

# High Temperature and High Pressure Cobalt Cementation onto Zinc Dust

by

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B.Sc., Sharif University of Technology, Iran, 2011

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

(Materials Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA  
(Vancouver)

January 2015

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## **Abstract**

Trace amounts of electrolyte cobalt during zinc electrowinning (EW) significantly decrease the current efficiency of the EW process by accelerating the parasitic hydrogen evolution reaction. The maximum tolerable level of cobalt in zinc EW can be as low as 0.1- 0.3 mg/L. The typical method to remove cobalt from zinc electrolyte, which is based on cementation onto zinc dust at approximately 85°C, is not an efficient process. It suffers from long retention times (2-3 hours) and high consumption of reagents; especially zinc dust.

The aim of the present research was to study cobalt cementation at high temperature and high pressure (HT/HP) to accelerate the rate of cobalt removal and reduce the consumption of the reagents (zinc dust and activators). Experimental variables included temperature (85-150°C), pressure (0-100 psig), zinc dust dosage, zinc dust particle size, and activators (copper and antimony).

Based on this research, the following results were obtained:

1. Increasing temperature had a significant effect on the rate of cobalt removal. The optimum temperature was found to be 125°C - temperature at which the target level of cobalt (0.1 mg/L) could be met in 20 min.
2. At 125°C and in the presence of 2.5 mg/L Sb and 45 mg/L Cu, 3.5 g/L zinc dust was found as the optimum zinc dust addition to lower cobalt concentration from the initial level of 15 mg/L to below 0.1 mg/L.
3. Smaller zinc particles showed better cobalt removal results, but the cement redissolution was also more severe with these particles.

4. The role of Sb in the activation system was more important than Cu. However, the best result in terms of the rate and extent of cobalt removal was achieved when both of the activators were added to the solution together.
5. As expected, increasing the overhead pressure of N<sub>2</sub> (tested at 85°C) did not alter the cobalt removal profile greatly. Also, the effect of increasing the partial pressure of H<sub>2</sub> (tested at 125°C, and above the amount generated in situ by the reaction) on cobalt removal was negligible.

## **Preface**

This research work was conducted with the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC), Hydro-Quebec and Canadian Electrolytic Zinc (CEZinc). The results obtained in this research were presented in poster format at the 7<sup>th</sup> international hydrometallurgy conference in Victoria (Canada) and at the 2014 COM conference in Vancouver (Canada).

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## Nomenclature

Symbol	Definition
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$A_c(t)$	Area per unit volume of the fluid, available at time $t$ for Co (II) reduction ( $\text{m}^2 \text{m}^{-3}$ )
$A_c^*$	Area per unit mass of noble metal (Cu and Sb) available for Co (II) reduction ( $\text{m}^2 \text{kg}^{-1}$ )
$\alpha^*$	Superficial area of Zn per unit mass of it ( $\text{m}^2 \text{kg}^{-1}$ )
$C$	Concentration ( $\text{mg L}^{-1}$ )
$C_0$	Concentration at $t = 0$ min ( $\text{mg L}^{-1}$ )
$k$	Rate constant ( $\text{min}^{-1}$ )
$k_m$	Mass transfer coefficient ( $\text{m s}^{-1}$ )
$m$	Mass of zinc per unit volume of the solution ( $\text{kg m}^{-3}$ )
$M_t(t)$	Amount of noble metal (Cu and Sb) deposited at time $t$ ( $\text{kg m}^{-3}$ )
$M^0$	Total amount of noble metals (Cu and Sb) added to the solution ( $\text{kg m}^{-3}$ )
$t$	Time (min)

## Acknowledgements

Definitely this research could not have been completed without the help of a great number of people. First of all, I would like to express my acknowledgement to my dear supervisor Dr. Edouard Asselin for his continuous support and kind guidance. He provided me with valuable input throughout the progression of this research, while gave me the freedom to pursue various paths in my research and to enjoy my study.

I also would like to express my appreciation to the industry representative of this project Mr. Georges Houlachi from Hydro Quebec. Mr. Houlachi's valuable research and industrial experience played a significant role in directing this research. He also contributed to this study by supplying the required industrial materials.

My special thanks go to my post-doc fellow, Dr. Hamidreza Zebardast, for his assistance in making the experimental setup and developing the solution analysis procedure. Many thanks to my dear fellows in materials engineering department of UBC, Dr. Ali Shafie, Parisa Abbasi, and Maryam Rasouli who helped me a lot in running the experiments.

Last but not least, the financial support from Natural Science and Engineering Research Council of Canada (NSERC) and Hydro-Quebec Company is greatly appreciated.

## **Dedication**

*To my dear parents,*

*Jila and Abdollah*



# **1 Introduction**

## **1.1 Zinc Uses**

Zinc is a common base metal with diverse uses in the modern world. Its major use is for the corrosion protection or galvanization of steel, and it achieves this protection property by forming a surface barrier as well as by corroding preferentially (acting as sacrificial anode) to the underlying steel. It is also used in producing brasses where it is alloyed with copper in different proportions to make brasses with various properties. In addition, zinc has uses as an oxide in the formulation of rubber, in fertilisers and in various minor medical applications (Sinclair 2005).

With respect to the above mentioned uses for zinc, its consumption grew from around 5 million tonne per year in 1970 to 9.7 million tonne per year in 2003 (Sinclair 2005). Zinc is produced either from primary resources (mine production) or from secondary resources (recycled materials). Although because of environmental concerns more emphasis is given to increasing the production of zinc from secondary resources, the majority of the world's zinc is still derived from mining. Canada has three active zinc plants (Teck in BC, CEZinc in QC, and Hudbay in MB) and it is an important producer of zinc in the world. In 2011, the world total zinc production was 13,100,000 metric tons, from which Canada produced 662,151 metric tons as primary zinc (U.S. Geological Survey 2012). This is around 5% of the world zinc production and signifies the importance of Canada in zinc industry.

## **1.2 Zinc Mineralogy**

There are basically three types of zinc ores in the Earth's crust; oxidized, carbonated and sulfur including zinc ores (Kayin 2003). But, zinc sulfide ore which is known as "zinc blende" or

“sphalerite” is the most important ore in zinc production; other zinc minerals are only of local importance (Habashi 1997). The common zinc minerals are introduced in Table 1-1.

Table 1-1. Mineralogy of zinc (Sinclair 2005).

<b>Mineral</b>	<b>Formula</b>	<b>Zinc content %</b>
<b>Sphalerite</b>	ZnS	67.1
<b>Marmatite</b>	(Zn,Fe)S	< 67.0
<b>Smithsonite</b>	ZnCO <sub>3</sub>	52.2
<b>Hydrozincite</b>	3ZnO.2ZnCO <sub>3</sub> .3H <sub>2</sub> O	59.5
<b>Willemite</b>	2ZnO.SiO <sub>2</sub>	58.7
<b>Hemimorphite</b>	4ZnO.2SiO <sub>2</sub> .2H <sub>2</sub> O	54.3
<b>Zincite</b>	ZnO	80.4

### 1.3 Hydrometallurgical Production of Zinc

Roast-Leach-Electrowinning (RLE) process is the most common route to produce zinc from sphalerite. In this process, sphalerite (ZnS), which is insoluble in dilute sulphuric acid, is firstly converted to soluble zinc calcine (ZnO) in roasters. The produced zinc calcine is leached by the spent electrolyte (H<sub>2</sub>SO<sub>4</sub>) so that zinc is liberated as well as impurities such as iron, cobalt, copper, cadmium and nickel.

In recent years new leaching processes have been adopted to directly extract zinc from ZnS (i.e. without having roasting stage). These processes are divided into two categories: ZnS pressure leaching and atmospheric leaching (Xu, Jiang, and Wang 2013). In these leaching processes, using oxygen or ferric ion as oxidant, zinc is extracted directly from sphalerite while

sulphidic sulfur is oxidized to its elemental form. Although the direct leaching processes are gaining market share (Jiang, Wang, and Li 2014), more than 85% of the world's zinc is still produced by the RLE process (Xu, Jiang, and Wang 2013).

Regardless of the leaching method or process employed, the obtained PLS must be extremely well purified prior to being fed to the electrowinning (EW) stage. Removal of impurities from the PLS is achieved by neutralization-precipitation (removal of Fe) and by cementation with zinc dust (removal of Cu, Cd, Co and Ni). Zinc EW is thermodynamically an impossible process because, based on the standard reduction potentials,  $H^+$  should be reduced rather than  $Zn^{2+}$  at the cathode. However, zinc electrowinning is practiced widely in industry due to the slow kinetics of the  $H^+$  reduction reaction. The overall sketch of the RLE process and the main reactions, which happen in the different stages, are presented in Figure 1-1 and Table 1-2 respectively.

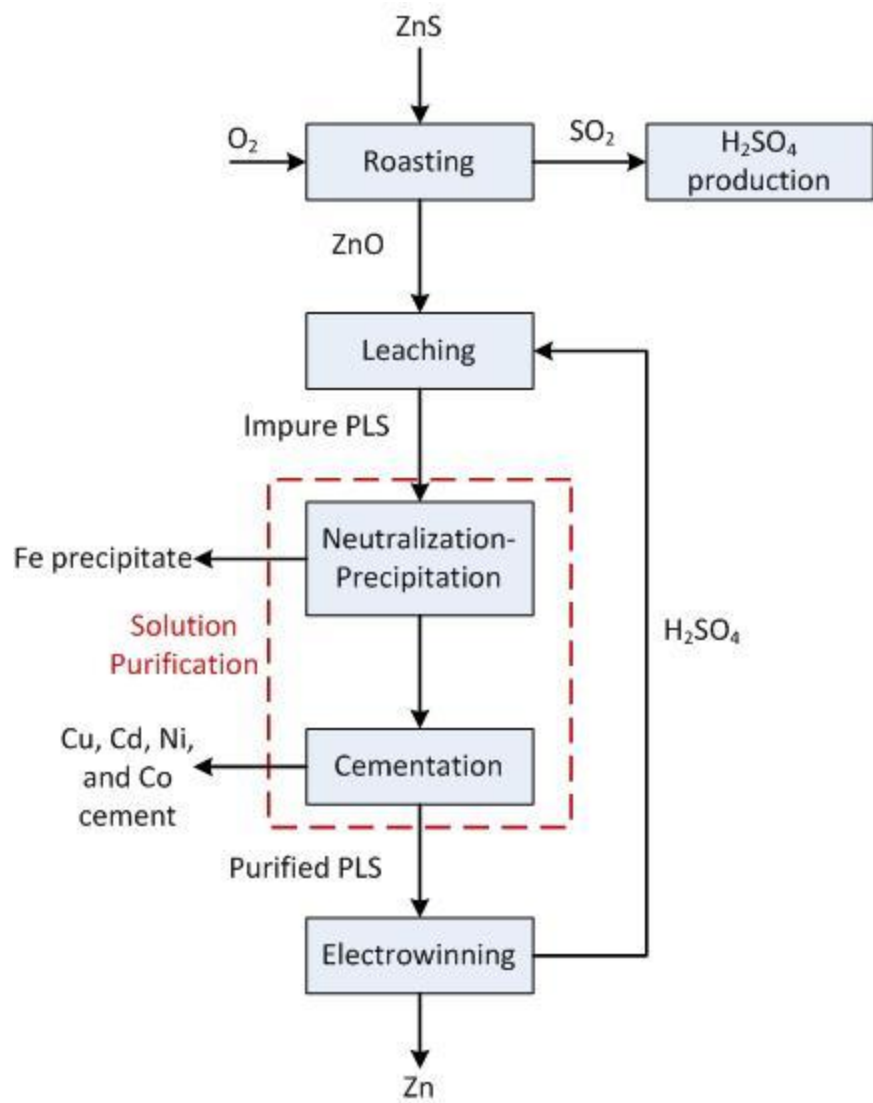


Figure 1-1. Roast-Leach-Electrowinning process for zinc production.

Table 1-2. Reactions occurred in the RLE zinc production process.

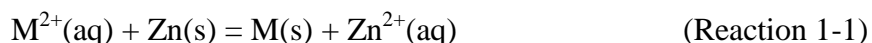
Operation stage	Reaction
Roasting of ZnS	$\text{ZnS(s)} + 1.5\text{O}_2\text{(g)} = \text{ZnO(s)} + \text{SO}_2\text{(g)}$
Leaching of ZnO	$\text{ZnO(s)} + \text{H}_2\text{SO}_4\text{(aq)} = \text{ZnSO}_4\text{(aq)} + \text{H}_2\text{O(l)}$
Direct leaching of ZnS	$\text{ZnS(s)} + \text{H}_2\text{SO}_4\text{(aq)} + 0.5\text{O}_2\text{(g)} = \text{ZnSO}_4\text{(aq)} + \text{H}_2\text{O(l)} + \text{S(s)}$
Cementation of impurities (e.g. Co cementation)	$\text{Co}^{2+}\text{(aq)} + \text{Zn(s)} = \text{Co(s)} + \text{Zn}^{2+}\text{(aq)}$
Electrowinning of Zn	$\text{ZnSO}_4\text{(aq)} + \text{H}_2\text{O(l)} = \text{Zn(s)} + 0.5\text{O}_2\text{(g)} + \text{H}_2\text{SO}_4\text{(aq)}$

## 1.4 Purification of PLS in the RLE Process

As mentioned in section 1.3, in general there are two steps in purification of zinc electrolyte; neutralization-precipitation and cementation. Neutralization-precipitation takes place right after the leaching step and as iron is the major impurity, which is removed in this step, it is also called an iron removal step. In this process, the pH of the PLS as well as other operational parameters is adjusted so that iron ions can precipitate either as goethite, jarosite or hematite. Among the iron precipitates, jarosite is the most common and cost effective (Sinclair 2005). During iron removal, some other impurities such as As, Sb, Ge, Te, Na and K also co-precipitate with iron to a great extent (Sinclair 2005; van der Pas 1995).

In the second step, remaining impurities like Co, Cu, Cd, and Ni are removed from the solution with cementation onto zinc dust. Cementation is an electrochemical process during which a solution containing a more noble metal ion is kept in contact with a less noble metal so that the noble metal ions can be deposited spontaneously on the less noble metal which, in turn, progressively dissolves. The process can be interpreted by means of a corrosion cell model so

that some parts of the less noble metal (substrate) behave like cathodic sites on which deposition of the more noble metal occurs, whereas on the rest of the substrate, which assumes anodic characteristics, the dissolution of the less noble metal takes place (Polcaro, Palmas, and Dernini 1995). Reaction 1-1 represents a typical cementation process for an impurity  $M^{2+}$  (M can be Cu, Co, Ni or Cd).



It was already stated that electrowinning of zinc from acidic solution can be practiced only because of the slow rate of hydrogen reduction at cathodes. Remaining electrolyte impurities like Co during EW can act as catalyst and accelerate the hydrogen evolution at cathodes. Thus, purification of the PLS in the electrolytic zinc production is of great importance not only because the remaining impurities reduce the quality and purity of the final product, but also more importantly because they can render the deposition of zinc impossible. The upper limit of common impurities during the EW stage is presented in Table 1-3. This table highlights the extreme PLS purification required prior the EW.

Table 1-3. Upper limits of common impurities during zinc electrowinning.

<b>Impurity(mg/L)</b>	<b>CEZinc</b>	<b>Cominco</b>	<b>Hoboken-Overpelt</b>	<b>Port Pirie</b>
	(Nelson et al. 2000)	(Tozawa et al. 1992)	(Tozawa et al. 1992)	(Tozawa et al. 1992)
<b>Cu</b>	0.1	-	0.2	0.15
<b>Cd</b>	1.0	0.3	1.0	0.35
<b>Co</b>	0.2	0.3	1.0	<0.05
<b>Ni</b>	-	-	0.050	<0.05
<b>Fe</b>	-	<5	20	8
<b>As</b>	0.02	-	0.020	0.01
<b>Sb</b>	-	0.03	0.020	0.025

## 1.5 Removal of Cobalt from the Electrolyte

### 1.5.1 Harmful Effects of Cobalt during Zinc EW

Among common zinc electrolyte impurities, cobalt is one of the most detrimental impurities during zinc EW. Trace amounts of cobalt during the EW, not only reduces the quality and purity of the final zinc deposit, but also significantly decreases the current efficiency of the cell house. Problems raised from the presence of cobalt in the electrolyte can be classified in two categories:

First, cobalt even in trace amounts deposits with zinc at cathodes and acts as catalyst for the hydrogen evolution reaction. The hydrogen evolution reaction has a high overvoltage on zinc deposits, while the co-deposited cobalt with zinc lowers this high overvoltage and allows the evolution of hydrogen to be the dominant reaction at cathodes. The fast hydrogen evolution

reaction decreases the current efficiency of the EW stage significantly and consequently leads to an increase in the energy consumption. Maja and Spinelli (Maja and Spinelli 1971) have classified cobalt as the fourth worst impurity in terms of decreasing CE of zinc EW. In this classification, the following impurities have less detrimental effects on the CE, respectively: Ge, Sb, Ni, Co, Bi, Cu, As, Sn, and Fe. Beside the effect of hydrogen evolution on the CE, the evolved hydrogen bubbles also change the morphology of the zinc deposit and cause a spongy deposit, which is of lower quality (van der Pas 1995). Moreover, increasing the rate of hydrogen gas evolution increases the risk of H<sub>2</sub> fires. H<sub>2</sub> fires in zinc EW have forced shut downs in recent years (Musadaidzwa and Tshiningayamwe 2009).

Second, the co-deposition of cobalt (as an element that is more noble than zinc) with zinc at cathodes reduces the purity of the final product. More importantly, the co-deposited cobalt induces dissolution of the deposited zinc (Mureşan et al. 1996) by forming microgalvanic cells with it (Boyanov, Konareva, and Kolev 2004b). The local dissolutions of zinc lower the quality of the deposit by forming round holes in it (van der Pas 1995).

The deleterious effects of cobalt can also be intensified if it co-exists with some other electrolyte impurities. For instance, Figure 1-2 shows that antimony (0.08 mg/L) interacts synergistically with Co in lowering the CE (Mackinnon, Morrison, and Brannen 1986). In addition, Morrison et al. (Morrison et al. 1992) reported that the combination of iron with cobalt leads to a lower CE, although iron itself doesn't show a noticeable effect. With respect to the synergistic interactions of cobalt with other impurities, its maximum tolerable level in zinc EW stage can change dependent on the composition of the electrolyte. However, most zinc plants reportedly cannot tolerate cobalt concentrations above 0.3 mg/L or even 0.1 mg/L.



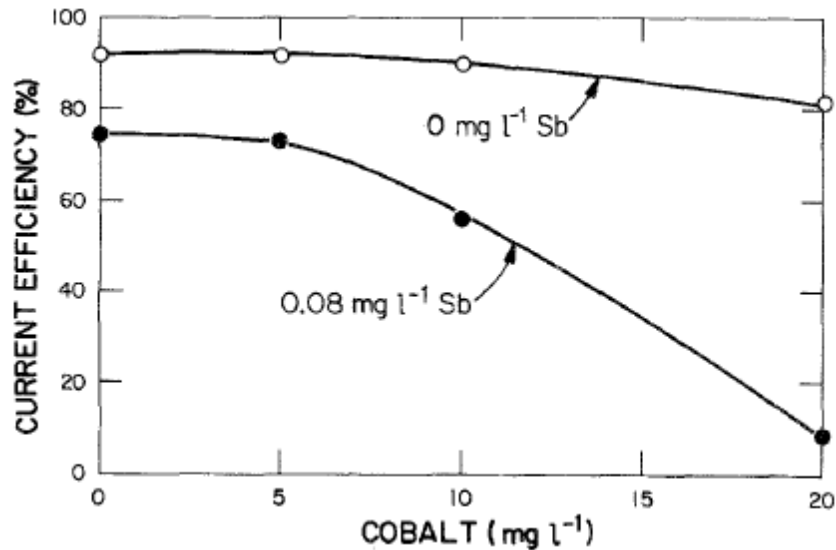


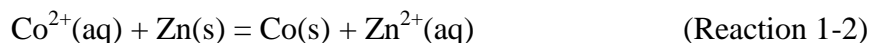
Figure 1-2. Effect of Co in the presence/absence of Sb on the CE for 1 hour zinc deposition at  $430 \text{ A m}^{-2}$  from industrial acid sulfate electrolyte (Mackinnon, Morrison, and Brannen 1986).

### 1.5.2 Difficulties Associated with the Cobalt Removal

As stated, cobalt is removed from zinc electrolyte by cementation onto zinc dust (Reaction 1-2). According to the standard reduction potentials, the reduction of cobalt ions with metallic zinc is thermodynamically favourable ( $E_{\text{reaction}} > 0$ ), but kinetic studies show that this reaction is very slow in the presence of zinc ions. It has been proposed that zinc ions, in the form of  $\text{ZnOH}^+$ , adsorb on the surface of zinc dust and block the deposition of cobalt (West-Sells 1996).

In order to accelerate the slow rate of the cobalt reduction, the cementation process needs to be performed at elevated temperatures near to the boiling point of the solution. In addition, in contrast to the cementations of impurities such as Cu, Cd and Ni, which happen easily with addition of only a little excess zinc dust, Co cementation requires a great excess (much above stoichiometric) of zinc dust. Both the high operation temperature and the large excess of zinc dust usage translate to high operation costs for the process. Besides these issues, the cobalt

cementation process is practicable only when small amounts of additives like arsenic or antimony along with copper are introduced to the solution. Arsenic and antimony compounds are toxic for workers' health.



$$\Delta E^{\circ} = E^{\circ}_{\text{Co}^{2+}/\text{Co}} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.280 - (-0.760) = 0.480 \text{ V} \quad (\text{vs. SHE at } 25^{\circ}\text{C})$$

These difficulties have rendered the cobalt cementation process inefficient. Therefore, much research has investigated alternative ways to remove cobalt from zinc electrolyte in past decades (Table 1-4). However, among these investigations only a few have shown promising results for application in industrial plants and it can be asserted that the removal of cobalt from zinc electrolytes still relies on the use of zinc dust. In the next section, a summary of the typical cobalt removal procedures that are (or were) practiced in industrial zinc plants will be presented.

