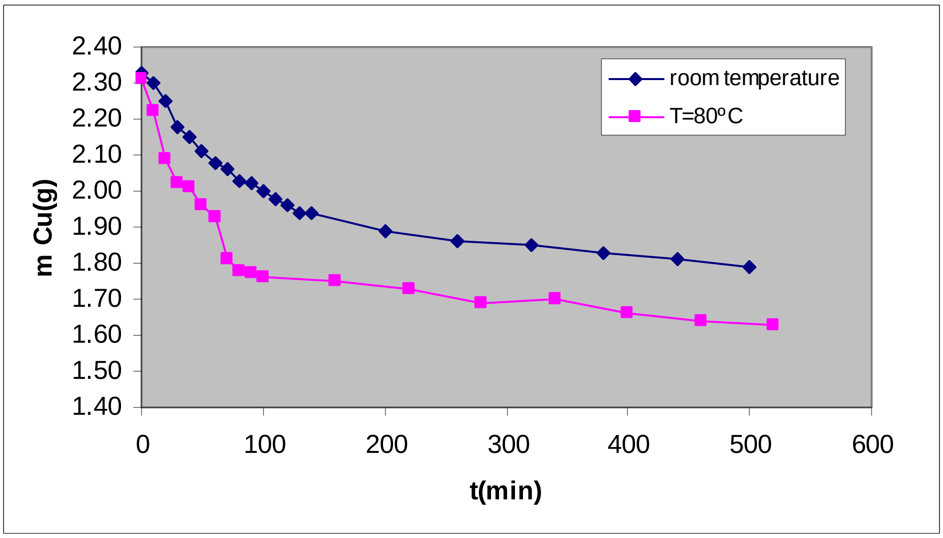


Figure 3.9 – Variation of weight of copper in 0.2M $CuCl_2.2H_2O$ / 50w% CC at room temperature and 80ºC

m_{Cu} which is possible to dissolve = 0.51g (consult appendix 6.2.2.)

m_{Cu} dissolved at room temperature = 0.54g

m_{Cu} dissolved at 80ºC = 0.68g

After one hour of leaching at room temperature the solution becomes cloudy and dark green because there is more Cu(II) present in solution which came from dissolution of copper and formation of Cu(I) precipitates.

In figure 3.9 it can be observed that at 80ºC leaching was faster than room temperature. At 100 minutes of leaching, at room temperature 0.55g of copper was dissolved and at 80ºC only was dissolved 0.33g. Theoretically, this solution is able to dissolve 0.508g but more than expected was dissolved both at room temperature (0.54g) and 80ºC (0.68g).

- Tin

Figures 3.10 and 3.11 show the pieces of tin used during the experiment and its dissolution, respectively.

Figure 3.10 – Pieces of tin

Figure 3.11 – Dissolution of tin

In figure 3.12 the variation of mass of tin piece during the leaching is presented.

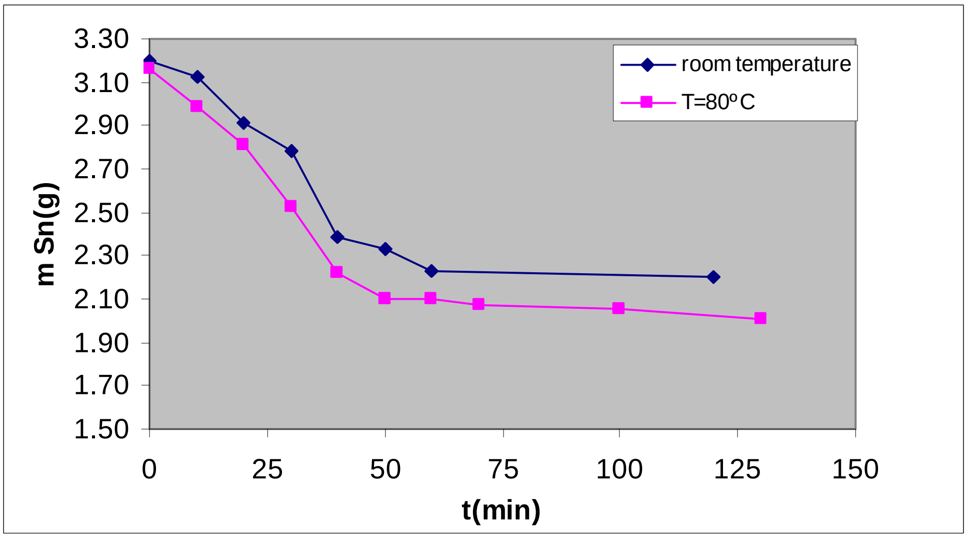


Figure 3.12 – Variation of weight of tin in 0.2M $CuCl_2.2H_2O$ / 50w% CC at room temperature and 80ºC

m_{Sn} which is possible to dissolve = 0.95g (consult appendix 6.2.2.)

m_{Sn} dissolved at room temperature = 1.00g

m_{Sn} dissolved at 80ºC = 1.15g

After one hour of leaching the solution was with almost colourless to very light-green. Deposition of copper on the tin pieces is observed. After two hours, the solution turned grey because Sn became Sn(II).

In the figure 3.12, it can be seen the dissolution initially occurs fast during the first hour of leaching. After one hour of leaching the weight of tin pieces was more or less constant.

Comparing both conditions, room temperature and 80ºC, it can be concluded at 80ºC, the leaching is faster than at room temperature. After one hour of leaching at room temperature, the mass of tin dissolved was 0.41g and for 80ºC it was 1.06g.

After 13 hours of leaching the weight remains more or less constant. For tin, at 80ºC 1.15g was dissolved and at room temperature 1.00g. Both situations dissolved more than expected (0.95g).

- Silver

In figure 3.13 the variation of mass of silver piece during the leaching is presented.

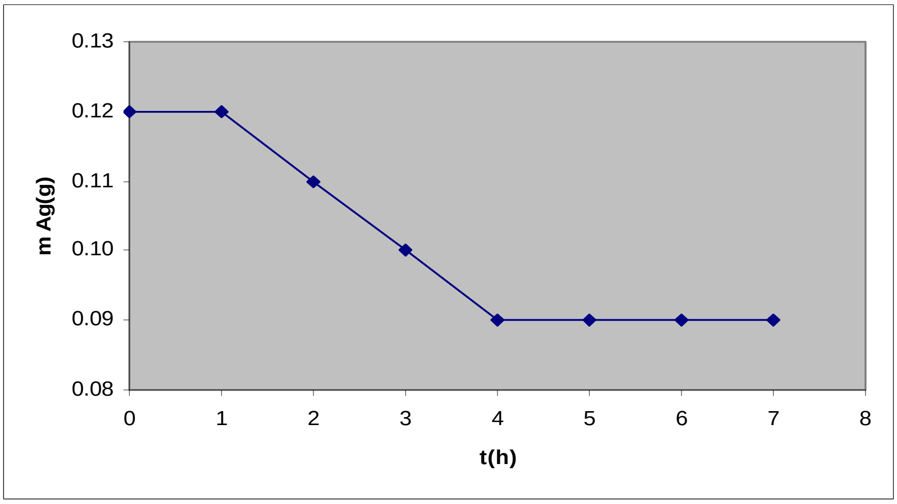


Figure 3.13 – Variation of weight of silver in 0.2M $CuCl_2.2H_2O$ / 50w% CC at room temperature

m_{Ag} which is possible to dissolve = 0.86g (consult appendix 6.2.2.)

m_{Ag} dissolved at room temperature = 0.03g

In figure 3.13 it can be observed that leaching the dissolution starts only after one hour. The dissolution occurs between one hour and four hours of leaching and the mass dissolved was only 0.03g. After four hours of leaching the weight remains constant. It can be concluded that this solution is not suitable for the leaching of silver.

- Zinc

Figures 3.14 and 3.15 show the pieces of zinc used for the experiment and the result of its dissolution, respectively.

Figure 3.14 – Pieces of zinc

Figure 3.15 – Dissolution of zinc

Figure 3.16 compares the leaching of zinc at room temperature and 80ºC.

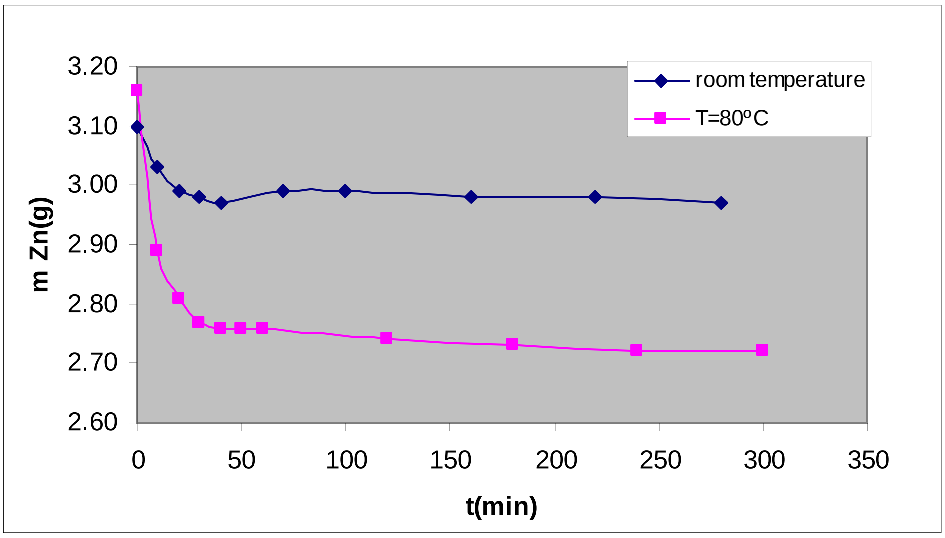


Figure 3.16 – Variation of weight of zinc in 0.2M $CuCl_2.2H_2O$ / 50w% CC at room temperature and 80ºC

m_{Zn} which is possible to dissolve = 0.52g (consult appendix 6.2.2.)

m_{Zn} dissolved at room temperature = 0.13g

m_{Zn} dissolved at 80ºC = 0.52g

After ten minutes of leaching the solution for both conditions turned from light green to dark green. In the first ten minutes, the leaching was faster at 80ºC; 0.48g of zinc was dissolved. At room temperature only 0.07g was dissolved over the same period. After this, the weight stays more or less constant at room temperature and at 80ºC.

After 20 minutes the solutions became colourless because the Cu(II) of the solution precipitated as Cu in the form of flakes.

The leaching was faster at 80ºC and in total 0.52g was dissolved, the same that would be expected and at room temperature 0.13g was dissolved, much less that would be expected.

- Lead

Figures 3.17 and 3.18 show the piece of lead used for the experiment and the result of its dissolution, respectively.

Figure 3.17– Piece of lead

Figure 3.18 – Dissolution of lead

In figure 3.19 the comparison of leaching at room temperature and 80ºC is presented.

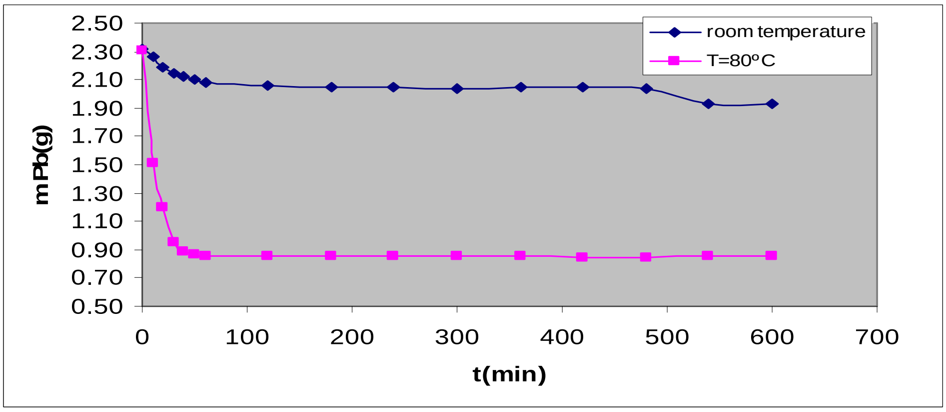


Figure 3.19 – Variation of weight of lead in 0.2M $CuCl_2.2H_2O$ / 50w% CC at room temperature and 80ºC

m_{Pb} which is possible to dissolve = 1.66g (consult appendix 6.2.2.)

m_{Pb} dissolved at room temperature = 1.08g

m_{Pb} dissolved at 80ºC = 1.46g

In first 20 minutes, leaching was very fast at 80ºC 1.11g was dissolved and the solution turned white cloudy because all Cu(II) in solution was had disappeared and Pb(II) was formed. At room temperature only 0.13g was dissolved and the colour of solution stayed green but cloudy too. After one hour of leaching the weight was more or less the same for both conditions. At 600 minutes, at 80ºC 1.46g of lead was dissolved, which is less than it would be expected from theoretical calculations; at room temperature 1.08g was dissolved.

- Nickel

Figures 3.20 and 3.21 show the pieces of nickel used during the experiment and the result of its dissolution, respectively.

Figure 3.20 – Piece of nickel

Figure 3.21– Dissolution of nickel

In figure 3.22 the leaching for nickel is presented.

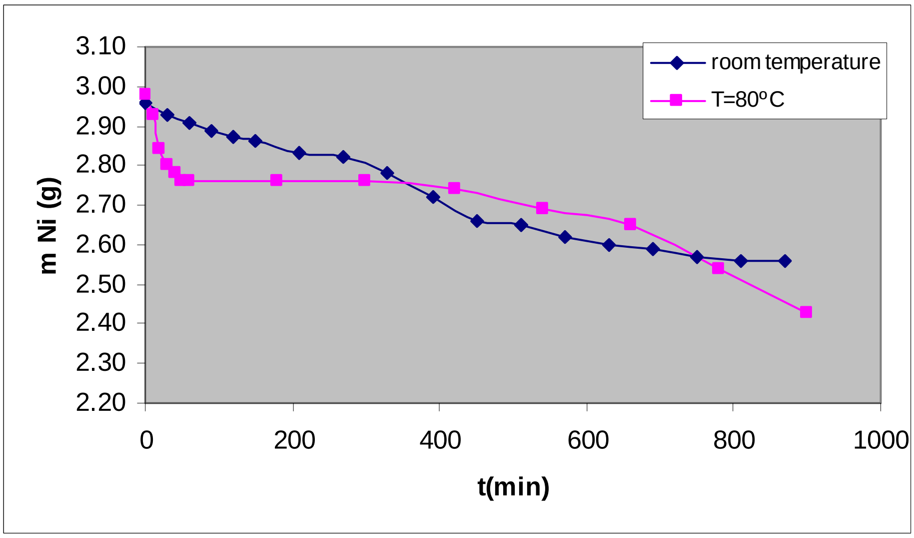


Figure 3.22 – Variation of weight of zinc in 0.2M $CuCl_2.2H_2O$ / 50w% CC at room temperature and 80ºC

m_{Ni} which is possible to dissolve = 0.47g (consult appendix 6.2.2.)

m_{Ni} dissolved at room temperature = 0.40g

m_{Ni} dissolved at 80ºC = 0.55g

As it can be seen in figure 3.22 in the first hour the leaching was faster at 80ºC than at room temperature: 0.22g was dissolved, while only 0.05g at room temperature. Later, the weight remained constant until after 400 minutes, probably due to the formation of a protective layer. Then, the weight starts to decrease again because the layer was destroyed at higher temperature. After 900 minutes of leaching, 0.4g was dissolved at room temperature, which is close to the theoretically expected value. At 80ºC 0.55g was dissolved, which is more than expected.

- Gold

Figure 3.23 shows the piece of gold used for the experiment.

Figure 3.23 - Piece of gold

The weight of a piece of gold immersed in 0.2M $CuCl_2.2H_2O$ / 50w% CC for several days at room temperature and 80ºC remained identical (0.39g). We can conclude that this solution is not able to leach gold.

3.2. Study of the influence of the CC concentration in copper dissolution at room temperature and 80ºC

This study was made only in first hour of leaching because in the beginning we noticed the most important changes.

- 0w% choline chloride

In figure 3.24 the comparison between room temperature and 80ºC during leaching of copper is showed.

