Cementation as a means for leachate liquor purification

Bachelor Thesis in Chemical Engineering

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Abstract

The metal oxide varistor (MOV) is an electrical component mainly used for limiting overvoltage in electrical lines caused by lightning strikes etc. The electrical properties of the MOV come from different metal oxide compounds that are present in the varistor material (VM). However, the combination of these metal oxides makes the recycling process of the VM difficult. As of now there is no well-defined method to recycle the VM. However, the VM can be dissolved into a varistor material leachate (VM leachate) using acids. The resulting leachate is a solution that contains mostly zinc and impurity metals. The impurity metals would need to be removed to be able to recover the zinc. With inspiration from industrial zinc refining, where cementation on zinc dust is a widely used purification method, a similar procedure might be applied to the VM leachate.

The overall purpose of this project was to examine if cementation reactions could be used as a means to purify VM leachate. To evaluate the effectiveness of the cementation reactions, an “artificial system” that contained dissolved salts of cobalt, antimony, copper and zinc was studied. Temperature, zinc dust concentration as well as metal ion concentrations were varied to evaluate their effect on the cementation reactions. It was found that cobalt was the biggest challenge to remove. Copper cemented readily out of solution in all observed cases. Antimony could potentially be removed completely under good conditions, but in most observed cases it was removed to an intermediate degree. Most of the reactions, including that of cobalt sometimes, initially proceeded at a high rate but were also halted relatively fast.

Sammanfattning

Metalloxidvaristorn (MOV) är en elektrisk komponent som främst används för att begränsa överspänningar i elnätet orsakade av blixtnedslag etc. Dess elektriska egenskaper är en direkt följd av de metalloxider som finns i varistormaterialet (VM). Kombinationen av dessa metalloxider försvårar dock återvinningsprocessen av VM. Det finns därför för närvarande ingen väldefinierad metod för att kunna återvinna VM. Varistormaterialet kan lösas upp till en lakvätska med hjälp av syror. Den resulterande lakvätskan är en lösning innehållande främst zink, men även föroreningar i form av andra metaller. Föroreningsmetallerna måste separeras bort från lakvätskan för att det ska gå att återvinna zinkmetallen. Med tanke på att elektrokemisk utfällning med hjälp av zinkpulver är en vanligt förekommande separationsmetod inom zinkindustrin, finns det en potential till att samma metod kan användas för att rena VM-lakvätska.

Det huvudsakliga syftet med projektet var att undersöka huruvida elektrokemiska utfällningsreaktioner är lämpade att användas för att rena VM-lakvätskor. Ett ”artificiellt system” innehållande upplösta salter av kobolt, antimon, koppar och zink studerades för att utvärdera de elektrokemiska utfällningsreaktionernas effektivitet. Temperatur, koncentration av zinkpulver samt metalljonskoncentrationer varierades för att utvärdera deras inverkan på utfällningsreaktionerna. Resultatet visade att kobolt var den största utmaningen att avlägsna från systemet. Koppar fälldes enkelt ut i alla experiment. Antimon skulle potentiellt kunna avlägsnas helt under goda betingelser, men i de flesta fall var borttagningsgraden av antimon måttlig. Initialt hade de flesta reaktionerna en hög reaktionshastighet, även kobolt i vissa fall. Dock avstannade reaktionerna relativt tidigt.

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1. Introduction

It is a fact that the earth has limited resources and therefore recycling materials is an important step towards a more sustainable society. Not only the environment would benefit from increased recycling, there is often also a potential profit to be made. Countries or organisations that cannot afford material recycling often resort to landfilling which is a growing problem in today's society [1].The same happens when there is no well-defined method available for recycling specific materials.

To be able to handle the increasing amount of waste and increasing need for metals worldwide it is of great importance to continue to develop the already existing separation technologies as well as developing new ones [1].

One specific product that as of now lacks a well-defined method of recycling and therefore ends up in landfills is the metal oxide varistor (MOV) [2]. The MOV is found within polymeric housings in electrical lines and substations, on trains, and is present in a smaller form in household appliances [3]. This work will focus on zinc oxide varistor which has nonlinear current-voltage characteristics enabling it to limit overvoltages caused by lightning strikes and other sudden power surges in electrical lines [3]. The ZnO itself is a semiconducting material and has a linear current-voltage behaviour [3]. Pure ZnO would not be sufficient to produce the electrical properties needed in the varistor [3]. To achieve the nonlinear current-voltage behaviour that is necessary for the varistor to be functional, multiple other metal oxides such as Bi_2O_3, Sb_2O_3, Co_2O_3 and MnO_2 are needed in the varistor material [3].

In the varistor material (VM), ZnO comprises around 90 mol %, Bi_2O_3 and Sb_2O_3, around 3 mol % each, and Co_2O_3, MnO_2, and NiO in smaller amounts with a total of 4 mol % [2]. It is difficult to recycle the zinc in the ZnO varistor because other metal ions (Bi^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+} and Sb^{3+}) co-leach along with zinc and can be difficult to separate from the zinc leachate [2]. Some of the ions even inhibit current recycling techniques used to recycle zinc, such as electrowinning [4]. Consequently, it is this complexity that leads to the recycling difficulties and that varistors often end up in landfills when they are no longer functional [2].

There are benefits to recycling varistors other than just keeping them out of landfills. The most obvious benefit is the recovery of zinc since that composes most of the VM. Even though zinc is present in the earth's crust in great amounts, the recovery of it is still interesting because of its many applications and its steady rate of consumption [2]. Antimony, also present in the varistor, is listed as a critical metal in the European Union [5]. Currently, there is no antimony produced in Europe [5]. The principal source of antimony comes from China and it is important to recycle the antimony from products in which it has been used to get a more independent resource market [2, 5]. Aside from zinc and antimony, the bismuth in the VM would also be useful to recover. Bismuth is approximately as abundant as silver and is mostly produced as a by-product when refining other metals such as lead, tungsten and copper [6].

Previous work by Gutknecht et al. on acid leaching of the VM showed that leaching with sulphuric acid solutions at pH 3 resulted in all zinc being leached from pulverized VM [2]. However, along with zinc, impurities such as antimony, cobalt, nickel and manganese were also co-leached [2]. It would be ideal to avoid the co-leaching of these metals as the zinc then could be directly electrowon from the leaching solution [2]. Since leaching of the VM was not ideal and co-leaching of other metals could not be avoided the leachate needed to be purified [2].

Not many studies have been conducted on purification of leached VM. However, there is a good amount of literature dealing with similar systems [7-10]. Most of the literature comes from the hydrometallurgical zinc industry where zinc solutions are purified from impurity metals. While the concentrations in these solutions are unlike those in VM leachate, the solutions often contain the same species [2, 7]. The finished product in both cases would be a sufficiently pure zinc solution for use in electrolysis [4].

In the hydrometallurgical process, ores containing zinc are pretreated in hot conditions and then dissolved using sulphuric acids into a zinc sulphate solution [9]. This solution is then purified from various impurity metals such as cobalt, nickel, cadmium and antimony by cementation [9]. These metal ions must be removed as they would disturb the following electrolysis of zinc [11]. Cobalt and related metals such as nickel cause damage to the cathode used in the electrolysis process as well as contributing to redissolution of zinc [4]. Metals such as antimony and germanium also cause zinc to redissolve as well as reduce the hydrogen overpotential causing a loss of current efficiency and making the entire process unfeasible [7, 10]. For the electrolyte to be usable, the literature reports acceptable limits for cobalt ranging between 0.2 – 1 ppm [7] and for antimony even lower, ranging between 0.012-0.03 ppm [12]. After the electrolysis, high purity metallic zinc is obtained [11].

Due to the relatively low concentration limits, the preparatory purification is of great importance [12]. The purification is achieved through electrochemical reactions causing the impurity metals to precipitate on the surface of zinc dust. These reactions are commonly known as cementation reactions [13]. Because the zinc sulphate solution is similar to the VM leachate, it is logical to try to use cementation reactions for separation of the metal ions in the leachate.

However, the VM leachate is very complex and contains multiple metals and metal complexes in solution [2]. To understand the more complex system a more simple system, an “artificial system”, will be investigated. The advantages of an artificial system are many. As an example, the composition of the system is always known from the beginning. It is also simple to adjust different ratios between the ingoing species, as well as vary their concentrations. The artificial solution to be studied will contain a fixed concentration of zinc and antimony along with various amounts of cobalt. It has also been reported that copper acts as an activator in the cementation of cobalt so it will be added to the artificial solution to promote the cementation reactions [9, 14].

1.1. Purpose

The overall purpose of the project is to examine if cementation reactions have the potential to be used as an effective method for purification of leach solutions of VM. The reactions would need to result in a pure zinc electrolyte that could be used in electrolytic zinc production.

To evaluate the potential of the reactions there is a need for a better understanding of how they behave under conditions similar to those in the VM leachate. Initially, this was thought to be achieved by studying the activation energy for the reactions. This has since then been revaluated and the study focuses in a more general way on how different parameters affect the reactions. The parameters investigated are temperature, amount of zinc dust, and concentrations of the metal ions involved.

The investigation will be conducted by studying an artificial system, a simplification of the VM leachate. The goal is to separate the impurity metals in an artificial system and from doing this derive information which later on can be applied to the VM leachate. Specifically, the report will result in data for the cementation reactions useful for further research conducted on this subject.

2. Theory

Cementation is widely used in hydrometallurgical zinc refining to purify zinc sulphate solutions from impurities [15]. In this section, a description of the reactions in the studied system is presented. A review of parameters that affect the cementation reactions then follows. Focus is on zinc dust addition, solution pH, temperature, and effect of additives such as copper and antimony. Lastly, theories on cobalt cementation and its problems are described.

A cementation reaction can be described as electrochemical precipitation where the most noble metal ions in a solution are reduced to solid metal through deposition on the surface of a less noble metal which is oxidized [13]. In the case of zinc purification, the impurity metals are the nobler metals that are to be reduced while zinc, often in the form of zinc dust, is the less noble metal providing the electrons [9, 13].

A cementation reaction is in an ideal situation summarized into the following 5 steps: [9, 13]

1. Metals ions more noble than zinc are transported from the bulk of the solution to the zinc surface through diffusion or electrostatic forces.
2. Electron transport from the dissolving zinc metal to the noble metal ion reduces the metal ion to its neutral state.
3. The deposited metal forms a crystal structure on the zinc metal surface.
4. Zinc ions desorb from the zinc surface.
5. Dissolved zinc ions are transported from the zinc surface to the bulk through diffusion, evening out the concentration gradient and making it easier for the process to start anew.

All of these steps need to happen for the cementation to occur. If any of them are inhibited, the entire reaction can be severely slowed or even stopped [9]. In the same manner, the step that has the slowest rate determines the overall rate of the reaction [9]. Which step this is may vary during the course of the cementation, making it a complicated process to analyse [9, 13]. For example, if step 1 or 5 is the rate-determining step then the process is mass transfer limited [9, 13]. The reaction is then limited by how fast the relevant ions can move through the solution. However, step 2, 3 and 4 are about different surface reaction limitations [8]. These steps are dependent on both the amount of free zinc surface as well as the total area available for deposition [8]. Depending on which metals deposit and how they deposit, the limiting factor can vary greatly throughout the cementation [9, 13].

2.1. Cementation Reactions of Cobalt, Antimony and Copper

For the artificial system studied, the main reactions are the cementation of cobalt, antimony and copper. However, there are other reactions occurring that can influence the rate of cementation. In Table 1 some important reduction reactions in the system are presented.

Table 1. The standard potentials at 298 K of the reduction reactions of the metals studied in the artificial system [9, 16].