Table 1-4. Studied alternative methods to remove cobalt from zinc electrolyte.

Method	Possibility of Industrial Use	Reference
Cobalt cementation with ferromanganese	No	(Cao and Duby 2001)
Cobalt precipitation by reduction with sodium borohydride	No	(Lu, Dreisinger, and Cooper 1997)
Cobalt removal with Solvent Extraction method	No	(Friedrich, Kruger, and Graciela 2001; Sandberg and Hebble 1978)
Oxidation-precipitation of Co using Caro's acid	No	(Owusu 1998)
Cobalt removal by Molecular Recognition Technology (MRT)	Yes	(Van Tonder et al. 2002)
Solvent Extraction method for separating zinc from zinc PLS	Yes	(Musadaidzwa and Tshiningayamwe 2009)
Cobalt precipitation with potassium permanganate	Yes	(Safarzadeh et al. 2011)

### 1.5.3 Industrial Processes to Remove Cobalt from Zinc Electrolyte

#### 1.5.3.1 Cold Beta Purification

The elimination of cobalt using the organic compound alpha-nitroso-beta-naphthol is an old technology that is still practiced in a few zinc plants (Figure 1-3). In this process, Cu, Cd and Ni

are removed from the electrolyte by cementation on zinc dust in the first stage. In the second stage, alpha-nitroso-beta-naphthol is added to the semi-purified solution to precipitate Co. This step is followed by activated charcoal treatment to remove the excess organic (Raghavan, Mohanan, and Verma 1999). In comparison to other purification procedures, cold beta purification does not require heating the solution to higher temperatures and also a little zinc is lost with the cake. But, there is always a risk of organics remaining in the purified solution, which can cause power consumption increases in the cell house (Singh 1996). This drawback has restricted the use of the cold beta purification procedure in zinc plants.

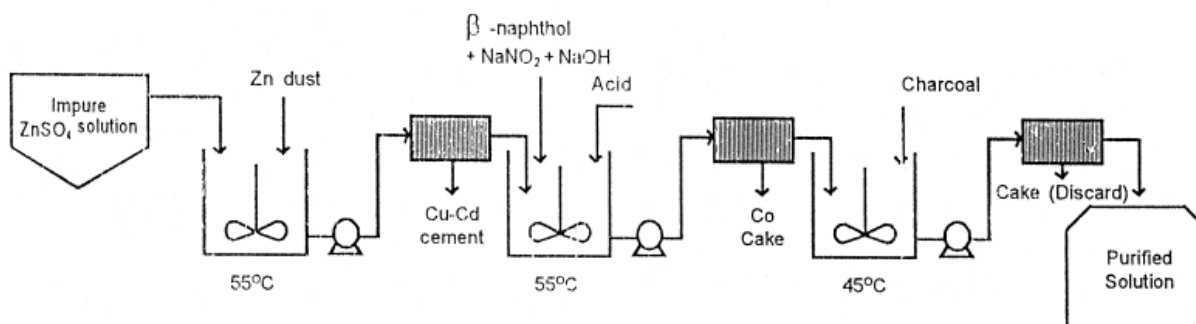


Figure 1-3.Cold beta purification process (Raghavan, Mohanan, and Verma 1999).

### 1.5.3.2 Hot Arsenic Purification

This technology (Figure 1-4) includes cobalt and nickel removal at almost 90°C, using zinc dust and in the presence of  $As_2O_3$  and  $CuSO_4$ . After removing cobalt, in the next stage, residual Cd and Ni are simply removed from the solution by addition of zinc dust (Raghavan, Mohanan, and Verma 1999). Hot arsenic purification is usually conducted in zinc plants which deal with high concentrations of cobalt in the PLS since arsenic (compared to antimony) appears to

eliminate cobalt more effectively. However, the use of this purification method is limited due to the environmental problems caused by arsenic (Singh 1996).

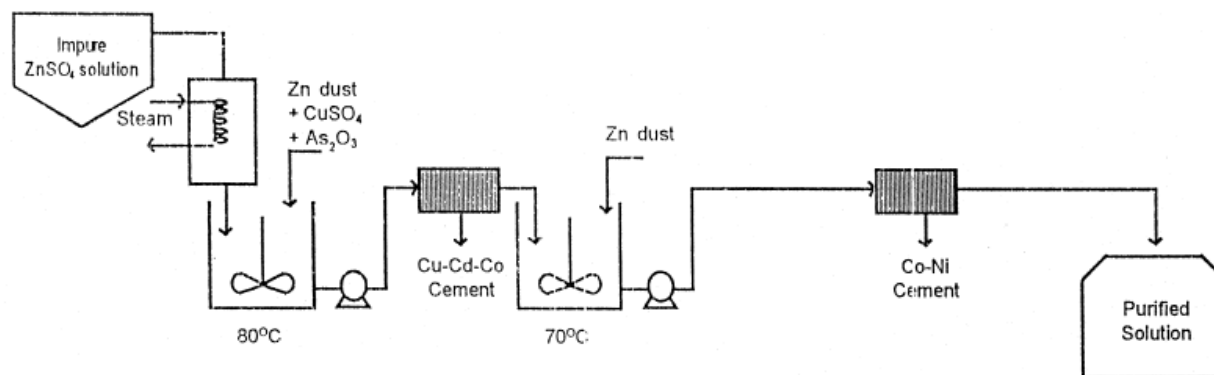


Figure 1-4. Hot arsenic purification process (Raghavan, Mohanan, and Verma 1999).

### 1.5.3.3 Cold- Hot Purification

In this procedure (Figure 1-5), cementation of Cd, Cu and Ni occurs at 50°C, the so-called “cold” condition. After that, the solution is heated to almost 90°C to remove cobalt by zinc dust and in the presence of copper and antimony compounds, antimony trioxide or potassium antimony tartrate (PAT). The modified hot purification process (Figure 1-6) is another version of the cold-hot purification process in which all the impurities can be removed from the solution in a single stage at 80-90°C with the addition of zinc dust and PAT. Although the modified hot purification process was originally a single stage process, an optional second purification stage (polishing stage) can also be operated (Raghavan, Mohanan, and Verma 1999). Table 1-5 classifies some of the world’s zinc plants in terms of the technology that they use for removing cobalt.

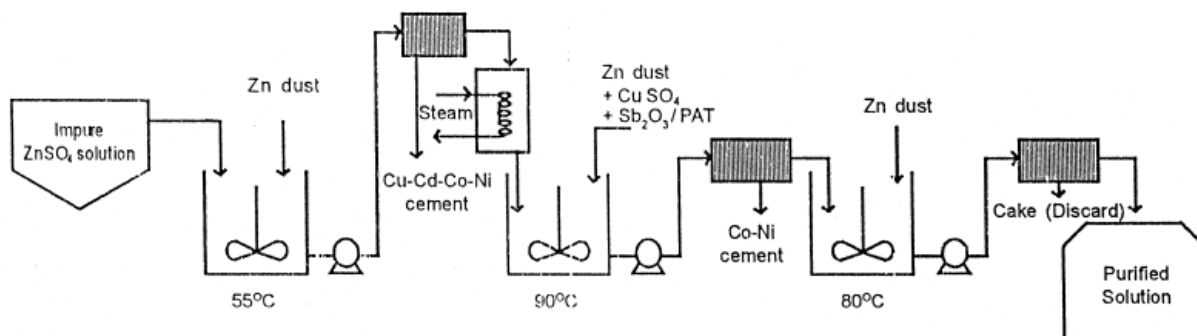


Figure 1-5. Cold-hot purification process (Raghavan, Mohanan, and Verma 1999).

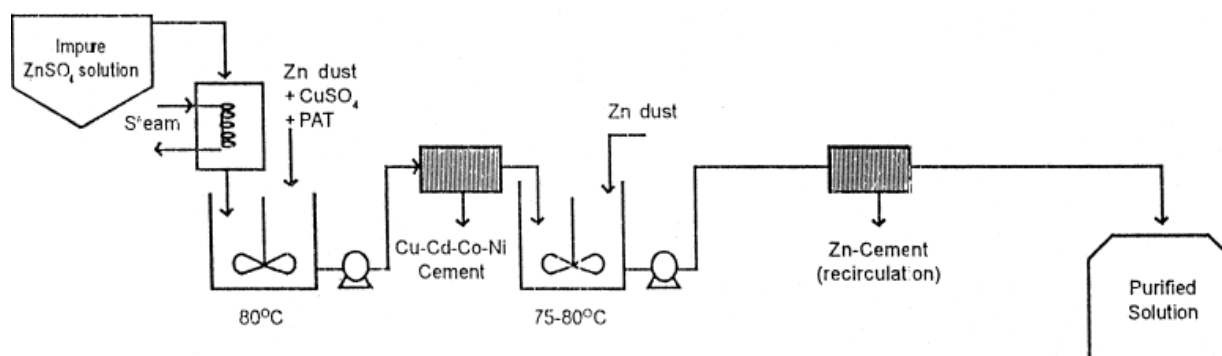


Figure 1-6. Modified hot purification process (Raghavan, Mohanan, and Verma 1999).

Table 1-5. Purification technologies adapted at various zinc plants (Raghavan, Mohanan, and Verma 1999).

Purification technology	Reagents used	Name of the plant
<b>Cobalt beta purification</b>	Beta-naphthol + zinc dust	EZ, Risdon, Australia
<b>Hot purification</b>	$\text{As}_2\text{O}_3$ + $\text{CuSO}_4$ + zinc dust	IMMSA, San Luis Potosi, Mexico
		Zinc of South Africa, Vogelstruisbult
		BHAS, Australia
		Preussag Zinc, Germany
		Kidd Creek, Falcon Bridge, Canada
		Amax Zinc, USA
		Sulfacid, Argentina
		MM&S, Kamioka, Japan
		MMC, Akita, Japan
		Akita Zinc, Ijima, Japan
		Outokumpu, Kokkola, Finland
<b>Cold-hot purification</b>	$\text{Sb}_2\text{O}_3$ + $\text{CuSO}_4$ + zinc dust	Cinkur, Turkey
		VM Balen, Belgium
		HBMS, Flin Flon, USA
		MHO, Belgium
		Jersey Miniere Zinc, USA
		COMINCO, Trail, Canada
		Zorcasabc, Yugoslavia
		Bleiberger, Berguerus, Austria
		Minero Peru, Peru
		Geca Mines, Zaire
		SMMC, Harima, Japan
		Toho Zinc, Japan

Purification technology	Reagents used	Name of the plant
	PAT + CuSO <sub>4</sub> + zinc dust	Hosakur, Japan
		CEZinc, Valleyfield, Canada
		Binani Zinc, India
		SMM Pertusola, Crotone, Italy
		Buldelco, Holland
		SAMIM, Italy
		Asturiana de Zinc, Aviles, Spain
		Norzink, Norway
Modified hot purification	PAT + CuSO <sub>4</sub> + zinc dust	Hindustan Zinc, India



## **2 Literature Review**

### **2.1 Products Formed during Cobalt Cementation**

Although Reaction 1-2 was presented in section 1.5.2 as the reaction for cobalt cementation on zinc dust, it is well documented that in the presence of zinc ions, cobalt cannot be deposited in a pure form, but is deposited as a cobalt-zinc alloy with very low amounts of cobalt. The formation of this cobalt-zinc alloy is also referred to as anomalous deposition since a less noble metal (zinc) is deposited preferentially over a more noble metal (cobalt). As a result, one can conclude that the value of potential difference suggested by Reaction 1-2 is not an accurate representation of the driving force for cobalt cementation, and to have a more precise estimation, the potential difference between metallic zinc and the formed cobalt alloy(s) should be taken into account (van der Pas 1995; van der Pas and Dreisinger 1996).

Bockman and Ostvold (Bøckman and Østvold 2000b) reported that the removal of cobalt from zinc sulfate electrolyte during cementation on zinc dust is due to two types of reactions. One reaction is the formation of Co alloys (e.g. Co-Zn alloy) and another is the formation of basic cobalt salts. According to this study, formation of the basic cobalt salts is a strong function of high local pH at the zinc dust surface. The high pH near to the surface of zinc dust is created by the evolution of hydrogen. However, when all the available metallic zinc dust is consumed (it is consumed either by the hydrogen evolution reaction or cementation reactions of the impurities), this high pH drops and therefore the basic cobalt salts start to redissolve. Bockman et al. believe that redissolution of the basic cobalt salts is the major reason for the cobalt cement redissolution; the technical problem that occurs in cobalt removal stages in an extended time. In contrast to the basic cobalt salts, the portion of the cement product which is present as Co alloys was reported to be resistant to acidic condition.

In another study by Bockman et al. (Bøckman et al. 2000) micro-Raman spectroscopy was used to characterize the cement products formed during cobalt cementation. The results of this study indicated that a large fraction of the cemented  $\text{Co}^{2+}$  exists as a mixture of cobalt containing oxide and hydroxide (cobalt basic salts). The observed spectrum for these compounds was reported to be similar to those of  $\text{Co}(\text{OH})_2$  in a ZnO matrix. The occurrence of the peak related to these compounds decreased considerably during redissolution of the cobalt cement, showing that these basic salts of cobalt are the main source of the cobalt cement redissolution.

It should be mentioned that the products formed during cobalt cementation are greatly dependent on the activation system employed in the process. For instance, Tozawa et al. (Tozawa et al. 1992) showed that in the Cu-As activation system, arsenic also forms alloys with cobalt in the cement, while it is well known that the Cu-Sb activation system doesn't promote cobalt cementation by forming alloys with Sb (van der Pas and Dreisinger 1996). The role of the activators in the cobalt cementation process will be discussed in more details in section 2.8.

## **2.2 Effect of Temperature on the Cobalt Cementation Process**

Temperature is one of the most important parameters for cobalt cementation (Blaser and O'Keefe 1983). As the cobalt cementation reaction is chemically or electrochemically controlled (Lew 1994; van der Pas and Dreisinger 1996), increasing temperature enhances the kinetics of the reaction considerably (Boyanov, Konareva, and Kolev 2004a; Jun et al. 2002; Lew 1994; Tozawa et al. 1992; Yang et al. 2006). However, it should be noted that increasing temperature also promotes the rate of the parasitic hydrogen evolution reaction. Therefore, some researchers suggest an optimum temperature, beyond which, a further increase contributes to the rate of the hydrogen evolution reaction more than it does to the cobalt cementation reaction.

In general, the studies in which the effect of temperature on cobalt cementation has been investigated can be classified into two categories:

- A. Studies that show that increasing temperature continually leads to an increase in the cobalt cementation rate. In such studies, the highest rate of cobalt removal was reported at the highest investigated temperature.
- B. Studies which report that there is an optimum temperature (85°C) at which the cobalt removal has the highest rate, beyond which a significant drop occurs in the rate of cobalt cementation.

Table 2-1 summarizes results of some studies regarding the effect of temperature on the rate of cobalt cementation.

Table 2-1. Reported results regarding the effect of temperature on the rate of cobalt cementation.

<b>Tested temperatures (°C)</b>	<b>Highest rate occurred at (°C)</b>	<b>Experimental condition</b>	<b>Can be put in category</b>	<b>Reference</b>
75, 85, 95	95	Natural pH, 5 g/L zinc dust, no additives	A	(Nelson 1998)
65, 73, 80, 85, 90	90	Natural pH, 4 g/L zinc dust, 46 mg/L Cu, 1.5 mg/L Sb	A	(Lew 1994)
55, 65, 75, 85, 95	85	5 g/L zinc dust, antimony trioxide rude	B	(Jun et al. 2002)
75, 80, 85	80	1500 % stoichiometrically required quantity zinc dust, 200 mg/L Cu , 1:1 ratio for $G_{Sb}/G_{Co}$	B	(Boyanov, Konareva, and Kolev 2004b)
50, 60, 70, 80, 90	90	pH controlled at 4, stoichiometric amount of zinc dust	A	(Yang et al. 2006)
70, 75, 80	80	pH 4.6, 2.5 g/L zinc dust, 590 mg/L Cd, 125 mg/L Cu, 5 mg/L Sb	A	(Brove and Ostvold 1994)
75, 80, 90	90	Rotating zinc disc, 10 mg/L Sb, 20 mg/L Cu	A	(Tozawa et al. 1992)
50, 60, 73, 85, 90	85	Electrodeposition of Co on Sb substrate, 30 A/m <sup>2</sup> current density, initial pH 4	B	(van der Pas 1995)
85, 90, 95	85	pH controlled at 4, different sets of additives tested, 5 g/L zinc dust	B	(Dreher et al. 2001)

To gain a better understanding of the way that temperature affects cobalt cementation, it is worth discussing the results of some of these studies in more detail.

Van der pas and Dreisinger (van der Pas 1995; van der Pas and Dreisinger 1996) studied mechanistic and kinetic aspects of cobalt removal from zinc electrolyte by depositing cobalt on an antimony substrate in an electrochemical cell. Investigated temperatures in this study were in the range of 50 to 90°C. They reported the existence of an optimum operating temperature at 85°C. According to this study Van der pas and Dreisinger found that:

1. In the temperature range of 50 to 85°C, cobalt content of the deposit increased exponentially with temperature. This increase was substantially higher than the expected values at 90°C. Morphology of the deposit also changed by increasing temperature; this change in morphology was attributed to the change in the cobalt content of the deposit. (Table 2-2)

Table 2-2. Cobalt content and morphology of cobalt-zinc deposits on antimony substrate as a function of temperature, 30 ppm Co, 30 A/m<sup>2</sup>, initial pH 3 (van der Pas 1995).

Temperature (°C)	Co (wt. %)	Deposit morphology
50	1.0	Hexagonal
60	1.8	Hexagonal
73	4.2	Nodular/ hexagonal
80	5.1	Nodular
85	8.8	Nodular
90	74.0	Smooth film

2. By increasing temperature from 50 to 85°C, a higher cobalt removal rate was obtained. However, the rate of cobalt removal dropped considerably when increasing temperature from 85 to 90°C. Van der Pas and Dreisinger attributed this unexpected drop to the

accelerated hydrogen evolution reaction at 90°C. Their study on distribution of the current between cathodic reactions (cobalt reduction, zinc reduction, and hydrogen evolution) showed that upon increasing temperature to 90°C, hydrogen evolution became the most prominent consumer of the cathodic current (Table 2-3). Van der Pas and Dreisinger believe that the increase in hydrogen evolution is most likely caused by the increase in the cobalt content of the deposit. As Table 2-3 shows, at 85°C, the main constituent of the deposit was zinc which is known for its high hydrogen evolution overpotential. But, as temperature increased to 90°C, cobalt, which is known for its catalytic effect on hydrogen evolution, became the major part of the deposit.

Table 2-3. Cobalt removal, deposit composition and estimated cathodic current distribution on antimony substrate as a function of temperature, 30 ppm Co, 30 A/m<sup>2</sup>, initial pH 4 (van der Pas 1995).

Temperature	$k_{Co}$	Co in deposit	Zn in deposit	$i_{Co}$	$i_{Zn}$	$i_{H_2}$
(°C)	(m/s)	(wt%)	(wt%)	(%)	(%)	(%)
85	$10.3 \times 10^{-5}$	7	93	3.5	46.5	50
90	$4.4 \times 10^{-5}$	76	24	1.5	0.5	98

In contrast to Van der Pas's study, which was conducted in an electrochemical cell (and may not represent the industrial condition for cobalt removal), Dreher et al. (Dreher et al. 2001) carried out an optimization study for cobalt cementation onto zinc dust. They investigated performance of different sets of additives (including Cu-Sb, Cu-Cd-Sb, Cu-Cd-Pb-Sb, and Cu-Cd-Sn) at temperatures of 85, 90, and 95°C. According to this study, 85°C appeared to be the optimum temperature since at this temperature more sets of the additives could reach the target

concentration of cobalt (0.1 ppm). Moreover, Dreher et al. reported that the dissolution of the zinc dust at 90 and 95°C was greater than that at 85°C for almost all sets of the tested additives. Noting that significant percentage of the zinc dust dissolution is due to the hydrogen evolution reaction, these results also confirm that at temperatures above 85°C the hydrogen evolution reaction becomes the dominant reaction.

From an economical point of view, industry is always interested in conducting the cementation process at as low temperature as possible to reduce energy consumption. In the case of the cobalt removal process, energy is consumed not only for heating zinc electrolyte prior to the cobalt cementation stage, but also for cooling the purified hot solution prior to the EW stage since zinc electrowinning takes place at temperatures lower than the purification stage temperature.

### **2.3 High Temperature/ High Pressure Cobalt Cementation on Zinc Dust**

Cobalt cementation at High Temperature/ High Pressure (HT/HP) is a relatively new process that has been reported by Houlachi et al. (Houlachi, Leroux, and Saint-Onge 1995). Cementation of cobalt on zinc dust is performed in a high-pressure vessel at temperatures above the normal boiling point of the solution. Houlachi et al. studied the kinetics of cobalt removal in the temperature range of 98-150°C and at the vapor pressure of the solution. The results of this study indicate that 130°C is the optimum temperature for which the desired cobalt removal (reaching the cobalt concentration of 0.2 ppm) occurs in 40 min. This is a significant improvement in the cobalt removal rate compared to the more than 120 min required to reach the same cobalt concentration at 98°C. However, this study shows that increasing temperature beyond 130°C causes a noticeable increase in the residual cobalt concentration after 60 min.