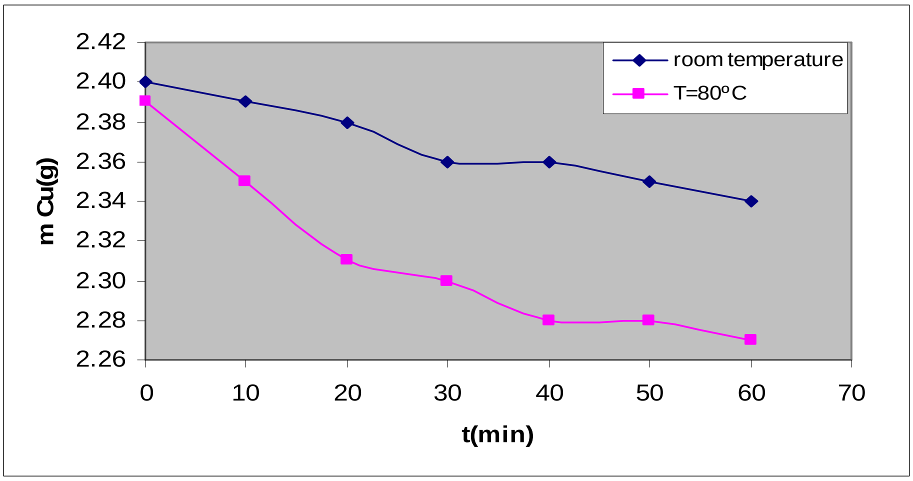


Figure 3.24 - Dissolution of copper in 0w% CC at room temperature and 80ºC

From figure 3.24 it can be concluded that with 0w% CC, copper dissolution was faster at 80ºC than at room temperature. The mass dissolved in one hour at room temperature was 0.06g and 0.12g at 80ºC.

- 10w% choline chloride

Figure 3.25 shows the leaching of copper with 10w% CC.

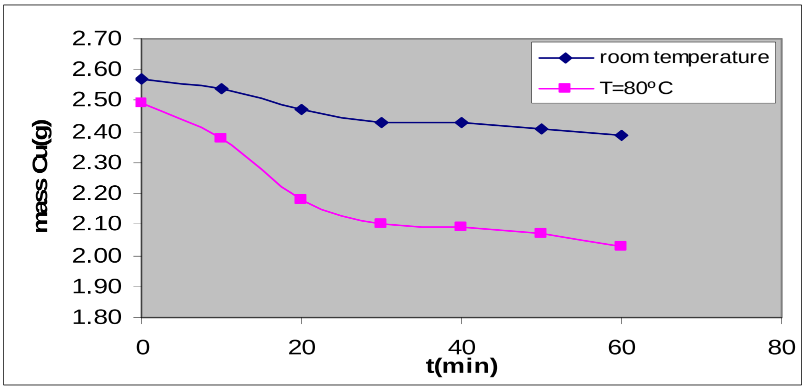


Figure 3.25 - Dissolution of copper in 10w% CC at room temperature and 80ºC

Using a solution with 10w% of CC at 80ºC the dissolution is faster than at room temperature too. At room temperature, after 60 minutes the mass dissolved was 0.18g and 0.46g at 80ºC.

- 20w% choline chloride

Figure 3.26 shows the leaching of copper with 20w% CC:

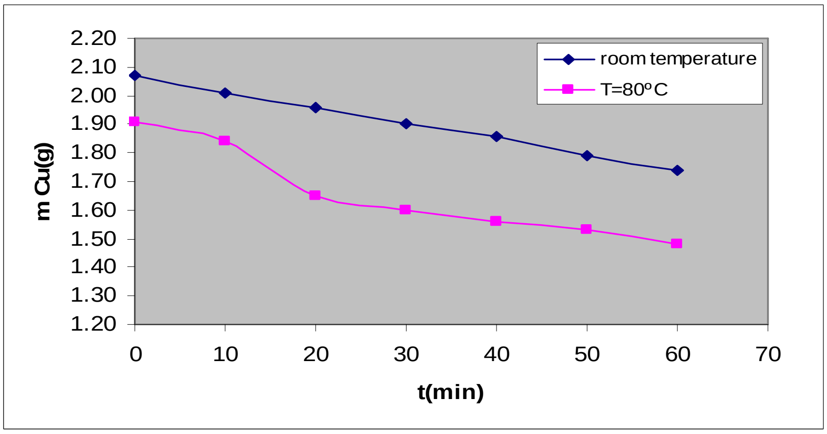


Figure 3.26 - Dissolution of copper in 20w% CC at room temperature and 80ºC

At 80ºC we have a fast dissolution too. It was possible to dissolve 0.43g and at room temperature 0.33g.

- 30w% choline chloride

Figure 3.27 shows the leaching of copper with 30w% CC.

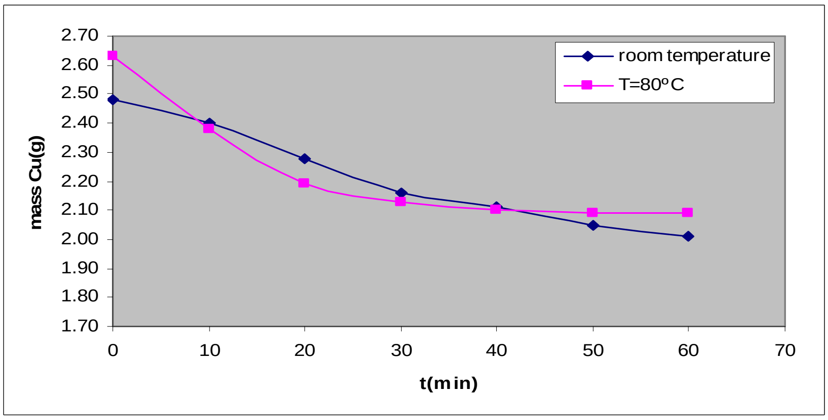


Figure 3.27 - Dissolution of copper in 30w% CC at room temperature and 80ºC

From figure 3.27 it can be seen for both conditions that the behaviour of dissolution was similar but in the first 20 minutes the dissolution was faster at 80ºC. After 60 minutes leaching at 80ºC it was found that more mass of copper could be dissolved than theoretically expected. This can be ascribed to the regeneration of Cu(II) in contact with air.

- 50w% choline chloride

Figure 3.28 shows the leaching of copper with 50w% CC.

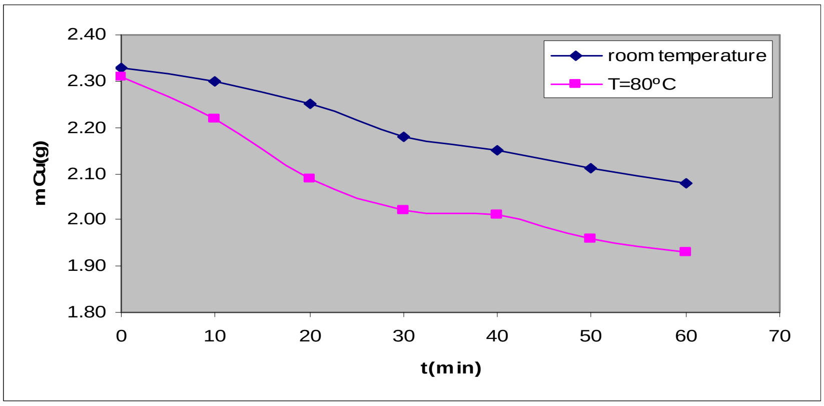


Figure 3.28 - Dissolution of copper in 50w% CC at room temperature and 80ºC

With 50w% of CC a fast dissolution during the initial 20 minutes is observed at 80ºC. Compared with room temperature, the dissolution of copper at 80ºC was faster. After one hour 0.38g of copper was dissolved at 80ºC and 0.25g at room temperature.

- 70w% choline chloride

Figure 3.29 shows the leaching of copper with 70w% CC.

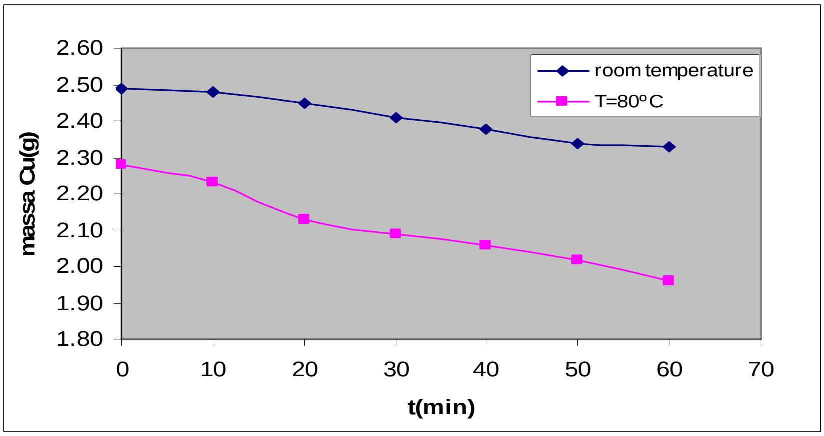


Figure 3.29 - Dissolution of copper in 70w% CC at room temperature and 80ºC

Using 70w% of CC the dissolution of copper was faster too at 80ºC. In one hour at room temperature 0.16g was dissolved and 0.32g at 80ºC.

- 90w% choline chloride

Figure 3.30 shows the leaching of copper with 90w% CC.

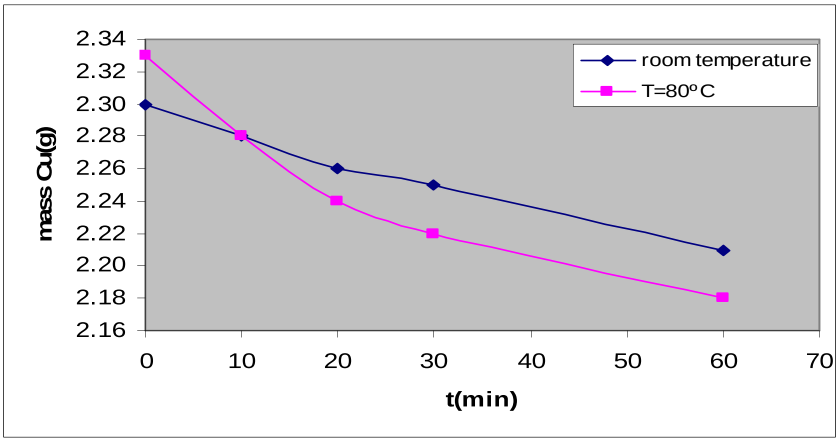


Figure 3.30 - Dissolution of copper in 90w% CC at room temperature and 80ºC

With 90w% of CC a fast dissolution during the initial 20 minutes is observed at 80ºC. During this period 0.15g was dissolved at 80ºC and 0.09g at room temperature.

In each case it can be concluded for all different concentrations of CC the leaching of copper is faster at 80ºC.

In table 3.1 the values of the leaching rate of copper for all investigated concentrations of CC are shown.

Table 3.1- Leaching rate of copper for different concentration of CC at room temperature

CC (w%)	Leaching rate (g/m^2.h)
0	59.68
10	171.63
20	365.61
30	444.32
50	285.49
70	162.38
90	106.26

Figure 3.31 shows the relation between leaching rate for copper and different concentration in CC, at room temperature.

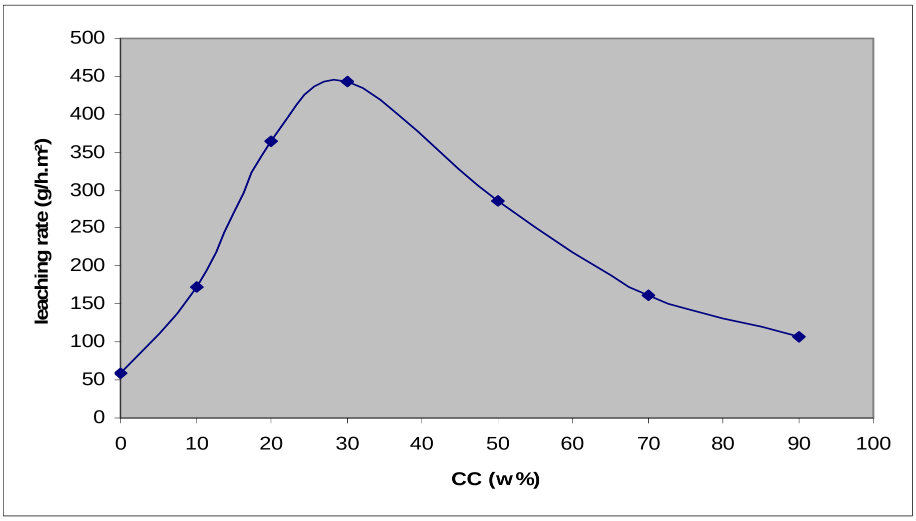


Figure 3.31 – Leaching rate vs concentration of CC at room temperature

From figure 3.31 it can be concluded that the best solution at room temperature to leach copper is the 30w% CC solution. However, regenerability of the solution is another aspect and the value of the leaching rate gives no information about that.

When the best solution for leaching copper was found ($CuCl_2.2H_2O$ / 30 w% CC) it was investigated if the solution could be regenerated with different oxidizing agents. The results are presented in section 3.3.

3.3. Copper leaching

3.3.1. Copper (II) recovery by oxidizing agents

In these tests, solutions with Cu(I) obtained after dissolution of Cu in 0.2M $CuCl_2.2H_2O$/ 20w% CC in different conditions, were treated with several oxidizing agents in order to investigate the possibility to regenerate Cu(II) in this way. Table 3.2 presents the results for each oxidizing agent.

Table 3.2 – Observations and conclusions for each oxidizing agent

Solution	Oxidizing agent	Observations	Conclusions
1	O_2	The solution was with appearance similar to milk with green colour.	• No presence of Cu^{2+}, if there, is reduced. • O_2 is a slow oxidizing agent
2	H_2O_2	The solution was blue “sulphate”	Presence of Cu^{2+}
2	O_2	The solution was blue “sulphate”	Presence of Cu^{2+}
3	H_2O_2	Formation of a black powder.	Passivation of copper
3	NH_3	The solution was with a light blue tone (almost colourless).	Cu^{2+} present but in less quantity..
3	NaOCl	Formation of a black powder.	Passivation of copper

Legend:

Solution 1: Cu^+ obtained after dissolution of one piece of copper in a solution of 0.2M $CuCl_2.2H_2O$ and 20w% CC while one hour of leaching.

Solution 2: Cu^+ obtained after dissolution of one piece of copper in a solution of 0.2M $CuCl_2.2H_2O$ and 20w%CC with 0.1M HCl, while one hour of leaching.

Solution 3: Cu^+ obtained after dissolution of one piece of copper in a solution of 0.2M $CuCl_2.2H_2O$ and 20w%CC with 0.1M HCl, with 17 hours of leaching.

H_2O_2 is a typical strong oxidizing agent and it was used to oxidize Cu(I) in solution 2 and 3; the behaviour in both solutions was different. For solution 2, the colour turned blue which confirmed the presence of Cu(II) and in solution 3 a black powder is formed. The leaching for solution 3 was slower which suggests the copper surface is passivated by the oxidant. The same is true for NaOCl. For solution 3, NH_3 was used because it is known that aqueous NH_3 solutions are used as well to leach copper and these solutions are readily regenerated; only a blue tone could be observed, which indicates that only a small quantity of Cu(II) was formed.

In case of solution 2, both oxidizing agents were efficient and the presence of Cu(II) was observed.

Comparing solution 1 and solution 2 where O_2 was used as an oxidant, we can see that in solution 2 the oxidation was more significant than in solution 1 because the presence of HCl in solution 2 accelerated the leaching.

3.3.2. Copper leaching in an electrochemical cell

After studying the leaching of copper with different oxidizing agents, an electrochemical cell was tested with the same objective. In table 3.3 the variation of the mass of copper and cathode during the experiment is shown.

Table 3.3 - Variation of mass of cathode and piece of copper

	m_i(g)	m_f(g)	Δm(g)
Cathode	14.72	13.52	1.2
Cu	11.98	10.54	1.94

Reactions at the cathode: $Cu^{2+}+2e^{-}\rightarrow Cu$

$2H^{+}+2e^{-}\rightarrow H_2$

Reaction at the anode: $H_2O\rightarrow 1/2\ O_2+2H^{+}+2e^{-}$

Typically, an electrochemical cell is efficient for recovery of metals, while simultaneously the consumption of chemical products is reduced. Disadvantages are the formation of H_2-gas and low efficiencies for metal recovery in solutions when concentration of metals in solution is low. [10]

In table 3.4 the concentration of copper in the beginning, after 30 minutes and one hour is given.

Table 3.4 - Concentration of copper in the beginning, after 30 and 60 minutes

Time (min)	Dilution factor	Absorbance	$C_{Cu(II)}$ (ppm)
0	500000	0.025	126307
30	500000	0.053	248258
60	500000	0.037	178571

Theoretically, the concentration of copper can only increase over time. However, the value in table 3.4 after 30 minutes leaching is higher than after 60 minutes. This is possibly due to formation of precipitates during the dissolution process.

3.3.3. Copper leaching by solution 0.2M $CuSO_4.5H_2O$ / 20w% CC

Because the presence of chloride can lead to formation of Cl_2 in an electrochemical cell, copper leaching in absence of the chloride of the metal salt is tested. Copper leaching with this solution was performed with cyclic voltammetry. Figure 3.32 shows the cyclic voltammogram of a solution with 0.2M $CuSO_4.5H_2O$ / 20w% CC.