Chemical Reaction	Standard Potential	Reaction
$Zn^{2+} + 2e^- \rightarrow Zn$	$E^\circ = -0.762\ V$	i
$Co^{2+} + 2e^- \rightarrow Co$	$E^\circ = -0.280\ V$	ii
$2H^+ + 2e^- \rightarrow H_2$	$E^\circ = 0\ V$	iii
$SbO^+ + 2H^+ + 3e^- \rightarrow Sb + H_20$	$E^\circ = +0.204\ \mathrm{V}$	iv
$Cu^{2+} + 2e^- \rightarrow Cu$	$E^\circ = +0.340\ V$	v

Reaction **ii**, **iv** and **v** in Table 1 show the reduction of cobalt, antimony, and copper respectively. These three in combination with the oxidation of zinc, which can be seen as the inverse of reaction **i**, make up the desired cementation system [9, 13]. Reaction **iii** is the reduction of hydrogen ions into hydrogen gas, causing what is known as hydrogen evolution, which inhibits the cementation reactions [8, 9, 15, 17]. The cementation reactions seem to be first order reactions according to Polcaro et. al [17].

Furthermore, literature states that the rate of the cementation reaction of both copper and antimony is high and therefore low concentrations of them are expected in a short amount of time, around 10 minutes, according to A. Nelson et al. [7, 8]. The high reaction rate is supported by thermodynamics and can be understood by comparing the standard potentials of copper and antimony to that of zinc as seen in Table 1 [9]. Cobalt however, is more difficult to cement and therefore will be discussed in greater detail.

2.1.1. Zinc Dust

The electrons needed for the cementation reactions come from the oxidation of a less noble metal than the metals to be cemented [13]. In this study, metallic zinc dust is preferred to add because the system already contains zinc ions. Addition of more zinc will only cause the concentration of zinc to increase. Other metals could be used but would contaminate the zinc-antimony-cobalt-copper system [9]. Since cementation reactions take place on the surface of the added metal, it is of importance that a large surface area is available for the reactions [14, 17]. For this reason, zinc dust is widely used to cement out impurities in zinc solutions. By using zinc dust with a smaller grain size a larger surface area can be achieved. This can be beneficial to the rate of cementation according to Børve and Ostvold [15]. However, other authors argue that the morphology of the zinc dust is even more important than the amount of surface area. They propose that small pores and cracks in the zinc particles could capture bubbles of hydrogen gas formed through hydrogen evolution, closing off the surfaces within the pores [8]. The closed surfaces constitute passive areas in regards to the cementation reactions [8].

Literature suggests that there is an optimal value of zinc dust, 4 g/L, for a system containing copper, antimony and cobalt [7, 14]. However, in industrial production of zinc, common amounts of zinc dust are between 4-6 g/L [7]. Note that these concentrations do not necessarily apply to purification of VM leachate since there is a difference in concentration magnitudes between the VM leachate and typical concentration used in industry [9, 15].

2.1.2. Temperature

For many chemical reactions, a high temperature is beneficial in order to achieve a higher reaction rate. This applies to the cementation reaction of at least cobalt [8, 15]. Note however, that a high temperature also affects the reactions competing with the cementation reactions, such as hydrogen evolution [7]. For example, according to Van Der Pas and Dreisinger, the rate of cobalt removal from a zinc solution is optimal at around 85 °C [14]. They state that temperatures lower than 70 °C result in a lower reaction rate for the cementation of cobalt [14]. Furthermore, they suggest that temperatures higher than 85 °C will benefit hydrogen evolution to a greater extent which competes for the available zinc and therefore inhibits the cementation reactions [14]. Hydrogen evolution also has the undesired effect of forming passive areas on the zinc surface as mentioned before [8, 9]. Therefore it is important to minimise hydrogen evolution, in order to increase the rate of cementation and decrease the amount of zinc dust used. Thus the temperature should be kept as low as possible while still achieving timely cobalt cementation reactions, preferably around 85 °C [8, 14].

2.1.3. Influence of pH

The pH value in solution is a significant parameter that affects the cementation [7]. With a too high local pH, basic zinc sulphate ($ZnSO_4 \cdot 3Zn(OH)_2 \cdot 4H_2O$) [9] as well as zinc hydroxide ($Zn(OH)_2$) can be formed in the solution [7, 8, 17, 18]. Formations of basic zinc salts can create a layer blocking the zinc dust surface from reaction with metal ions in solution [7, 10]. At a low pH ($pH<4$) the hydrogen reduction rate increases and competes with the cobalt cementation reactions [9]. The increase can be understood by taking into consideration that a low pH means there are more hydrogen ions in solution available for reduction. According to Polcaro et al. the pH in an unbuffered cementation system has been observed to rise during reaction to a final value of around 5.5 [17]. The optimal pH for cementation varies between 4.0 and 4.4 according to literature [7].

2.1.4. Cementation of Cobalt

Cobalt has a standard potential of -0.280 V and zinc has a standard potential of -0.762 V compared to the standard hydrogen electrode (SHE) as can be seen in Table 1. The reaction between cobalt in solution and zinc dust is described in the chemical reaction **vi** [9].

$$\boldsymbol{Zn(s) + Co^{2+}(aq) \rightarrow Zn^{2+}(aq) + Co(s)} \tag{vi}$$

The standard cell potential (E°_{cell}) for the chemical reaction **vi** can be calculated to 0.482 V using the noted standard potentials for cobalt and zinc. Thermodynamics state that the reaction between cobalt in solution and zinc dust should be favourable. This thermodynamic statement can be understood by using Equation 1 that can be derived from the Nernst Equation at equilibrium [9, 19].

$$\boldsymbol{K = exp\left(\frac{n \cdot F \cdot E^{\circ}_{cell}}{R \cdot T}\right)} \tag{1}$$

Where K is the equilibrium constant, n is the number of electrons (in this case two), F is Faraday's constant 96 485 [J/V·mol], R is the ideal gas constant 8.314 [J/K·mol] and T is the temperature [K] [19].

A K-value for the chemical reaction **vi** can be calculated to a value of $2 \cdot 10^{16}$ under standard conditions. The high value suggests that cobalt would deposit on the zinc surface without any additives [14] and that any redissolution of cobalt should be insignificant [9]. However, experimental studies report redissolution of cobalt over time and slow kinetics [20]. Furthermore, cobalt removal without any additives, has a low yield and very slow reaction kinetics [14, 17, 21] which is caused by kinetic barriers of the cobalt reduction [7].

A proposed explanation of the kinetic barriers involved is that zinc ions, present in the system, can adsorb to the zinc dust surface making it unavailable as a reaction site [7-9]. The adsorption leads to accumulation of positively charged ions in a layer around the zinc particles [7, 8]. The layer of positive ions then decreases the electrostatic forces between the cobalt ions and the zinc surface [8]. The transport of cobalt ions to the zinc surface is therefore hindered [8]. An abundance of zinc ions also facilitates the forming of zinc salts due to a high local pH as previously stated [8]. Together these two effects cause a lower amount of surface area available for the cementation reactions and result in a slower rate of reaction. This explanation is supported by the fact that cobalt cements out easily in a solution where no zinc ions are present [7, 8]. With antimony in the system, this adsorption of zinc ions may be avoided to some extent [7].

2.1.5. Activators

In order to increase the rate of cobalt removal, additives commonly known as activators, are widely used. The most common additives for this type of systems in the industry are either arsenic or antimony together with copper [7]. Since antimony is a component of the varistor material it fits well to use that over arsenic, even more so due to the toxic nature of arsenic. Studies regarding purification of zinc sulphate solutions indicate that addition of activators has an increasing effect on the rate of cobalt removal [7, 9, 14, 22]. But the studies have different results regarding how the cementation mechanism actually works. Despite this lack of a complete fundamental understanding, there are ways that the additives are known to enhance the rate of cobalt cementation. Firstly, the additives tend to minimize the amount of salts and passivating layers which block the zinc surface [9]. Secondly, they provide increased cathodic surface as well as inhibiting the ability of the deposited metals to redissolve [9, 14]. Optimal concentrations for the additives antimony and copper are reported to be around 3-4 mg/L and 50-100 mg/L respectively [7].

2.1.6. Suggested Mechanisms of Cobalt Cementation

Many studies suggest different alloys are formed during cementation. For example copper- and antimony alloys as well as intermetallic compounds or mixed phases with cobalt [18, 20]. Another alloy frequently mentioned in literature is between cobalt and zinc [14, 18, 20]. Some authors even argue that, as long as zinc ions even in very small amounts are present in solution, cobalt does not deposit as pure cobalt but as a zinc-cobalt alloy with mixed composition [7, 14, 18]. These alloys are thought to be more stable than cobalt alone and have a stronger thermodynamic driving force towards deposition [9, 14]. Together this is said to make the alloys deposit faster and redissolve less frequently [9]. As an addition to this theory, explaining the observed redissolution, B. Boyanov et al. state that in addition to formation of alloys, formation of basic cobalt salts occurs [20]. The formation of salts is dependent on a high local pH, caused by hydrogen evolution [20]. When the zinc dust is exhausted, the hydrogen formation stops, and redissolution of the basic cobalt salts can occur [20].

Other authors have theories that antimony and copper precipitate on the zinc dust surface and form a substrate that an alloy of zinc-cobalt later could deposit upon [14, 23]. In an Ideal case according to one such theory, when zinc dust is introduced to a solution containing zinc, copper, antimony, and cobalt, the copper ions in the solution reacts with the zinc dust resulting in a layer of solid copper on the zinc dust surface. On top of this newly formed copper layer, antimony ions react and form a solid antimony layer. Finally an alloy of cobalt and zinc is deposited on the antimony surface [7, 8].

2.2. Theory Summary

Solutions containing zinc ions and impurity metals are complex systems and the cementation reactions involved in their purification are hard to predict [9]. The reactions, being composed of several steps involving both mass and surface limited processes, can be influenced by several factors [9]. Temperature, amount of zinc dust, concentrations of ingoing ions as well as morphology of the solid species has the potential to affect the cementation [7, 8].

The most effective cementation reactions for systems containing copper, antimony, cobalt and zinc has been reported to take place at a temperature of 85 °C [14] and at a pH range of 4.0-4.4 [7]. The concentrations of activators have been suggested to be optimal around 3-5 mg/L antimony and 50-100 mg/L copper [7]. The zinc industry typically uses a zinc dust concentration of 4-6 g/L [7, 8].

The mechanisms behind the reactions and the explanation of why they are halted are currently unknown. Further studies are still needed before a more complete understanding exists.

3. Materials and Method

An artificial system, less complex than the actual VM leachate, was studied with all the ingoing components and their amounts known. Chemicals used in this system were potassium antimony tartrate hydrate ($C_8H_4K_2O_{12}Sb_2 \cdot 3H_2O$), cobalt sulphate heptahydrate ($CoSO_4 \cdot 7H_2O$), copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$) and zinc sulphate heptahydrate ($ZnSO_4 \cdot 7H_2O$). Zinc dust with a particle size of 325 mesh was used. Samples were taken during the cementation reaction and diluted with 0.1 M HNO_3 to allow for the samples to be analysed with ICP-OES (iCAP 6500, Thermo Fischer) and ICP-MS (iCAP Q, Thermo Fischer). Calibration curves were made using ICP-OES standards (1000 ppm) and ICP-MS (10 µg/mL±0.5% in 2% HNO_3+ Trace HF) standards. If solutions needed to be pH adjusted to a desired range, either NaOH or HNO_3 was used depending on if the pH needed to be raised or lowered, respectively. To calibrate the pH-meter (Metrohm 827pH lab KCl-electrode 6.0228.010), pH buffers were used with pH 1, 4, 7 and 9.

3.1. Artificial System Solution

As previously stated, the artificial solution is based on a more complex leaching solution obtained from sulphuric acid leaching of the VM. The composition of the VM leachate is given in Table 2 along with the typical concentrations of metals present in the artificial system. The artificial system is based on the VM leachate but is simplified by eliminating metal ions other than antimony, cobalt and zinc. Thus the interaction between only these metals is studied. Other differences are that copper is added to the artificial system even though it is not present in the VM leachate, also the zinc concentration is halved. The copper was added to promote the cementation reactions and the zinc was halved since that was believed to facilitate the cobalt cementation [7].