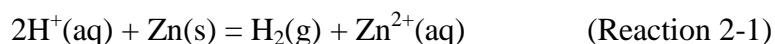
## 2.4 Effect of pH on the Cobalt Cementation Process

Although Blaser and O'Keefe (Blaser and O'Keefe 1983) mentioned that pH is a less influential parameter than temperature and reagent concentrations on the cobalt removal process, conducting the process at pH other than the optimum pH can lead to elevated terminal cobalt concentrations. In order to decrease hydrogen ion activity and consequently the rate of the parasitic hydrogen evolution reaction, the pH of the solution should be as high as possible. However, too high a pH increases the risk of zinc dust passivation through the formation of basic zinc sulfate or zinc hydroxide (Lew 1994; Nelson et al. 2000; Nelson 1998; Tozawa et al. 1992). Many researchers have stated that there is a window for pH operation in which the hydrogen evolution reaction is not severe and also there is no serious risk of zinc dust passivation. For instance, the optimum pH ranges of 4- 4.4 at an operating temperature of 73°C ((Lew 1994)) and 3.30- 3.75 at 90°C ((Tozawa et al. 1992)) have been reported in the literature.

An optimization study on the VZS plant (Raghavan, Mohanan, and Verma 1999) showed that the minimum reachable cobalt concentration in the cobalt removal stage could be lowered from 0.3 to 0.1 ppm by decreasing the operating pH from 5 to 4.5 (The pH values reported in this study were based on pH of the solution at room temperature). In contrast to this study, Brove et al. (Brove and Ostvold 1994) reported that in their experiments, which were carried out at two different pH of 4 and 4.7, the final cobalt concentration was independent of the initial pH. However, the authors also observed that the cementation kinetics in the first 60 min was slightly slower for the test carried out at the initial pH of 4 compared to pH 4.7. According to this observation, Brove et al. concluded that the accelerated hydrogen evolution reaction is more detrimental than zinc salt precipitation during cobalt cementation. Thus, in the cobalt removal stage, it is important to prevent a situation in which  $\text{pH} < 4$  rather than the situation of  $\text{pH} > 4$ .



During cobalt cementation, the pH of the solution increases due to the consumption of  $H^+$  ions by the hydrogen evolution reaction (Reaction 2-1). This increase in pH may lead to passivation of the zinc dust which may hinder cobalt cementation. Also, the formation of massive zinc salt precipitates on zinc dust makes filtration of the solution very difficult. To address these issues, it is often proposed to control pH of the solution close to its initial value by adding  $H_2SO_4$ . However, adding  $H_2SO_4$  to the solution promotes the hydrogen evolution reaction, and causes a significant increase in zinc dust dissolution (consumption). To avoid high zinc dust consumptions, industrial zinc plants (Harlamovs and Sharpe 2014) reportedly prefer to leave pH of the solution uncontrolled during the cobalt cementation process. In this approach, the difficulty of filtering the cement residues is solved by adding small amounts of  $H_2SO_4$  to the solution just prior to filtration (Harlamovs and Sharpe 2014; Nelson, Demopoulos, and Houlachi 2000). The effect of pH control on the cobalt cementation will be discussed in more details in section 5.1.



## 2.5 Effect of Zinc Ions on the Cobalt Cementation Process

In zinc production plants, cobalt cementation occurs in a solution which typically contains 145-160 g/L  $Zn^{2+}$  ions (Blander and Winand 1975; Fugleberg, Jarvinen, and Sipila 1980; Rodier 1980). “In a solution containing no zinc ions, cobalt cementation reaction proceeds rapidly and has an activation energy of 13 KJ/mol, indicating that the reaction is under mass transfer control” (Nelson et al. 2000). But the same reaction is hindered severely in the presence of even small

amounts of  $\text{Zn}^{2+}$  ions, and consequently, the activation energy of the reaction increases showing that the reaction becomes chemically controlled. A study done by Nelson et al. (Nelson, Demopoulos, and Houlachi 2000) showed that when no zinc ion is present in the solution (and in the absence of activators), cobalt cements out of the solution in less than 20 min. However, the same reaction is inhibited considerably as the zinc concentration of the solution increases. Nelson et al. believe that this inhibitory effect of zinc ions on the cobalt cementation reaction is because of adsorption of  $\text{Zn}^{2+}$  ions on the surface of the zinc dust which in effect passivate it.

Lew (Lew 1994) believes that the inhibition of cobalt cementation by zinc ions arises from the precipitation of zinc oxide or zinc hydroxide species on the zinc dust. The author attributed the formation of the mentioned species to the high pH and zinc ion concentration created at the surface of the zinc dust. The parasitic hydrogen evolution reaction, which takes place rapidly at elevated temperatures, consumes  $\text{H}^+$  ions and causes an increase in the local pH near the surface of the zinc dust. On the other hand, zinc dust dissolution which occurs as the anodic reaction along with the reduction reactions produces  $\text{Zn}^{2+}$  ions. The produced  $\text{Zn}^{2+}$  ions have relatively smaller mass transfer coefficient and therefore are accumulated in the boundary layer of the zinc dust to some extent. The relatively high  $\text{Zn}^{2+}$  and  $\text{OH}^-$  concentration at the surface of the zinc dust result in forming  $\text{ZnO}$  and  $\text{Zn(OH)}_2$  species which eventually passivate the zinc dust.

It has been mentioned in (van der Pas and Dreisinger 1996) that in the solutions containing zinc ions, zinc co-deposits with cobalt and produces the major content of the deposit. Yununs et al. (Yunus, Capel-Boute, and Decroly 1965) showed that obtaining zinc free cobalt deposit from sulphate solutions containing even traces of zinc ions is impossible. Yamashita et al. (Yamashita, Hata, and Goto 1997) reported that in the electrolytic reduction of cobalt from zinc electrolyte,

zinc could be found in the deposit at potentials as large as -580 mV, although theoretically, zinc ions can be reduced only at potentials lower than -760 mV.

## **2.6 Effect of Zinc Dust on the Cobalt Cementation Process**

The typical amount of the zinc dust used in the cobalt removal stage is in the range of 4- 6 grams per liter of the electrolyte (Nelson et al. 2000). “Depending on the purification process selected, the amount of impurities in the raw material feed, and the purity required for electrolysis, zinc dust consumption in the cementation stages may equal to 8% of the cathode zinc production, although stoichiometrically, no more than 0.5- 1.5% would be needed” (Esna-Ashari 1983). Such large zinc dust consumptions in the purification stages, especially in the cobalt removal stage, represent a large cost for zinc plants. Thus, reducing zinc dust consumption has always been one of the objectives of cobalt cementation studies.

Increase in zinc dust surface, which can be achieved by increasing zinc dust dosage or using smaller zinc particles, improves the cobalt cementation reaction. For instance, the beneficial impact of increasing the zinc dust dosage on the cobalt cementation kinetics was shown in (Boyanov, Konareva, and Kolev 2004a; Dreher et al. 2001; Raghavan, Mohanan, and Verma 1999). Brove (Brove and Ostvold 1994) also showed that decreasing the size of the zinc particles results in lower final cobalt concentrations and faster cementation kinetics. However, Dreher et al. (Dreher et al. 2001) believe that for a given concentration of the activators, there is always a maximum number of the active sites that can be formed on the zinc dust, and as soon as this number is reached, further increase in zinc dust dosage, or more precisely, further increase in the zinc dust surface area, cannot be more effective. In the same study, Dreher et al. also reported that they found an inverse relationship between the quantity of the added zinc dust and its

dissolution during the cementation process, so that by decreasing zinc dust dosage, the percentage of its dissolution increased. The authors believe that this observation was likely “due to extensive coverage of zinc dust by cobalt impurity, which is known to be an effective catalyst for hydrogen evolution”.

Bockman and Ostvold (Bøckman and Østvold 2000b) studied the effect of zinc dust particle size in more detail. According to their tests, the initial cementation rate of cobalt was the same, when the zinc dust surface area was kept constant. This means that during the tests for which the total surface area of the zinc dust was constant, but for which the zinc dust concentration varied from test to test, the same initial cobalt removal rate was obtained. In the same study, the effect of particle size on the cobalt redissolution was also investigated. According to the results of this study, for a constant amount of the zinc dust, smaller particles gave higher initial cobalt cementation rate (as expected), but the redissolution of the cemented cobalt was also higher in these cases. The larger particles showed little cementation, but also very little redissolution.

Raghavan (Raghavan, Mohanan, and Verma 1999) reported that leaded zinc dust, i.e. zinc dust which is activated by lead, is helpful in preventing redissolution of the cemented impurities. In addition to lead, a beneficial effect of tin-containing zinc dust has been reported by Kayin (Kayin 2003). Kayin studied the efficiency of 4% Sn-Zn alloy and 10% Sn-Zn alloy powders in removing cobalt from a synthetic zinc electrolyte, and compared the results with that of the pure Zn dust. According to the results of this study, both the tin containing alloys worked better than pure zinc dust in cementing cobalt, however the 4% Sn-Zn alloy showed better results than the 10% Sn-Zn alloy. It was reported in Kayin’s study that using tin containing zinc powder, instead of pure zinc powder, could remove the need for arsenic trioxide, the toxic activator that is used in

the cobalt cementation stage; although an excessive use of the Sn-Zn powder (e.g. 14 g/L 10% Sn-Zn powder) would be required.

Laboratory and plant scale work conducted by Singh (Singh 1996) indicated that recycling filter cake from the second Co purification stage (polishing stage) to the first Co purification stage improves the cobalt removal while decreases the fresh zinc dust consumption. Indeed, Singh found that combination of the recycled zinc dust and the fresh zinc dust gives better results than the fresh zinc dust alone, not only in the rate but also in the extent of the cobalt removal. The improved reactivity of zinc dust in the presence of the recycled cake was explained by the cleaning of the zinc dust surface with the help of Cu, Cd and Sb ions which present in the recycled cake. As reported by Singh, the implementation of this strategy (recycling the second stage filter cake to the first stage cobalt removal) in the Electrolytic Zinc Plant at Debari and the second plant of Hindustan Zinc Limited at Vizag has markedly decreased the consumption of the zinc dust in these plants.

## **2.7 Effect of Residual Organics on the Cobalt Cementation Process**

In general, organic chemicals that are used in the hydrometallurgical zinc production processes include flocculants, that are used in thickeners, and glue and foaming agents which are used in electrowinning tank houses. Although most of these organics are degraded by time or temperature, it is possible that small amounts enter the purification stages and interfere with cobalt cementation (Lew 1994; Nelson 1998). There are a number of hypotheses proposed to explain the inhibiting mechanism of organics in the cobalt cementation process (Lew 1994; van der Pas 1995):

1. Organics may have chelation interaction with cobalt ions and make complex compounds which are reduced on the zinc dust surface more difficultly than the cobalt ion itself.
2. Organics may agglomerate/flocculate the zinc dust and therefore reduce the available zinc dust surface for the reduction of cobalt.
3. Organics may be adsorbed on the zinc dust surface and block the active cathodic sites for the cobalt reduction.

Houlachi et al. (Houlachi, Belanger, and Principe 1990) reported that small amounts (even as low as 0.5 ppm) of animal glue, Percol 156 and Saponin significantly decrease the cobalt cementation rate. The deleterious effect of animal glue, Percol 351 and lignin sulphonic acid was also confirmed by Lew (Lew 1994). According to the Lew's study, these organics, in concentrations as low as 2 ppm, can hinder the cementation of cobalt greatly. Lew believes that the adsorption of the organics on zinc dust is the most probable mechanism through which organics interfere with cobalt removal.

Van der Pas and Dreisinger (van der Pas 1995) studied the influence of Percol 338, the flocculant which is used in the iron removal stage. According to the results of this study, while antimony addition as an activator increases the cobalt content in the cement deposit, the presence of 3 ppm Percol 338 totally eliminates this increase. The theory developed in Van der Pas' work explains that antimony cements on the cathodic surface in the early stages and decreases the surface energy barrier for cobalt reduction. However, when small amounts of the organics are present in the solution, they adsorb on the deposited antimony earlier than cobalt, and increase the energy barrier for cobalt cementation due to the need for electron transfer through the adsorbed organic layer. In addition to the effect of Percol 338 on the cobalt content of the deposit, its effect on the rate of the cobalt removal was also examined in Van der Pas's work.

The results showed that the organic compound, in the concentration of 3 ppm, reduced the cobalt removal rate by approximately 70%. The authors believe that since organics can inhibit the cementation process, even when the organic:cobalt ratio is low, blocking the active cathode sites for cobalt reduction, as explained, is the most likely mechanism for the inhibiting role of organics.

Karavasteva (Karavasteva 2001) investigated the effect of nonylphenolpolyethylene glycol with molecular weight 900 (D1), dinaphthylmethane-4,4'-disulphonic acid (D2) and polyethylene glycol with molecular weight 400 (D3) on cobalt cementation in the presence of copper (200 mg/L) and antimony (200 mg/L). According to Karavasteva's study, addition of the surfactants D1 (30 mg/L) and D3 (15 mg/L) decreased the cobalt cementation rate in the presence of copper or antimony. It was reported in the same study that the morphology of the cemented products changed to a cement with decreased crystallites size and porosity upon the addition of D1 and D3 to the solution. In contrast to D1 and D3 surfactants, no evidence was found in Karavasteva's study regarding the inhibition effect of D2 on the cobalt cementation process.

In addition to the mentioned organics, tartrate ( $\text{C}_4\text{H}_4\text{O}_6^{2-}$ ) is another organic compound which exists in the cobalt cementation stage in the plants which use potassium antimony tartrate (PAT) as a cementation aid. A study done by Bockman and Ostvold (Bøckman and Østvold 2000a) showed that a high concentration of tartrate in zinc solution, not only inhibits the cobalt cementation, but also decreases the cementation rates of  $\text{Cu}^{2+}$ ,  $\text{Sb}^{3+}$  and  $\text{Cd}^{2+}$ . However, the effect of tartrate on  $\text{Co}^{2+}$  cementation was reported to be more substantial. In the same work, it was indicated that the detrimental influence of tartrate is also dependent on the solution pH, since in high pH (e.g.  $\text{pH} > 4.5$  compared to  $\text{pH} 4$ ) the tartrate-metal complexes are more easily

formed. Although tartrate is introduced to the zinc electrolyte in very small amounts, it may accumulate in the electrolyte and can reach concentrations as high as 50-250 mg/L - concentrations that can cause serious problems for the cobalt cementation process.

## **2.8 Additives in the Cobalt Cementation Process**

Currently, the zinc industry uses two types of additive combinations to activate the cobalt cementation process; the Cu-Sb activation system (Brove and Ostvold 1994; Painter 1980; Raghavan, Mohanan, and Verma 1999; Rodier 1980; Singh 1996) and the Cu-As activation system (Huggare, Ojanen, and Kuivala 1973). In general, most zinc plants that deal with high cobalt concentrations in the PLS (higher than 15- 20 mg/L) use Cu-As as As appears to be suitable for high cobalt loadings (Singh 1996). Also, zinc dust consumption in the Cu-As activation system is less than that in the Cu-Sb activation system. However, the use of Cu-Sb is preferred because it presents less environmental hazards (Singh 1996; van der Pas 1995). In this section we will discuss the mechanisms associated with Cu-Sb and Cu-As activation as well as some other novel activators used to promote the cobalt cementation process.

### **2.8.1 Cu-Sb Activation System**

In an early study by Blander and Winand (Blander and Winand 1975) it was claimed that Cu-Sb accelerates cobalt removal by forming a Cu-Sb-Co alloy. These authors mentioned that the triple alloy of Co resists anodic corrosion in the presence of cathodic hydrogen evolution. It was also reported that in the accelerated cobalt removal from zinc solution, copper appeared to have a higher accelerating effect than antimony while antimony stabilized the deposit.

Tozawa et al. (Tozawa et al. 1992) constructed the Eh-pH diagram (Figure 2-1) for the system of M-Sb-H<sub>2</sub>O in which M can be cobalt, nickel or copper at the 10<sup>-5</sup> molar concentration level.



According to this diagram, in the pH range of 3-5, where the cobalt cementation takes place, antimonide alloys of Co and Ni are more stable than pure metallic Co and Ni. Therefore, Tozawa et al. inferred that Sb might enhance the cobalt cementation reaction by forming CoSb. Reaction 2-2 was presented in Tozawa's work for the cementation of cobalt in the presence of antimony trioxide. However, in the same work, the authors reported that their SEM analysis on the deposit products didn't show the coexistence of Co and Sb.

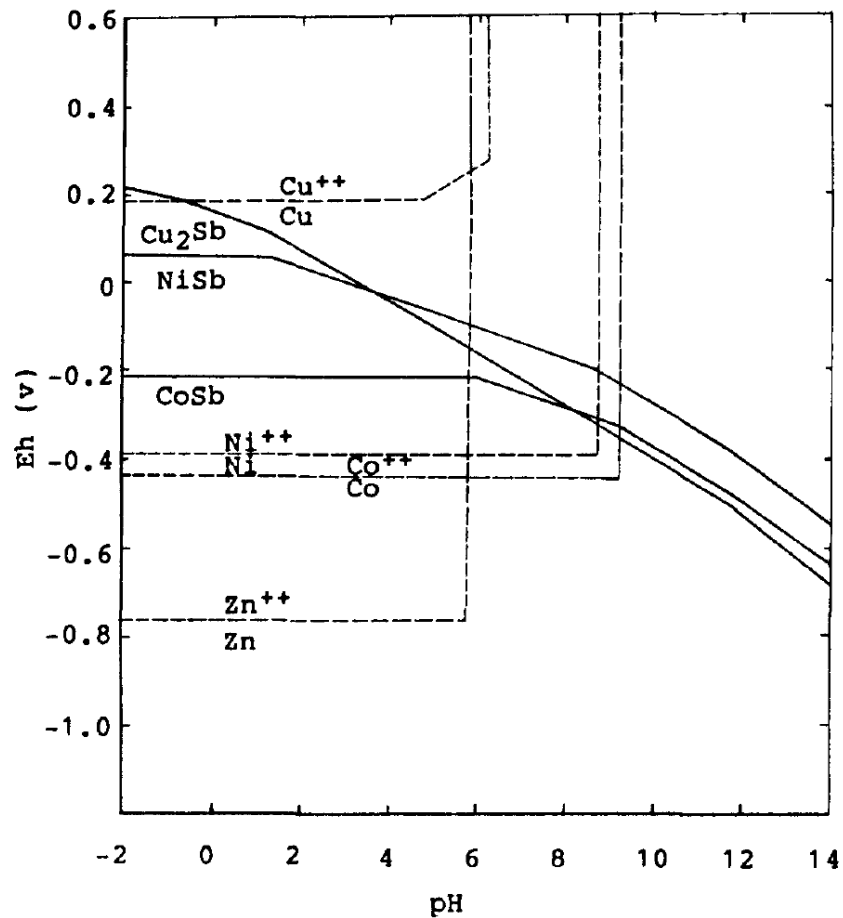


Figure 2-1. Potential-pH diagram for the M-Sb-H<sub>2</sub>O system ([Cu]= [Ni]= [Co]= [Sb]= 10<sup>-5</sup> mol/L, [Zn]= 1 mol/L) (Tozawa et al. 1992).

More recent studies done by Lew (Lew 1994) and Van der Pas (van der Pas 1995; van der Pas and Dreisinger 1996) clarified that the Cu-Sb additives improve the cobalt cementation, not by forming alloys with cobalt, but by providing a substrate onto which cobalt cements preferentially.

Lew's study (Lew 1994) indicated that the cobalt cementation process is enhanced more significantly when Cu and Sb are added to the solution together compared to the condition where they are introduced alone. In the same work, it was shown that both of the additives cement out of the solution in the first 10 min of the experiments, although the mechanisms that each of the additives contributes to the cobalt cementation were found to be different. Lew believes that Sb probably facilitates Co removal by providing a preferential substrate for cobalt deposition and by increasing the hydrogen overpotential on the zinc dust. But, Cu on its own has no effect on the hydrogen evolution and probably just provides cathodic surface area on which Co cements preferably. In Lew's study, experiments run with zinc dust pre-coated by Cu and Sb, and with no addition of the activators, gave the same results that were achieved in the Cu-Sb activation system. This verifies that co-deposition of cobalt with copper and antimony does not necessarily occur.

The results reported by Lew are verified in Van der Pas's studies (van der Pas 1995; van der Pas and Dreisinger 1996). According to these studies, "in the presence of zinc ions, cobalt cannot be deposited in a pure form, but is deposited as a cobalt-zinc alloy which consists primarily of anomalously deposited zinc" (van der Pas and Dreisinger 1996). Van der Pas believes that Sb increases the cobalt content of the cemented Co-Zn alloy by cementing earlier on the zinc dust and forming nuclei on which the Co-Zn alloy with increased cobalt content can form and grow. On the other hand, these authors also proposed that copper contributes to the cobalt cementation

by forming dendritic deposits on zinc dust and enlarging the surface area for the cementation reaction.

As discussed in section 2.1, Bockman and Ostvold (Bøckman and Østvold 2000b) believe that the cemented cobalt on the zinc dust is comprised of two parts; basic cobalt salts which easily dissolve in acidic condition, and cobalt in alloy form or in a solid solution which is resistant to redissolution under acidic conditions. These researchers showed that the addition of  $\text{Sb}^{3+}$  and  $\text{Cu}^{2+}$  to the solution during the cobalt cementation process increases the extent of un-dissolvable Co cement (i.e. Co alloys) and consequently leads to an increase in cobalt cementation rate. However, the amount of Co salts in the cement was reportedly constant and independent of the initial concentrations of the activators.