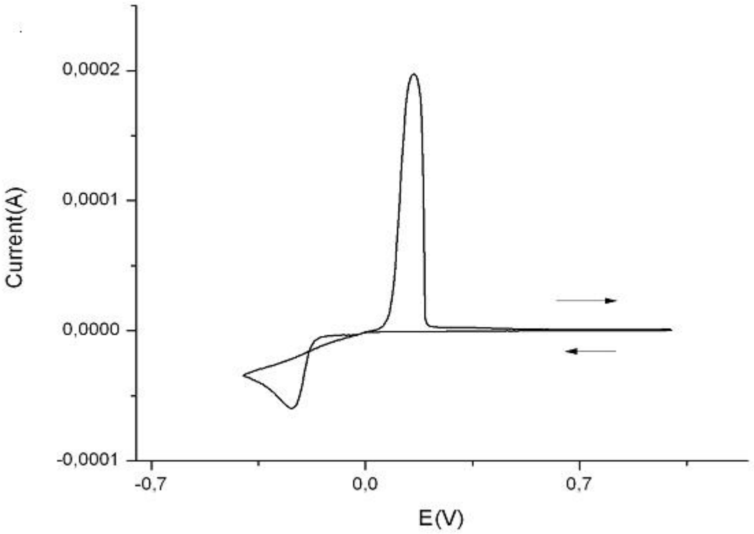


Figure 3.32 – A cyclic voltammogram of 0.2M $CuSO_4.5H_2O$ with 20w% CC in water at room temperature; step = 5mV; v=20mV/s; work electrode: Pt-disk (φ=1mm); counter: RuO_2/IrO_2 DSA; reference: 0.1M $Ag/AgNO_3$ with 0.2M kryptant in acetonitrile

In figure 3.32 it can be observed copper deposited at about -0.25 V vs. Ag/Ag-cryptand. The peak corresponding to the Cu(II)/Cu(I) couple did not appear. At about -0.18V the two lines make a intersection which is referred to as “nucleation loop”. This is related with the deposition of a metal. This is confirmed by the stripping peak in the reversal scan.

3.3.4. Copper leaching by solution 0.2M $CuCl_2.2H_2O$ / 20w% of CC and 0.1M HCl

Copper leaching was tested with a solution of 0.2M $CuCl_2.2H_2O$ with CC and HCl. Its effect in copper leaching was investigated with cyclic voltammetry. In figure 3.33 a cyclic voltammogram for this experiment is presented.

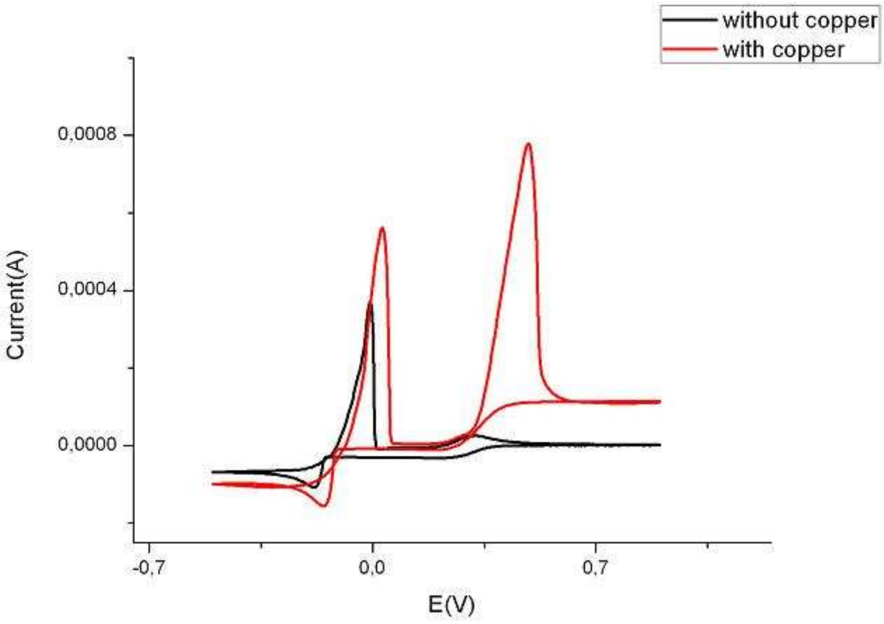


Figure 3.33 – A cyclic voltammogram of 0.2M $CuCl_2.2H_2O$ with 20w% CC and 0.1M HCl in water without and with piece of copper at room temperature ; step = 5mV; v=20mV/s; work electrode: Pt-disk (φ=1mm) ; counter: RuO_2/IrO_2 DSA; reference: Ag/$AgNO_3$ 0.1M with 0.2M kryptant in acetonitrile

Cyclic voltammograms of $CuCl_2.2H_2O$ in aqueous CC solutions that have been used for copper leaching, show a remarkable behaviour. As it can be seen in figure 3.33 the reversal is featured by two consecutive stripping peaks. This can be explained as follows. Initially, Cu(II) is reduced to Cu(I) in a homogeneous process. Then copper deposits as expected. On reversal, a first stripping peak appears; this peak is related with the oxidation of Cu to Cu(I), but due to the high concentration of Cu(I) in the bulk solution, because of the leaching, the Cu(I) precipitates as CuCl and a new deposit is formed. At more positive potentials the CuCl is oxidized to Cu(II) which is observed again as a stripping peak because of the limited thickness of the CuCl layer.

After studying copper leaching in solutions containing Cu(II), the effect of Fe(III) was tested. In point 3.3.5 and 3.3.6 the results for different experiments with Fe(III), CC and CCC are shown.

3.3.5. Copper leaching in 0.2M $FeCl_3.6H_2O$ / 50w% CC

In this experiment after 2h hours of copper dissolution the solution turned green. This colour can be a combination between Cu(II) (blue) and Fe(III) (yellow) or formation of Fe(II) cations (green). In table 3.5, the values of pH and weight of copper in the beginning and in the end are recorded.

Table 3.5 – Initial and final values of pH and mass of copper

	pH	m Cu(g)
Initial	1.83	2.33
final	2.33	1.29

$C_{Cu^{2+}\text{ in solution}} = 0.118M$

Concentration of Fe(II) expected for each possibility:

1st possibility: $C_{Fe(II)=}0.1M$ (if Cu(II) was formed)

2nd possibility: $C_{Fe(II)=}0.2M$ (if Cu(I) was formed)

Analysing both concentrations we can conclude that the species formed is Cu(I) because the concentration of copper dissolved was 0.118M (measured with AAS). However, the appearance of the solution is more similar to a Cu(II) solution. To check this, solutions were analysed by UV-Vis spectrometry. Figure 3.34 shows UV-Vis spectra for different solutions of Fe.

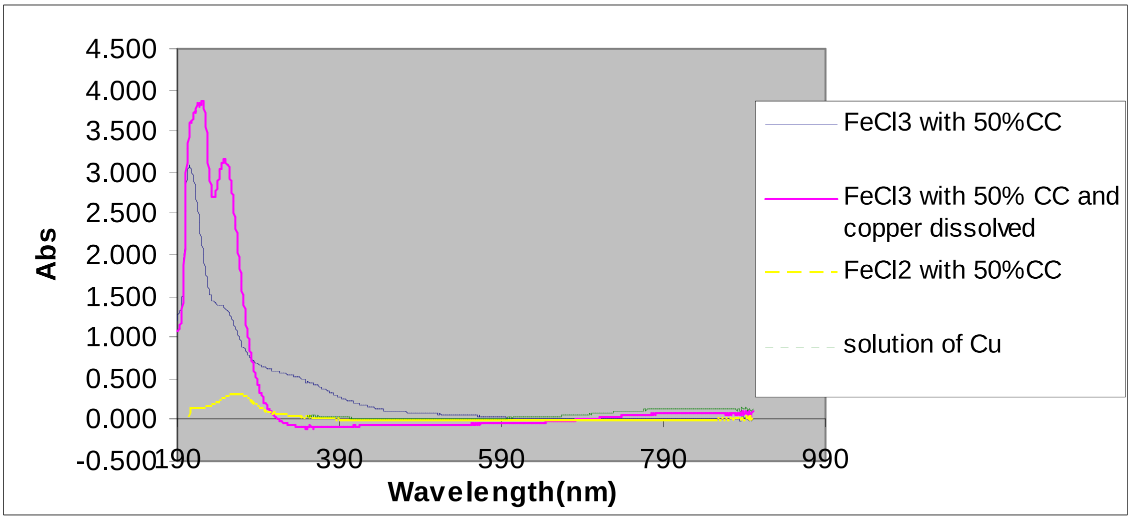


Figure 3.34 - UV-Vis spectra for solution $FeCl_3$ with 50%CC; $FeCl_3$ / 50% CC and copper dissolved: $FeCl_2$ / 50% CC and solution of copper

In figure 3.34 the yellow line recorded with a $FeCl_2$ solution has a peak at approximately 260nm which is associated with Fe(II). At 200nm the blue and pink peak represent Fe(III).

3.3.6. Copper leaching in 0.2M $FeCl_3.6H_2O$ / 30w% CC and 30w% CCC

In this experiment leaching with an Fe(III) solution with similar quantities of either CC or CCC is tested.

Figure 3.35 represents the copper leaching in a solution 0.2M $FeCl_3.6H_2O$ with 30%CC without air agitation.

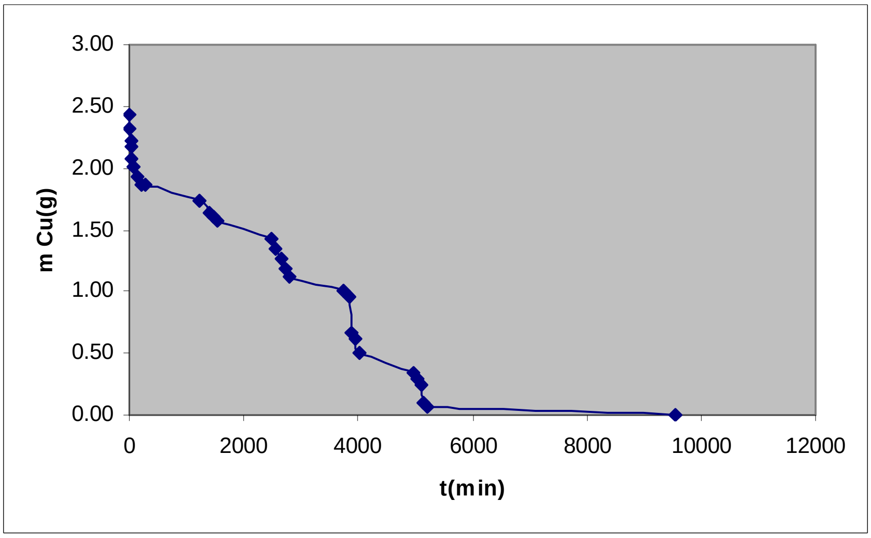


Figure 3.35 – Copper dissolution with 0.2M $FeCl_3.6H_2O$ / 30w% CC

As it can be observed in figure 3.35 almost 170 hours were required in order to leach the complete piece of copper.

Figure 3.36 represents the difference of weight for a piece of copper in 0.2M $FeCl_3.6H_2O$ and 30w% CCC without air agitation.

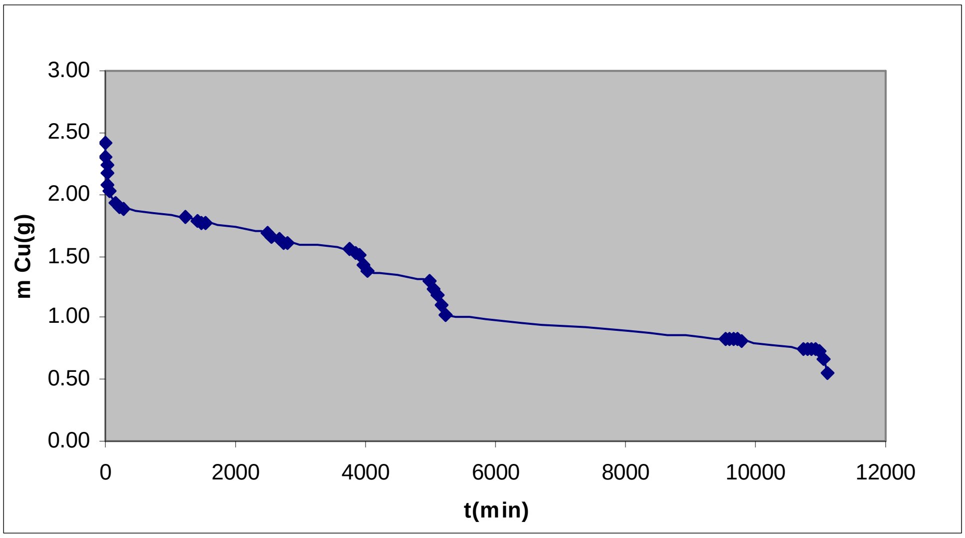


Figure 3.36 – Copper dissolution in 0.2M $FeCl_3.6H_2O$ / 30w% CCC

When CCC and CC solutions are compared, the leaching was faster using the CC. At 184 hours (approximately 11000 minutes) the piece of copper in CCC solution was not dissolved and at almost 167 hours (approximately 10000 minutes using CC without air agitation the piece of copper dissolved totally. The leaching power of solutions with CC was tested further in presence of air and N_2. Figures 3.36 and 3.37 show the result of leaching in presence of air and N_2, respectively.

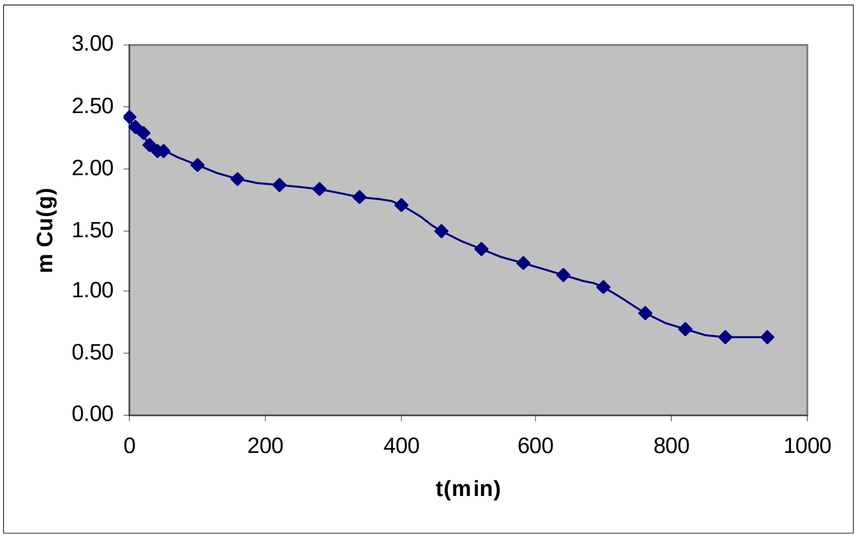


Figure 3.37 – Copper dissolution in with 0.2M $FeCl_3.6H_2O$ / 30w% CC with air bubbling

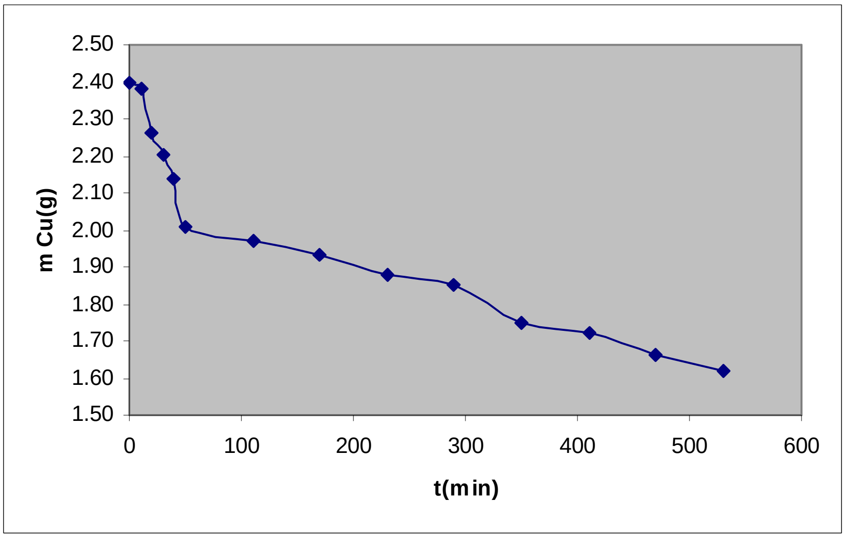


Figure 3.38– Copper dissolution with 0.2M $FeCl_3.6H_2O$ / 30w% CC with N_2 bubbling

Comparing both curves it can be concluded that leaching in the initial stage (50 minutes) was faster using N_2 instead of air, but when the experiment with N_2 bubbling was stopped at 530 minutes, the mass of copper dissolved was 0.78g and with air bubbling 1.08g was dissolved. We can conclude that for leaching of copper with iron solutions the use of air is better because the O_2 regenerates the Fe(III) oxidant, which results in a larger concentration of the active Fe(III) oxidant.