Table 2. A comparison between the composition of the VM leachate and a typical artificial system used in this study.

Metal	VM leachate (mg/L)	Artificial System (mg/L)
Antimony	70	100
Bismuth	-	-
Cobalt	400	500
Copper	-	500
Manganese	66.4	-
Nickel	65.7	-
Zinc	64600	32690

The VM contains a high concentration of metal ions such as cobalt, antimony and copper when compared to literature data [7]. In zinc production, the concentration of cobalt and antimony is several orders of magnitude lower than for the VM leachate and thus the artificial system [7]. Several parameters were studied with the artificial system such as the effect of copper and cobalt concentrations, temperature and zinc dust addition.

When adjusting the concentration of the metal ions, it was of importance to keep in mind that some concentrations were preferred not to be changed to any great extent. This preference applies specifically to cobalt and zinc, due to the desired resemblance to the VM leachate. However, the concentration of the additives, copper and antimony, could be changed. Antimony should always be present in at least small amounts since it is so in the VM and since it acts as an activator. In general, when adjusting parameters, it was important to change only one parameter at a time in order to be able to compare the experiments and thereby determine what gives a certain difference in the reaction.

The copper concentration ranged from 200-1500 ppm. Initially, 200 ppm copper were used, but it was early on concluded that this concentration was too low compared to what was found to be optimal in other studies [17]. The concentration of the antimony ranged from 1-200 ppm where 100 ppm was used in most experiments. The cobalt concentration ranged from 100-500 ppm, where 500 ppm was the most frequently used but due to conclusions from other studies, a decrease in cobalt concentration was done in order to study its effect [17].

The zinc-dust amount varied from 100-900 % excess of the needed stoichiometric amount. Note that the percentage was on a molar basis and not necessarily related to the needed surface area. An example calculation of the zinc dust amount can be found in Appendix B.2. Over 900 % would not be convenient at this high concentration scale since that would turn the solution into sludge. The temperature was also varied and it ranged from 25-70 °C. It was known from other studies that the higher the temperature, the higher the cobalt removal to a certain point [14]. The upper limit of this project was due to practical limitations; the tubing was not suitable for temperatures above 75 °C because of the risk of melting and also sample evaporation.

With set concentrations in the sample solution containing cobalt (Co), antimony (Sb), zinc (Zn) and copper (Cu), the required masses of the different metal compounds could be calculated using stoichiometry and the information in Table 3. Examples of these stoichiometric calculations can be seen in Appendix B.1.

Table 3. An owerview of the metal componds used in the experiments and their molar masses.

Metal in solution	M_W [g/mol]	Metal compound	M_W [g/mol]
Co	58.93	$CoSO_4·7H_2O$	281.10
Sb	121.76	$C_8H_4K_2O_{12}Sb_2·3H_2O$	667.88
Zn	65.41	$ZnSO_4·7H_2O$	287.56
Cu	63.55	$CuSO_4·5H_2O$	249.68

3.2. Artificial Solution Preparation

Sample solutions were prepared to a total volume of 50 mL or 100 mL. The solutions were made using a solution of Milli-Q water and surfactant which was prepared by adding two drops of the surfactant Triton-X-100 per 500 mL Milli-Q water. The purpose of the surfactant was to decrease the surface tension of the solution so the zinc dust would coalesce with solution. The process of preparing a sample solution is exemplified below with respect to a total volume of 100 mL.

Initially, the calculated masses of the metal compounds were weighed in a plastic boat. The four metal compounds were then poured into a glass beaker and 80 mL of the surfactant water was added. A high stirring rate was maintained until all the metal compounds had been dissolved entirely. Then the pH of the solution was measured and adjusted from around 3.5 to 3.9-4.1. While making pH adjustments, it was concluded that a too high concentrated NaOH solution could cause unwanted precipitations when added to the sample solution. These precipitations were probably formed due to high local pH in the sample solution. If precipitations were observed, the sample solution had to be stirred for a long time to make them dissolve or solutions were remade.

The solution was transferred to a 100 mL volumetric flask and was diluted to the 100 mL mark with Milli-Q water containing surfactant. The pH of the solution was again measured and adjusted if needed, to achieve a final pH ranging from 4.0 to 4.5.

An important part of the laboratory sessions was the measuring of the pH for the constituent solutions. There are many ways to measure the pH, but in this case the most common method was used and that is measuring with a pH meter consisting of a glass electrode, an electrode with a glass membrane bulb at the bottom of it [24].

In order to be accurate, the pH meter needs to be calibrated each time a test is carried out [24]. However, this is too time-consuming and a calibration once a week is well enough in order to get reliable values in this case. The reason why the pH meter needs to be calibrated is that the substance in the porous plug tends to precipitate if the analyte contains a reducing agent and this causes a slow drift of the pH reading [24]. To see if the pH meter needs to be calibrated, a simple procedure could be done by plotting a certain number of values that the apparatus measures and plot these against the known pH of the standard buffer solutions. The standard buffer solutions always contain a weak acid and the conjugate base.

In an example of a performed calibration check, the measured voltage of each buffer standard was plotted against their respective pH 1, 4, 7 and 9. The correlation coefficient squared of the resulting graph should be equal to 1 if it is perfectly linear. As can be seen in Figure 1, the calculated value is then obtained to 0.99995, which is very close, therefore the pH meter is considered calibrated.

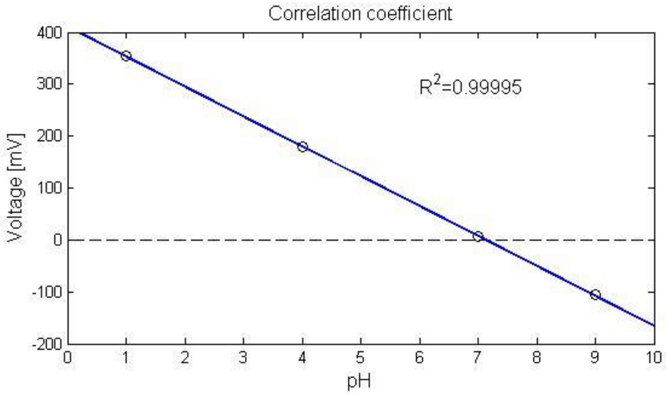

Figure 1. *pH meter calibration curve that shows if calibration is needed or not.*

3.3. Cementation Experiment

The experimental equipment consisted of a reaction vessel connected with plastic tubes to a heater and a pump, a lab stand holding a thermometer and a magnetic stirrer. Before each experiment, the reaction vessel was cleaned thoroughly with distilled-water followed by rinsing with acetone. The heater was set to the chosen temperature for the experiment and the pump was put on early when performing experiments since it was time consuming to wait for the temperature in the reaction vessel to stabilize. 12 mL of sample solution was measured with volumetric flasks and was then poured into the reaction vessel. A thermometer was put in the solution as well as a magnetic stir bar and a stirring rate at a level of 450 rpm was held constant. Figure 2 shows a picture of the experimental setup used. The thermometer can be seen coming down from above in Figure 2 as well as the magnetic stir bar visible as a white spot in the reaction vessel. The tubes on the right side of the reaction vessel transported the heating water with a pump.

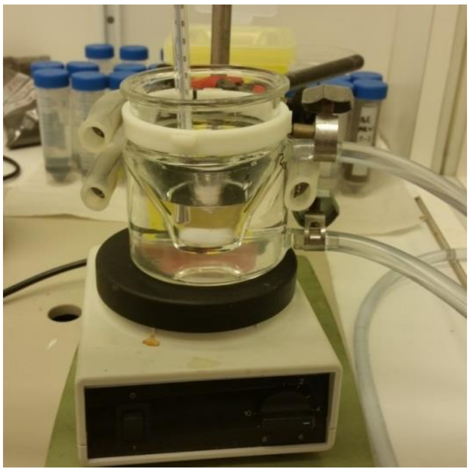

Figure 2. *Laboratory Equipment, with a heated reaction vessel and magnetic stirrer. The tubes were connected to a heater below the lab bench.*

While waiting for the temperature to stabilize, all the test tubes that were to be used in the experiment were marked with their series number and times. Syringes with filters (0.45 µm pore size) were also prepared. The test tubes were weighed and their weights were recorded in an Excel document. After the test tubes were weighed, 9.9 mL 0.1 M HNO3 was pipetted with a micro pipette and added to the test tubes. The test tubes were weighed once again.

When the temperature was close enough to the set temperature (±1 ˚C), the zero sample (t=0), 0.1 mL, could be taken from the reaction vessel with a micro pipette. The sample was transferred to the corresponding test tube. The test tube with HNO_3 and sample was weighed and its weight was noted. The next step was to weigh the amount of zinc dust in a plastic boat. The zinc dust was added to the solution and at the same time a timer was started because at this point the cementation reactions started. Also the stirring rate was increased in order to mix the zinc dust in the solution and to prevent a zinc layer that usually was formed on the surface of the solution. When the solution was thoroughly mixed the stirring rate was again set to a level of 450 rpm and was kept constant through the rest of the experiment.

At specific time intervals, 0.3 mL samples were pipetted from the reaction vessel and filtered into a plastic cup. The specific time intervals were reevaluated several times during course of the project, but they commonly contained seven to ten different samples. The filtration was done to get rid of the metal particles so that no further reactions could occur in solution. A 0.1 mL sample was pipetted from the plastic cup and transferred to its test tube. The samples were weighed and their weights were noted. At this point, dilution factors for all the samples were calculated and compared to the

desired 100x dilution factor (0.1 mL sample to 9.9 mL HNO_3). The total experimental kinetic time of the different series was ranging from 15-60 minutes.
Finally, the samples were ready to be analysed with either ICP-OES or ICP-MS depending on the magnitudes of the sample concentrations. If the samples were to be analysed with ICP-MS, they had to be diluted another 10x with 0.1 M HNO_3, resulting in a total of 1000x dilution, meaning that another series of test tubes were needed. The test tubes were weighed empty, after addition of 9 mL HNO_3 as well as with both 1 mL of sample and 9 mL HNO_3 giving a second dilution factor.

3.4. Sample Analysis

To determine the concentration of metal ions in a solution, inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) can be used. These methods allow for measuring of up to 70 elements simultaneously [24]. Standards with known concentrations are used to quantify the metal ions in the sample.

Both techniques utilize an inert argon gas to transport the sample and to produce plasma [24]. The plasma is produced when an induction current, generated by a coil, heats and ionizes the argon gas which results in Ar^+ ions and electrons [24]. The temperature of the plasma ranges from 6000-10000 K and is high enough to atomize the sample [24]. The temperature of the plasma affects how much of the analytes that end up in an excited or ionized state [24].

The excited electrons of the analytes can relax back to their ground state, by an emission of a photon of a specific wavelength [24]. The ICP-OES utilizes the fact that each element has a unique wavelength which makes it possible to identify the analytes [24]. ICP-OES is a very sensitive analytical instrument with detection limits ranging from about 0.5-50 ppm [24].

The ICP MS, on the other hand, uses a quadruple mass filter (QMF) to separate the atoms based on their mass-to-charge-ratio (m/z) [24]. AC voltage and DC voltage is applied on four different rods in the QMF, which makes the separation of the ions with the proper m/z-ratio possible [24]. Ions with an incorrect m/z-ratio will collide with the rods [24]. Ions that pass through the filter are then measured with a detector [24]. ICP-MS is an extremely sensitive analytical instrument and can detect concentrations from 0.1 to 50 ppb [24].