Nelson et al. (Nelson, Demopoulos, and Houlachi 2000) believe that partial hydrolysis of metallic ions is a precursor to adsorption on the surface of zinc dust. In the case of zinc ions, the formation of the precursor ( $\text{ZnOH}^+$ ) and its adsorption on the zinc dust surface would lead to passivation of the zinc dust. However, Nelson believes that when additives (like copper and antimony) exist in the solution, they form hydrolyzed species and adsorb on zinc dust in the place of  $\text{ZnOH}^+$ . Once the hydrolyzed species of the additives are adsorbed, they reduce to their metallic form and form a substrate on which  $\text{ZnOH}^+$  does not adsorb, allowing cobalt to reach the zinc dust surface and discharge.

### **2.8.2 Cu-As Activation System**

In the Cu-As activation system, Cu and As are added to the solution typically in the concentrations of 200 mg/L and 50-200 mg/L, respectively (van der Pas 1995). These concentrations are noticeably higher than Sb and Cu concentrations in the Cu-Sb activation system where concentrations are normally in the range of 2-4 mg/L and 50-100 mg/L,

respectively. There is adequate evidence indicating that the mechanism of cobalt removal with Cu-As is different from that with Cu-Sb. For instance, comparison of removal rates of arsenic and antimony during the cementation process (Figure 2-2) indicates that arsenic and cobalt cement out of the solution almost simultaneously, while as mentioned in section 2.8.1, antimony is removed from the solution much faster than cobalt. It is believed that in contrast to antimony, arsenic promotes the cobalt cementation reaction by forming alloys with cobalt; these alloys may have a higher rate of cementation or be more stable than cobalt cement alone (Nelson et al. 2000).

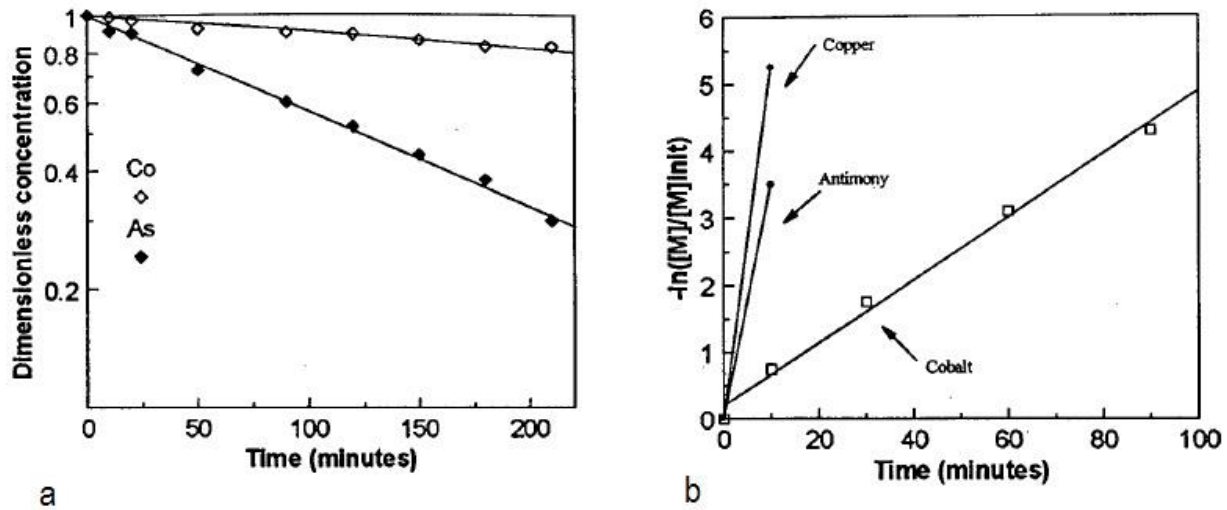


Figure 2-2. Removal rates of arsenic (a) antimony, and copper (b) compared to the cobalt cementation rate (van der Pas 1995).

Tozawa et al. (Tozawa et al. 1992) confirmed the coexistence of Co and As in the deposit by SEM analysis. Thermodynamic studies conducted in Tozawa's work shows that in the condition of the cobalt removal stage, cobalt arsenide (CoAs) is more stable than metallic cobalt (Figure 2-3). The authors proposed Reaction 2-3 for CoAs formation from  $As_2O_3$  and Co ions. Based on experiments from the same study, the presence and concentration of Cu in the Cu-As

system played an important role in increasing the rate of cobalt removal, whereas Sb could remove an appreciable amount of Co, even in absence of Cu.

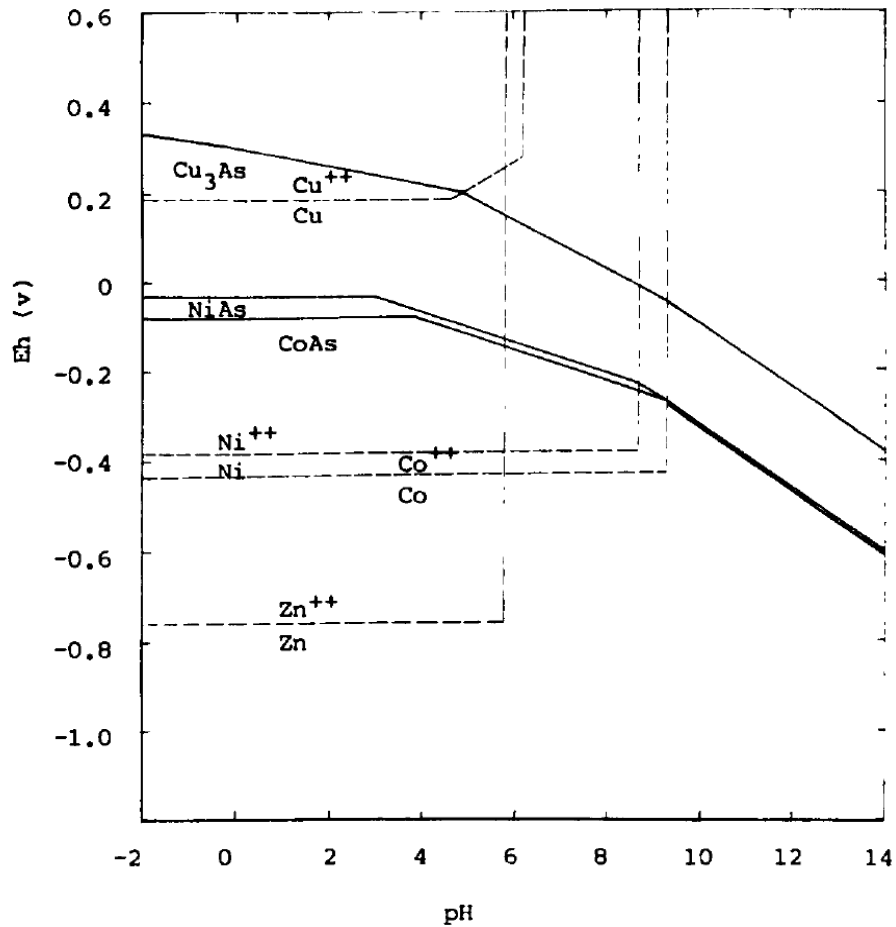


Figure 2-3. Potential-pH diagram for the M-As-H<sub>2</sub>O system ([Cu]= [Ni]= [Co]= [As]= 10<sup>-5</sup> mol/L, [Zn]= 1 mol/L) (Tozawa et al. 1992).

Yamashita et al. (Yamashita et al. 1997) believe that in the Cu-As activation system, copper cements on zinc dust first and forms a galvanic cell with zinc. At the cathodic site of this galvanic cell, cobalt is deposited on copper as CoAs and at the anodic site zinc dissolves.

### 2.8.3 Other Novel Activators

#### 2.8.3.1 Cadmium

The impact of adding Cd in the Cu-Sb activation system has been studied by Nelson et al. (Nelson, Demopoulos, and Houlachi 2000). Their experiments showed that Cd in small quantities ( $[Cd] < 100$  mg/L) works synergistically with Sb and Cu in decreasing the final cobalt concentration; but has little effect on the initial cobalt removal rate. Increasing Cd concentration above 100 mg/L resulted in a higher final cobalt concentration. It was also stated in Nelson's work that cobalt removal in the presence of Sb and Cd was very similar to that in the presence of Sb and Cu. Thus, Nelson et al. postulated that Cd probably improves cobalt cementation in the same way that Cu does; by forming a dendritic deposit on the zinc dust and enlarging the reaction surface area.

The beneficial effect of cadmium on the cobalt removal was also investigated by Yang et al. (Yang et al. 2006). The results of this study (Figure 2-4) indicated that adding Cd (up to 300 mg/L) to the synthetic zinc electrolyte, containing 140 g/L  $Zn^{2+}$  and 3 g/L  $Co^{2+}$ , causes a linear increase in the cobalt removal extent. However, further increase in the Cd concentration (especially for  $[Cd^{2+}] > 400$  mg/L) led to a plateau in the cobalt removal. In sum, from (Nelson, Demopoulos, and Houlachi 2000) and (Yang et al. 2006), it can be inferred that Cd, in small quantities, improves cobalt cementation, therefore complete elimination of this element, prior to the Co cementation stage, is not necessarily recommended.

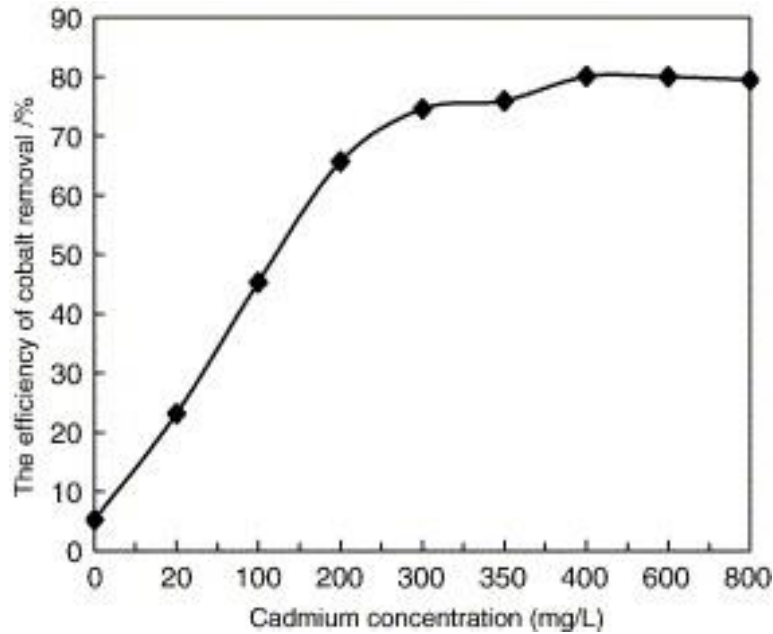


Figure 2-4. Effect of Cadmium concentration in the solution on cobalt removal (Yang et al. 2006).

### 2.8.3.2 Tin

Nelson et al. (Nelson, Demopoulos, and Houlachi 2000; Nelson 1998) tested the suitability of  $\text{As}^{3+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Te}^{4+}$ ,  $\text{In}^{3+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Se}^{4+}$ ,  $\text{Ge}^{4+}$  and  $\text{Ag}^{+}$  as a replacement for antimony in the Cu-Sb activation system. The elements were studied from three aspects:

1. Their ability to be removed from the solution effectively since many of the studied elements were more harmful than cobalt itself for zinc EW.
2. Their ability to lower cobalt concentrations to acceptable levels.
3. Their contribution to the zinc dust consumption.

According to the obtained results, almost all of the tested elements fulfilled the first criterion since their concentration went down to levels lower than detectable limits of ICP-MS (0.1-1 part per trillion) within 40 min. In terms of the rate of cobalt removal (the second criterion), the following order was reported for the tested elements (from the most effective to

the least effective): Sn, Sb, Te, In, Bi, Cu, Se, As, Ag, Pb, Hg, Ge. Nelson et al. observed that not only the extent of cobalt removal, but also the trend of decreasing cobalt concentration as a function of time varied from element to element. For instance, they observed that Sb and Sn give very rapid cobalt removal at the beginning, but reach a plateau after 20 min. In contrast, Te, In and Bi showed slow but linear cobalt removal with time which never reached a plateau. Nelson et al. reported that between different characteristics of the tested elements, the hydrolysis constant ( $K_{OH}$ ) was the best parameter to predict the cobalt removal efficiency of the elements, so that elements with higher  $K_{OH}$  were the best in terms of cobalt removal.

Regarding zinc dust consumption (the third criterion), Nelson's studies showed that in general, those elements which worked better in cobalt removal led to more zinc dust dissolution as well. However, tin interestingly led to a lower zinc dust dissolution compared to antimony. These researchers believe that zinc dust consumption is linked to the hydrogen exchange current density on the activator so that metals with large hydrogen exchange current densities act as catalyst for hydrogen evolution and lead to an increase in zinc dust consumption. Nelson et al. reported tin as an element that is equally as effective as antimony for cobalt removal.

Dreher et al. (Dreher et al. 2001) confirmed that tin works more efficiently than antimony in terms of zinc dust dissolution. However, their experiments showed that to obtain a satisfactory cobalt removal, a substantially higher quantity of tin, compared to antimony, should be used in the cementation process. Noting that tin is more expensive than antimony, using higher quantities of it in the process may render the process uneconomical.

#### **2.8.3.3 Chloride**

According to (Nelson, Demopoulos, and Houlachi 2000), chloride ( $Cl^-$ ) even in concentrations as low as a few hundred mg/L improves the extent of cobalt removal. Although



based on Nelson's work, adding  $\text{Cl}^-$  at higher levels (600 mg/L) resulted in a significant increase in the cobalt removal kinetics, such high levels of chloride in zinc electrolyte cannot be tolerated during electrowinning. Tanabe et al. (Tanabe et al. 1995) related the beneficial effect of chloride to its catalytic capability, but no explanation has been provided regarding the mechanism of this catalytic effect.

## 2.9 The Kinetics of the Cobalt Cementation Reaction

It is normally assumed that the cobalt cementation reaction follows apparent first-order reaction kinetics (Dreher et al. 2001; Tozawa et al. 1992). Therefore, the concentration of cobalt can be predicted by Equation 2-1, in which,  $k$  represents the rate constant of the reaction and is dependent on many parameters including temperature, zinc dust surface area, surface concentration of the activators, solution composition, and pH.

$$\ln C/C_0 = -kt \quad (\text{Equation 2-1})$$

Dreher et al. (Dreher et al. 2001) showed that in Cu-Cd-Sb activated cobalt cementation, the rate constant ( $k$ ) is independent of the initial cobalt concentration (1.5- 30 mg/L), while it is affected by the initial concentration of the activators (in a certain range) and zinc dust surface area. Dib and Makhoulfi (Dib and Makhoulfi 2006; Dib and Makhoulfi 2007) studied the effect of different parameters including temperature and solution stirring speed on the rate constant of the simultaneous cobalt and nickel cementation reactions. According to these studies, the responses that the cobalt and nickel cementation reactions showed to varying operating parameters (temperature, agitation) were interestingly different, showing that these reactions are controlled by different mechanisms. Dib and Makhoulfi observed that rate constant of the cobalt cementation reaction was improved significantly by increasing temperature while it didn't

change noticeably with varying the solution stirring rate. On the other hand, the rate constant of the nickel cementation reaction was increased by increasing agitation but was not considerably affected by changing temperature.

Polcaro et al. (Polcaro, Palmas, and Dernini 1995) believe that a few modifications should be made in the typical first-order kinetics equation (Equation 2-1) to perfectly represent kinetics of the cobalt cementation reaction. They believe:

1. Because the cobalt cementation occurs only on the sites of the zinc dust which already have been activated by additives (Cu-Sb), there should be a term in the kinetic equations representing the area of these active sites as a function of time.
2. Since cobalt concentration after an initial rapid decrease reaches a limit ( $C_{as}$ ) around 0.1 ppm beyond which it cannot proceed further, this limit should also be included in the kinetics model.

To satisfy both of the above mentioned modifications, Polcaro et al. presented Equation 2-2, where  $\bar{C} = C - C_{as}$  represents the difference between the bulk concentration of Co(II) and the minimum achievable Co(II) concentration,  $A_c(t)$  represents the active cathodic site area on which Co(II) reduction can occur, and  $k_m$  represents the mass transfer coefficient for Co(II).

$$d\bar{C}/dt = -A_c(t)k_m\bar{C} \quad (\text{Equation 2-2})$$

$A_c(t)$  in Equation 2-2 can be calculated by Equation 2-3:

$$A_c(t) = A_c^* M(t) \quad (\text{Equation 2-3})$$

Where  $A_c^*$  is the specific area of the noble metal (activators) sites and  $M(t)$  is the amount of the noble metals per unit volume of the solution deposited on the zinc dust at time  $t$ . Assuming that

deposition of the noble metals on the zinc dust surface takes place by a first-order reaction, and with the same mass transfer coefficient as the cobalt cementation reaction, Equation 2-4 can be presented to predict the residual concentrations of the noble metals in the solution. Then,  $M(t)$  can be determined from the difference between the initial and residual concentration of the noble metals in the solution (Equation 2-5).

$$C/C_0 = \exp(-\alpha^*mk_mt) \quad (\text{Equation 2-4})$$

$$M(t) = M^0[1 - \exp(-\alpha^*mk_mt)] \quad (\text{Equation 2-5})$$

By substituting Equation 2-5 in Equation 2-3,  $A_c(t)$  is determined (Equation 2-6).

$$A_c(t) = A_c^* M^0 [1 - \exp(-\alpha^*mk_mt)] \quad (\text{Equation 2-6})$$

Replacing  $A_c(t)$  from Equation 2-6 in Equation 2-2 and integrating, the following equation is obtained, presenting cobalt concentration in the solution ( $\bar{C}$ ) for time  $t$ .

$$\ln \bar{C}/\bar{C}_0 = -\frac{A_c^* M^0}{\alpha^*m} [\alpha^*mk_mt + \exp(-\alpha^*mk_mt) - 1] \quad (\text{Equation 2-7})$$

In fact, when  $t$  is sufficiently large (noble metals are completely deposited),  $A_c(t) = A_c^* M^0$  and Equation 2-7 can be converted to the following equation.

$$\ln \bar{C}/\bar{C}_0 = -\frac{A_c^* M^0}{\alpha^*m} [\alpha^*mk_mt - 1] \quad (\text{Equation 2-8})$$

In other words, Equation 2-8 gives a linear relationship between  $\ln \bar{C}/\bar{C}^0$  and  $t$  in which the slope and intercept are equal to  $-k_m A_c^* M^0$  and  $\frac{A_c^* M^0}{\alpha_m^*}$ , respectively.

### 3 Objectives

In the previous sections, the typical cobalt cementation process, hereafter referred to as LT/LP (Low Temperature/Low Pressure) cobalt cementation was introduced. It was shown that this process is challenging. A summary of the various studies that have been conducted over the past decades to better understand the cobalt cementation mechanism was also provided.

“High Temperature and High Pressure” cobalt cementation as a new approach to remove cobalt from zinc electrolyte was introduced in section 2.3. Although this technology was reported by Houlachi et al. (Houlachi, Leroux, and Saint-Onge 1995) almost twenty years ago, no academic investigation has been conducted to study it in depth. Thus, it was the aim of this research to study the HT/HP cobalt cementation process in order to answer the following questions, specifically:

1. What is the effect of high temperatures (100-150°C) on the rate and extent of cobalt removal?
2. Can the amount of zinc dust used for the cobalt cementation be reduced by conducting the process at HT/HP condition? Knowing that the parasitic hydrogen evolution reaction is the dominant zinc dust consumer, in fact it was the aim of this study to determine if this reaction can be suppressed by the application of pressure (e.g. increasing partial pressure of hydrogen gas in the autoclave).
3. Can the need for activators (Cu and Sb) be removed or reduced by performing the cobalt cementation process at HT/HP condition? Since at high temperatures, the kinetics of reactions are enhanced, it might be possible to remove the need for activators (especially Sb as it is toxic).

In general, based on the previous studies, two experimental approaches can be followed to simulate the cobalt cementation process; running the cementation tests in an electrochemical setup (i.e. rotating disc electrode) or with addition of zinc dust. Although running the cementation tests in an electrochemical cell can provide a better control on mass transfer as well as electrochemistry of the process, such a setup cannot ideally represent the industrial condition for the process. Thus, in this work, it was decided to conduct the cobalt cementation experiments with addition of zinc dust. A synthetic solution, with zinc content close to that of the industrial zinc electrolyte, was used in the experiments.

Effects of the following parameters on the kinetics of cobalt cementation at HT/HP condition were studied:

pH control (this parameter was studied at LT/LP condition), temperature (85-150°C), zinc dust dosage, zinc dust sizing, additives (Cu and Sb), and pressure.

## 4 Experimental Setup and Procedures

### 4.1 Chemicals

All the cobalt cementation tests were carried out using a synthetic zinc electrolyte containing 145 g/L  $\text{Zn}^{2+}$ , 15 mg/L  $\text{Co}^{2+}$ , 45 mg/L  $\text{Cu}^{2+}$ , and 2.5 mg/L  $\text{Sb}^{3+}$  (unless otherwise stated). All the solutions were prepared by dissolving suitable amounts of the compounds (Table 4-1) in the de-ionized water, which was treated by activated carbon beforehand. The activated carbon treatment of the de-ionized water was done in order to eliminate or reduce the concentration of any possible organics in the de-ionized water.

Table 4-1. Constituents of the synthetic zinc electrolyte.

Element	Added as	Typical concentration of the element
<b>Zn</b>	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	145 g/L
<b>Co</b>	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	15 mg/L
<b>Sb</b>	$\text{C}_8\text{H}_4\text{K}_2\text{O}_{12}\text{Sb}_2 \cdot 3\text{H}_2\text{O}$	2.5 mg/L
<b>Cu</b>	$\text{CuSO}_4$	45 mg/L

### 4.2 Zinc Dust

Two types of zinc dust were used in the tests; an industrial zinc dust provided by CEZinc (Quebec, Canada) and a zinc dust purchased from J.T.Baker Chemical Co. The concentration of the added zinc dust to the solution in each test was 3.5 g/L and it was screened to separate particles with diameter smaller than 75  $\mu\text{m}$  before use. In some tests, the quantity of the zinc dust used or its particle size was changed to study the effect of these parameters.