3.4. Metals dissolution from PCBs

3.4.1. Metals dissolution in a solution 0.2M $CuCl_2.2H_2O$ / 30w% CC

In figures 3.39 to 3.41 the PCB before and after leaching at room temperature and 80ºC are represented.

(a) (b)

Figure 3.39 – PCBs before dissolution in 0.2M $CuCl_2.2H_2O$ / 30w% CC: (a) front (b) back

(a) (b)

Figure 3.40 – PCBs after dissolution in 0.2M $CuCl_2.2H_2O$ / 30w% CC at room temperature (a) front (b) back

(a) (b)

Figure 3.41 – PCBs after dissolution in 0.2M $CuCl_2.2H_2O$ / 30w% CC at 80ºC: (a) front (b) back

As we can see in figures 3.40 and 3.41, at 80ºC the gold fingers were dissolved in larger quantity than at room temperature. Also, the plastic pieces unclasp more easily.

In table 3.6 the weight of PCBs before and after leaching is given.

Table 3.6 – Mass of PBCs at start and after dissolution with 0.2M $CuCl_2.2H_2O$ / 30w% CC

Temperature	m_i (g)	m_f(g)	Δm(g)
Room temperature	72.87	72.48	0.39
80ºC	72.23	71.26	0.97

From the table 3.6 it can be concluded that more mass of metal was dissolved at 80 ℃

In table 3.7 the absorbance and concentration of copper during 6 hours of leaching is represented.

Table 3.7– Concentration of copper during leaching of the PCB at room temperature and 80ºC

t(h)	Abs		Dilution factor	C_{Cu}(ppm)	
	room temperature	T=80ºC		room temperature	T=80ºC
1	0.333	0.367	8000	23765.5	26181.2
2	0.323	0.387	8000	23055.1	27602.1
3	0.334	0.360	8000	23836.6	25683.8
4	0.334	0.349	8000	23836.6	24902.3
5	0.337	0.359	8000	24049.7	25612.8
6	0.331	0.358	8000	23623.4	25541.7

In figure 3.42 the graphic representation of concentration of copper vs time of leaching is shown.

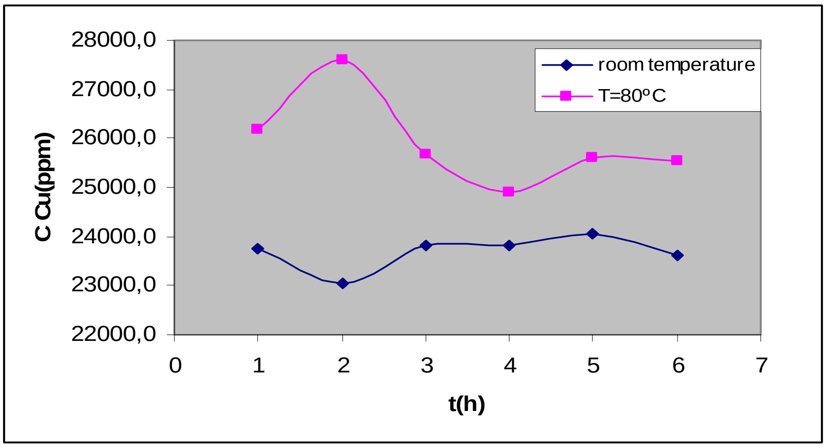


Figure 3.42 – Concentration of copper during PCB dissolution in 0.2 M $CuCl_2.2H_2O$ / 30w% CC at room temperature and at 80ºC

Theoretically, the concentration of copper should increase during the leaching process. However, it is observed the concentration of copper decreases after 3 hours and then increases again after 4 hours leaching. This effect is reproducible and is probably related with the formation of precipitates. The same was observed at room temperature after two hours of leaching. In this case, the leaching was slow.

In table 3.8 the concentration of lead during the experiment is given.

Table 3.8 – Concentration of lead during leaching of the PCB at room temperature and 80ºC

t(h)	Abs		Dilution factor	C_{Pb}(ppm)	
	room temperature	T=80ºC		room temperature	T=80ºC
1	0.098	0.113	50	104.0	118.9
2	0.122	0.136	50	127.8	141.7
3	0.162	0.148	50	167.6	153.7
4	0.187	0.159	50	192.4	164.6
5	0.198	0.170	50	203.4	175.5
6	0.204	0.182	50	209.3	187.5

In figure 3.43 the variation of lead against time of leaching is shown.

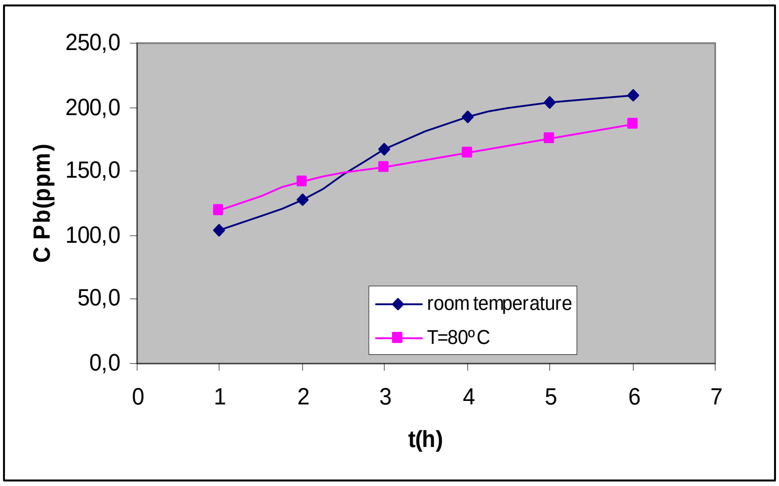


Figure 3.43 – Concentration of lead during PCB dissolution in 0.2 M $CuCl_2.2H_2O$ / 30w% CC at room temperature and at 80ºC

From figure 3.43 it can be seen that up till 2.5 hours the leaching at 80ºC was slightly faster than at room temperature. After this time leaching was faster at room temperature for this metal.

In table 3.9 the concentration of tin during the leaching is given.

Table 3.9 – Concentration of tin during leaching of the PCB at room temperature and 80ºC

t(h)	Abs		Dilution factor	C_{Sn}(ppm)	
	room temperature	T=80ºC		room temperature	T=80ºC
1	0.277	0.182	50	481.1	334.9
2	0.352	0.221	50	596.5	394.9
3	0.387	0.225	50	650.3	401.1
4	0.397	0.229	50	665.7	407.2
5	0.462	0.258	50	765.7	451.8
6	0.546	0.250	50	894.9	439.5

In figure 3.34 the comparison between both conditions is presented.

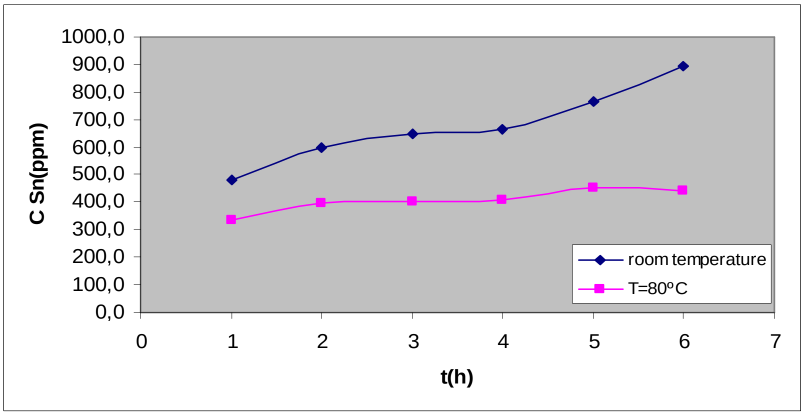


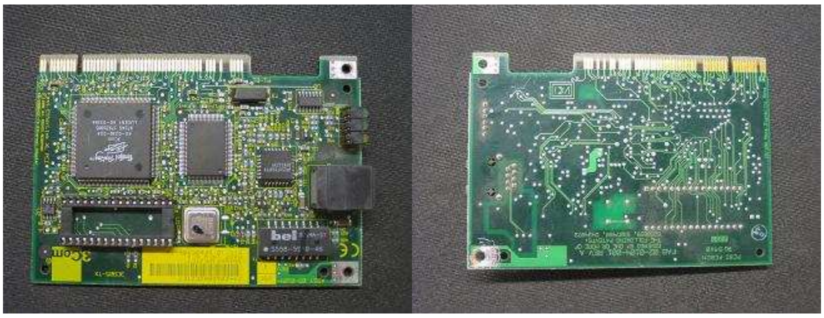
Figure 3.44 – Concentration of tin during PCB dissolution in 0.2 M $CuCl_2.2H_2O$ / 30w% CC at room temperature and at 80ºC

As can be seen in figure 3.34, at room temperature the leaching was faster than at 80 ℃. In preliminary work the leaching of some metals was investigated with a solution of 0.2M $CuCl_2.2H_2O$ / 50w% CC; the difference between both conditions was not significant, so for this metal it is better to use room temperature.

The leaching of PCB´s is studied further with a solution of 0.2M $FeCl_3.6H_2O$ / 30w% CC. The 30w% CC solution is used for reasons of comparison with the earlier results with the solution of 0.2M $CuCl_2.2H_2O$. The use of the iron solution was based on the experimental work made by Vanhoecke[9], who performed a study on the leaching of copper using solutions of 0.2M $FeCl_3.6H_2O$ with different concentrations of CC. In this experimental work the solution of 0.2M $FeCl_3.6H_2O$ with 30w% CC was the best leach for copper.

3.4.2. Metals dissolution in a solution 0.2M $FeCl_3.6H_2O$ / 30w% CC

In figures 3.45 to 3.47 the PCB before and after leaching at room temperature and 80ºC is shown.



(a) (b)

Figure 3.45 – PCBs before dissolution in 0.2M $FeCl_3.6H_2O$ / 30w% CC: (a) front (b)back

(a) (b)

Figure 3.46 – PCBs after dissolution in 0.2M $FeCl_3.6H_2O$ / 30w% CC at room temperature: (a) front (b) back


(a) (b)

Figure 3.47 – PCBs after dissolution in 0.2M $FeCl_3.6H_2O$ / 30w% CC at room 80ºC: (a) front (b) back

From figures 3.46 and 3.47, it can be seen that at 80ºC more gold fingers were dissolved than at room temperature. Also, the electronic components are detached more easily at 80ºC.

In table 3.10 the weight at the start, at the end and the difference is represented.

Table 3.10 – Mass of PCB´s at the start and after dissolution in 0.2 M $FeCl_3.6H_2O$ / 30w% CC

Temperature	m_i (g)	m_f(g)	Δm(g)
Room temperature	56.54	55.36	1.18
80ºC	58.51	55.84	2.67

With a solution of 0.2 M $FeCl_3.6H_2O$ plus 30w% CC, the leaching at 80ºC was faster than at room temperature. At 80ºC 2.67g was dissolved and 1.18g at room temperature.

In table 3.11 the variation of concentration of copper is presented.

Table 3.11– Concentration of copper during leaching of the PCB at room temperature and 80ºC

t(h)	Abs		Dilution factor	C_{Cu}(ppm)	
	room temperature	T=80ºC		room temperature	T=80ºC
1	0.006	0.093	5000	304.1	3978.0
2	0.011	0.202	5000	515.2	8581.1
3	0.051	0.255	5000	2204.4	10819.3
4	0.090	0.267	5000	3851.4	11326.0
5	0.131	0.280	5000	5582.8	11875.0
6	0.155	0.296	5000	6596.3	12550.7

The figure 3.48 shows the concentration of copper vs. time of leaching.

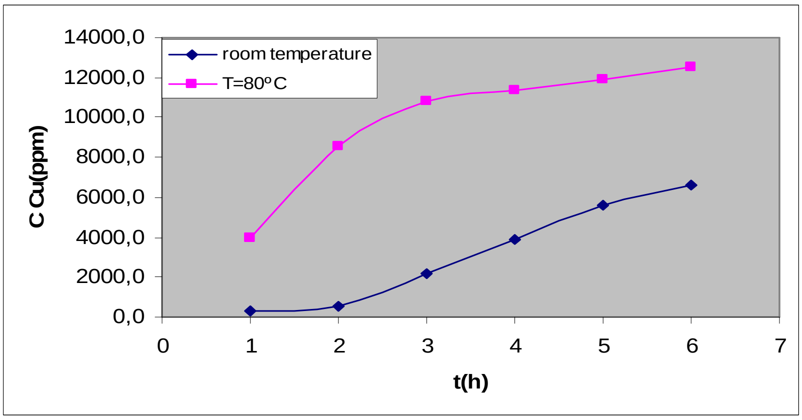


Figure 3.48 – Concentration of copper during PCB dissolution in 0.2 M $FeCl_3.6H_2O$ / 30w% CC at room temperature and at 80ºC

The concentration of copper increased during all experiments but the leaching was faster at 80ºC. After 6 hours of leaching the concentration of copper in solution at 80ºC was 12550.7ppm and at room temperature 6596.3ppm was measured.

In table 3.12 the variation of concentration of lead during the leaching is presented.

Table 3.12– Concentration of lead during leaching of PCB at room temperature and 80ºC

t(h)	Abs		Dilution factor	C_{Pb}(ppm)	
	room temperature	T=80ºC		room temperature	T=80ºC
1	0.003	0.036	5000	1288.1	5858.7
2	0.009	0.053	5000	2119.1	8213.3
3	0.017	0.059	5000	3227.1	9044.3
4	0.023	0.062	5000	4058.2	9459.8
5	0.027	0.066	5000	4612.2	10013.9
6	0.030	0.053	5000	5027.7	8213.3

In figure 3.49 the concentration of lead against time of dissolution is given.

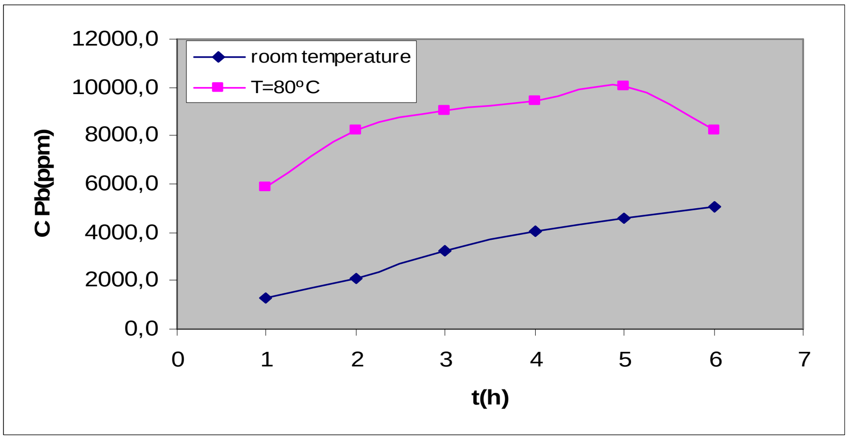


Figure 3.49 – Concentration of lead along PCB dissolution in 0.2 M $FeCl_3.6H_2O$ / 30w% CC at room temperature and at 80ºC

From figure 3.49 it is clear the dissolution of lead was faster at 80ºC. The last point represented at 80ºC shows the concentration decreased again, which is not expected. This is likely due to the formation of precipitates in the solutions.

In table 3.13 the variation of concentration of tin during six hours of leaching is presented.

Table 3.13– Concentration of tin during leaching of PCB at room temperature and 80ºC

t(h)	Abs		Dilution factor		C_{Sn}(ppm)	
	room temperature	T=80ºC	room temperature	T=80ºC	room temperature	T=80ºC
1	0.12	0.035	50	5000	773.2	1428.6
2	0.221	0.038	50	5000	1675.0	4107.1
3	0.372	0.041	50	5000	3023.2	6785.7
4	0.426	0.054	50	5000	3505.4	18392.9
5	0.483	0.059	50	5000	4014.3	22857.1
6	0.522	0.062	50	5000	4362.5	25535.7

Tin was dissolved very quickly. The absorbances obtained at 80ºC were high compared with the ones at room temperature that it was necessary to dilute 5000 times.

In figure 3.50 the graphic representation of the tin leaching is given.