These two techniques have the advantages that the high temperature of the plasma leads to lower interferences from the sample matrix and a complete ionization of the sample [24]. A disadvantage is that maintaining the plasma results in a relatively high consumption of argon gas [24].

Standard curves were needed for the ICP-OES and ICP-MS to be able to quantify the metal ions in the sample solutions. ICP-OES standards with concentrations of 20, 10, 5 and 2.5 ppm were prepared from stock solutions of Co, Cu and Sb salts, each stock solution holding a concentration of 1000 ppm. The dilutions involved were done using a 25 mL volumetric flask, a 50 mL volumetric flask and a supply of 0.1 M HNO_3. ICP-MS standards with a concentration of 50, 25, 12.5 and 6.25 ppb were made from an ICP-MS standard holding a concentration of 10 000 ppb ±0.5 % in 2 % HNO_3+ Trace HF, using simple solution chemistry. Dilutions were done with 25 and 50 mL volumetric flasks using 0.1 M HNO_3.

4. Results and Discussion

To be able to illustrate how the different parameters affected the cementation reactions, plots of concentration at time t divided by the initial concentration versus time was made (C/C_0 vs t). With these plots, it is possible to evaluate the yield of the cementation reactions as well as to observe potential trends. In this section, plots will only be visualized for the most important results obtained, although many other experiments were performed. More experimental data can be seen in Appendix C.1. In every study, it is desirable to make at least triplicates of the experiments performed in order to make sure that the experiments have reproducibility and can be validated. However, because of time constraints, only a duplicate of the effect of temperature experimental series could be performed. The duplicate can be seen in Appendix D. For the rest of the experiments the reproducibility was not investigated, but would need to be done for further work.

An important condition for all the experiments illustrated in the result section was that the initial pH of the solution was in the range of 4.0-4.4. After the end of the reactions, the final pH was measured for enough kinetic experiments to conclude that it was raised to around 5.3-5.5. Mass of zinc dust added to the solution was dependent on the concentrations of the metal ions in solution and was calculated using stoichiometry. If nothing else is mentioned, the sample solutions had a concentration of 0.5 M zinc.

4.1. Zinc Wire or Zinc Dust

A short investigation was done on whether zinc-dust or zinc wire was going to be used as the cementation reaction surface. Even though zinc wire provides smaller surface area than zinc dust, it was still investigated since the literature did not seem to have performed any similar experiments. In Figure 3 the data obtained from the zinc wire experiment are plotted. The zinc wire (Sigma-Aldrich ZN005132/1) was curled using a metal rod. It had a length of 0.5 m, 1 mm diameter, a total area of $1.57 \cdot 10^{-3}$ m^2 and a mass of 2.8 g with a purity of 99.99 %. Conditions of sample solution were isothermal at 40 °C and with an initial pH of 4.4. Concentrations were 500 ppm for Co, 100 ppm for Sb and 200 ppm for Cu. For the zinc-wire experiment 1.0 M HNO_3 was used for dilutions.

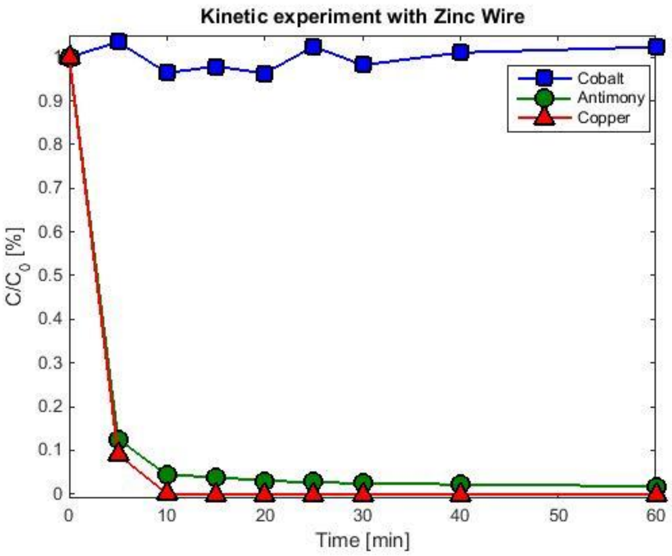

Figure 3: *Kinetic experiment performed where zinc wire acts as the reaction surface.*

Conclusions that can be made from Figure 3 are that copper is removed completely from the solution and antimony reaches a total removal of 95 % at the end of the experiment. In fact, the removal of antimony obtained from this experiment was the best achieved throughout the entire project. Thereby, if only antimony and copper were needed to be removed to obtain a pure zinc electrolyte, a zinc wire would probably be an effective choice of reaction surface. However, none of the cobalt was removed which was the main reason why the rest of the experiments performed in the project were done using zinc dust instead. Also, zinc dust offered more surface area for reaction.

To get a better understanding of the nucleation process that occurs on the zinc wire surface, a scanning electron microscope (SEM) image was taken and analysed which can be seen in Figure 4. The zinc wire (left side of the diagonal) was cut and the right side of the diagonal shows the surface where most likely flaky zinc salt formations has precipitated. Beneath this formation of zinc salt, there is precipitation of copper and antimony which is hard to identify in the SEM image alone. Therefore, an EDX (Energy dispersive X-ray analyser) analysis was done. From the data obtained in this analysis, a lot of different species can be identified but with some difficulty since zinc salt is in the way. However, in the cut-line of the zinc wire in Figure 4, there is some surface from beneath the zinc salt visible where copper is detected. That copper is present on the wire is supported by the experimental results from Figure 3.

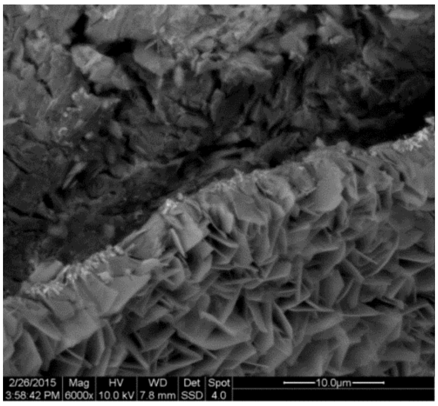

Figure 4. *SEM image visualizing a small cut of the zinc-wire after the reactions had ended.*

4.2. Effect of Copper Concentration

One of the parameters investigated in this report is how the copper concentration in solution affects the cementation reactions. Table 4 shows the experimental starting concentrations in solution of cobalt, antimony, and copper. The difference in amount of zinc dust added comes from the copper concentrations being varied. The temperature was kept constant at 40 °C during the experiments.

Table 4. Investigation of the effect of copper concentration: Initial composition and reaction conditions.

Experiment	Temperature [°C]	Co II [ppm]	Sb III [ppm]	Cu II [ppm]	Initial pH	Zinc Dust added [g/L]	Zinc Dust Excess [%]
A1	40	500	100	500	4.191	2.317	100
A2	40	500	100	800	4.199	2.858	100
A3	40	500	100	1500	4.137	4.317	100

Results are shown in Figure 5, to the left it can be noticed a trend for the cementation reaction of antimony with different concentrations of copper. A higher yield of cemented antimony on the zinc dust surface was achieved with an increased concentration of copper. The antimony removal was a lot better in run A2 than in run A1 (300 mg/L copper concentration difference). Furthermore, the difference in removal was not so distinctive when comparing run A2 to run A3 (700 mg/L copper concentration difference) which could indicate that there might be an optimal copper concentration. The right side of Figure 5, illustrates an enlarged version of the effect of copper concentration for cobalt only. It can be observed that there is a small trend that the cobalt removal is higher when the copper concentration is increased. Cobalt reaches a maximum of approximately 4 % removal with a copper concentration of 1500 mg/L (run A3), and then after 7 minutes the cobalt concentration in solution increases.

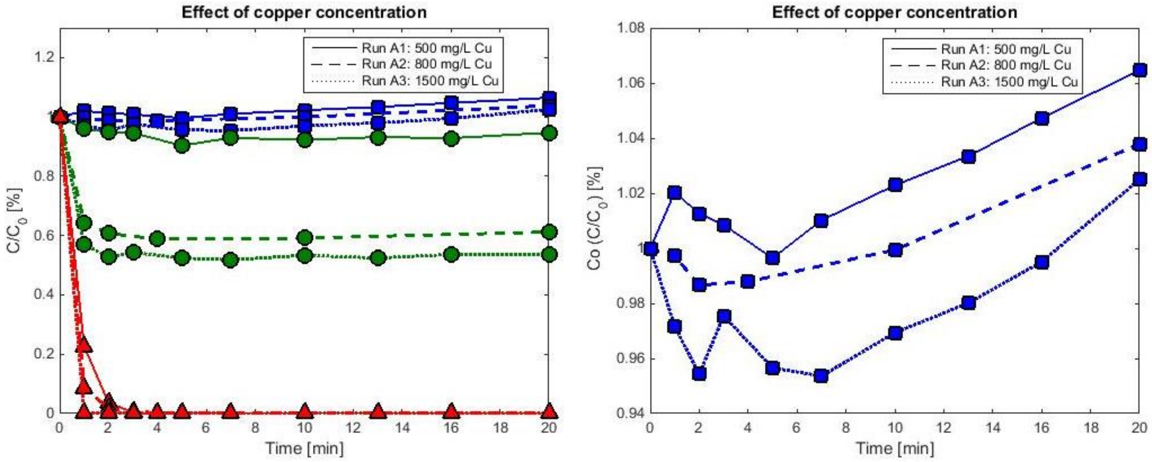

Figure 5. *The left figure illustrates the effect of copper concentration for the cementation reactions of cobalt (□), antimony (○) and copper (Δ) versus time. The right figure is a zoomed version of the cobalt cementation only.*

From Figure 5 it seems that antimony removal improves when the concentration of copper in solution is increased. This could indicate that copper deposits and forms a surface on the zinc dust to a greater extent, which in turn seems to affect the antimony removal in a positive way. The cobalt cementation seems to be only slightly affected by the copper concentration. The cobalt concentration quotient for all the runs in these experiments shows a decreasing trend until around six minutes into the cementation experiment. After that cobalt goes back into solution. This trend for cobalt precipitation and dissolution is common for other experiments and will be discussed more thoroughly in the general discussion section.

4.3. Effect of Cobalt Concentration

The following section explains results regarding how the cementation reactions are affected by a variation in cobalt concentration. Literature has shown that cobalt can be successfully removed to a greater extent [17]. However, the cobalt concentration is much higher in this work than what is reported in literature where only a few ppm of cobalt is present in solution [17]. Table 5 describes the experimental starting concentrations in solution of cobalt, antimony and copper. Note that the only concentration varied in run B1-B3 is the cobalt concentration. Temperature was maintained at 40 °C.

Table 5. Variation of cobalt concentration: Initial composition and reaction conditions.

Experiment	Temperature [°C]	Co II [ppm]	Sb III [ppm]	Cu II [ppm]	Initial pH	Zinc Dust added [g/L]	Zinc Dust Excess [%]
B1	40	100	100	500	4.140	1.375	100
B2	40	250	100	500	4.129	1.667	100
B3	40	500	100	500	4.191	2.317	100

Figure 6 demonstrates the effect of cobalt concentration in solution. The cobalt concentration seems to affect the removal of antimony to a high extent. During run B1 (100 ppm Co), the level of antimony removal was about 40 % already after 4 minutes and the concentration in solution was constant for the rest of the experiment. Run B1 can be compared to run B3 (500 ppm Co), which only resulted in a maximum of 10 % antimony removal.