It is interesting to mention that although the zinc dust was screened by 75 $\mu$ m sieve, particle size distribution (PSD) analysis on the sub-sieve dust revealed that a noticeable portion of the particles are larger than 75 $\mu$ m. P(80) for the zinc dust samples were on the order of 95 $\mu$ m. These PSD analyses were conducted with two different machines: a Malvern Mastersizer 2000 and Malvern Mastersizer 3000. This observation can be attributed to the shape of the zinc dust particles. SEM photos (given in Appendix A) show that majority of the zinc particles are in the shape of long cylinders with small diameters. Figure 4-1 shows the sub-sieve zinc particles under a microscope; according to this figure, the sub-sieve particles can be as long as 126 $\mu$ m, although they have narrow diameters and therefore can pass through the sieve. It is likely that in the PSD analysis, some of these long particles were oriented in a way so that the length of their longer dimension was measured by the machine. To provide a more accurate picture of the zinc dust that was used, a P(80) is always provided with the results.



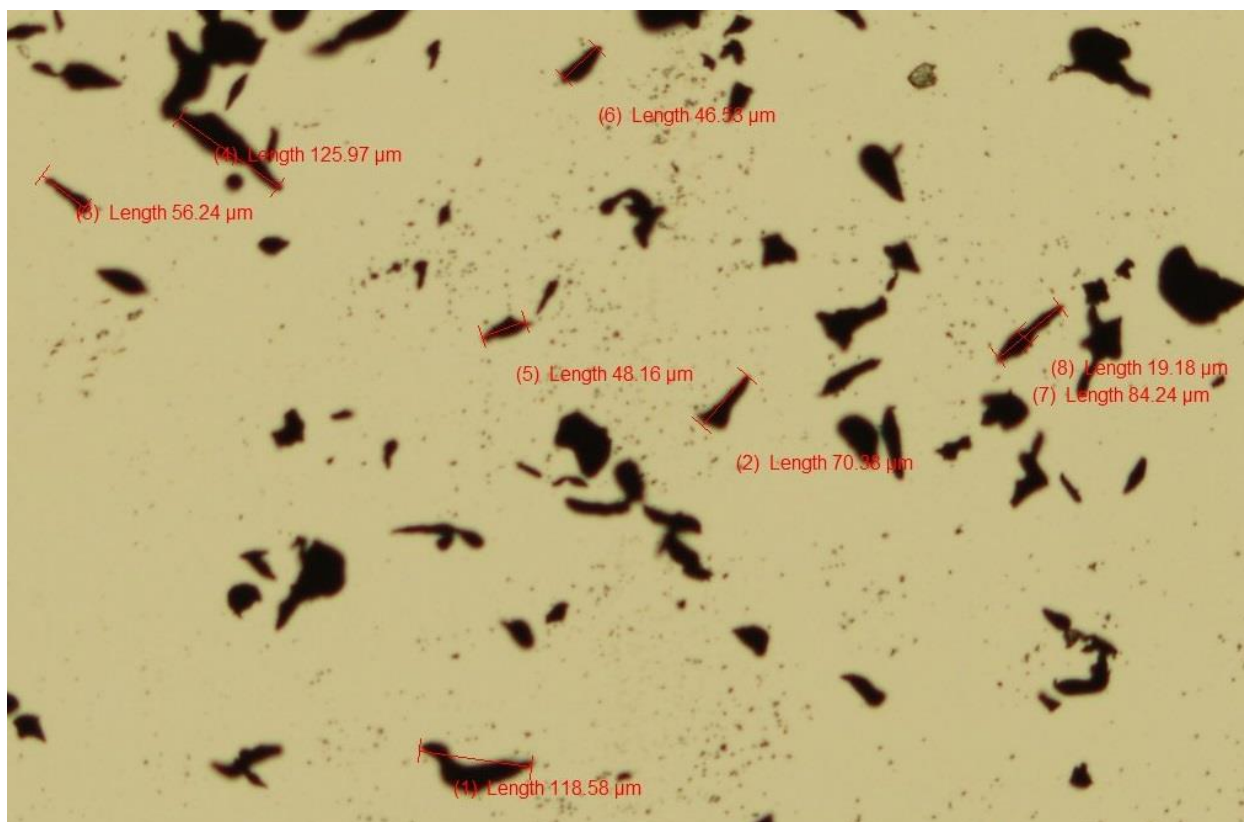


Figure 4-1. CEZinc zinc dust with  $D < 75\mu\text{m}$  by screening, as seen under microscope with some dimensions in excess of  $75\mu\text{m}$ .

Table 4-2 summarizes the characteristics of the zinc dusts. More details about surface morphology of the dusts and their surface composition are provided in Appendix A and B, respectively.

Table 4-2. Zinc dusts characteristics.

Supplier	Surface area	P(80)
	( $\text{m}^2/\text{g}$ )	( $\mu\text{m}$ )
CEZinc	0.236	93.63
J.T.Baker Chemical Co.	0.212	107.73

### 4.3 Experimental Apparatus

All the batch cementation tests were conducted in a 2 L autoclave made of inconel 625. Although for these test conditions, inconel 625 is corrosion resistant, and therefore would not interfere with the experiments, it was decided to use a glass liner inside the autoclave to alleviate any concerns associated with another metallic surface in the system (Figure 4-2). The temperature of the autoclave was controlled at the intended temperature for each test using an electrical heater and a touch screen temperature controller connected to the heater (Figure 4-3). Agitation of the solution was maintained at 1000 rpm using a 4-bladed Teflon impeller. Although the cobalt cementation reaction is chemically controlled, high agitation in the system was established to ensure sufficient suspension of zinc particles in the solution. At the head of the autoclave, there were some holes for installing required instruments such as a thermocouple, a sampling tube, a zinc dust injection tube, and baffle (Figure 4-4). Figure 4-5 shows a schematic of the experimental setup in more detail.

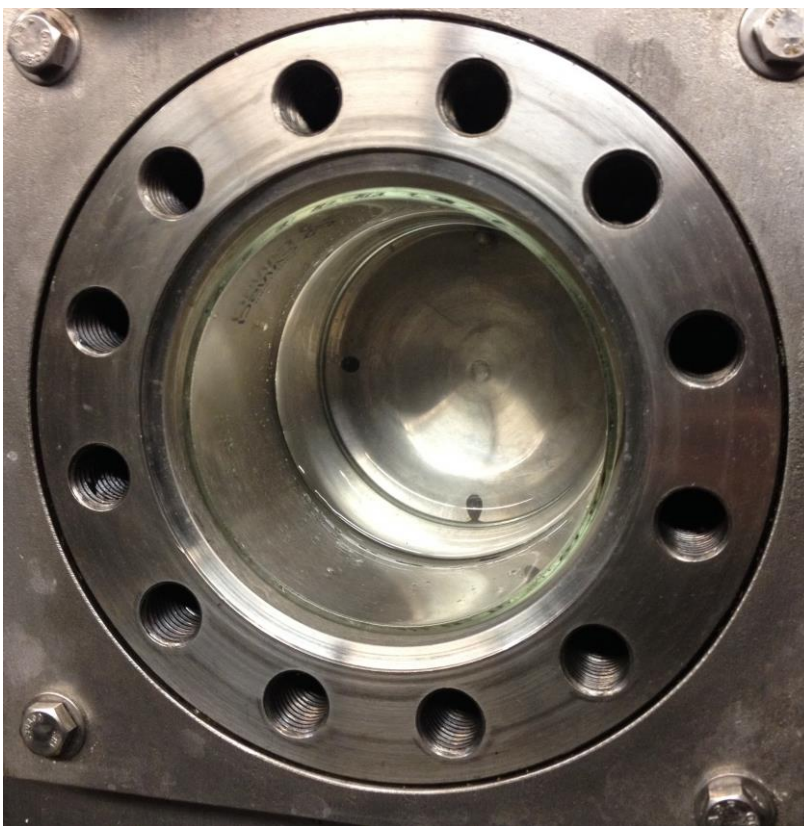


Figure 4-2. Top view of Inconel 625 autoclave with glass liner.

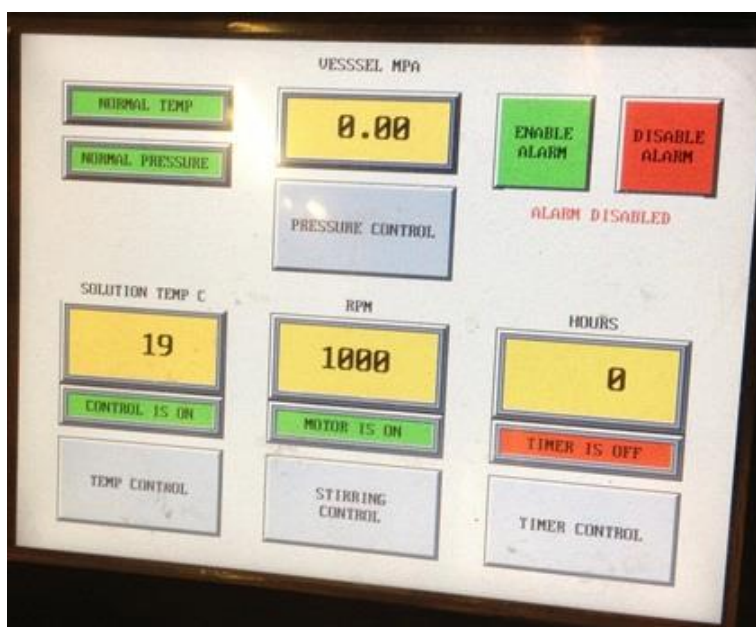


Figure 4-3. Touch screen controller of temperature and agitation.

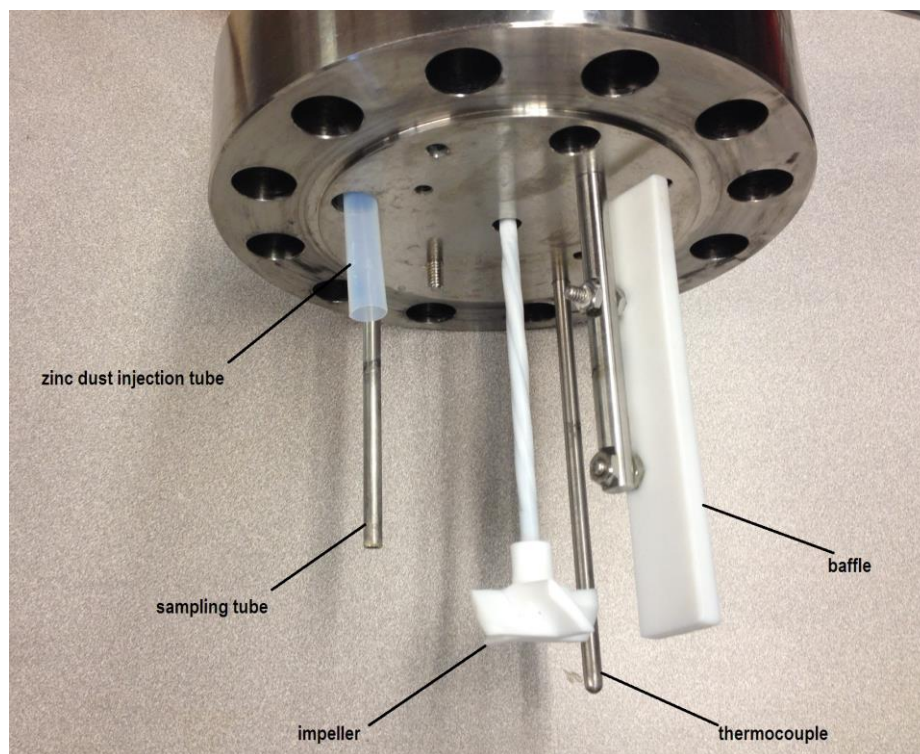


Figure 4-4. Head of the autoclave along with the installed parts.

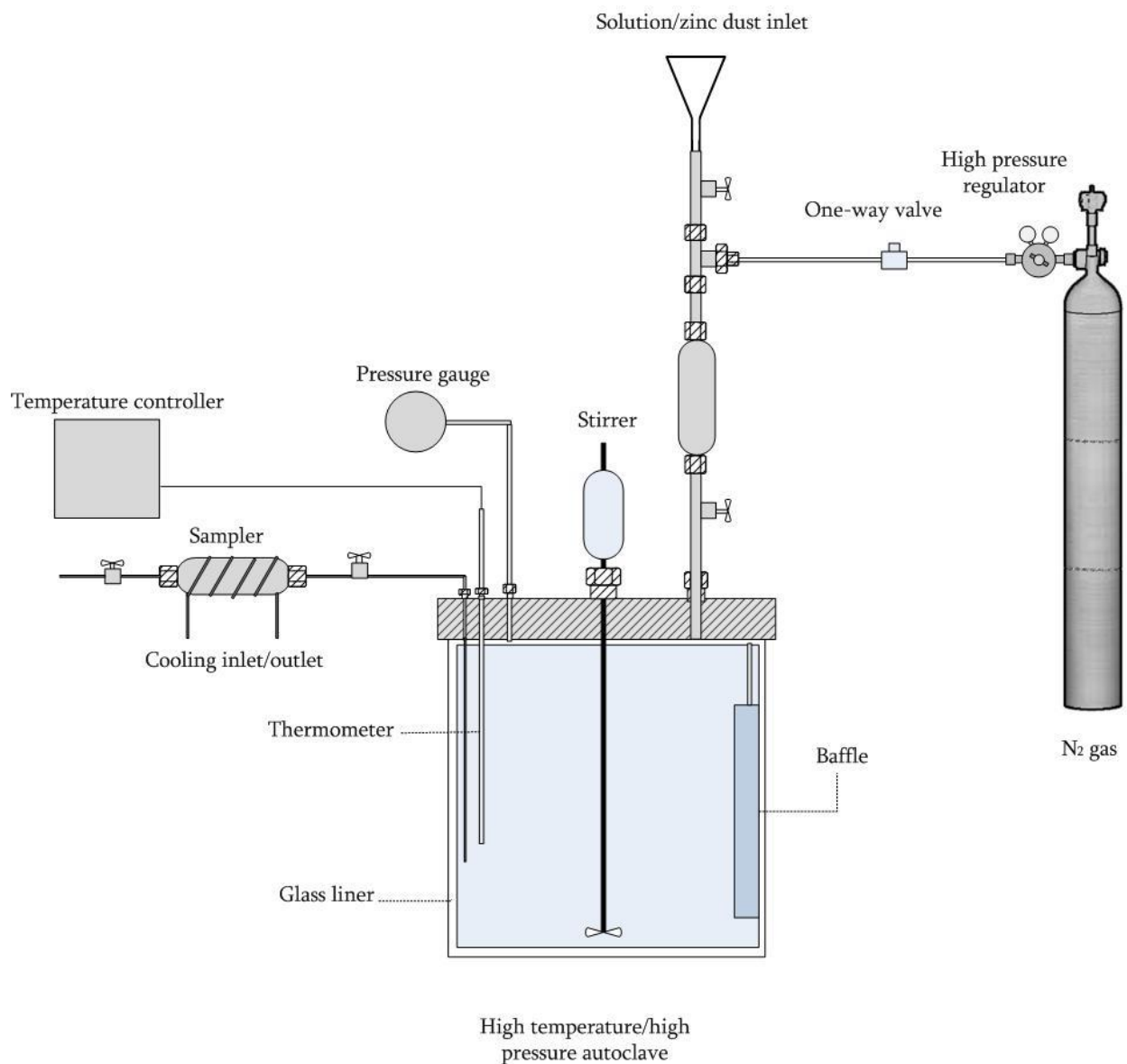


Figure 4-5. Schematic of the autoclave setup.

## 4.4 Experimental Procedure

The steps used to conduct the cobalt cementation tests can be summarized as follows:

1. 1L of the prepared synthetic zinc electrolyte, containing 145 g/L Zn<sup>2+</sup> and 15 mg/L Co<sup>2+</sup>, was used in each test. However, to start an experiment only 850 mL of the solution was

transferred to the autoclave and the remaining solution was kept for later use when zinc dust was injected to the system in slurry form.

2. Nitrogen gas sparging was employed for the first 15 min to eliminate oxygen from the solution and the autoclave atmosphere. Oxygen is undesirable during cobalt cementation as it can cause redissolution of the cemented cobalt (Lew 1994; van der Pas 1995).
3. While sparging nitrogen, the solution was also heated to 85°C.
4. At 85°C, the pH of the solution was adjusted to 4 by adding approximately 15 mL NaOH (0.5 M) (Figure 4-6).
5. In addition to the pH adjustment, the appropriate volumes of stock solution of the activators (potassium antimony tartrate and copper sulfate) were also added to the solution to establish the required concentrations of the activators in the solution.
6. Thereafter the autoclave was sealed and the solution heating was continued until a point 3°C above the intended operating temperature was reached.
7. When the desired temperature point was reached, a slurry of the zinc dust was made in the remaining 150 mL of the synthetic electrolyte and transferred to the autoclave with (or without) the help of external gas injection. Through experience it was found that using this strategy, the temperature of the combined solution was fairly close to the intended operating temperature for each test.
8. Immediately after injecting the zinc dust slurry to the system, the autoclave was pressurized to the operating pressure for each test. This moment was considered as the actual commencement of the experiment.
9. Depending on the test operating temperature, at specific time intervals, samples of 40 mL of the solution were withdrawn; at higher temperatures, the cobalt removal rate is faster

and therefore the samples were taken in shorter time intervals. The duration of the tests was between 60 and 120 min.

10. Each sample was filtered firstly by filter paper and secondly by disc filter (Figure 4-7).

The filter paper and disc filter had 2 and 0.20  $\mu\text{m}$  pore sizes, respectively. Special care was taken to filter the samples as quickly as possible since there is risk of redissolution of the cemented cobalt if the zinc particles stay in the solution for an extended time.

11. The filtrates were stored for solution analysis.

Since cobalt cementation tests are notoriously difficult to reproduce (Dreher et al. 2001), the tests that dealt with low cobalt concentrations (lower than 0.5 mg/L) were repeated two (or in some cases three) times, and the average value of the results was reported as the final result. In the case of three repeats, the error bars, which represent the standard deviation of the results from the average value, are shown in the figures.

The errors in the cobalt cementation tests can occur from the following sources:

1. Error from the solution analysis: When very low cobalt concentrations were analyzed, the obtained absorbance was lower than the optimum absorbance range of the UV-Vis Spectroscopy machine and therefore the uncertainty of the results was increased.
2. Error from failure to introduce the entire zinc dust charge into the system: The designed zinc dust injection system worked well in most tests, however in some of the tests, it was seen that a small amount of the zinc dust stuck to the injection tube and was not introduced to the solution. Failure in inserting all of the zinc dust into the solution would cause a significant error in the results.



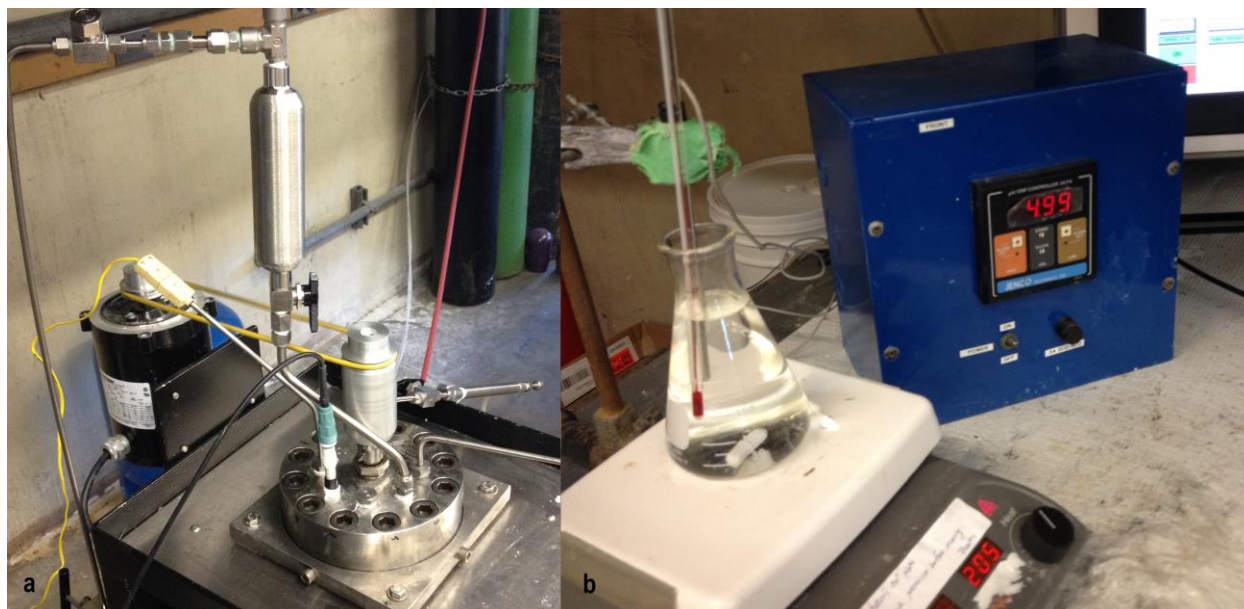


Figure 4-6. pH adjustment at 85°C (pH probe installed on the autoclave (a), pH meter and temperature compensation probe (b)).





Figure 4-7. Filtration of the samples with filter paper (a) and with disc filter (b).