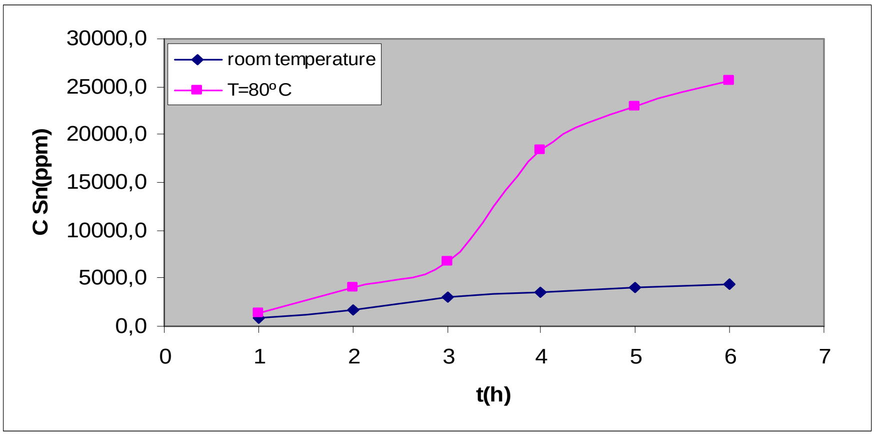


Figure 3.50 – Concentration of tin along PCB dissolution in 0.2 M $FeCl_3.6H_2O$ / 30w% CC at room temperature and at 80ºC

From the figure the fast dissolution of tin at 80ºC can be seen. However, at room temperature the leaching was much slower. At the end of the experiment 25535.7ppm of tin was obtained at 80ºC and only 4362.5ppm at room temperature.

3.5. Gold dissolution

3.5.1. Gold dissolution in different solutions at room temperature and 80ºC (gold powder)

In figure 3.51 the gold that was used for this experiment is presented.

Figure 3.51 – Gold powder

The leaching rate, the concentration of gold determined and expected are presented in table 3.14.

Table 3.14 - Concentration and leaching rate for each solution used to dissolve gold at room temperature

	Solution 1 (a)	Solution 2 (b)	Solution 3 (c)
Time of dissolution(h)	20	45	20
m $(Au)_i$ (mg)	3.7	3.5	7.9
m $(Au)_{filtered}$ (mg)	0.7	1.1	4.7
m $(Au)_{dissolved}$ (mg)	3.0	2.4	3.2
$C_{expected}$ (ppm)	12	12	16
C_{AA} (ppm)	7.36	8.59	0.060
Diluation factor	10	8	8
C (ppm)	73.6	68.7	0.48
Leaching rate (mg/h)	0.15	0.053	0.16

Legend:
(a) 0.2M $CuCl_2.2H_2O$ in Ethaline200
(b) 0.2M $FeCl_3.6H_2O$ in Ethaline200
(c) 15mL 0.2M $CuCl_2.2H_2O$ in Ethaline200 and 10mL of 45w% choline base

From table 3.14 we can see that some gold was dissolved in several solutions. However, these results are not conclusive because gold was used in powder form which is difficult to weigh. Therefore, the values of the remaining weight of gold can be due to dissolution or due to losses during the experiment, for example during the weighing and loss of material when transferring the powder.

The same experiment was repeated at 80ºC but with solution 1 and 2.

Table 3.15 represents the concentration of gold experimentally determined and calculated at 80ºC.

Table 3.15 – Results of concentration and leaching rate for each solution used to dissolve gold at 80ºC

	Solution 1(a)	Solution 2 (b)
nº hours of dissolution	20	45
$m(Au)_i$ (mg)	5.6	6.7
$m(Au)_{filtered}$ (mg)	0	3.2
$m(Au)_{dissolved}$ (mg)	5.6	3.5
$C_{expected}$ (ppm)	56	35
C_{AA} (ppm)	5.2	7.7
Diluation factor	4	4
C(ppm)	20.8	30.8
Leaching rate(mg/h)	0.28	0.24

With solution 1 all gold was dissolved and 3.5g was dissolved in solution 2, a quite significant quantity was dissolved. Here again, the measured mass is uncertain due to the use of gold powder. Nevertheless, it is clear the leaching of gold does occur at this high temperature, because in case of solution 1 all gold disappeared. It is better for this kind of experiments to use gold in solid form.

Solutions 3 are featured by a specific dark-blue colour which reminds of Cu(II) in presence of ammonia or amines. The leaching of gold was tested with solutions containing amines; Ethanolamine, Ammonia and [2-(methylamino)ethanol]. With Ethanolamine and Ammonia the solution turned blue purple and with [2-(methylamino)ethanol] dark-blue. They were tested during one hour leaching to check if they are able to leach gold, but the result was negative.

3.5.1.1. Results of cyclic voltammetry for gold dissolution

In figure 3.52 a cyclic voltammogram of Ethaline200 is represented. This analysis give us information about the “solvent limit”, the potentials between which we can work, that means the interval where the electro-activity of an added compound can be investigated without interference of the solvent deteriorating at the electrode.

In a cyclic voltammogram positive (oxidation) and negative (reduction) current peaks reveal information on the electro-active behaviour of the product.

The figure 3.52 shows the formation of one small peak at 1V after reversal of the scan. This peak is typical for ionic liquids and is due to the reduction of deterioration products that have been formed by oxidation of the solvent just before the reversal.

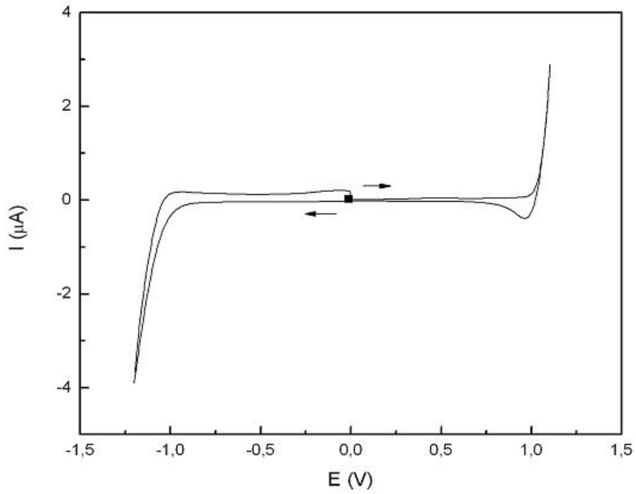


Figure 3.52 – A cyclic voltammogram of Ethaline200 at room temperature; step = 5mV; v=20mV/s; work electrode: Pt-disk (φ=1mm); counter: RuO_2/IrO_2 DSA; reference: 0.1M $Ag/AgNO_3$ with 0.2M kryptant in acetonitrile.

In figure 3.53 a cyclic voltammogram recorded before and after gold dissolution in 0.2 M $FeCl_3.6H_2O$ / Ethaline 200 is presented.

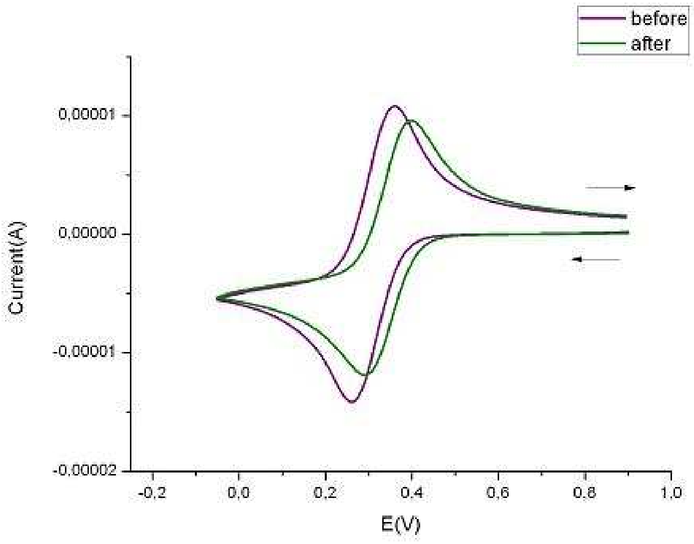


Figure 3.53 – A cyclic voltammogram of 0.2M $FeCl_3.6H_2O$ in Ethaline200 before and after gold dissolution at room temperature; step=5mV; v=20mV/s; work electrode: Pt-disk (φ=1mm); counter: RuO_2/IrO_2 DSA; reference: 0.1M $Ag/AgNO_3$ with 0.2M kryptant in acetonitrile.

From figure 3.53 it is not possible to extract information about gold leaching. There is no clear difference between both voltammograms. This figure only gives information about the reversibility of the solution: a fast reduction to Fe(II) and a fast oxidation to Fe(III). The reduction of Fe(III) occurs at potentials between 0.45V and 0.25V. At -0.15V the oxidation of Fe(II) occurs until 0.35V.

Figure 3.54 represents a cyclic voltammetry analysis of 0.2M $CuCl_2.2H_2O$ in Ethaline200 before and after dissolution of gold.

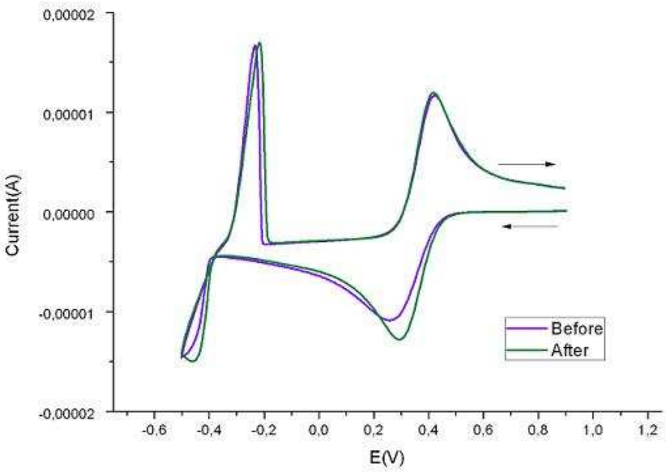


Figure 3.54 – A cyclic voltammogram of 0.2M $CuCl_2.2H_2O$ in Ethaline200 before and after gold dissolution at room temperature; step = 5mV; v=20mv/s; work electrode: Pt-disk (φ=1mm); counter: RuO_2/IrO_2 DSA; reference: 0.1M Ag/$AgNO_3$ with 0.2M kryptant in acetonitrile

In figure 3.54 it can be seen that the current starts at zero because only Cu(II) is present in solution and the initial value of the potential is too positive to induce reduction of Cu(II). At 0.45V the reduction of Cu(II) to Cu(I) starts. At -0.4V the current increases because of the reduction of Cu(I) to Cu. On reversal, the current becomes anodic and shows a typical stripping peak immediately because of the oxidation of Cu to Cu(I). At 0.2V the current is negative (cathodic); this is not expected because only oxidation currents are expected. Possibly the reduction current is due to reduction of Cu(II) that has been formed chemically. At 0.30V the current increases because Cu(I) is oxidized to Cu(II).

3.5.2. Gold dissolution in Ethaline200 in presence of Cl_2/ Cl_3^- (piece of gold)

3.5.2.1. Gold dissolution with Cl_2 produced with 1st method

After 2-3 minutes of Cl_2 production, the solution turned bright yellow due to an excess of Cl_2. At the end of the experiment (after 20 minutes) it was observed the solution turned colourless, possibly due to the release of Cl_2.

The solution was analysed with UV-Vis spectrophotometry with air as a reference.

In table 3.16 the content of water in Ethaline200 pure, Ethaline after 5 hours in oven (less water) and Ethaline200 with Cl_2 by Karl Fisher method is given.

Table 3.16 – Water content for the 1st method present in samples: Ethaline200; Ethaline "dry" and Ethaline "dry" with Cl_2

%H_2O Solution	1st	2nd	3rd
Ethaline 200	5,87%	5,34%	6,98%
Ethaline 200"dry"	4.49%	8.88%	5.28%
Ethaline with Cl_2 "dry"	2.30%	5.66%	6.42%

From table 3.16 it can be concluded that for the same solutions slightly different values were obtained. Ethaline200 made up with CC, which is highly hygroscopic, absorbs high quantity of water in contact with air.

The different solutions were analysed as well with UV-Vis spectrometry in order to identify the Cl_2 peak.

Figure 3.35 represents the analysis in UV-Vis spectrometry for the different solutions of Ethaline200.

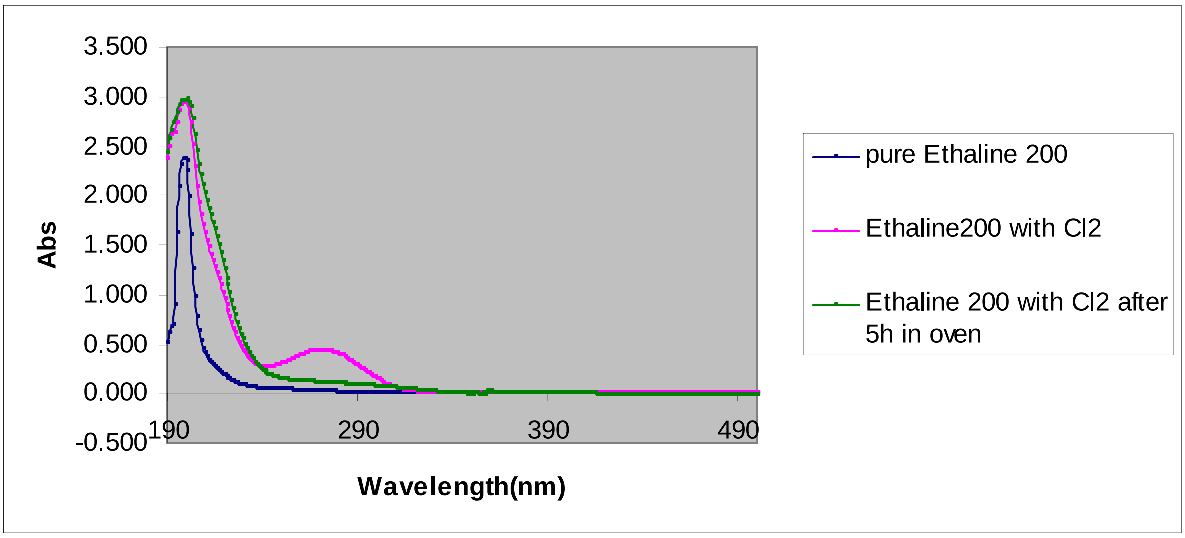


Figure 3.55 - UV-Vis spectra for pure Ethaline200; Ethaline with Cl_2; Ethaline200 with Cl_2 after 5h in oven

In the UV-Vis spectrum the peak which corresponds to Cl_2/Cl_3^- (270nm) and a big peak around 210nm which corresponds to water can be observed. To investigate this further, a sample of solution was placed in an oven for five hours to eliminate the water present. Then, the solution was again scanned spectrophotometrically.

After 5h in the oven it was observed that the absorbance of the water had decreased. The Cl_2 peak disappeared as well on heating.

It was not possible to dissolve gold with this solution, because it can be expected on basis of the spectra Cl_2 disappears slowly from the solution.

3.5.2.2. Gold dissolution with Cl_2 produced with 2nd method

In all experiments bubbles were formed at the anode, which indicates production of Cl_2.

Next table contains the water content for Ethaline200 pure, Ethaline200 after 24h in oven and Ethaline200 from anode measured by Karl Fisher method.

Table 3.17 – Water content for the 2nd method present in samples: Ethaline200; Ethaline "dry" and Ethaline "dry" with Cl_2

%H_2O / Solution	1st	2nd	3rd
Ethaline 200	6.98%	6.65%	6.31%
Ethaline 200"dry" after 24 hours	4.94%	3.25%	4.19%
Ethaline with Cl_2 (anode)	4.51%	3.91%	3.78%

From table 3.17 the percentage of H_2O for "dry" Ethaline200 and "dry" Ethaline200 with Cl_2 are lower than pure Ethaline200. This means that some water was evaporated. The difference in values between the readings are due the varying humidity of atmospheric air.

In figure 3.56 the results from UV-Vis spectrometry for the same solutions of Ethaline200 are represented.