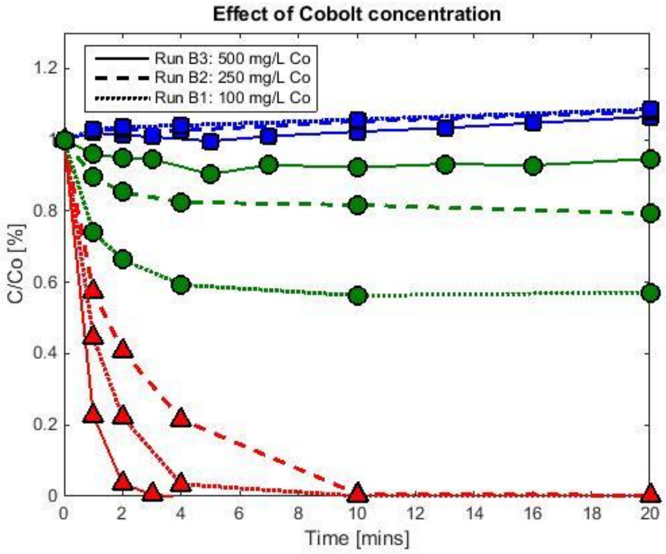

Figure 6. *The variation of cobalt concentration and its effects on the cementation reactions of cobalt (□), antimony (○) and copper (Δ) plotted versus time.*

From the result obtained from the effect of cobalt experiments, it seems possible that antimony removal is affected negatively with more cobalt present in solution. The copper in run B2 seems to cement slower compared to the average copper cementation reaction preformed in this project. An explanation might have been a small variation of the stirring rate when the zinc dust was added. However, this variation does not seem to affect the cementation of antimony in the same way.

4.4. Effect of Dilution

Another parameter investigated was if dilution of the sample solution affected the cementation reactions. In run C1-C3, as can be seen in Table 6, the ratio between the metal ions was the same just with different dilutions. All the initial concentrations of the metal ions and the initial conditions of the sample solution are specified in Table 6.

Table 6. Same concentration ratio for the metal ions: Co:Sb:Cu $(1:\frac{1}{5}:1)$.

Experiment	Temperature [°C]	Co II [ppm]	Sb III [ppm]	Cu II [ppm]	Initial pH	Zinc Dust added [g/L]	Zinc Dust Excess [%]
C1	40	100	20	100	4.162	0.450	100
C2	40	250	50	250	4.302	1.150	100
C3	40	500	100	500	4.191	2.317	100

As can be viewed in Figure 7, the copper seems to cement faster with higher concentrations in solution (run C3), even though the trend is marginal. The antimony removal varies a lot in the different experiments and the highest removal was achieved during run C2.

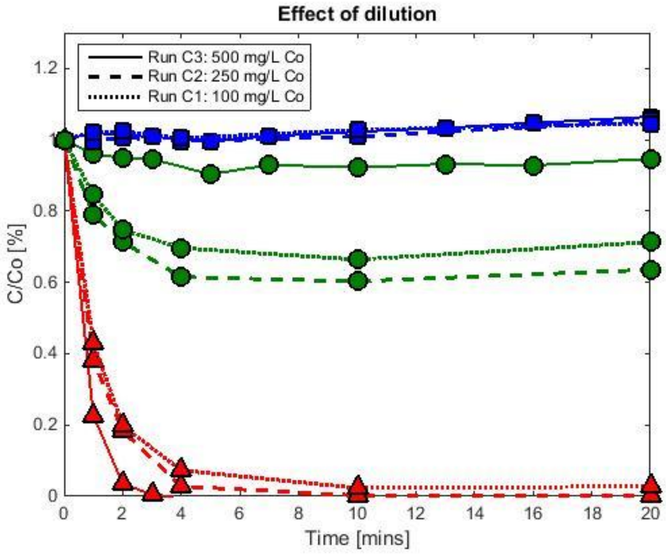

Figure 7. *The effect of dilutions for cementation reactions of cobalt (□), antimony (○) and copper (Δ).*

There are no obvious conclusions that can be made from Figure 7 regarding the removal of antimony. We think that the inconclusive result is because of a difference in initial pH, which was a bit higher during run C2 than in the other experiments. The motivation for this experiment was to investigate if the total amount of ions in solution affected the mass transport and thereby the rate of the reactions. Since there is a trend for copper in this experiment, but not for antimony and cobalt, the above mentioned hypothesis could not be confirmed nor neglected.

4.5. Effect of Temperature

The temperature dependence was studied for the system. Composition and conditions such as temperature of the solutions can be found in Table 7. The temperature was interesting to investigate since it is reported to have the greatest impact on the rate of the reactions [7, 8].

Table 7. Effect of variation in temperature. Initial composition and reaction conditions.

Experiment	Temperature [°C]	Co II [ppm]	Sb III [ppm]	Cu II [ppm]	Initial pH	Zinc Dust added [g/L]	Zinc Dust Excess [%]
D1	40	500	100	500	4.056	2.208	100
D2	50	500	100	500	4.056	2.217	100
D3	60	500	100	500	4.056	2.233	100

A higher temperature resulted in a positive effect on the removal of both cobalt and antimony in Figure 8. Also the rate of copper cementation seems to be faster with increased temperature, though the difference is not so distinctive. The concentration of cobalt increases after about 4-6 minutes and the antimony concentration increases after 6 minutes in both run D2 and D3. In run D1, both antimony and cobalt behave differently compared to in the other two runs. This difference can be noticed in the time interval of 6-20 minutes. Note that in some samples the C/C_0 is greater than one, this happened in several experiments, reasons for this is discussed in the general discussion section.

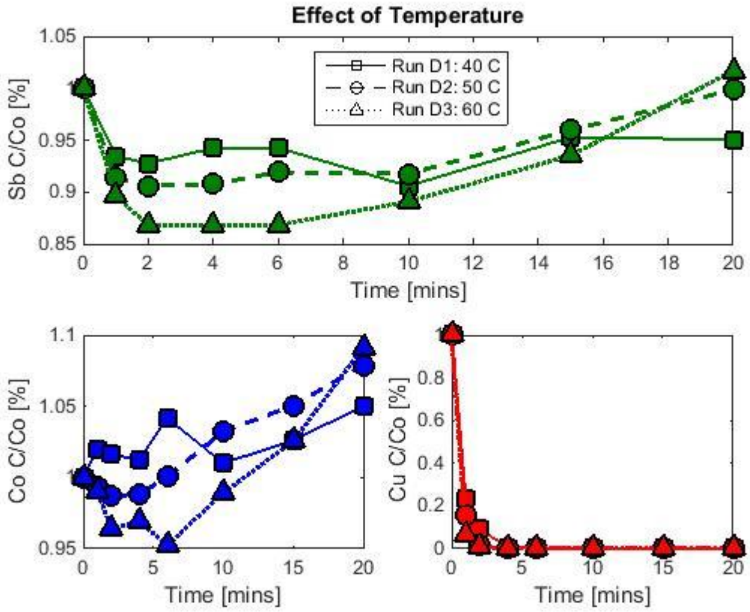

Figure 8. *Subplots of the cementation reactions at different temperatures, 40 °C (□), 50°C (○) and 60°C (Δ). The upper figure is showing how antimony is affected by the temperature The lower figures illustrate cobalt cementation to the left and copper cementation to the right.*

According to the literature, the temperature should have an impact on the cobalt kinetics with an optimal temperature of 85 °C [7]. Temperatures this high were not studied since the experimental equipment was not suitable for it. In common for both antimony and cobalt, the concentrations increase after certain period of time.

4.6. Effect of Zinc Dust Amount

Cementation reactions of copper, antimony and cobalt are dependent on how much zinc dust surface area that is exposed to the solution. In Table 8, initial conditions of run E1-E4 are described and the only parameter changed during these experiments is the zinc dust concentration.

Table 8. Effect of the mass of zinc dust added to sample solution. Initial composition and reaction conditions.

Experiment	Temperature [°C]	Co II [ppm]	Sb III [ppm]	Cu II [ppm]	Initial pH	Zinc Dust added [g/L]	Zinc Dust Excess [%]
E1	40	500	100	500	4.191	2.242	100
E2	40	500	100	500	4.191	5.614	400
E3	40	500	100	500	4.191	8.982	700
E4	40	500	100	500	4.191	11.227	900

In Figure 9 the result from run E1-E4 is plotted versus time. The highest antimony removal was achieved during run E2 (400 % excess of zinc dust) and the lowest antimony removal was reached during run E1 (100% excess of zinc dust). Figure 9 also shows that the cobalt and copper removal does not seem to change substantially with increasing zinc dust. The results from run E1-E4 suggest that there is an optimal value of the zinc dust concentration at around 5.61 g/L (run E2) but multiple experiments would need to be run to confirm this.

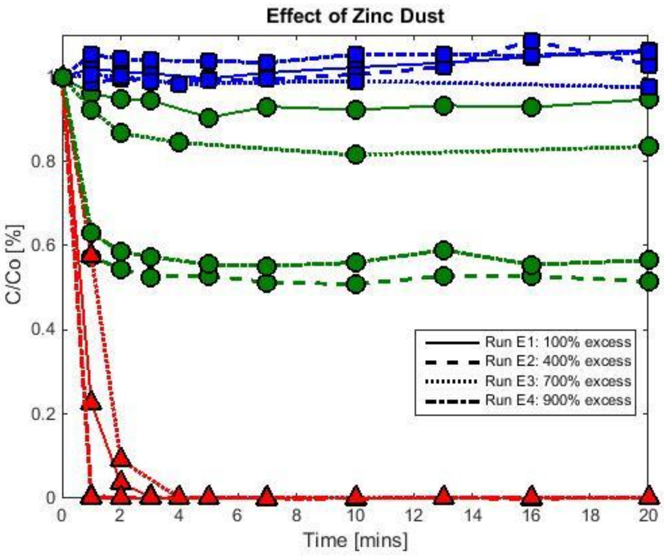

Figure 9. *The impact on cobalt (□), antimony (○) and copper (Δ) concentrations when raising the zinc dust amount added to the solution.*

As the literature states [7], the amount of zinc dust seems to have an optimal value. Not only does this optimal value give a better yield of cementation reactions, it is also favourable from an economical perspective not to use too much zinc dust. The best antimony removal, obtained during run E2, uses a zinc dust concentration similar to what the industry typically uses (as mentioned in the theory section). This similarity to industrial concentration levels is not necessarily to be expected since the proportions in our system is different from those in industry [9, 15].

4.7. Mimic of Literature Experiment

This experiment was done to investigate if it was possible to get similar linear behaviour of the cementation reactions as the literature had obtained [17]. The concentrations used in this literature experiment are in a comparable magnitude to those typically used in both other studies and industry [9, 15]. It would be possible to dilute the VM leachate to similar concentration levels. However, a dilution like that would decrease the concentration of zinc, meaning that the purification process would not be as profitable. Furthermore, the concentration ratios of cobalt, antimony and zinc, used in run Ea1 are not the same as in the VM leachate.

An example of an experiment performed with excellent data can be seen in Figure 10. Cobalt reaches a maximum of 15 % removal after 10 minutes. Also antimony is removed effectively ending up at a 92 % removal at its best. Although these numbers are high, they probably cannot be compared directly to the other results because concentrations of the metal ions were significantly higher in those.

In addition, Figure 10 indicates that cobalt has a linear region in the time interval 0-10 minutes (four dots). Copper and antimony shows a linear trend in the time interval 0-6 minutes (four dots). This type of linear behaviour is required when aiming for an activation energy study. It encouraged the group to do more experiments with the same sample solution but varying the temperature with a goal of obtaining the activation energy for these concentrations. However, this turned out not to be doable since the slope of the lines for cobalt, antimony and copper did not change as expected with temperature. The rest of the graphs for these experiments (Ea2-Ea6) can be seen in Appendix C.1. A brief explanation of the equations that initially were to be used for the activating energy study can be seen in Appendix C.