#### 4.5 Solution Analysis (UV-Vis Spectroscopy) Procedure

The determination of cobalt concentrations for this work was a challenging task, as cobalt should be present at low levels (0-15 mg/L) but in coexistence with high levels of zinc (145 g/L). Thus there is a serious risk of zinc interference in the results. Moreover, to avoid clogging the injection systems of analysis machines, it was necessary to dilute the samples at least 15 times. This would lead to very low cobalt concentrations, which were under the detectable level of Atomic Absorption Spectroscopy (AAS) and even ICP.

Noting these issues, it was decided to measure cobalt concentrations using UV-Vis Spectroscopy. The procedure that was used was reported by (Omar Zahir and Keshtkar 1998). This analysis method is based on selective complexation of the organic compound, 1-Nitroso-2-naphthol-3,6-disulfonic acid, disodium salt, with cobalt, which gives a specific color to the sample with respect to its cobalt content. The intensity of the color is measured with UV-Vis spectroscopy and compared with the color intensity of known standard solutions (Figure 4-8). A

summary of the steps followed in the preparation of the samples and the standards is presented below.

**Sample Preparation:**

1. 20 mL of the sample was transferred to a clean and dry 50 mL volumetric flask.
2. 5 mL sodium acetate solution (3.7 M) was added in to the flask.
3. 1 mL 1-Nitroso-2-naphthol-3,6-disulfonic acid, disodium salt solution (prepared by dissolving 1g of the salt in 100 mL de-ionized water) was added to the flask.
4. The volume of the solution inside the flask was made up to almost 40 mL with de-ionized water.
5. The flask was heated to- and maintained at 80-90°C for 1 hour. During the heating period, the flask was covered with a plastic film to avoid evaporative loss of the solution.
6. Immediately after the heating period, 5 mL concentrated HCl was added to the solution to destroy any complexes other than the cobalt complex.
7. The volume of the solution was adjusted to 50 mL and the solution was cooled.
8. The solution was transferred to a 10 cm cuvette (for low concentrations of cobalt) or to a 2 cm cuvette (for high concentrations of cobalt) and its absorption was measured at 550 nm by the Lambda 35 UV/VIS Spectrometer (Perkin Elmer). The best range of absorbance for this equipment was between 0.1 and 0.7.

### **Standards Preparation:**

The preparation of standard solutions was similar to the preparation of the samples with only a few differences in the first steps:

1. Appropriate volumes of the certified 1000 mg/L cobalt solution (or dilutions thereof) were transferred to clean and dry 50 mL flasks to make 0, 0.01, 0.05, 0.1, 1 and 2 mg/L cobalt standard solutions.
2. In order to have standard solutions with the same matrix as the samples, 20 mL of  $\text{ZnSO}_4$  solution (145 g/L  $\text{Zn}^{2+}$ ) was added to each flask.
3. Hereafter the steps 2-8, mentioned above, were followed.

Following this procedure, the standard solution with cobalt concentration of 0.01 mg/L had an absorbance in the range of 0.008-0.012 in a 10 cm cuvette.



Figure 4-8. Standard solutions prepared for the UV-Vis spectroscopy analysis (the number on each beaker shows the concentration of cobalt in mg/L).

## 5 Results and Discussion

### 5.1 pH Control

The role of pH in the cobalt cementation process was discussed in section 2.4. It was mentioned that the pH of the zinc electrolyte rises during cobalt cementation due to the consumption of hydrogen ions by the hydrogen evolution reaction. This increase in pH is more substantial near the surface of zinc dust, where the  $H^+$  ions get reduced. West-Sells (West-Sells 1996) reported that during electrodeposition of cobalt from zinc sulfate solution, pH at the cathode surface can reach values as high as 8 (at 75°C). At such a high pH, zinc salts can precipitate on cathodic sites and block them for cobalt reduction. To avoid this from happening, pH of the solution during laboratory experiment is often controlled close to the initial pH by adding  $H_2SO_4$  as the cobalt cementation process goes on (Nelson, Demopoulos, and Houlachi 2000). However, there are a number of studies reporting that the absence of pH control during the cobalt cementation process does not impede the process (Lew 1994; Nelson, Demopoulos, and Houlachi 2000). Since measuring pH at HT/HP conditions is challenging (it needs a sophisticated pH probe and controlling circuit), it seemed critical to investigate the impact of the presence/absence of pH control on cobalt removal. Verifying that pH control during the experiments is not imperative could significantly ease the operation of the tests.

For this purpose, at 85°C and atmospheric pressure, two sets of experiments were conducted at the same condition with and without controlling pH to 4. The cobalt removal profiles of these tests, given in Figure 5-1, show that the absence of pH control had a beneficial effect on the kinetics of cobalt removal, so that the cobalt level of 0.1 mg/L could be achieved in 60 min; this level could not be reached in earlier than 90 min when the pH was controlled at 4. However, it

seems that leaving the pH of the solution uncontrolled led to a minor redissolution of the cement at the end of the experiment.

Noting that a significant portion of the cobalt cement consists of basic cobalt salts (Bøckman et al. 2000), the beneficial effect of the absence of pH control can be justified as it can accelerate precipitation of the basic cobalt species on the zinc dust. The changes of pH during the process were also monitored (Figure 5-1, right-hand axis). It was observed that pH increased from the initial value of 4 to 4.5 in the first 40 min of the test and became almost constant and self-regulating for the remainder of the experiment. The results obtained in these tests are in agreement with (Lew 1994; Nelson, Demopoulos, and Houlachi 2000).

Nelson et al. (Nelson, Demopoulos, and Houlachi 2000) examined the range of the pH rise and also its influence during the cementation process. They observed that pH rises from the initial value of 4 to 4.3 in the first 40 min and then becomes constant. More importantly, they reported that the absence of pH control had a positive effect on the cobalt removal so that the final cobalt concentration became slightly lower compared to the experiments in which pH was controlled at 4. The authors attributed this result to a difference between the rates of cobalt cementation and the zinc salt precipitation. They believe that in their system, because of the presence of the activators, cobalt cementation occurred earlier than the zinc salt precipitation and most likely the formation of the zinc salts prevents oxidation or re-dissolution of the cemented cobalt.

Lew (Lew 1994) reported that cobalt cementation tests run at the natural pH of the solution had the highest rate constant. For those tests, pH increased from the initial value of 3.7 to the equilibrium value of 4.6 (both pH values measured at 73°C) during 90 min duration of the tests.

Van der Pas (van der Pas 1995) also confirmed that increasing pH beyond the point where basic zinc compounds form, does not inhibit the reduction of cobalt.

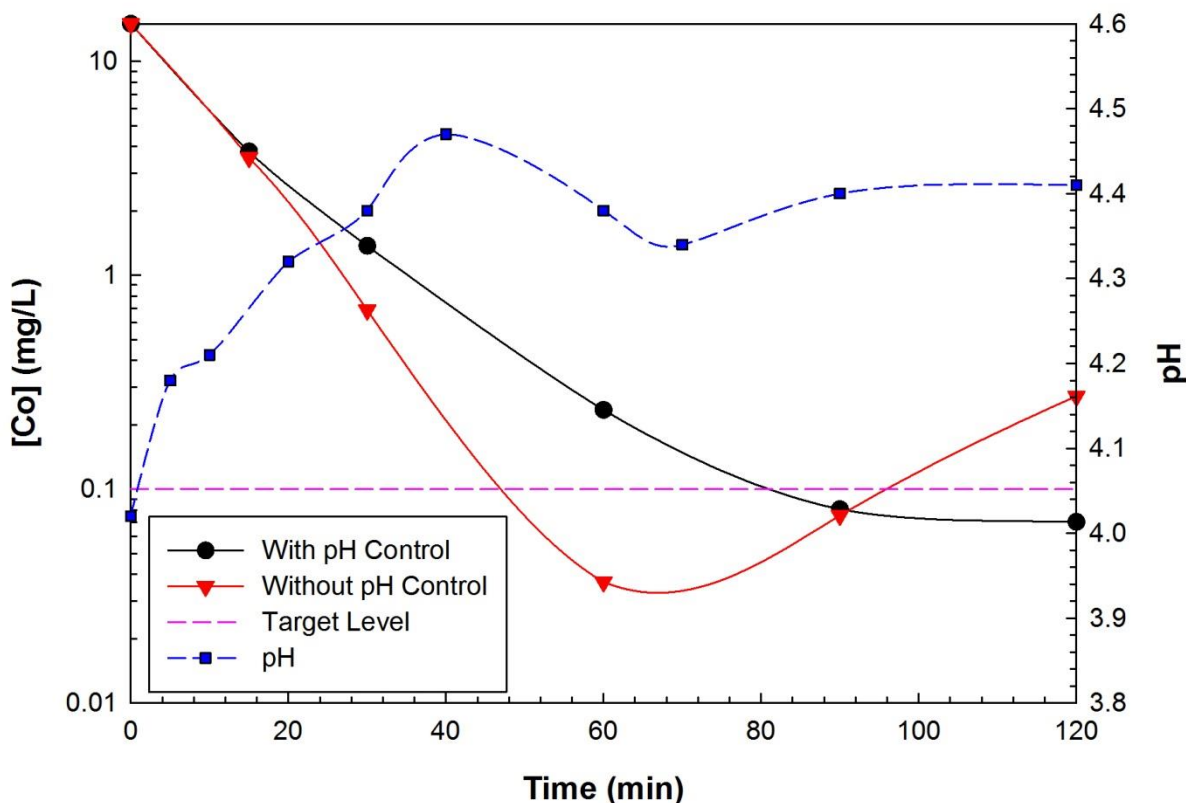


Figure 5-1. Cobalt cementation with and without pH control (85°C, 0 psig, 145 g/L  $\text{Zn}^{2+}$ , 45 mg/L  $\text{Cu}^{2+}$ , 2.5 mg/L  $\text{Sb}^{3+}$ , 3.5 g/L CEZinc zinc dust,  $P(80) = 94 \mu\text{m}$ ).

## 5.2 Temperature

The temperature range studied in this work was between 85 and 150°C. For the temperatures above the boiling point of the solution, the vapor pressure of the solution was in the range of 15-60 psig (1.02-4.08 atm) (Table 5-1 provides vapor pressure of the solution at each tested temperature). The tests needed to be carried out at pressures higher than the vapor pressure of the solution at each temperature since zinc dust slurry was injected into the system using the higher

pressure of the external gas. In order to separate the effect of pressure on the results, in all of the tests the total pressure over the solution was kept constant at 60 psig using N<sub>2</sub> gas (with just one exception at 150°C, where the pressure was maintained at 100 psig).

According to the results of these experiments, given in Figure 5-2, the following conclusions can be drawn regarding the effect of temperature on the cobalt cementation reaction:

1. Temperature had a significant effect on the kinetics of the cobalt cementation reaction.

Increasing temperature (from 85 to 125°C) enhanced the rate of the cobalt removal substantially so that the cobalt concentration of 0.1 mg/L, which could not be reached in earlier than 60 min at 85°C, could be reached in 20 min at 125°C. Houlachi et al. (Houlachi, Leroux, and Saint-Onge 1995) showed that by increasing temperature from 98 to 130°C, the required retention time to reach a cobalt concentration of 0.1 mg/L was reduced from over 120 min to 60 min. The relatively higher retention times reported in Houlachi's work can be attributed to the composition of the tested zinc solution as an industrial zinc electrolyte was used in Houlachi's study (compared to the synthetic zinc electrolyte which was used in this study).

2. 125°C appeared to be the optimum operation temperature beyond which a further temperature increase led to a lower extent of cobalt removal. In experiments conducted at 135 and 150°C, the lowest reachable cobalt concentration was above 1 mg/L, although a fast initial cobalt removal rate (compared to the cobalt removal rate at 85°C) was still observed at these temperatures. The observed drop in the cobalt removal extent might be related to the parasitic hydrogen evolution reaction which likely becomes the dominant zinc consuming reaction upon increasing temperature above 125°C. The existence of an

optimum temperature between 120 and 130°C was also confirmed in (Houlachi, Leroux, and Saint-Onge 1995).

3. Increasing the temperature not only improved the rate of cobalt removal, but also accelerated the rate of cobalt redissolution. The highest cobalt redissolution (defined here as the highest cobalt concentration at 60 min) occurred at 150°C - the highest tested temperature. In general, it seems that stability of the cobalt cement deteriorated as the temperature increased. This could be another explanation for not attaining low cobalt concentrations at 135 and 150°C.

Table 5-1. Vapor pressure of the solution at HT/HP tests.

<b>Tested temperature</b>	<b>Vapor pressure of the solution</b>
<b>(°C)</b>	<b>(psig)<sup>1</sup></b>
<b>110</b>	15
<b>125</b>	25
<b>135</b>	37
<b>150</b>	60

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<sup>1</sup> Vapor pressure of the solution at each tested temperature was lower than the vapor pressure of pure water at that temperature. This is because of the lower activity of H<sub>2</sub>O in the test solutions compared to that of pure water.



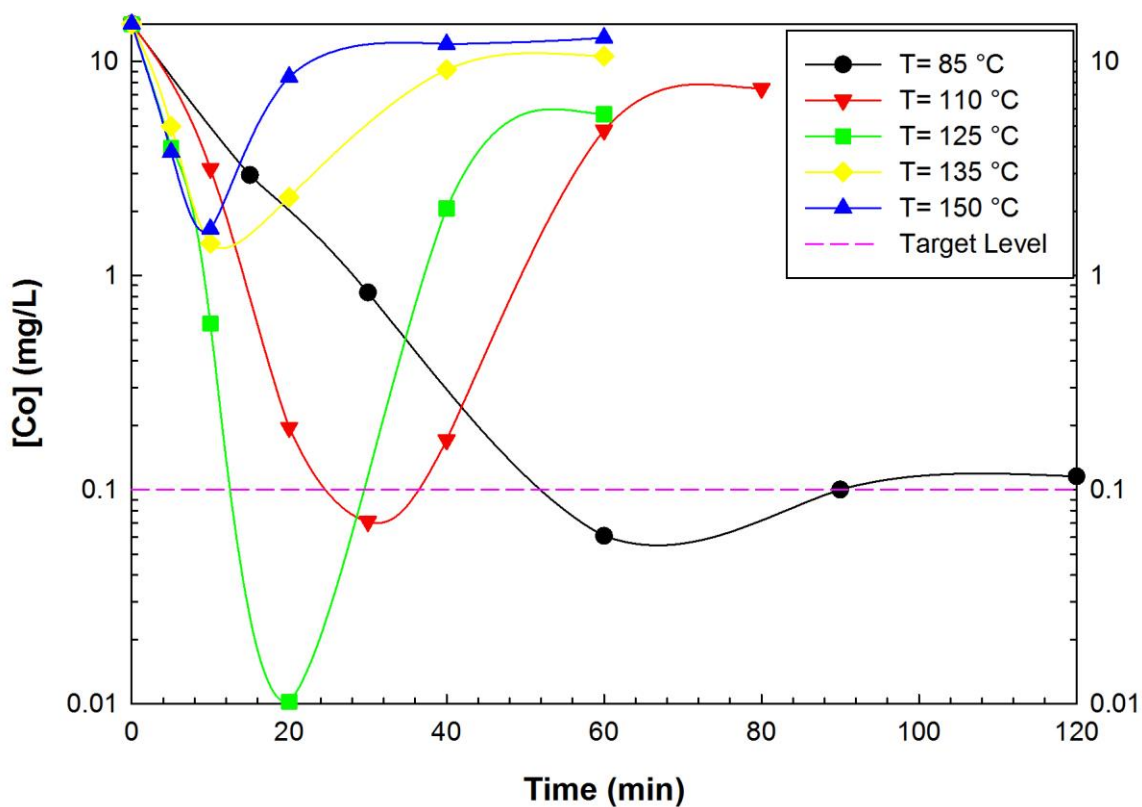


Figure 5-2. Effect of temperature on cobalt cementation (60 psig, 145 g/L  $\text{Zn}^{2+}$ , 45 mg/L  $\text{Cu}^{2+}$ , 2.5 mg/L  $\text{Sb}^{3+}$ , 3.5 g/L J.T.Baker zinc dust,  $P(80) = 95 \mu\text{m}$ ).

Increasing temperature affects reaction thermodynamics. The effect of temperature on electrochemical driving forces for the cobalt cementation and the hydrogen evolution reaction is shown in Figure 5-3 (The calculations have been provided in Appendix D). According to this figure, increasing temperature results in a decrease in the driving forces for both cobalt cementation and hydrogen evolution, however, the numbers presented in Table D-4 (presented in Appendix D) show that this decrease is more substantial for the hydrogen evolution reaction.

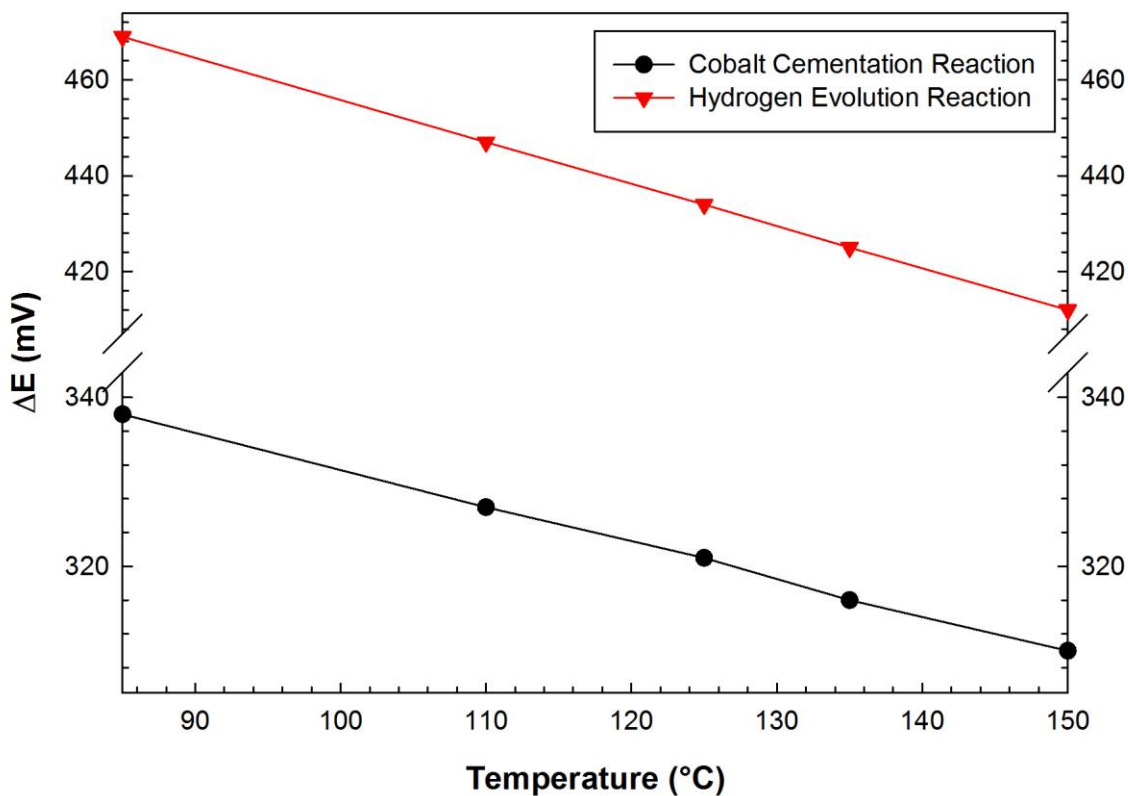


Figure 5-3. Effect of temperature on the electromotive driving force of the cobalt cementation and hydrogen evolution reaction.

### 5.3 Kinetic Studies

Many researchers have mentioned that cobalt cementation onto zinc dust follows a first order reaction mechanism ( $\ln C/C_0 = -kt$ ). This was investigated with the data provided in Figure 5-2. The results, provided in Figure 5-4, show that plotting  $-\ln C/C_0$  versus  $t$ , for all the tested temperatures, produced straight lines; this confirms the first order kinetics for the cobalt cementation reaction. The rate constant ( $k$ ) for the reaction at each tested temperature was obtained from the slope of the lines produced in Figure 5-4. These results (Table 5-2) show that

the rate constant increased with increasing temperature from 85 to 125°C (as expected) and then decreased as the temperature was increased to 135 and 150°C.

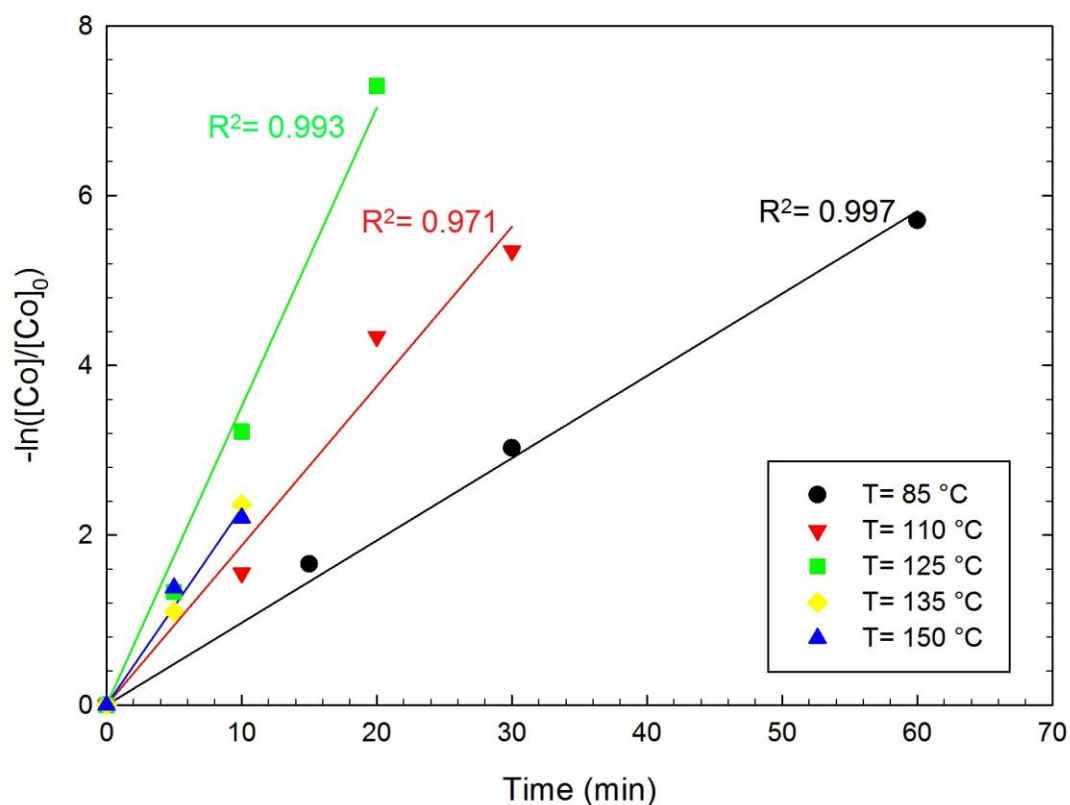


Figure 5-4. Effect of temperature on initial rate of cobalt removal (60 psig, 145 g/L  $Zn^{2+}$ , 45 mg/L  $Cu^{2+}$ , 2.5 mg/L  $Sb^{3+}$ , 3.5 g/L J.T.Baker zinc dust,  $P(80) = 95 \mu m$ ).