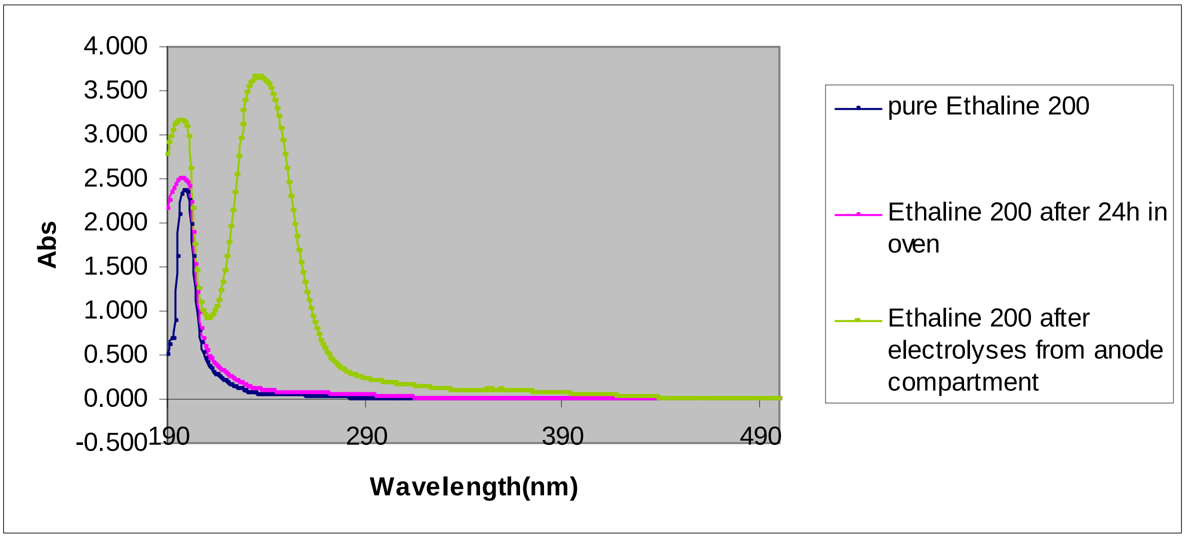


Figure 3.56 – UV-Vis spectra of solution Ethaline200; Ethaline200 after 24h in oven; Ethaline200 after electrolyses from anode compartment

In the figure a peak is observed at 210 nm which correspond to the water present. Comparing pure Ethaline200 with Ethaline after 24h in an oven at 70 ℃, there is not a big difference between both peaks. Perhaps Ethaline absorbed some humidity from air before the UV-Vis measurement was performed.

A sample was withdrawn near the anode and analysed too (green line in figure 3.56). It is possible to see a big peak at 240nm which correspond to Cl_2 and a peak of water but now the absorbance is higher, probably due to the humidity of air that the solution absorbed.

After making a solution with Ethaline200 and Cl_2 in the electrochemical cell a piece of gold was immersed for 5 hours. At end of this time the weight of the piece of gold was identical to the initial weight 0.39g.

3.5.3. Gold dissolution in presence of 0.2M $FeCl_3$ in Ethaline200 and 0.2M $FeCl_3$ in CCC and Ethaline200

After 17h in contact with solution of 0.2M $FeCl_3$ in Ethaline200 the piece of gold did not dissolve. Then, the same piece of gold was put in contact with 25mL of 0.2M $FeCl_3.6H_2O$ with 20w% CCC and Ethaline200 and did not dissolve too.

3.6. Analytical methods to quantify Fe(III) and Fe(II) in solutions

3.6.1. Study of Nernst Equation in solutions containing Fe(III) and Fe(II)

Figure 3.57 shows the relation ratio Fe(III)/Fe(II) against potential based in Nernst equation.

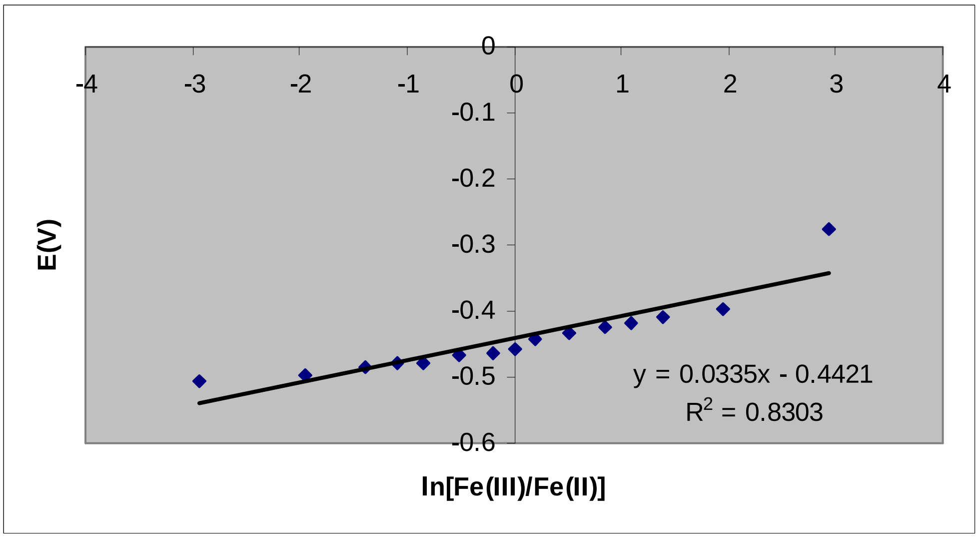


Figure 3.57 – Ratio Fe(III)/Fe(II) vs potencial

Analysing the figure the linear relation between potential and ratio Fe(III)/Fe(II) has a R^2=0.8303.

Note: It was despised two points which correspond at solution only with Fe(III) and other with only Fe(II).

3.6.2. Identification and quantification of Fe(III) and Fe(II) in different concentrations

In figures 3.58 and 3.59 the voltammetric results are shown for different concentrations of Fe(III) and Fe(II). The objective is to obtain a linear relation between current and concentration.

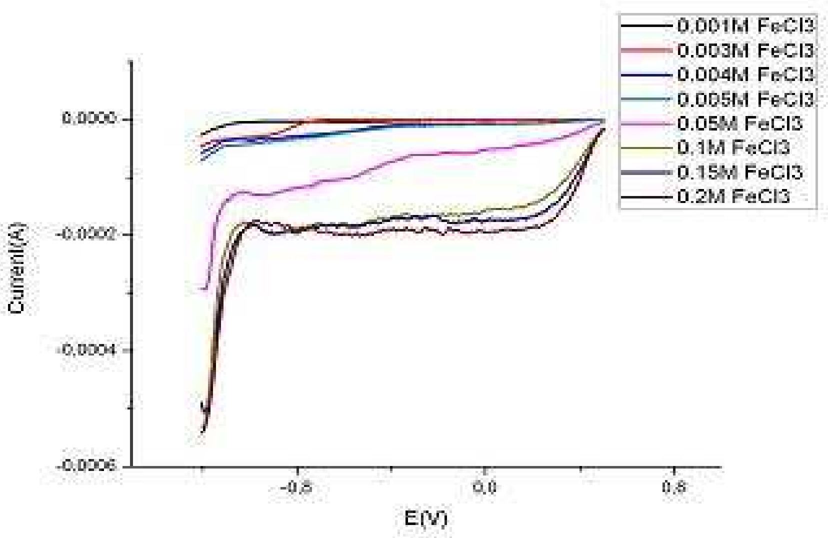


Figure 3.58 – A voltammogram of 0.2M $FeCl_3.6H_2O$ in 50w%CC at room temperature; step = 5mV; scan rate=0.01V/s; work electrode: platinum rotating electrode; counter: RuO_2/IrO_2 DSA; reference: 0.1M $Ag/AgNO_3$ with 0.2M kryptant in acetonitrile

For this experiment voltammograms were recorded for low and high concentration of Fe(II) and Fe(III). In the figure it can be seen that the reduction of Fe(III) to Fe(II) has reached the limiting current at about -0.4V. For low concentrations, [0.001-0.005]M the voltammograms are very similar. But in the latter case it is difficult to find a linear relation between concentration and current.

The next graph corresponds to Fe(II) solutions. Four solutions were made between 0.05 and 0.2M $FeCl_2$.

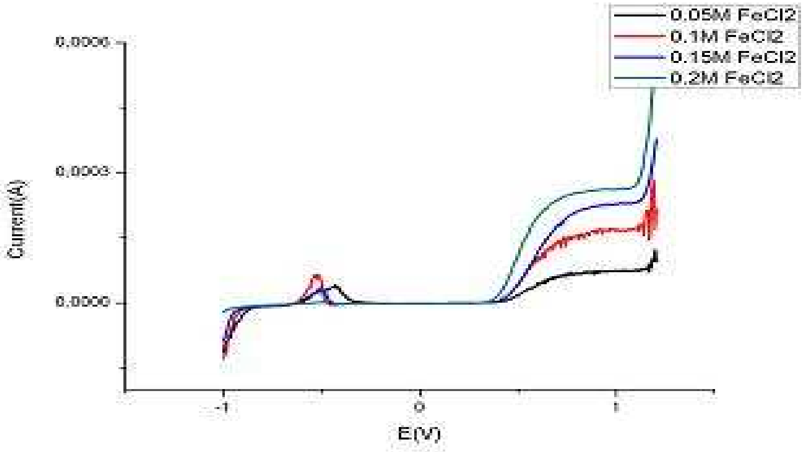


Figure 3.59 – A voltammogram of 0.2M $FeCl_2.4H_2O$ in 50w%CC at room temperature; step = 5mV; scan rate=0.05V/s; work electrode: platinum rotating electrode; counter: RuO_2/IrO_2 DSA; reference: 0.1M $Ag/AgNO_3$ with 0.2M kryptant in acetonitrile

In order to find a relation between current and concentration, the current at 0.7V was read because then the limiting current for formation of Fe(III) is reached. Figure 3.60 shows this relation.

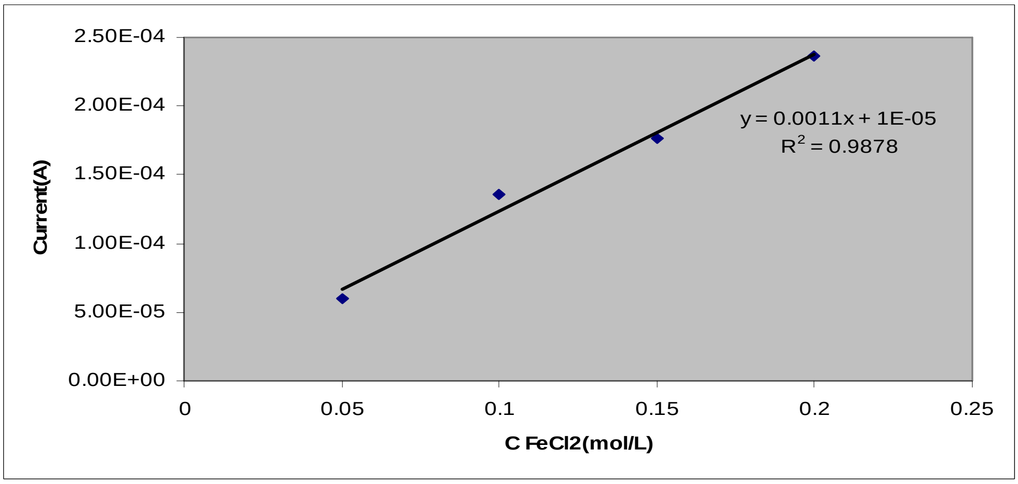


Figure 3.60 – Current vs concentration of $FeCl_2$ in 50w%CC at 0.7V

From figure 3.60 a linear relation with R^2=0.9878 is found.

4. Conclusions

The main objective of this project was to study the leaching effect of solutions based on ionic liquids on some metals commonly found in PCBs. These solutions are aqueous and contain either $CuCl_2.2H_2O$ or $FeCl_3.6H_2O$ as an oxidant and a quaternary ammonium salt. It is proven the typical properties ascribed to the use of ionic liquids, still prevail when quite large amounts of water are added. In case of $CuCl_2.2H_2O$ this 'ionic liquid property' is the existence of a stable Cu(I) component; in case of $FeCl_3.6H_2O$ this 'ionic liquid property' is the reversibility of the Fe(III)/Fe(II) redox couple, which is not true in pure water. Moreover, in the case of leaching solutions based on Cu(II) or Fe(III) and quaternary ammonium salts, the leaching effect clearly increases on addition of water, while the viscosity lowers, the conductivity increases and the use of hazardous ethylene glycol is not necessary.

In the preliminary work, the leaching effect of a 0.2M $CuCl_2.2H_2O$ / 50 w% CC solution was studied on several pure metals, which are present on PCBs. The leaching was investigated at room temperature and at 80ºC. In these experiments it was observed that aluminium dissolved fast at high temperature (80ºC). On the contrary, at room temperature the leaching stopped after 10 minutes presumably because of a protective layer formed on the aluminium surface. For copper and tin at 80ºC the leaching was faster than at room temperature but the difference was not significant. We can conclude for these metals the leaching can better be made at room temperature. For iron leaching at room temperature was faster than at 80ºC. But, for other metals the leaching rate is clearly larger at 80ºC as compared with room temperature. For zinc and lead this is ascribed to the impossibility of forming a protective layer at higher temperature. In the case of nickel the leaching at room temperature and 80ºC are more or less similar and thus the leaching of nickel is preferably done at room temperature. For gold, silver and other noble metals, this solution was not efficient. It seems that the presence of water is not advantageous in this case.

Copper being the metal of reference, the properties of Cu leaching were studied more in depth: its behaviour was investigated in 0.2M $CuCl_2$ at room temperature and 80ºC with different concentrations of CC. For several solutions, the leaching at 80ºC was faster than at room temperature but the highest leaching rate (444.32 $g/m^2.h$) was obtained with a solution of 0.2M $CuCl_2$ / 30w% CC at room temperature.

The leaching of copper was tested as well in solutions of Fe(III) with CC and CCC with various percentages of water. With Fe(III) an increase in pH is observed after some time of leaching.

This is ascribed to the replacement of a strong acid, Fe(III), to a weaker acid, Fe(II). By consequence, insoluble iron hydroxides precipitate, thus decreasing the concentration of the active component. The possibilities to regenerate these solutions composed of Fe(III) and CC was investigated by bubbling air through the solutions. Because of the constant flow of air Fe(II) oxidizes again to Fe(III). This is proven in an experiment where a copper plate with a weight several times more than the theoretical maximum that can be dissolved by the volume of etching solution, is dissolved completely when air is bubbled continuously through the solution.

With the 0.2M $CuCl_2$ / 30w% CC and 0.2M $FeCl_3.6H_2O$ / 30w% CC solutions at room temperature, leaching experiments on PCBs were performed. The results with both solutions were satisfactory and at 80℃ the efficiency is still better, but the formation of precipitates explained earlier is disturbing the process. The leaching effect of the Fe(III) solutions on gold were tested as well, but it can be concluded that gold cannot be leached at all due to the presence of water in the solutions.

Because of the troublesome Cu(I) precipitates formed with Cu(II) leaching solutions, we prefer the Fe(III) solutions. The solution selected is composed of $FeCl_3.6H_2O$ and CC. The latter is preferred over CCC because CCC is classified as a chlorinated organic component and is therefore to be avoided. Moreover, the solubility of $FeCl_3.6H_2O$ in CCC is lower as compared to CC. Thus, increase of the leaching strength by increasing the concentration of the oxidant is limited with CCC. For future experiments we suggest to investigate the possibility to counter the pH increase of Fe(III) leaching solutions by continuous regeneration in an electrochemical cell. The regeneration of Fe(III) at the anode will lead to a pH decrease. It is important when a continuous electrochemical regeneration is targeted, the copper deposited at the cathode is protected against leaching; if not, the electrochemical efficiency will decrease. Furthermore, we suggest to further investigate the chemical regeneration with oxygen and the influence on the pH.

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Appendix A

A.1 Analytical Equipment

- Atomic Absorption Spectrometer Unicam Solar 989
- Cary 100 Bio UV-Vis Spectrophotometer
- The potentiostat is a Eco Chemie Autolab PG-STAT12 potentiostat. The software used was "General Purpose Electrochemical System version 4.9"

- For the Karl Fischer-titrations:
  It's a Metrohm 787 KF Titrino with 703 Ti Stand and a Pt-electrode. As titrant you use Fluka Hydranal - Composite 5 and the solvent is Fluka Hydranal Methanol Rapid.

A.2 Calculations

A.2.1. Preparation of 0.2M $CuCl_2.2H_2O$ with 50w% CC (procedure 3.1.)

V= 1L

1- Calculation of mass of $CuCl_2.2H_2O$ necessary

$$n = c \times V = 0.2 \times 1 = 0.2 mol$$
$$m = n \times M = 0.2 \times 170.48 = 34.1 g$$

2- Mass of choline chloride

To make 50w% of choline chloride was used 500 g of this reagent in one litter.

A.2.2. Mass of each metal which is possible to dissolve in 40mL of 0.2M $CuCl_2.2H_2O$ (procedure 2.1.1.)