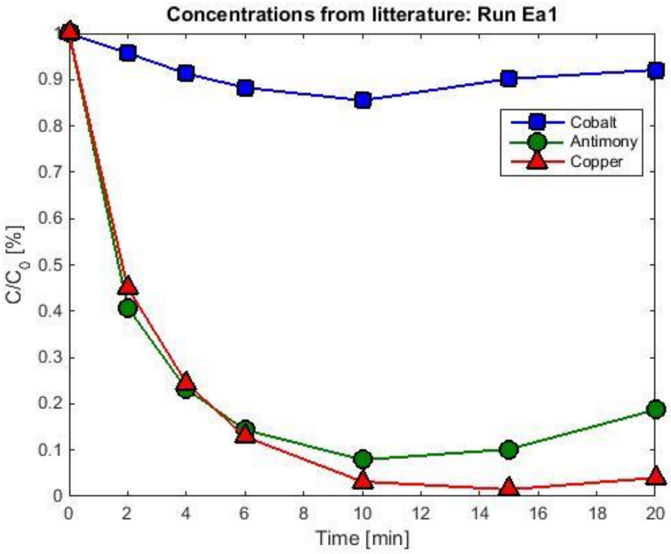

Figure 10. *Kinetic experiment performed using concentrations from the literature. The following concentrations were used: Co 9 ppm, Sb 1 ppm, Cu 17 ppm, zinc 0.3 M and zinc dust 2 g/L. The temperature was maintained at 25 °C (room temperature) and the initial pH was 4.32.*

4.8. General Discussion of the Results

The following section is a general discussion of the obtained results. It also explains some problems that arose during the experiments which we think contributed to the behaviour the cementation reactions exhibited. Furthermore, suggestions for improvements when it comes to the experimental equipment will also be proposed.

A result common for all performed experiments is that all copper in solution cements on the surface of the zinc dust after 3-10 minutes, which agrees with the results of other studies performing cementation reactions with the same species [7]. According to literature, copper needs to be in solution to initiate the cementation of cobalt [7]. However, copper is not originally present in the VM leachate and would therefore have to be added. For zinc electrowinning the copper concentration in solution needs to be minimised. This means that copper has to be removed completely after it has been used. Our experiments indicate that no matter how much copper is added to the solution it can be removed.

As can be observed in especially Figures 5, 6, 7 and 9 the concentration quotient of antimony, Sb C/C_0, tends to remain at a constant level after 1-4 minutes. Other research on similar subjects does not get similar behaviour for the removal of antimony [8, 9, 17]. Therefore, we think that there were a number of factors contributing to a passivation of the reaction surface. Firstly, an inhibiting step could have been the formation of basic zinc salts. Secondly, hydrogen ions probably reacted on the zinc dust surface forming hydrogen gas. This hydrogen formation is negative since it is a competing reaction. Lastly, Zn^{2+} ions could have adsorbed to the zinc dust surface. If the reaction surface was passivated by any of the discussed factors to a greater extent, this could explain the halted cementation.

By comparing the results obtained from the wide range of different experiments performed, it is common that cobalt is only removed with a few percentages and under some conditions it is not removed at all. It can also be noticed from the experimental data that the concentration quotient (C/C_0) is often above one for cobalt. This indicates that cobalt is somehow produced in the system, which obviously should not be possible.

A contributory reason for values above one of the concentration quotient is believed to be the laboratory setup. During the experiments evaporation of sample solution was observed to some extent already at 40-50 °C. A hypothesis is that this caused a loss in sample volume leading to higher concentrations of the metal ions in solution. To reduce the impact of evaporation, a watch-glass was put on the reaction vessel to condense vapour and recirculate some of the sample solution. However, this was of course not the best solution; it would have been desirable to have a reaction vessel that was isolated and sealed with a condenser. In addition, with a setup like that, the optimal temperature for cobalt cementation according to the literature, 85 °C [7], could have been investigated. Furthermore, the effect of the evaporation could have be decreased if a larger sample solution volume were used (12 mL sample solution were used in our experiments). A larger volume of sample solution would in turn require a reaction vessel with a larger volume. Another possible reason for the anomalous concentration quotient might have been that the sample volume was reduced due to hydrogen formation.

The increase of cobalt and antimony concentration after a certain time, as can be noticed in especially Figure 5, 8 and 10, might indicate that neither of them forms a stable deposition and therefore redissolves back in solution as reported by other literature [4]. However, evaporation could also be another explanation for the increase in concentration.

As mentioned earlier, in the result section, the pH of the sample solution increased as the reaction proceeded and the final pH usually landed on around 5.3-5.5. Increase in pH is probably due to hydrogen evolution that occurs when zinc dust is added to the solution. With a pH this high, it is likely that there is even a higher local pH in the solution. Basic zinc salts are then formed, which can passivate the zinc dust surface [9]. With this in mind it would have been interesting to try the same experiments with an automatic titration equipment, continuously correcting the pH to be in the interval of 4.0-4.4 or just use a buffer to make the pH more stable.

During the laboratory sessions there were some complications with the use of the zinc dust because it tended to form a layer on the surface of the sample solution. A countermeasure for this was obviously to increase the stirring rate when adding the zinc dust, but also addition of surfactant to reduce surface tension in the sample solution. This seemed to work reasonably well because sometimes a zinc layer was not formed. However, if the surfactant affected the cementation reaction itself was not investigated. Such an investigation would require additional knowledge of the molecular behaviour of this surfactant, Triton-X-100, in a system containing similar components. In our case further investigation was deemed to not be of great necessity, due to the lack of time.

When using zinc wire instead of zinc dust the removal of antimony was high (see Figure 3) and there could be many reasons. One reason could be surface area. While the zinc dust is presumed to have a higher surface area compared to the wire, it is also more prone to form lumps and aggregates when introduced to the solution. These formations might lead to a decrease in the effective surface area available. Since the wire is more static it does not have these problems. Another speculation is that the higher degree of cementation was facilitated by better electron transport within the wire. While a small zinc particle may be made inert by a layer of cemented material the wire has the potential to remain negatively charged throughout the entire structure, provided that there still is at least one spot where zinc can dissolve at.

However, neither higher surface area nor better electron transport can explain why the cobalt was left uncemented while copper and antimony was not. Our current explanation for this is that the experiment was conducted at a low temperature, 40 ^{o}C compared to the recommended 85 ^{o}C from literature [7]. Furthermore, the cobalt may have been a part of the reaction in a small rate and then redissolved fast, or it simply never took part in the reaction. The latter is more likely according to Figure 3 since there is little indication of cobalt precipitation at all. Even more likely is that the formed zinc salt (seen in Figure 4) blocked all surface of the zinc-wire so that cobalt never could react. However, these reasons can only be speculative, since no detailed investigation was done.

It is difficult to predict whether cementation reactions would be an industrially feasible separation method for purifying VM leachate. Based on our results, the cementation reactions would need to be performed in several batches in order to remove the impurity metals to the required low levels. In a process like this, the zinc dust consumption would be high since it would have to be added to every batch. In addition, the pH of solution would probably be needed to be adjusted during the reactions, meaning that there would be constant consumption of acid. However, if further studies on the cementation reactions establish them to be effective means for purifying VM leachate systems from impurity metals, they have good potential to be applied industrially in the future.

In addition, the precipitated metals on the zinc dust surface are also of importance to recover. If we had had more time it would have been interesting to investigate how to separate the different metals precipitated on the zinc dust.

5. Conclusions

The focus of this study was to investigate how the cementation reactions of cobalt, antimony and copper in an artificial system, similar to acid leached varistor material, were affected by temperature, zinc dust concentration and different concentrations of the ingoing metal ions.

Some trends were obtained from the experiments and those were mainly for antimony. The removal of antimony seems to increase with an increased concentration of copper. However, the antimony removal ceased to increase at a certain point were further added copper did not result higher removal. In addition, a decreased concentration of cobalt turned out to have a positive effect on the removal of antimony. The best antimony removal with similar concentrations to that of the VM leachate was obtained using a zinc wire instead of zinc dust as a reaction surface.

It was difficult to observe trends regarding the removal of cobalt since it tended not to react to any greater extent. However, the removal of cobalt seemed to increase with an increased copper concentration in solution. It has been found that the copper in solution (500-1500 mg/L) can be totally removed by cementation on zinc dust with a very high rate. In the VM leachate copper would need to be added, however it would also need to be removed as any other impurity before electrolysis. The high rate of copper removal is therefore positive since it indicates that the removal of copper can be done even with larger additions of copper.

The increasing concentrations of cobalt and antimony after a certain time of reaction made interpretation of the results difficult. Possible reasons for these increasing concentrations could have been redissolution of cemented metals and/or evaporation of sample solution.

To meet the requirement of a pure zinc sulphate solution, the impurity metals have to be removed to a very high extent. With a single reactor, as used in this study, the required purity would probably not be possible to achieve. However, if reactors in series were to be used, the removal of impurity metals would be increased significantly.

Finally, cementation reactions can potentially be used as a separation method for purifying VM leachate for use in zinc electrowinning. However, further studies needs to be conducted in the subject in order to increase the effectiveness of the cementation reactions. In addition, cementation of metals in actual VM leachate needs to be studied in order to see if the information achieved in this project can be applied on the VM system.

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Appendices

Appendix A. Discussion of the Projects Progression

Originally, the plan with this project was to investigate the behaviour of the cementation reactions in an artificial system of cobalt, antimony, copper and zinc as an introduction before moving on to performing cementation reactions in the VM leachate. The project aimed to result in data for the activation energy for the cementation reactions of cobalt, antimony and copper with set initial concentrations of the metal ions. The motivation for this was to gain a better understanding of the nucleation mechanism and reaction kinetics of the system. However, it was concluded early on that the results from the experiments on the artificial system were not optimal for an activation energy study because of several reasons. For an example, there were not enough linear regions in the graphs analysed for any of the cementation reactions. A linear region is a key factor when aiming for a value of an activation energy that is scientifically reliable. The region could not be observed since copper and antimony cemented out too quickly and cobalt removal was poor. This meant that further investigation had to be done on the artificial system. With doing so, the plan of conducting experiments on the varistor material was abandoned, and the focus rather went to an investigation of the effect of changing different parameters in order to get a better understanding of the reactions.

Initially, when we performed experiments on the artificial system, 1.0 M HNO_3 acid was used to dilute the samples. However, since the obtained graphs did not look as expected, we had to reevaluate. A hypothesis was that the acid for dilution had a too low pH. We believed that the 1.0 M HNO_3 caused the zinc-dust with precipitated material to dissolve when adding the 0.1 mL sample to the test tube with the HNO_3. The concentration of HNO_3 was changed to 0.1 M and to make sure that the problem was avoided totally, a filtration was done before adding the sample to the HNO_3, instead of filtering the diluted sample.

Further studies on cementation in VM leachate would need to investigate how the reactions behave at higher temperatures, preferably around 85 ^{o}C. They would also have to conduct experiments using a sealed reaction vessel to offset the effects of evaporation etc. Furthermore, the effect of pH and ways to control the pH during the cementation should be considered. Lastly more tests have to be conducted using solid zinc with different morphology, different wire or different dust particles most likely affects the cementation.

Appendix B. Calculations

B.1. Preparation of sample solution

Before every laboratory session there were calculations needed to be carried out so that they would run smoothly without interruptions. The more thoroughly the preparations are executed the more accurate the data for the reactions will be.

The artificial system is set to contain of:

$ZnSO_4 \cdot 7H_2O, CoSO_4 \cdot 7H_2O, CuSO_4 \cdot 5H_2O$ and $C_8H_4O_{12}Sb_2 \cdot 3H_2O$.

Each metal compound are weighed as carefully as possible to the calculated value for the mass, then solved in a jar and diluted with Milli-Q water to a desired volume. It is important to dissolve all metals and therefore the solution is stirred until it is considered to be completely free from solid particles. All the calculation steps needed for this computation can be visualized below in a general form and will be followed with a specific example from this project.