Table 5-2. Rate constant of cobalt removal at tested temperatures.

Temperature (°C)	Rate constant (min <sup>-1</sup> )	Normalized rate constant
85	0.0934	0.27
110	0.1878	0.53
125	0.3518	1
135	0.2331	0.66
150	0.2315	0.66

According to Arrhenius's law,  $k = A \exp\left(-\frac{E}{RT}\right)$ , plotting  $\ln k$  versus the inverse of absolute temperature yields a straight line, the slope of which represents  $-\frac{E}{R}$ , where  $E$  is the activation energy for the reaction and  $R$  is the gas constant (8.314 J/mol.K). Based on Arrhenius's law, the rate constant should be continuously increased with increasing temperature. However, as mentioned, the rate constant for the cobalt cementation reaction decreased with the increasing temperature above 125°C. This decrease in the rate constant might be explained as below:

1. The parasitic hydrogen evolution reaction, which competes with the cobalt cementation reaction to get electrons from the added zinc dust, probably became the dominant reaction at temperatures above 125°C. Therefore, as the amount of the added zinc dust to the solution was constant for all the tested temperatures, one can assume that the amount of zinc dust available for the cobalt cementation reaction significantly decreased at temperatures above 125°C. This could lead to a slow and incomplete cobalt removal or, in other words, to a decrease in the observed rate constant. This theory was proposed by Van der Pas (van der Pas 1995) to explain the drop observed in the rate of cobalt deposition from a zinc electrolyte when the temperature increased from 85 to 90°C.

2. The decrease in the rate of cobalt removal at temperatures above 125°C might also be related to severe cobalt cement redissolution at these temperatures. It should be noted that the rate of cobalt removal is determined from the trend of cobalt concentration in the solution during the experiments, and the cobalt concentration in the solution is the result of two reactions; the cobalt cementation reaction that consumes  $\text{Co}^{2+}$  ions and the cobalt cement redissolution reaction that generates  $\text{Co}^{2+}$  ions. It is apparent from Figure 5-2 that increasing the temperature above 125°C makes cobalt cement redissolution more severe (i.e. cobalt cement redissolution occurs more quickly). Therefore, one may postulate that at temperatures above 125°C, a very low cobalt concentration (i.e. a very high cobalt removal rate), cannot be attained because a significant portion of the cemented cobalt redissolves very quickly.

In Figure 5-5,  $\ln k$  versus  $\frac{1}{T}$  for temperatures 85, 110, and 125°C has been plotted. As Figure 5-5 shows, the data fits a straight line very well. The activation energy calculated from the slope of this line is 38 KJ/mol. This value for the activation energy for the cobalt cementation reaction is noticeably lower than the values reported in the literature (Table 5-3). The reported values in the literature indicate that the cobalt cementation reaction (at LT/LP conditions) is under chemical-reaction control. However, the lower activation energy obtained in this work suggests a mixed-control mechanism for the reaction. The observed difference in the activation energies (and subsequently in the proposed rate controlling steps) might indicate that the reaction (or mechanism) for cobalt removal changes when the operating temperature for the process is increased to temperatures higher than the boiling point of the solution. However, since in this study, cobalt cementation was not studied from a mechanistic viewpoint (e.g. morphology of the

cobalt cement was not studied), a comment regarding the details of this possible change cannot be provided.

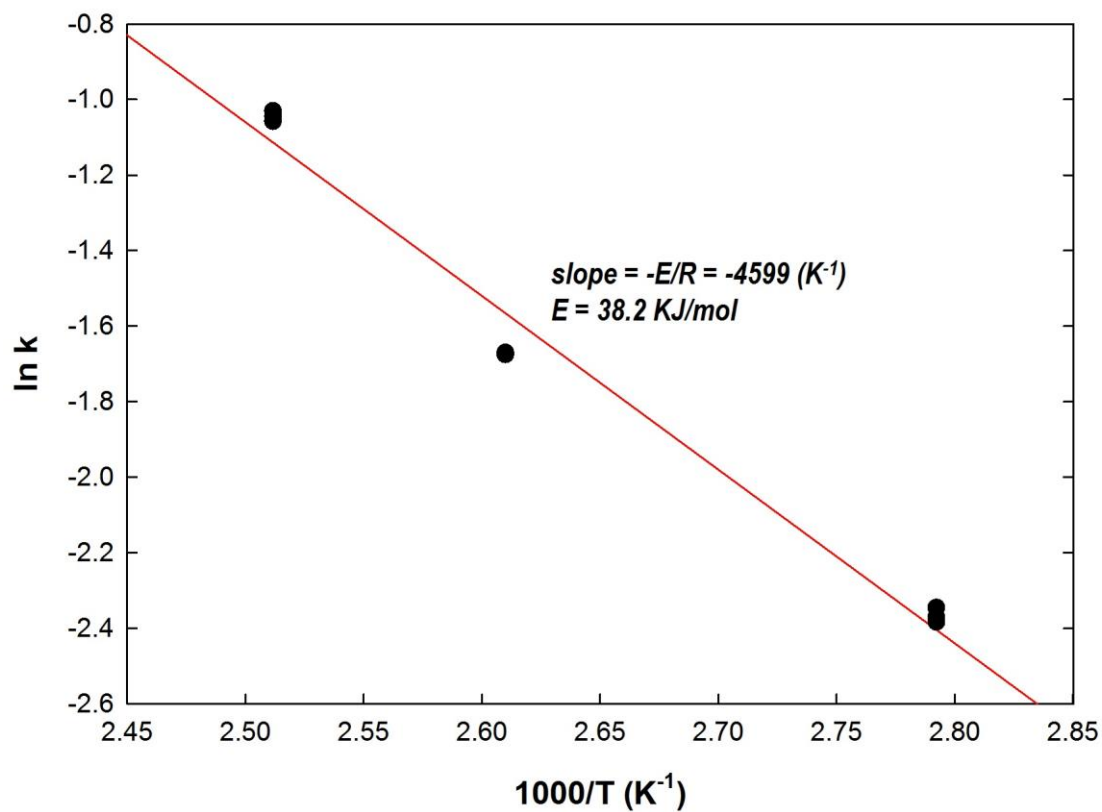


Figure 5-5. Arrhenius plot for the cobalt cementation reaction (85-125°C, 60 psig, 145 g/L  $Zn^{2+}$ , 45 mg/L  $Cu^{2+}$ , 2.5 mg/L  $Sb^{3+}$ , 3.5 g/L J.T.Baker zinc dust, P(80) = 95  $\mu m$ ).

Table 5-3. Reported values for the activation energy of the cobalt cementation reaction.

Reported Value (KJ/mol)	Tested temperatures (°C)	Test condition	Reference
86.6	65, 73, 80, 85, 90	46 mg/L Cu, 1.5 mg/L Sb, 4 g/L zinc dust	(Lew 1994)
51	85, 90, 95	30 mg/L Cu, 30 mg/L Cd, 30 mg/L Pb, 2 mg/L Sb, 5 g/L zinc dust	(Dreher et al. 2001)
80 ± 3	60, 65, 70, 75, 80, 85	200 mg/L Cu, 2 g/L zinc dust	(Dib and Makhoulfi 2006)
65	50, 60, 73, 85	Electrodeposition on Sb substrate, 30 A/m <sup>2</sup> current density	(van der Pas 1995)

#### 5.4 Zinc Dust Dosage

Zinc dust is certainly the most costly reagent used in the cobalt cementation process, thus reducing its quantity and finding its minimum required amount to meet the desired removal of cobalt is at the core of optimization studies done on the process. The effect of the initial concentration of the added zinc dust was investigated at 125°C and 60 psig and in the presence of 2.5 and 45 mg/L Sb and Cu, respectively. The quantity of zinc dust used in the experiments was 2.5, 3, 3.5, and 4 g/L which, noting the initial concentration of Co in the solution (15 mg/L), respectively corresponded to 150, 180, 210, and 240 times the stoichiometrically-required quantity for the cementation of Co.

From the obtained results, given in Figure 5-6, it can be inferred that an increase of zinc dust dosage from 2.5 to 3.5 g/L expectedly led to an increase in the degree of cobalt removal. 3.5 g/L zinc dust was found to be optimum for zinc dust addition, with which the target level of cobalt (0.1 mg/L) could be easily met in 20 min. Increasing zinc dust dosage from 3.5 to 4 g/L did not contribute to the cobalt removal extent (this might be related to the problem of reproducibility of the results for very low cobalt concentrations), however using 4 g/L zinc dust had a beneficial effect on decreasing the rate of the cobalt cement redissolution. In general, as the amount of zinc dust addition decreased, the cobalt cement redissolution became more severe.



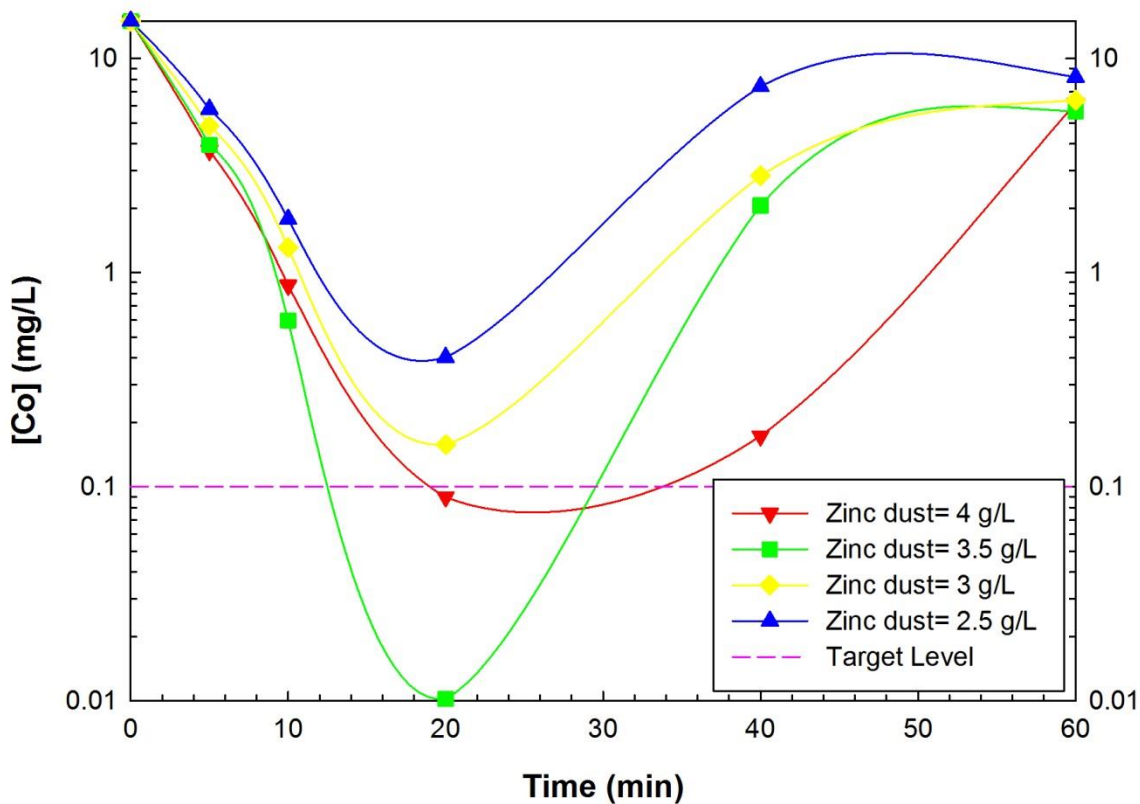


Figure 5-6. Effect of zinc dust dosage on cobalt cementation (125°C, 145 g/L  $\text{Zn}^{2+}$ , 45 mg/L  $\text{Cu}^{2+}$ , 2.5 mg/L  $\text{Sb}^{3+}$ , J.T.Baker zinc dust,  $P(80) = 95 \mu\text{m}$ ).

As the results show, even in laboratory scale work, a large excess of zinc dust addition is required to reach the desired cobalt removal. The amount of zinc dust excess can be higher in the industrial plants due to the complexity of the industrial electrolytes. It might be interesting to track the added zinc dust to determine how and where it deports. In total, one can assume three different destinations (paths) for the zinc dust added to the cobalt cementation stage:

1. A very small portion of the zinc dust is consumed (dissolved) with the cementation of cobalt and the activators (Cu and Sb in this work). This is the ideal usage for the added zinc dust.

2. A large portion of the zinc dust is consumed (dissolved) with the hydrogen evolution reaction. (Lu and Dreisinger 2014) reported that  $H_2$  evolution consumes over 100 times more zinc dust than the cobalt cementation. Although the dissolved zinc dust eventually gets recovered from the electrolyte at the EW stage, and theoretically can be recycled to the purification stages, the process of electrowinning consumes a significant amount of energy. As an example, the data provided in Appendix C show that introducing 6 g/L zinc dust for removal of Cu (1 g/L), Cd (1 g/L), and Co (20 mg/L), instead of 1.6 g/L (the stoichiometrically-required amount), leads to an approximately 2 million dollars per year of extra cost for zinc electrowinning (Houlachi 2012). To have a precise estimate for the cost of zinc dust recovery, the additional cost required for processing zinc to zinc dust should also be added to the mentioned value.
3. Besides the consumption of zinc dust with the hydrogen evolution reaction, passivation of the dust with zinc salts is another parasitic phenomenon which makes zinc dust inaccessible for the cobalt reduction reaction. The passivated (unreacted) zinc dust is transferred to the filter cake in the solid-liquid separation stages. Depending on the purification method, the zinc content in the cobalt-purification filter cake can vary from plant to plant. For instance, zinc contents of 75% (Rodier 1980) and 15% (Huggare, Ojanen, and Kuivala 1973) in the cobalt filter cake have been reported. One potentially economical approach to treat the cobalt-purification filter cake is to selectively leach the zinc content of the cake and recycle it to the zinc production circuit. The residue of the leaching can then be enriched and sold for its cobalt (Painter 1980; Stanojević, Nikolić, and Todorović 2000). In addition to the extra cost needed for extracting zinc from the cobalt-purification filter cake, specific care should be taken during leaching the filter

cake since redissolving cobalt can cause re-circulation of this impurity to the zinc production circuit.

## **5.5 Zinc Dust Particle Size**

Zinc dust particles with four different sizes (-75, -149 +75, -300 +149, and +300  $\mu\text{m}$  ) were used in this study to establish the effect of particle size on the cobalt cementation process at 125°C and 60 psig. The initial concentration of the zinc dust added was kept constant at 3.5 g/L in all the tests examining particle size effects. The results, presented in Figure 5-7, show that the rate of cobalt cementation increased with decreasing particle size (as expected). This is obviously because of the larger surface area provided by the smaller particles.

Besides the effect of particle size on the cobalt cementation, its impact on the cement redissolution is also interesting. As Figure 5-7 shows, for the smallest particles (-75  $\mu\text{m}$ ), the cemented cobalt started to redissolve after 20 min. This happened a little later for the particles within the range of -149 +75  $\mu\text{m}$ , and in the case of particles within the -300 +149  $\mu\text{m}$  and +300  $\mu\text{m}$  ranges, the cobalt redissolution did not occur over the 60 min duration of the experiments. The observed results for the effect of zinc dust particle size on the cobalt cementation and redissolution are the same when the process is practiced at LT/LP condition (Bøckman and Østvold 2000b; Zeng, Li, and Xie 2012).

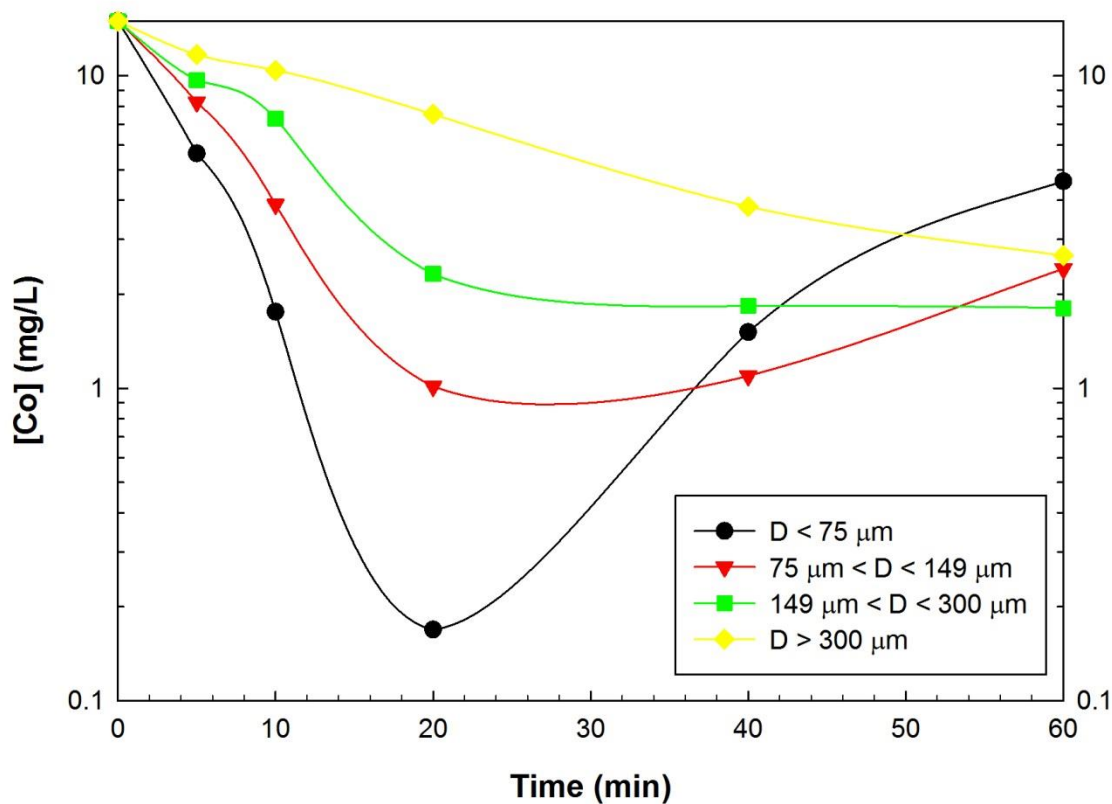


Figure 5-7. Effect of zinc dust particle size on cobalt cementation ( $125^{\circ}\text{C}$ ,  $145 \text{ g/L Zn}^{2+}$ ,  $45 \text{ mg/L Cu}^{2+}$ ,  $2.5 \text{ mg/L Sb}^{3+}$ ,  $3.5 \text{ g/L CEZinc}$  zinc dust).

## 5.6 Additives

One aim of this study was to determine if the need for the addition of activators can be removed by running the cobalt cementation process at HT/HP condition. To test this the cementation experiments were run: without any activator, with  $45 \text{ mg/L Cu}$ , and with  $2.5 \text{ mg/L Sb}$ . The results were compared with the baseline experiment, where both of the activators ( $45 \text{ mg/L Cu} + 2.5 \text{ mg/L Sb}$ ) were present in the solution. According to the obtained results (Figure 5-8):

1. Cobalt removal in the absence of the activators is almost negligible even at the HT/HP condition. In this test, the cobalt concentration went down from the initial level of 15 mg/L to 11 mg/L in the first 5 min and did not change significantly for the remainder of the test.
2. Addition of copper improved cobalt removal to some extent. In this test the minimum cobalt concentration (5.7 mg/L) was reached at 60 min and after that a minor cement redissolution was observed, so that the cobalt concentration at 90 min became 5.8 mg/L.
3. Removal of cobalt was significantly enhanced in the presence of Sb. With the presence of Sb in solution, a cobalt concentration as low as 0.27 mg/L was observed at 60 min, and after that the cement started to redissolve. Although the minimum reachable cobalt concentration in this test was close to that of the baseline experiment (0.17 mg/L), the rate of cobalt removal was significantly slower.

The observed effect of the activators at HT/HP condition was similar to their effect at LT/LP condition. The cobalt cementation tests at typical LT/LP condition also showed that Sb gives better results than Cu in terms of cobalt removal; however, the best cobalt removal was achieved when both of the activators were present in the solution (Lew 1994; Nelson 1998).