- Cu

$Cu^{2+} + e^- \leftrightarrow Cu^+$

$Cu^0 \leftrightarrow Cu^+ + e^-$

$\overline{Cu^{2+} + Cu^0 \leftrightarrow Cu^+ + Cu^+}$

M(Cu)= 63.55 g/mol

$n(Cu)=0.2 \times 40 \times 10^{-3} = 8 \times 10^{-3} mol$

$m(Cu)= 8 \times 10^{-3} \times 63.55 = 0.51 g$

- Fe

$3Cu^{2+} + 2e^{-} \leftrightarrow Cu^{0}$

$2Fe \leftrightarrow Fe^{3+} + 3e^{-}$

$Cu^{2+} + \frac{2}{3}\, Fe \leftrightarrow 3\, Cu^{0} + 2Fe^{3+}$

M(Fe)= 55.8 g/mol

$n(Fe) = \frac{2}{3} \times 8 \times 10^{-3} = 5.33 \times 10^{-3}$mol

$m(Fe) = 5.33 \times 10^{-3} \times 55.8 = 0.29$g

- Al

$3Cu^{2+} + 2e^{-} \leftrightarrow Cu^{0}$

$2Al \leftrightarrow Al^{3+} + 3e^{-}$

$Cu^{2+} + \frac{2}{3}\, Al \leftrightarrow 3\, Cu^{0} + 2Al^{3+}$

M(Al)= 26.98 g/mol

$n(Al) = \frac{2}{3} \times 8 \times 10^{-3} = 5.33 \times 10^{-3}$mol

$m(Al) = 5.33 \times 10^{-3} \times 26.98 = 0.14$g

- Sn

$Cu^{2+} + 2e^{-} \leftrightarrow Cu^{0}$

$Sn \leftrightarrow Sn^{2+} + 2e^{-}$

$Cu^{2+} + Sn \leftrightarrow Cu^{0} + Sn^{2+}$

M(Sn)= 118.69 g/mol

By stoichiometry of reaction n(Cu) = n(Sn)

$n(Sn) = 0.2 \times 40 \times 10^{-3} = 8 \times 10^{-3}$mol

$m(Sn) = 8 \times 10^{-3} \times 118.69 = 0.95$g

- Ag

$Cu^{2+}+e^{-} \leftrightarrow Cu^{+}$

$Ag \leftrightarrow Ag^{+} + e^{-}$

$\overline{Cu^{2+} + Ag \leftrightarrow Cu^{+} + Ag^{+}}$

M(Ag)= 108 g/mol

By stoichiometry of reaction n(Cu) = n(Ag)

$n(Ag)=0.2\times40\times10^{-3}=8\times10^{-3}mol$

$m(Ag)= 8\times10^{-3}\times108=0.86g$

- Zn

$Cu^{2+}+2e^{-} \leftrightarrow Cu^{0}$

$Zn \leftrightarrow Zn^{2+} + 2e^{-}$

$\overline{Cu^{2+} + Zn \leftrightarrow Cu^{0} + Zn^{2+}}$

M(Zn)= 65.39 g/mol

By stoichiometry of reaction n(Cu) = n(Zn)

$n(Ag)=0.2\times40\times10^{-3}=8\times10^{-3}mol$

$m(Ag)= 8\times10^{-3}\times65.39=0.52g$

- Ni

$Cu^{2+}+2e^{-} \leftrightarrow Cu^{0}$

$Ni \leftrightarrow Ni^{2+} + 2e^{-}$

$\overline{Cu^{2+} + Ni \leftrightarrow Cu^{0} + Ni^{2+}}$

M(Ni)= 58.7 g/mol

By stoichiometry of reaction n(Cu) = n(Ni)

$n(Ni)=0.2\times40\times10^{-3}=8\times10^{-3}mol$

$m(Ni)= 8\times10^{-3}\times58.7=0.47g$

- Pb

$Cu^{2+} + 2e^{-} \leftrightarrow Cu^{0}$

$Pb \leftrightarrow Pb^{2+} + 2e^{-}$

$Cu^{2+} + Pb \leftrightarrow Cu^{0} + Pb^{2+}$

M(Pb)= 207.20 g/mol

By stoichiometry of reaction n(Cu) = n(Pb)

$n(Pb)=0.2\times40\times10^{-3}=8\times10^{-3}$mol

$m(Pb)= 8\times10^{-3}\times207.20=1.66$g

A.2.3. Calculation example of leaching rate for 0w% CC at room temperature (procedure 3.2.)

Trend line equation: y=-0.001x+2.3986
(trend line equation of blue line represented in figure 3.24)

With : y – mass of copper
x - time

Area(Cu)=10.06cm^2

$m(Cu)_i$=2.40g

1 – Calculation of time to dissolve all piece

$$0 = -0.001x + 2.3986 \Leftrightarrow x = 2398.6\,\text{min}$$

2 – Calculation of leaching rate

$$v_L = \frac{2.40}{10.06 \times 2398.6} = 59.68 g/m^2.h$$

A.2.4. Calculations for the procedure of gold dissolution

- Calculation of mass necessary to make 0.2M of $FeCl_3.6H_2O$

V=100mL

$$n = c \times V = 0.2 \times 0.1 = 0.02 mol$$
$$m = n \times M = 0.02 \times 270.3 = 5.4 g$$

- Example calculation for C_{AA} in gold dissolution in 0.2M $CuCl_2.2H_2O$ at room temperature

$$C_{\exp} = \frac{m_{diss}}{V} = \frac{3}{0.250} = 12\, ppm$$

In figure A.1 calibration curve for gold is presented:

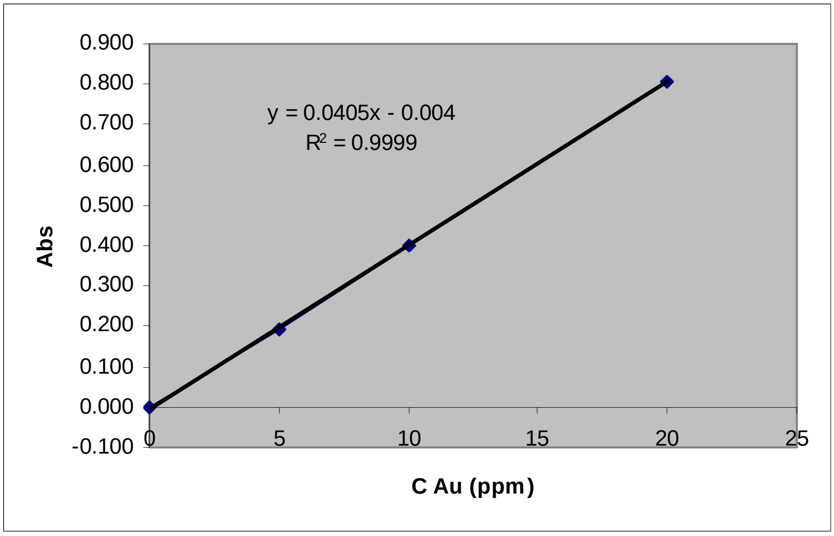

Figure A.1 – Gold calibration curve for leaching in 0.2M $CuCl_2.2H_2O$

By the calibration curve:

$$C_{AA} = \frac{A + 0.004}{0,0405} = \frac{0.294 + 0.004}{0.0405} = 7.36\,ppm$$

$$C = C_{AA} \times df = 7.36 \times 10 = 73.6\,ppm$$

$$df = \frac{V_{vf}}{V_{sample}} = \frac{250}{25} = 10$$

- Example of calculation for dissolution rate of gold in 0.2M $CuCl_2.2H_2O$ at room temperature

$$v_{diss} = \frac{m_{diss}}{t_{diss}} = \frac{3}{20} = 0.15 mg/h$$

- Calculation of the volume necessary of CCC and water to make 25mL of 0.2M $FeCl_3$ with CCC(Calculations for procedure 2.4.3)

Properties of CCC solution: 66w% CCC and the rest is water.

$$V_{CCC} = \frac{20\% \times 25}{66\%} = 7.57 mL$$

$$V_{H_2O} = 25 - 7.57 = 17.43 mL$$

A.3. Results

A.3.1. Variation of mass for each metal while leaching in 0.2M $CuCl_2.2H_2O$ / 50w% CC

Tables A.1 and A.2 show the decrease of aluminium mass with time for both conditions, room temperature and 80ºC respectively .

Table A.1 – Evolution of aluminium mass by dissolution in 0.2M $CuCl_2.2H_2O$ / 50w% CC at room temperature

t(min)	m $_{Al}$(g)	t(min)	m $_{Al}$(g)
0	3.05	60	2.92
10	2.92	120	2.92
20	2.92	180	2.92
30	2.92	240	2.92
40	2.92	300	2.92
50	2.92	360	2.92

Table A.2 – Evolution of aluminium mass by dissolution in 0.2M $CuCl_2.2H_2O$ / 50w% CC at 80ºC

t(min)	m_{Al}(g)	t(min)	m_{Al}(g)
0	3.12	100	2.84
10	2.91	160	2.83
20	2.89	220	2.81
30	2.87	280	2.79
40	2.86	340	2.79

Tables A.3 and A.4 show the difference of iron mass with time at room temperature and 80ºC, respectively.

Table A.3 – Evolution of iron mass by dissolution in 0.2M $CuCl_2.2H_2O$ / 50w% CC at room temperature

t(min)	m_{Fe}(g)	t(min)	m_{Fe}(g)
0	3.53	60	3.11
10	3.43	120	3.05
20	3.25	180	3.05
30	3.16	240	3.05
40	3.13	300	3.03
50	3.11		

Table A.4 – Evolution of iron mass by dissolution in 0.2M $CuCl_2.2H_2O$ / 50w% CC at 80ºC

t(min)	m_{Fe}(g)	t(min)	m_{Fe}(g)
0	3.52	50	3.16
10	3.41	110	3.13
20	3.25	170	3.13
30	3.19	230	3.13
40	3.15	290	3.13

Tables A.5 and A.6 represent mass variation of one piece of copper with time at room temperature and 80ºC.

Table A.5 – Evolution of copper mass by dissolution in 0.2M $CuCl_2.2H_2O$ / 50w% CC at room temperature

t(min)	m_{Cu}(g)	t(min)	m_{Cu}(g)
0	2.33	100	2.00
10	2.30	110	1.98
20	2.25	120	1.96
30	2.18	130	1.94
40	2.15	140	1.94
50	2.11	200	1.89
60	2.08	260	1.86
70	2.06	320	1.85
80	2.03	380	1.83
90	2.02	440	1.81
		500	1.79

Table A.6 – Evolution of copper mass by dissolution in 0.2M $CuCl_2.2H_2O$ / 50w% CC at 80ºC

t(min)	m_{Cu}(g)	t(min)	m_{Cu}(g)
0	2.31	90	1.77
10	2.22	100	1.76
20	2.09	160	1.75
30	2.02	220	1.73
40	2.01	280	1.69
50	1.96	340	1.70
60	1.93	400	1.66
70	1.81	460	1.64
80	1.78	520	1.63

Table A.7 and A.8 show the difference of mass of with dissolution time at room temperature and 80ºC.

Table A.7 – Evolution of tin mass by dissolution in 0.2M $CuCl_2.2H_2O$ / 50w% CC at room temperature

t(min)	m_{Sn}(g)	t(min)	m_{Sn}(g)
0	3.20	50	2.33
10	3.12	60	2.23
20	2.91	120	2.20
30	2.78	180	2.18
40	2.39	240	1.95

Table A.8 – Evolution of tin mass by dissolution in 0.2M $CuCl_2.2H_2O$ / 50w% CC at 80ºC

t(min)	m_{Sn}(g)	t(min)	m_{Sn}(g)
0	3.16	50	2.10
10	2.99	60	2.10
20	2.81	70	2.07
30	2.52	100	2.05
40	2.22	130	2.01

Table A.9 and A.10 show the difference of mass of zinc with time at room temperature and 80ºC.

Table A.9 – Evolution of zinc mass by dissolution in 0.2M $CuCl_2.2H_2O$ / 50w% CC at room temperature

t(min)	m_{Zn}(g)	t(min)	m_{Zn}(g)
0	3.10	70	2.99
10	3.03	100	2.99
20	2.99	160	2.98
30	2.98	220	2.98
40	2.97	280	2.97

Table A.10 – Evolution of zinc mass by dissolution in 0.2M $CuCl_2.2H_2O$ / 50w% CC at 80ºC

t(min)	m_{Zn}(g)	t(min)	m_{Zn}(g)
0	3.16	60	2.76
10	2.89	120	2.74
20	2.81	180	2.73
30	2.77	240	2.72
40	2.76	300	2.72
50	2.76		

Next tables A.11 and A.12 show the variation of lead with time at room temperature and 80ºC respectively.

Table A.11 – Evolution of lead mass by dissolution in 0.2M $CuCl_2.2H_2O$ / 50w% CC at room temperature

t(min)	m_{Pb}(g)	t(min)	m_{Pb}(g)
0	2.32	180	2.05
10	2.26	240	2.05
20	2.19	300	2.04
30	2.15	360	2.05
40	2.12	420	2.05
50	2.10	480	2.04
60	2.08	540	1.93
120	2.06	600	1.93

Table A.12– Evolution of lead mass by dissolution in 0.2M $CuCl_2.2H_2O$ / 50w% CC at 80ºC

t(min)	m_{Pb}(g)	t(min)	m_{Pb}(g)
0	2.31	180	0.86
10	1.51	240	0.86
20	1.20	300	0.86
30	0.95	360	0.85
40	0.89	420	0.84
50	0.87	480	0.84
60	0.86	540	0.85
120	0.86	600	0.85

A.3.2. Variation of copper for different concentration of CC at room temperature and 80ºC (procedure 2.1.2)

Next tables represent the difference of mass for copper in several solutions of CC.

Table A.13 – Evolution of copper mass by dissolution in 0w% CC at room temperature and 80ºC

t(min)	m Cu(g)	
	Room temperature	T=80ºC
0	2.40	2.39
10	2.39	2.35
20	2.38	2.31
30	2.36	2.30
40	2.36	2.28
50	2.35	2.28
60	2.34	2.27
A_{Cu}(cm^2)	10.06	10.08

Table A.14 – Evolution of copper mass by dissolution in 10w% CC at room temperature and 80ºC

t(min)	m Cu(g)	
	Room temperature	T=80ºC
0	2.57	2.49
10	2.54	2.38
20	2.47	2.18
30	2.43	2.10
40	2.43	2.09
50	2.41	2.07
60	2.39	2.03
$A_{Cu}(cm^2)$	10.56	10.64

Table A.15 – Evolution of copper mass by dissolution in 20w% CC at room temperature and 80ºC

t(min)	m Cu(g)	
	Room temperature	T=80ºC
0	2.07	1.91
10	2.01	1.84
20	1.96	1.65
30	1.90	1.60
40	1.86	1.56
50	1.79	1.53
60	1.74	1.48
$A_{Cu}(cm^2)$	9.03	8.80

Table A.16 – Evolution of copper mass by dissolution in 30w% CC at room temperature and 80ºC

t(min)	m Cu(g)	
	Room temperature	T=80ºC
0	2.48	2.63
10	2.40	2.38
20	2.28	2.19
30	2.16	2.13
40	2.11	2.10
50	2.05	2.09
60	2.01	2.09
$A_{Cu}(cm^2)$	11.04	11.50

Table A.17 – Evolution of copper mass by dissolution in 50w% CC at room temperature and 80ºC

t(min)	m Cu(g)	
	Room temperature	T=80ºC
0	2.33	2.31
10	2.30	2.22
20	2.25	2.09
30	2.18	2.02
40	2.15	2.01
50	2.11	1.96
60	2.08	1.93
$A_{Cu}(cm^2)$	10.98	10.95

Table A.18 – Evolution of copper mass by dissolution in 70w% CC at room temperature and 80ºC

t(min)	m Cu(g)	
	Room temperature	T=80ºC
0	2.49	2.28
10	2.48	2.23
20	2.45	2.13
30	2.41	2.09
40	2.38	2.06
50	2.34	2.02
60	2.33	1.96
$A_{Cu}(cm^2)$	11.04	9.60

Table A.19 – Evolution of copper mass by dissolution in 90w% CC at room temperature and 80ºC

t(min)	m Cu(g)	
	Room temperature	T=80ºC
0	2.30	2.33
10	2.28	2.28
20	2.26	2.24
30	2.25	2.22
60	2.21	2.18
$A_{Cu}(cm^2)$	9.62	9.72

A.3.3. Variation of copper in different solutions of $FeCl_3$ with CC and CCC (procedure 2.2.4.)

In tables A.20 to A.23 the variation of mass for copper in different conditions, using solution of $FeCl_3$ is represented.