Amount of added mass to sample solution:

$$\boldsymbol{c_{metal}}\left[\frac{mole}{l}\right] = \frac{c_{metal\ in\ solution}}{M_{metal}}\left[\frac{\frac{g}{l}}{\frac{g}{mole}}\right] \tag{2}$$

Decide the ratio: $\boldsymbol{n_{metal\ compound}}: \boldsymbol{n_{metal\ in\ solution}}$

$$\Rightarrow \boldsymbol{n_{metal\ compound}}[\boldsymbol{mol}] = \boldsymbol{V_{Sample\ solution}}[\boldsymbol{l}] * \boldsymbol{c_{metal\ in\ solution}}\left[\frac{mole}{l}\right] \tag{3}$$

$$\boldsymbol{m_{metal\ compound}}[\boldsymbol{g}] = \boldsymbol{n_{metal\ compoud}}[\boldsymbol{mole}] * \boldsymbol{M_{metal\ compound}}\left[\frac{g}{mol}\right] \tag{4}$$

Where c is the concentration, M the molar mass, n the amount of substance and V the volume. The molar mass can be visualized in table 3 and the concentration setup can be found in table 4 and these are decided in advance.

Example:
Choose concentration setup from experiment A1 in table 4 and the total volume is decided to be 100 ml then the calculations will be following:

Cobalt:

$$c_{Co} = \frac{500*10^{-3}}{58.93} = 0.0084846428\left[\frac{mole}{l}\right]$$

$$n_{CoSO_4 \cdot 7H_2O}: n_{Co} \leftrightarrow 1:1$$

$$\Rightarrow n_{CoSO_4 \cdot 7H_2O} = 100 * 10^{-3} * 0.0084846428 = 8.484642797 * 10^{-4}\ mole$$

And then $m_{CoSO_4 \cdot 7H_2O} = 8.484642797 * 10^{-4} * 281.10 = 0.238503309\ \mathrm{g}$

Thus 0.239 grams of Cobalt (II) Sulfate Heptahydrate needs to be weighted.

Antimony:

$$c_{Sb} = \frac{100*10^{-3}}{121.76} = 8.212877792 * 10^{-4} \left[\frac{mole}{l}\right]$$

$$n_{C_8H_4O_{12}Sb_2 \cdot 3H_2O} : n_{Sb} \leftrightarrow 1:2$$

$$\Rightarrow n_{C_8H_4O_{12}Sb_2 \cdot 3H_2O} = \frac{100 * 10^{-3} * 8.212877792 * 10^{-4}}{2} = 4.106438896 * 10^{-5}\, mole$$

And then $m_{C_8H_4O_{12}Sb_2 \cdot 3H_2O} = 4.106438896 * 10^{-5} * 667.88 = 0.0274260841$ g

Thus 0.0274 grams of Antinomy potassium tartrate needs to be weighted.

Copper:

$$c_{Cu} = \frac{500*10^{-3}}{63.55} = 0.0078678206 \left[\frac{mole}{l}\right]$$

$$n_{CuSO_4 \cdot 5H_2O} : n_{Cu} \leftrightarrow 1:1$$

$$\Rightarrow n_{CuSO_4 \cdot 5H_2O} = 100 * 10^{-3} * 0.0078678206 = 7.867820614 * 10^{-4}\, mole$$

And then $m_{CuSO_4 \cdot 5H_2O} = 7.867820614 * 10^{-4} * 249.68 = 0.1964437451$ g

Thus 0.196 grams of copper (II) sulfate pentahydrate needs to be weighted.

All the weighted substances are mixed then diluted to total volume of 100 ml with stirring and thereby an artificial system of the varistor material is obtained with the concentration setup A1.

B.2. Zinc dust amount

When the artificial system, sample solution, is obtained the experiment can be executed and for the reaction to start the zinc-dust have to be added. The zinc-dust amount will be varied depending on the sample solution and therefore the needed mass must be calculated in various laboratory sessions and this is done accordingly:

$$\boldsymbol{n_{metal\ compound}}\ [\boldsymbol{mole}] = \frac{\boldsymbol{m_{weighted\ metal\ compound}}[\boldsymbol{g}]}{\boldsymbol{M_{metal\ compound}}\left[\frac{\boldsymbol{g}}{\boldsymbol{mole}}\right]} \qquad (5)$$

Decide the ratio: $\boldsymbol{n_{metal\ compound}} : \boldsymbol{n_{metal\ ion}}$

Then $$\boldsymbol{c_{metal\ ion\ in\ sample\ solution}} \left[\frac{\boldsymbol{mole}}{\boldsymbol{l}}\right] = \frac{\boldsymbol{n_{metal\ ion\ in\ sample\ solution}}\ [\boldsymbol{mole}]}{\boldsymbol{V_{sample\ solution}}[\boldsymbol{l}]} \qquad (6)$$

$$\boldsymbol{n_{metal\ ion\ in\ reaction\ vessel}}[\boldsymbol{mole}] = \boldsymbol{c_{metal\ ion\ in\ sample\ solution}} \left[\frac{\boldsymbol{mole}}{\boldsymbol{l}}\right] * \boldsymbol{V_{reaction\ vessel}}\ [\boldsymbol{l}] \qquad (7)$$

Here $$\sum \boldsymbol{n_{metal\ ions\ in\ reaction}} = \boldsymbol{n_{Co}} + \boldsymbol{n_{Cu}} + \boldsymbol{n_{Sb}} \qquad (8)$$

Since the Zinc compound will not take part in the reaction it is not relevant to add its amount of substance here.

$$\boldsymbol{m_{Zinc\ dust\ needed\ for\ reaction}} = \sum \boldsymbol{n_{metal\ ions\ in\ reaction}} * \boldsymbol{M_{zinc}} \qquad (9)$$

$$\Rightarrow \boldsymbol{m}_{\boldsymbol{Zinc\ dust\ in\ excess}} = \boldsymbol{m}_{\boldsymbol{Zinc\ dust\ needed\ for\ reaction}} * \boldsymbol{X}_{\boldsymbol{factor\ excess}} \qquad \textbf{(10)}$$

Example:
If an experiment with setup A1 from table 4 with 100 % excess, 100 ml sample solution and 12 ml to reaction vessel would be done the needed amount of zinc-dust would be accordingly:

If $m_{weighted\ metal\ compound}$ is close to the calculated value from preparation of sample solution then:

Cobalt:

$$n_{CoSO_4 \cdot 7H_2O} = \frac{0.239}{281.10} = 8.502312344 * 10^{-4}\ mole$$

$$n_{CoSO_4 \cdot 7H_2O} : n_{Co} \leftrightarrow 1:1$$

$$c_{Co} = \frac{8.502312344 * 10^{-4}}{100 * 10^{-3}} = 0.0085023123\ \left[\frac{mole}{l}\right]$$

$$\Rightarrow n_{Co\ in\ reaction\ vessel} \approx 0.00102\ [mole]$$

Antimony:

$$n_{C_8H_4O_{12}Sb_2 \cdot 3H_2O} = \frac{0.0274}{667.88} = 4.102533389 * 10^{-5}\ mole$$

$$n_{C_8H_4O_{12}Sb_2 \cdot 3H_2O} : n_{Sb} \leftrightarrow 1:2$$

$$c_{Sb} = \frac{4.102533389 * 10^{-5}}{100 * 10^{-3}} * 2 = 8.205066778 * 10^{-4}\ \left[\frac{mole}{l}\right]$$

$$\Rightarrow n_{Sb\ in\ reaction\ vessel} \approx 9.85 * 10^{-6}\ [mole]$$

Copper:

$$n_{CuSO_4 \cdot 5H_2O} = \frac{0.196}{249.68} = 7.850048062 * 10^{-4}\ mole$$

$$n_{CuSO_4 \cdot 5H_2O} : n_{Cu} \leftrightarrow 1:1$$

$$c_{Cu} = \frac{7.850048062 * 10^{-4}}{100 * 10^{-3}} = 0.0078500481\ \left[\frac{mole}{l}\right]$$

$$\Rightarrow n_{Cu\ in\ reaction\ vessel} \approx 9.420 * 10^{-5}\ [mole]$$

And $\sum n_{metal\ ions\ in\ reaction} = 2.057 * 10^{-4}\ [mole]$

$$m_{Zinc\ dust} = 2.057 * 10^{-4} * 65.41 = 0.013569883\ [g]$$

$$\Rightarrow m_{Zinc\ dust\ in\ excess} = \{100\%\ excess\} = 0.013569883\ * 2 = 0.0269139766\ [g]$$

Thus approximately $\underline{\underline{0.0270}}$ grams of zinc-dust must be added to the sample solution in order to get the reaction started.

B.3. Preparation of ICP run

In an analysis using ICP, the samples need to be diluted a certain number of times if it is to work and if accurate values is to be obtained.

100x dilution for ICP-OES:

$$c_{sample}\left[\frac{mole}{l}\right] * V_{sample}[l] = c_{dilute}\left[\frac{mole}{l}\right] * V_{dilute}[l] \quad (11)$$

The volume in the sample is then the volume needed to be pipetted from the sample to an acidic solution of appropriate volume.
For the ICP-MS the procedure is carried out equally except the extra dilution with the same volume as V_{sample} added from the acidic solution to another test tube with more acidic solution of appropriate volume.

Appendix C. Activation energy study

The following equations were initially supposed to be used in an activation energy study of the artificial system. The section explains the process that was initially to be used for calculating the activation energy.

Equation 12 describes how the concentration of the studied metals varies in the leaching solution over a certain period of time.

$$\frac{dC}{dt} = \frac{-k \cdot A \cdot C}{V} \quad (12)$$

Where $C\ (mol \cdot dm^{-3})$ is the concentration of the studied metal, $t\ (s)$ is the time, $k\ (cm \cdot s^{-1})$ is the rate constant, $A\ (cm^2)$ is surface area of the zinc dust that is exposed and $V\ (cm^3)$ is the volume of the solution [8].

A simple integration of equation 12 from the initial concentration (C_0) to the final concentration (C) at time t can be done. The result is Equation 13.

$$V \cdot \ln\left(\frac{C_0}{C}\right) = k \cdot A \cdot t \quad (13)$$

With equation 13, a plot of $\ln\left(\frac{C_0}{C}\right)$ versus the time t can be made. With a linear regression the value of the rate constant k at different temperatures can be determined from the slope of the line.

The rate constants are then used to make an Arrhenius plot using equation 14.

$$\ln(k) = \ln(A_{pre}) - \frac{E_a}{R} \cdot \left(\frac{1}{T}\right) \quad (14)$$

In equation 14 A_{pre} is a pre-exponential factor, $E_a\ (kJ \cdot mol^{-1})$ is the activation energy, $R\ (J \cdot mol^{-1} \cdot K^{-1})$ is the ideal gas constant and $T\ (K)$ is the temperature. This will make a linear curve where $\ln(A_{pre})$ is the intercept with the y-axis where $\left(\frac{1}{T}\right)$ equals zero and $-\frac{E_a}{R}$ is the slope of the curve. From the slope of the curve the activation energy can easily be obtained [12].

From the activation energy the enthalpy of activation $\Delta H^{\ddagger}$ $(kJ \cdot mol^{-1})$, the entropy of activation $\Delta S^{\ddagger}(J \cdot mol^{-1} \cdot K^{-1})$ and the Gibbs free energy of activation $\Delta G^{\ddagger}(kJ \cdot mol^{-1})$ can be determined from the equations 15, 16, 17 respectively.

$$\Delta \boldsymbol{H}^{\ddagger} = \boldsymbol{E}_{a} - \boldsymbol{R} \cdot \boldsymbol{T} \qquad \textbf{(15)}$$

$$\Delta \boldsymbol{S}^{\ddagger} = \boldsymbol{R} \cdot \ln\left(\frac{A_{pre} \cdot \boldsymbol{h} \cdot \boldsymbol{N}}{\boldsymbol{e} \cdot \boldsymbol{R} \cdot \boldsymbol{T}}\right) \qquad \textbf{(16)}$$

$$\Delta \boldsymbol{G}^{\ddagger} = \Delta \boldsymbol{H}^{\ddagger} - \boldsymbol{T} \cdot \Delta \boldsymbol{S}^{\ddagger} \qquad \textbf{(17)}$$

In Equation 16 h $(J \cdot s)$ is Planck's constant, N (mol^{-1}) is Avogadro's Constant and e (coulomb) is the elementary charge [8].

C.1. Mimic of literature experiment

The activation energy for the "mimic of literature experiment" was attempted to be obtained. However, as can be seen in figures 11-15, the reactions occurred fast which resulted in that the desired linearity was not achieved. In addition, the slope of the lines for the cementation reactions did not change as expected with an increased temperature. The initial compositions used for run Ea2-Ea6 are visualized in Table 9.

Table 9. Initial conditions and concentrations of sample solution used of the activation energy experiments.

Experiment	Temperature [°C]	Co II [ppm]	Sb III [ppm]	Cu II [ppm]	Initial pH	Zinc Dust added [g/L]
Ea2	30	9	1	17	4.32	2.008
Ea3	40	9	1	17	4.32	2.000
Ea4	50	9	1	17	4.32	2.025
Ea5	60	9	1	17	4.32	2.017
Ea6	70	9	1	17	4.32	2.033

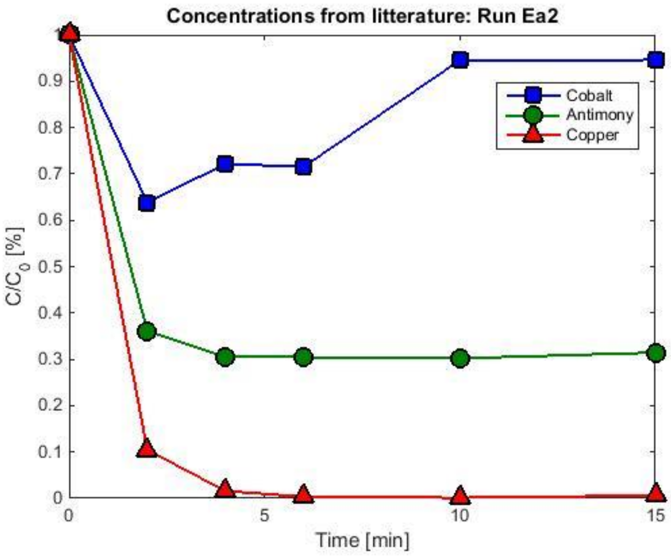

Figure 11. *Kinetic experiment performed using concentrations from the literature. The temperature used in this run was 30°C.*

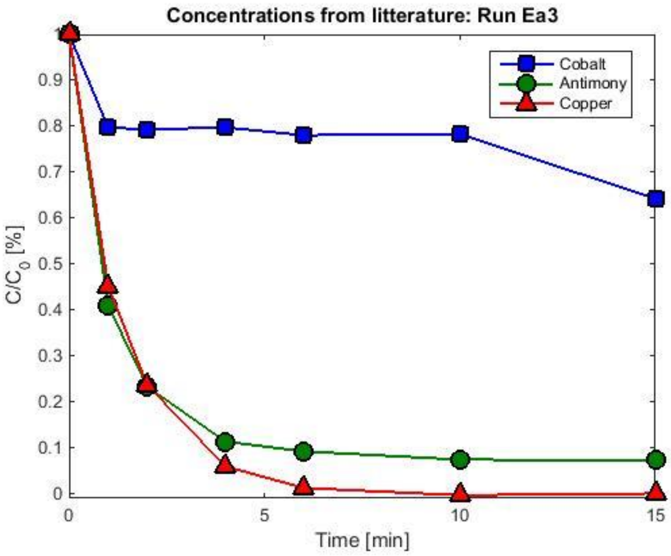

Figure 12. *Kinetic experiment performed using concentrations from the literature. The temperature used in this run was 40°C.*

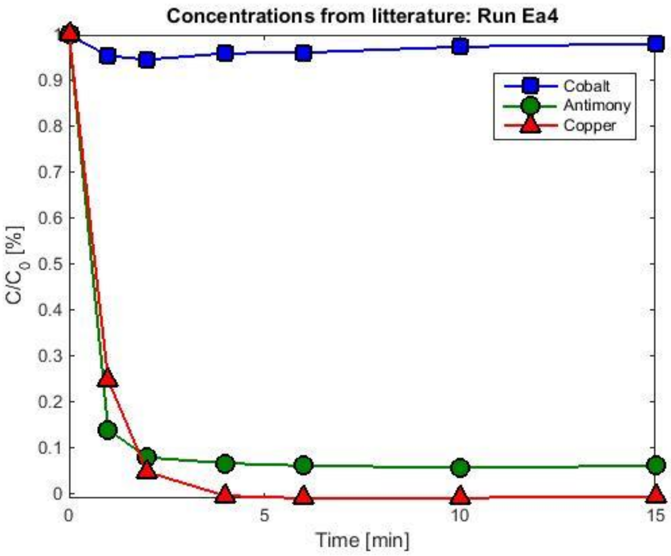

Figure 13. *Kinetic experiment performed using concentrations from the literature. The temperature used in this run was 50°C.*

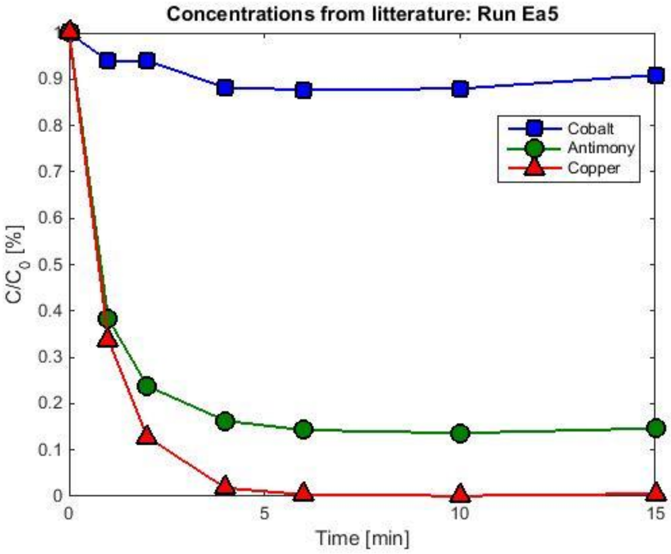

Figure 14. *Kinetic experiment performed using concentrations from the literature. The temperature used in this run was 60°C.*

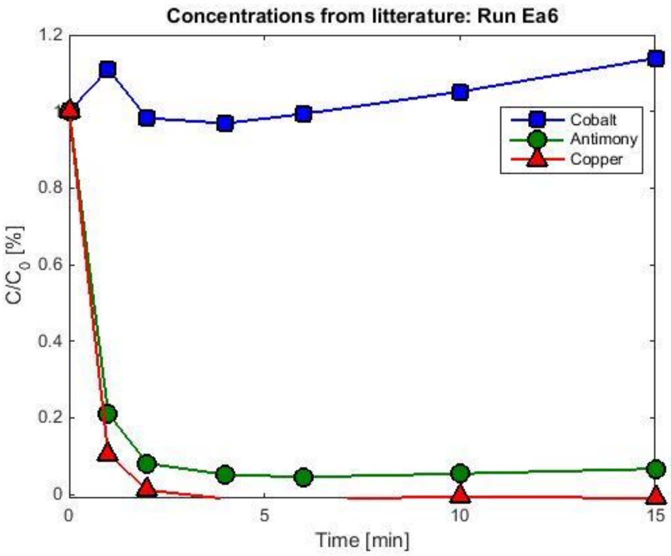

Figure 15. *Kinetic experiment performed using concentrations from the literature. The temperature used in this run was 70°C.*

Appendix D. Replicates

D.1. Effect of temperature

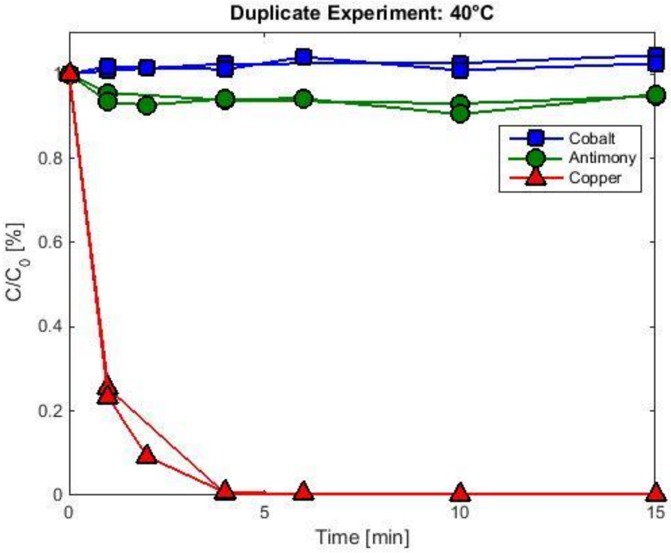

Figure 16. *Effect of temperature experiment performed in a duplicate. The temperature used in these runs was 40°C.*

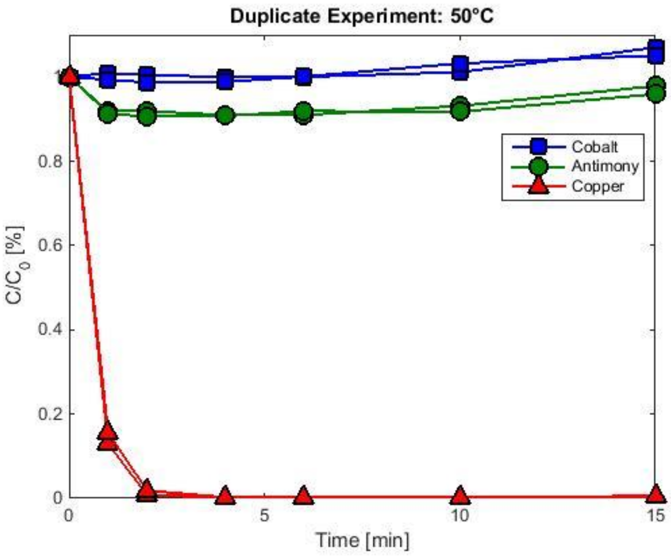

Figure 16. *Effect of temperature experiment performed in a duplicate. The temperature used in these runs was 50°C.*

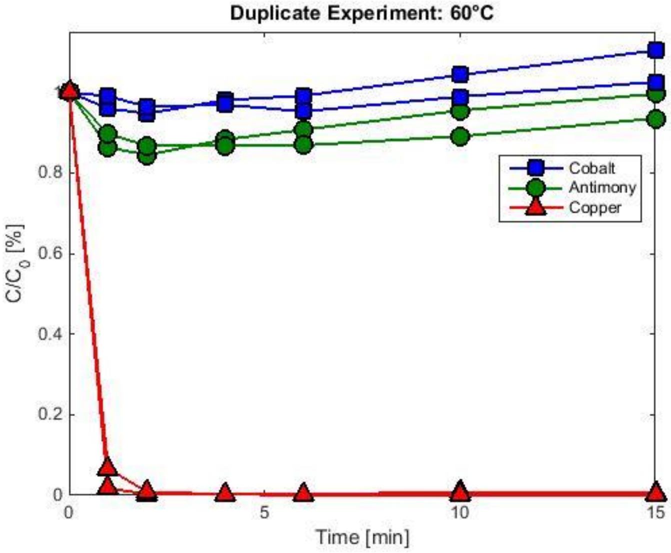

Figure 17.*Effect of temperature experiment performed in a duplicate. The temperature used in these runs was 60°C.*