Table A.20 – Evolution of copper mass by dissolution in solution of 0.2M $FeCl_3.6H_2O$ / 30w% CC

t(min)	m_{Cu}(g)	t(min)	m_{Cu}(g)
0	2.44	2670	1.27
10	2.32	2730	1.18
20	2.22	2790	1.12
30	2.17	3750	1.00
40	2.08	3840	0.96
60	2.01	3900	0.67
150	1.93	3960	0.62
210	1.87	4020	0.50
270	1.87	4980	0.34
1230	1.73	5040	0.30
1410	1.64	5100	0.24
1470	1.61	5160	0.10
1530	1.57	5220	0.06
2490	1.42	9540	0.00
2550	1.35		

Table A.21 - Evolution of copper mass by dissolution in solution of 0.2M $FeCl_3.6H_2O$ / 30w% CC with bubbling air

t(min)	m_{Cu}(g)	t(min)	m_{Cu}(g)
0	2.44	400	1.27
10	2.32	460	1.18
20	2.22	520	1.12
30	2.17	580	1.00
40	2.08	640	0.96
50	2.01	700	0.67
100	1.93	760	0.62
160	1.87	820	0.50
220	1.87	880	0.34
280	1.73	940	0.30
340	1.64		

Table A.22– Evolution of copper mass by dissolution in solution of 0.2M $FeCl_3.6H_2O$ / 30w% CC with bubbling N_2

t(min)	m_{Cu}(g)	t(min)	m_{Cu}(g)
0	2.44	170	1.27
10	2.32	230	1.18
20	2.22	290	1.12
30	2.17	350	1.00
40	2.08	410	0.96
50	2.01	470	0.67
110	1.93	530	0.62

Table A.23 – Evolution of copper mass by dissolution in solution of 0.2M $FeCl_3.6H_2O$ / 30w% CCC

t(min)	m_{Cu}(g)	t(min)	m_{Cu}(g)
0	2.42	4020	1.38
10	2.30	4980	1.30
20	2.23	5040	1.24
30	2.17	5100	1.19
40	2.08	5160	1.10
60	2.03	5220	1.02
150	1.93	9540	0.82
210	1.89	9600	0.82
270	1.88	9660	0.82
1230	1.82	9720	0.82
1410	1.79	9780	0.81
1470	1.77	10740	0.75
1530	1.76	10800	0.74
2490	1.69	10860	0.74
2550	1.66	10920	0.74
2670	1.64	10980	0.73
2730	1.60	11040	0.67
2790	1.60	11100	0.55
3750	1.56	11160	0.55
3840	1.53	11220	0.46
3900	1.51		
3960	1.42		

A.3.4. Calibration curves for PCB leaching

- **Calibration curves for leaching in 0.2M $CuCl_2.2H_2O$ / 30w% CC**

- **Copper**

Table A.24 – Absorbance for copper standard solutions to leaching in 0.2M $CuCl_2.2H_2O$ / 30w% CC

C_{Cu}(ppm)	Absorbance
0.00	0.000
1.50	0.165
2.50	0.280
4.00	0.450

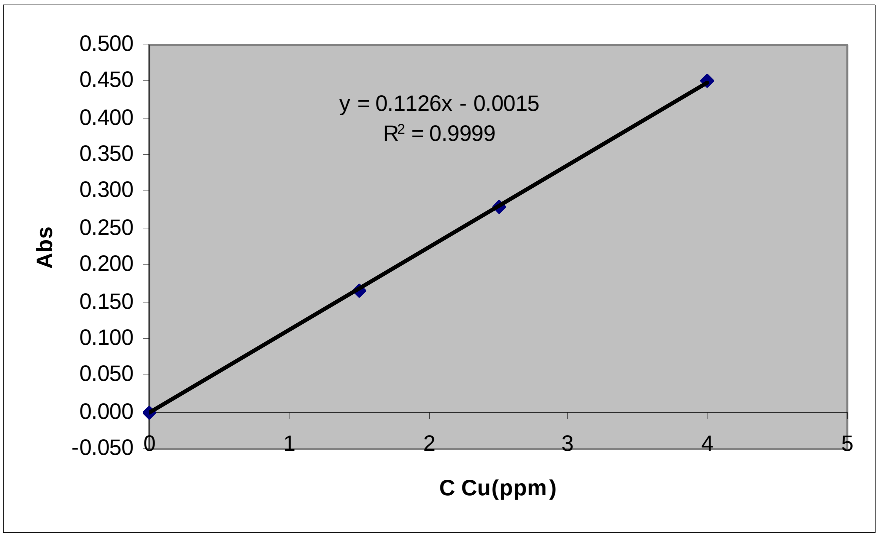

Figure A.2 – Copper calibration curve for leaching in 0.2M $CuCl_2.2H_2O$ / 30w% CC

- **Lead**

Table A.25 – Absorbance for lead standard solutions to leaching in 0.2M $CuCl_2.2H_2O$ / 30w% CC

C_{Pb}(ppm)	Absorbance
0.00	0.000
3.00	0.136
6.00	0.292
9.00	0.451

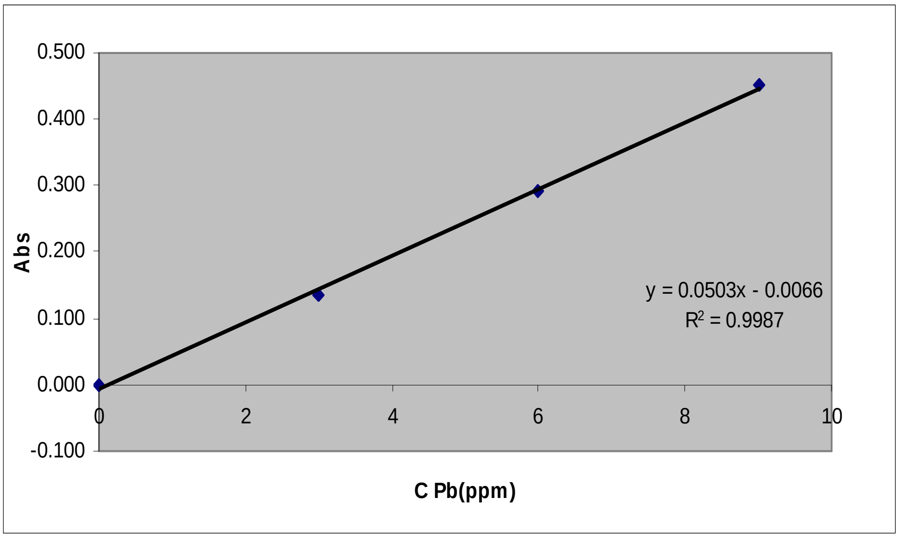

Figure A.3 –Lead calibration curve for leaching in 0.2M $CuCl_2.2H_2O$ / 30w% CC

- **Tin**

Table A.26 – Absorbance for tin standard solutions to leaching in 0.2M $CuCl_2.2H_2O$ / 30w% CC

C_{Sn}(ppm)	Absorbance
0.00	0.007
10.0	0.318
50.0	1.450
100.0	3.277

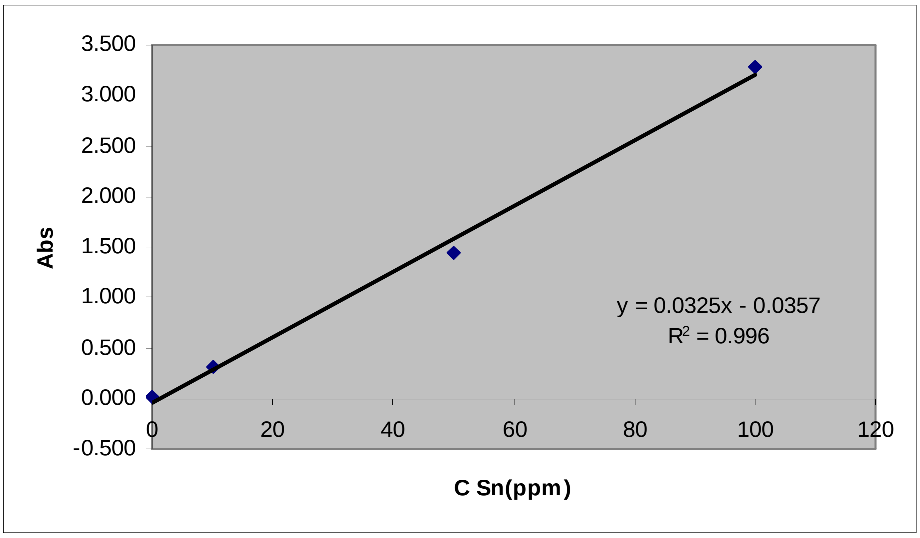

Figure A.4– Tin calibration curve for leaching in 0.2M $CuCl_2.2H_2O$ / 30w% CC

Calibration curves for leaching in 0.2M $FeCl_3.6H_2O$ / 30w% CC

Copper

Table A.27 – Absorbance for copper standard solutions to leaching in 0.2M $FeCl_3.6H_2O$ / 30w% CC

C_{Cu}(ppm)	Absorbance
0.00	0.000
1.50	0.173
2.50	0.297
4.00	0.472

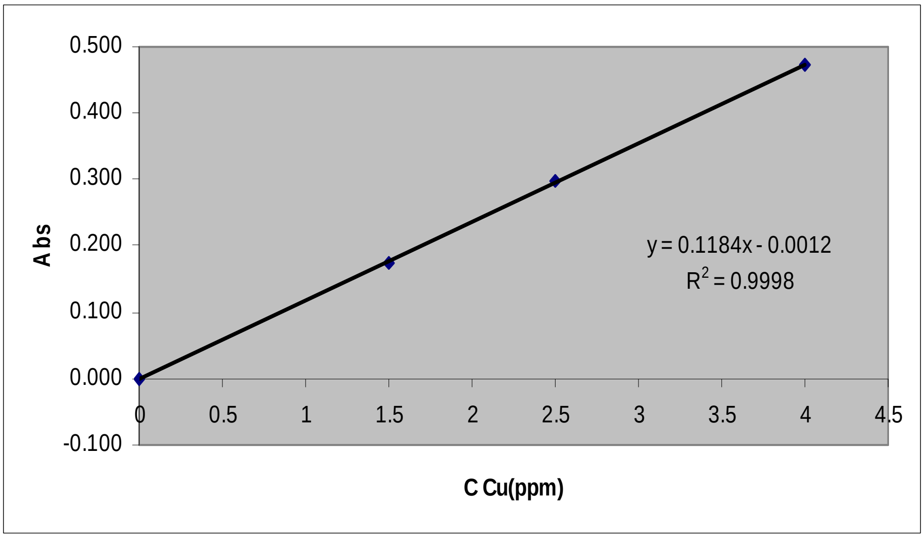

Figure A.5– Copper calibration curve for leaching in 0.2M $FeCl_3.6H_2O$ / 30w% CC

- **Lead**

Table A.28 – Absorbance for lead standard solutions to leaching in 0.2M $FeCl_3.6H_2O$ / 30w% CC

C_{Pb}(ppm)	Absorbance
0.00	-0.002
3.00	0.097
6.00	0.207
9.00	0.322

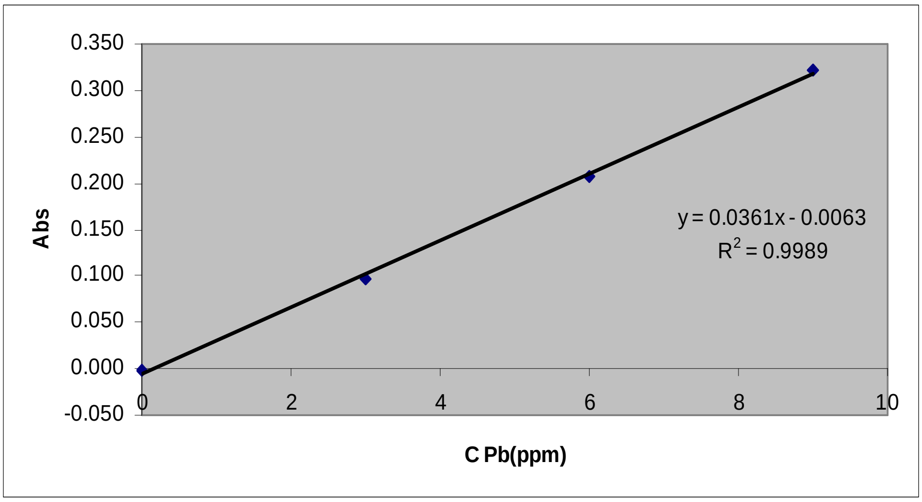

Figure A.6 – Lead calibration curve for leaching in 0.2M $FeCl_3.6H_2O$ / 30w% CC

- **Tin**

Table A.29 – Absorbance for tin standard solutions to leaching in 0.2M $FeCl_3.6H_2O$ / 30w% CC

C_{Sn}(ppm)	Absorbance
0.00	0.004
10.0	0.121
50.0	0.315
100.0	0.589

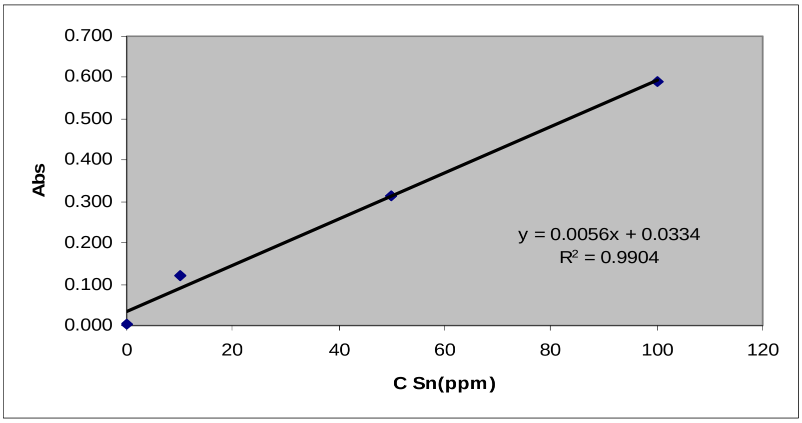

Figure A.7 – Tin calibration curve for leaching in 0.2M $FeCl_3.6H_2O$ / 30w% CC

A.3.5. Potential for different ratio Fe(III)/Fe(II) (procedure 2.7.1)

Table A.30 represents the variation of potential for several mixtures of Fe(III) and Fe(II):

Table A.30 – Potential for different ratio of Fe(III) / Fe(II):

$V(Fe^{3+})/V(Fe^{2+})$	$ln[C(Fe^{3+})/C(Fe^{2+})]$	E (V)
40/0	indetermination	-0.0660
38/2	-2.944	-0.5050
35/5	-1.946	-0.4970
32/8	-1.386	-0.4848
30/10	-1.099	-0.4788
28/12	-0.847	-0.4773
25/15	-0.511	-0.4678
22/18	-0.201	-0.4628
20/20	0.000	-0.4570
18/22	0.201	-0.4435
15/25	0.511	-0.4340
12/28	0.847	-0.4249
10/30	1.099	-0.4175
8/32	1.386	-0.4102
5/35	1.946	-0.3955
2/38	2.944	-0.2750
0/40	indetermination	-0.1140

A.4. Conditions of measurement in CV

A.4.1. Conditions of cyclic voltammetry analysis for leaching gold (procedure 2.4.1)

- Conditions of blank measurement (Ethaline200)

Conditioning potential: 0V

Duration: 10s

Start potential: 0V

First vertex potential: -1.4V

Second vertex potential: 1.4V

Step potential: 5mV

Scan rate: 0.02V/s

- Conditions of solutions measurement

Conditioning potential: 0.9V

Duration: 60s

Start potential: 0.9V

First vertex potential: -0.05V

Second vertex potential: 0.9V

Step potential: 5mV

Scan rate: 0.02V/s

A.4.2. Conditions of voltammetry analysis for solutions of Fe(III) and Fe(II) (procedure 2.7.2.)

1- Conditions to measure the Fe(III) solutions

- Pretreatment

First conditioning potencial: 0.75V
Duration: 10s

- Measurement

Number of scans: 1
Stanby potential: 0.5V

- Potentials

Begin potential: 0.5V
End potential: -1.2V
Step potencial: 5mV
Scan rate: 0.01 V/s

2- Conditions to measure the Fe(II) solutions

- Pretreatment

First conditioning potencial: -1.5V
Duration: 0s

- Measurement

Number of scans: 1
Stanby potential: 0.5V

- Potentials

Begin potential: -1V
End potential: 1.2V
Step potencial: 5mV
Scan rate: 0.05 V/s

A.5. Technical Bulletin

Choline Chloride

- Hazardus identification

- Inhalation: no information found, but compound should be handled as a potential health hazard
- Ingestion: no information found, but compound should be handled as a potential health hazard
- Skin contact: may cause irritation with redness and pain
- Eye contact: may cause irritation, redness and pain
- Chronic exposure: no information found
- Aggravation of pre-existing conditions: no information found

- Other Information

- Label hazard warning: may be harmful if swallowed or inhaled. May cause irritation to skin, eyes and respiratory tract.

Chlormequat Chloride

- R-Phrase: R21/22
- S-Phrase: S2-13-20/21-36/37-46
- Hazards Identification:

- Harmful if swallowed
- Harmful in contact with skin
- Mild eye irritation
- Corrosive in contact with metals

- Toxicological Information

Human experience: Overexposure may cause nausea, vomiting, sweating, diarrhoea, salivation, visual disturbances, cardiac irregularities and unconsciousness.

Xn- Harmful

Choline Base

- R-Phrase: R34
- S-Phrase: S26-27-28-36/37/39
- Hazards Identification:

- Causes burns
- Caution: substance not yet fully tested

C- Corrosive

- Toxicological Information

Human experience: causes severe burns; Inhalation of mist causes irritation of respiratory system; main symptoms; cough; shortness of breath; nausea; vomiting; aspiration may cause pulmonary oedema and pneumonitis.