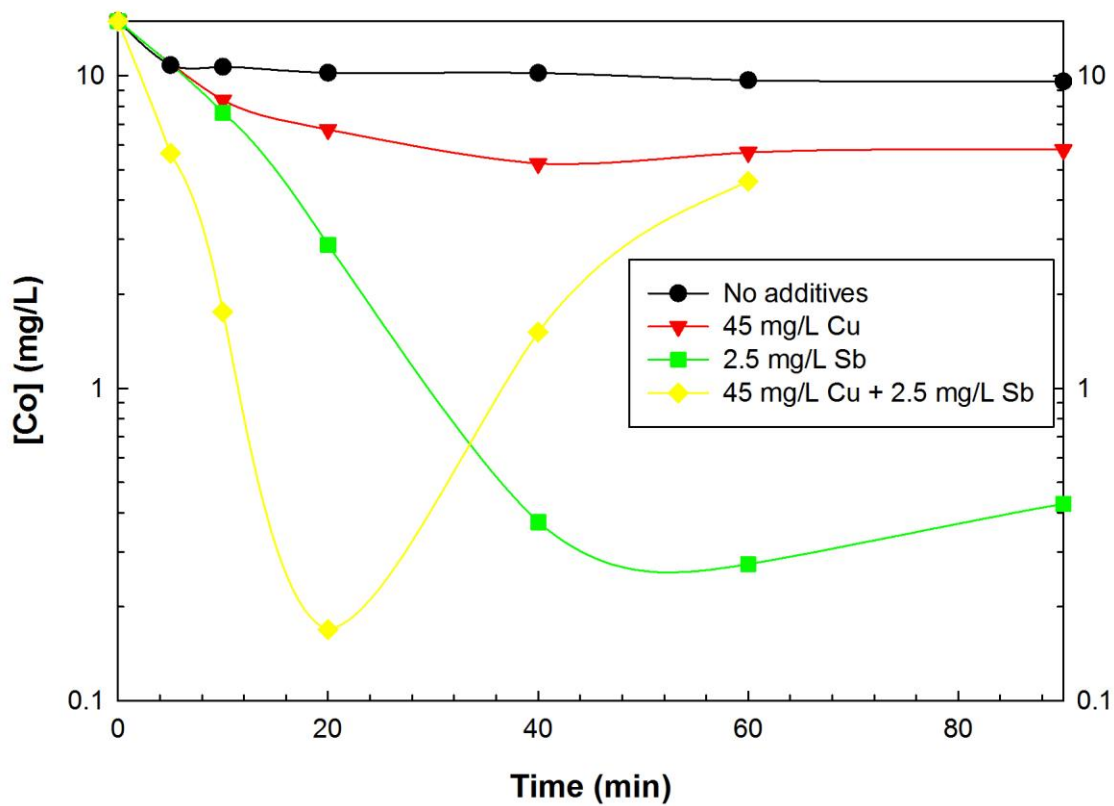


Figure 5-8. Effect of additives on cobalt cementation (125°C, 60 psig, 145 g/L Zn<sup>+</sup>, 3.5 g/L CEZinc zinc dust, P(80) = 94 μm).

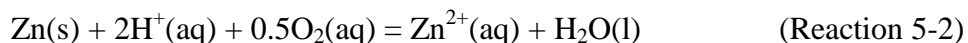
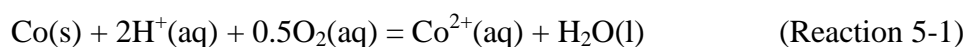
## 5.7 Cobalt Cement Redissolution

One of the issues that can be noticed from the cobalt removal profile at HT/HP condition is the severe cobalt cement redissolution, which can begin as early as 20 min from the commencement of the experiments. Cobalt cement redissolution is also a problem that occurs during LT/LP cobalt cementation (Boyanov, Konareva, and Kolev 2004a; Zeng, Li, and Xie 2012), however, it is intensified as the process is operated at higher temperatures. There are different theories proposed to explain the redissolution of cobalt cement. Although all of these

theories have been proposed for the cementation process carried out in the typical LT/LP condition, they might be helpful in explaining the observed cobalt redissolution during the HT/HP tests, too.

### ***1. Oxygen***

Dissolved oxygen in the solution is one of the well-known sources for the cobalt cement redissolution. The presence of oxygen in the solution will cause the following reactions (Nelson 1998):



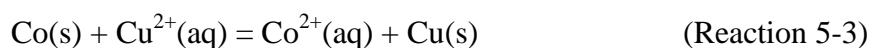
At 95°C and atmospheric condition, oxygen solubility in zinc electrolyte is less than 9 mg/L, but even such a low concentration can have a significant impact on the cobalt cement redissolution and zinc dust consumption (Nelson 1998). Bubbling nitrogen gas in the solution is the common way to deoxygenate the solution, however, its implementation in the industrial zinc purification stages may be considered too expensive (Zeng, Li, and Xie 2012).

Zeng's experiments (Zeng, Li, and Xie 2012) showed that putting Ni-Co purification residues in contact with air (for 7 days) increases the solubility (redissolution) of Co and Cd in zinc electrolyte considerably. During the selective leaching of zinc from the cobalt-purification filter cake, it is important to prevent oxidation of cobalt by air since cobalt oxide is much easier to dissolve in sulfuric acid than the metallic cobalt (Stanojević, Nikolić, and Todorović 2000).

Although oxygen can play a significant role in redissolution of the cobalt cement in industrial zinc plants, it does not seem to be the reason of the observed cobalt cement redissolution in this work, because the test solution as well as the autoclave atmosphere was deoxygenated with N<sub>2</sub> sparging before commencement of the experiments. Also, all the tests were carried out under a nitrogen atmosphere, thus it would not be possible for oxygen to enter the solution during the experiment to redissolve the cobalt cement.

## **2. Additives (Cu)**

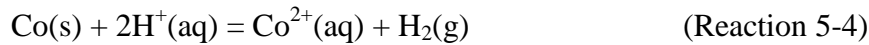
Salin (Salin 1964) explained the redissolution of cobalt by Reaction 5-3, and he believes that this reaction will occur even if the zinc dust dosage is enough to cement Cu<sup>2+</sup> ions. Zeng et al. (Zeng, Li, and Xie 2012) showed that the cobalt cement redissolution does not occur in the absence of copper in the solution. However, these researchers believe that copper cannot cause the cobalt cement redissolution with the mechanism proposed by Salin, because their experiments showed that the copper cement redissolution also takes place simultaneously with the cobalt redissolution. Zeng et al. believe that the role of copper in the cobalt cement redissolution can be indirect; for example, they noticed that addition of copper to the cementation system results in formation of Co(OH)<sub>2</sub> in the cement; the species that is known to be less stable and easily dissolvable in acidic conditions (Bøckman and Østvold 2000b). The role of cobalt basic salts in the cobalt cement redissolution will be discussed in more detail later in this section.





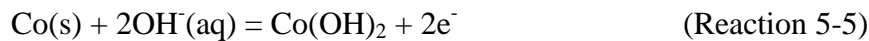
### 3. Hydrogen Evolution

Corrosion of the cobalt cement by the hydrogen evolution reaction (Reaction 5-4) has also been proposed as the mechanism for the cobalt cement redissolution (Dib and Makhoulfi 2007). From a thermodynamic viewpoint,  $H^+$  ions prefer to get electrons from Zn compared to Co. However when all the available metallic zinc has been used or passivated so that  $H^+$  ions cannot reach the zinc dust surface, it is possible that these ions start to get reduced on the cobalt cement- the reaction which progressively dissolves the cobalt cement.



### 4. Transformation of Co to $Co(OH)_2$

West-Sells (West-Sells 1996) has proposed Reaction 5-5 as an explanation for the cobalt deposit redissolution during electrodeposition of cobalt from zinc containing electrolyte. According to the West-Sells' experiments, and the Eh-pH diagram for Co-Zn- $H_2O$  system, at  $75^\circ C$ , Reaction 5-5 takes place at  $-0.700\text{ V}$  (vs SCE), and pH higher than 8. West-Sells believes that this high pH can be reached on the cathode surface when  $Zn(OH)_2$  precipitates on the interface and blocks ionic diffusion of  $H^+$  to the solid surface. In this condition, the bulk pH is still around 5, and therefore a pH difference in the order of 3 can be observed between the bulk of the solution and the solid surface.



## 5. Cobalt Basic Salts

Bockman and Ostvold (Bøckman and Østvold 2000b) believe that the redissolution of cobalt cement is from the part of the cement which is in the form of basic cobalt salts. Dissolution tests performed in Bockman's study showed that these basic salts redissolved in 0.1 M HCl in about 20 s, while the part of the cement which was in the form of metallic cobalt or cobalt in solid solution showed no redissolution. The formation of basic cobalt salts on zinc dust is related to high local pH on the zinc dust surface, which is created by the hydrogen evolution reaction. Bockman and Ostvold believe that when all the metallic zinc is consumed, this high pH on the zinc dust surface cannot be maintained, and in consequence the basic cobalt salts start to redissolve.

From these theories, it can be concluded that the cobalt cement redissolution is affected by many parameters and sometimes the presented explanations for the redissolution mechanism are contradictory. For instance, as mentioned, West-sells (West-Sells 1996) attributes the cobalt cement redissolution to a high pH (i.e. pH 8) reached on the solid-liquid interface due to the passivation of the solid surface by zinc salts. On the other hand Bockman and Ostvold (Bøckman and Østvold 2000b) believe that the cobalt cement starts to redissolve when the local high pH on the surface of zinc dust cannot be maintained. It would definitely be ideal if there was a way to monitor pH at the surface of the zinc particles at HT/HP conditions to know whether West-Sells' or Bockman and Ostvold's explanation is applicable to the observed cobalt redissolution in this work. However, noting the above mentioned theories and with respect to the effects of the tested variables on the cobalt cement redissolution, the following conclusions can be drawn regarding the cobalt cement redissolution at HT/HP conditions:

1. In contrast to Bockman and Ostvold's theory, basic cobalt salts are not the only source of cobalt redissolution at HT/HP conditions. The results of the cobalt cementation tests, especially those run at 135 and 150°C, show that almost all of the cemented cobalt redissolves in 40 min. Therefore it can be inferred that in addition to the basic cobalt salts, the stability of the metallic cobalt cement (or cobalt in solid solution) also decreases upon increasing temperature.
2. The lower stability of the cobalt cement at higher temperatures can be related to the accelerated hydrogen evolution reaction at these temperatures, which corrode the cobalt cement when the metallic zinc is inaccessible. The fact that increasing zinc dust dosage suppresses (or delays) the cobalt cement redissolution could be evidence for the importance of hydrogen evolution on the cobalt cement redissolution.
3. According to the results presented in section 5.6, cobalt cement redissolution is very slow and negligible when the activators are introduced to the solution individually, although the rate of cobalt removal is slow in these cases as well. In general, it can be stated that at HT/HP condition when the rate of cobalt removal is fast, the cobalt cement redissolution occurs rapidly, too.

## **5.8 Pressure**

Studying the effect of pressure on cobalt cementation is divided into two subsections; pressure applied with 100% N<sub>2</sub> gas and pressure applied with 98% N<sub>2</sub> + 2% H<sub>2</sub> gas.

### **5.8.1 Pressure Applied with 100% N<sub>2</sub> Gas**

The impact of solution's overhead pressure, created by 100% N<sub>2</sub> gas, on the cobalt removal was studied at 85°C. As N<sub>2</sub> has no effect in the reactions occurring during the cobalt removal

process, it was not expected that changing  $N_2$  pressure would significantly alter the cobalt cementation process. Its impact could be limited to some physical parameters. The results, presented in Figure 5-9, show that increasing  $N_2$  pressure did not affect the kinetics of cobalt cementation. It caused minor differences in the extent of cobalt removal and the cobalt cement redissolution, however, a solid conclusion regarding the effect of  $N_2$  pressure cannot be made based on these differences. These differences might have arisen from the poor reproducibility of the results at low cobalt concentrations ( $[Co] < 0.1$  mg/L).

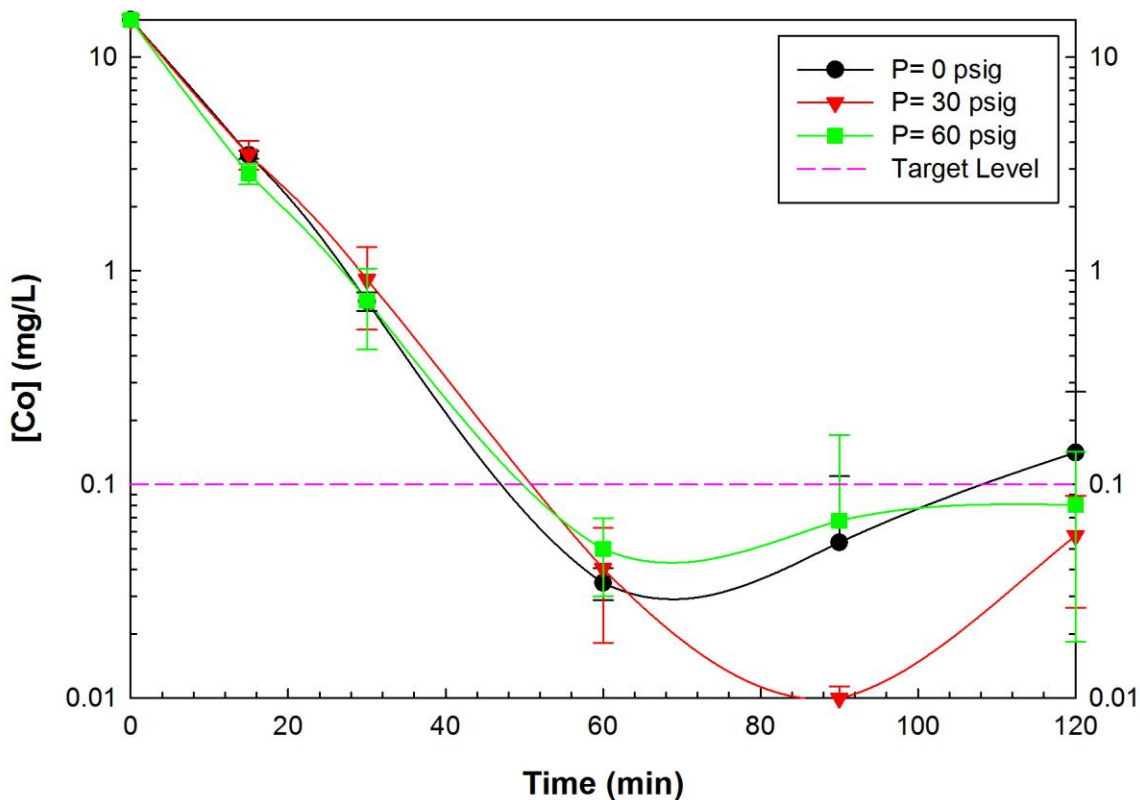


Figure 5-9. Effect of pressure on cobalt cementation ( $85^{\circ}\text{C}$ ,  $145$  g/L  $\text{Zn}^{2+}$ ,  $45$  mg/L  $\text{Cu}^{2+}$ ,  $2.5$  mg/L  $\text{Sb}^{3+}$ ,  $3.5$  g/L CEZinc zinc dust,  $P(80) = 94$   $\mu\text{m}$ ).

### 5.8.2 Pressure Applied with 98% N<sub>2</sub> and 2% H<sub>2</sub> Gas

Increasing partial pressure of H<sub>2</sub> in the reactor is important because it leads to a decrease in the electromotive driving force for the hydrogen evolution reaction and consequently can suppress this reaction. Suppressing the hydrogen evolution reaction is critical since it can save a significant amount of zinc dust for the cobalt cementation reaction. The effect of  $P_{H_2}$  on the electromotive driving force of the hydrogen evolution reaction can be predicted by the Nernst equation (calculations are provided in Appendix D); the results in the  $P_{H_2}$  range of 0.56-3 atm (8.2- 44.1 psig) are shown in (Figure 5-10).

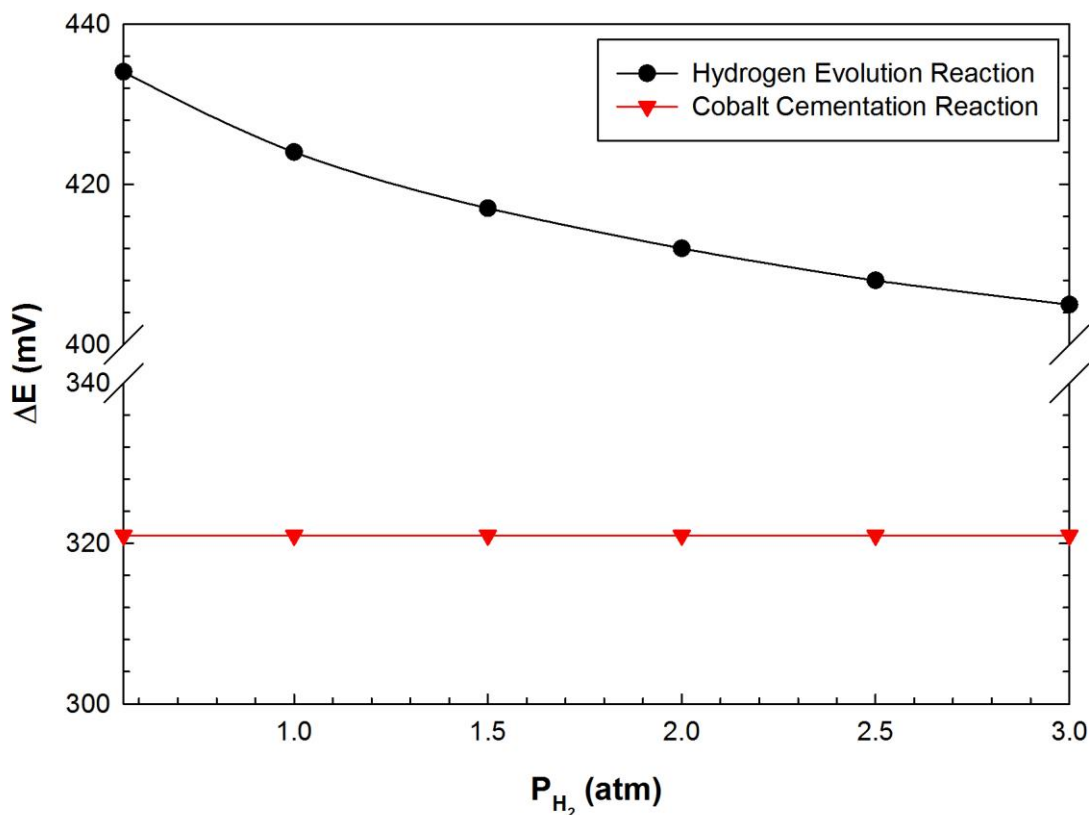


Figure 5-10. Effect of partial pressure of hydrogen gas on the electromotive driving force of the hydrogen evolution reaction.

In HT/HP cobalt cementation process,  $P_{H_2}$  is governed by two sources:

1. The hydrogen evolution reaction itself generates  $H_2$  gas and therefore leads to a continuous increase in  $P_{H_2}$  as the process goes forward. The amount of evolved hydrogen gas can be significant; this can be noticed from the large amount of zinc dust consumed by the hydrogen evolution reaction. As an example, Lu (Lu and Dreisinger 2014) reported that at  $85^\circ\text{C}$  (and with experimental conditions very close to those of this study) in total, 19 mmol  $H_2$  (per liter of the solution) evolves during 90 min the cobalt cementation process. Considering the volume of the autoclave, this amount of  $H_2$  corresponds to a  $P_{H_2}$  of 0.56 atm or 8.2 psig (The detailed calculations have been provided on page 107). However, it should be noted that the  $P_{H_2}$  created by the hydrogen evolution reaction is not a constant value in course of the experiment's time, so that it increases from the initial value of 0 psig (when zinc dust is added to the solution) to its maximum value at the end of the experiment.
2.  $P_{H_2}$  in the autoclave can also be increased by injecting  $H_2$  gas through the application of an external gas source. In contrast to the previous source of  $H_2$ , which cannot be controlled during the process, the amount of  $H_2$  injected to the reactor can be changed as an experimental variable. However, it should be noted that from a safety perspective using  $H_2$  gas with high purities is not recommended since it can be extremely explosive. In this research, a gas with 2%  $H_2$  and 98%  $N_2$ , which is not explosive, was used.

Two sets of experiments were carried out at  $125^\circ\text{C}$  to study the effect of  $P_{H_2}$ ; In the first experiment the total pressure over the solution was 60 psig and in the second 100 psig (as mentioned, the external gas composition was 2%  $H_2$  and 98%  $N_2$  in these tests). Cobalt removal

in these experiments was compared with the baseline experiment at 125°C, where the total pressure over the solution was kept constant at 60 psig using 100% N<sub>2</sub> gas. According to the obtained results, given in Figure 5-11, the cobalt removal profile in these experiments did not change noticeably. This might be explained as follows:

1. The increase in the  $P_{H_2}$  was not significant. For example, in the experiment with  $P_t = 100$  psig, the  $P_{H_2}$  created by the external gas was only 1.5 psig<sup>1</sup> (0.1 atm). This causes a very small change in  $P_{H_2}$  because in all the three experiments, regardless of the composition of the applied external gas, a high  $P_{H_2}$  is created by the hydrogen evolution reaction, as discussed before. In order to generate a noticeable increase in  $P_{H_2}$  with an external gas, a gas with very high purity of H<sub>2</sub> should be used.
2. Although the development of hydrogen overpressure decreases the electromotive driving force for the hydrogen evolution reaction on zinc dust, the reaction in practice is so favorable that any “back reaction” impact is unlikely to be effective in stopping it.

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<sup>1</sup>100 psig (total pressure) – 25 psig (vapor pressure of the solution at 125°C) =  
75 psig (pressure of the applied external gas)

75 psig (pressure of the applied gas) × 2% = 1.5 psig (partial pressure of H<sub>2</sub>)

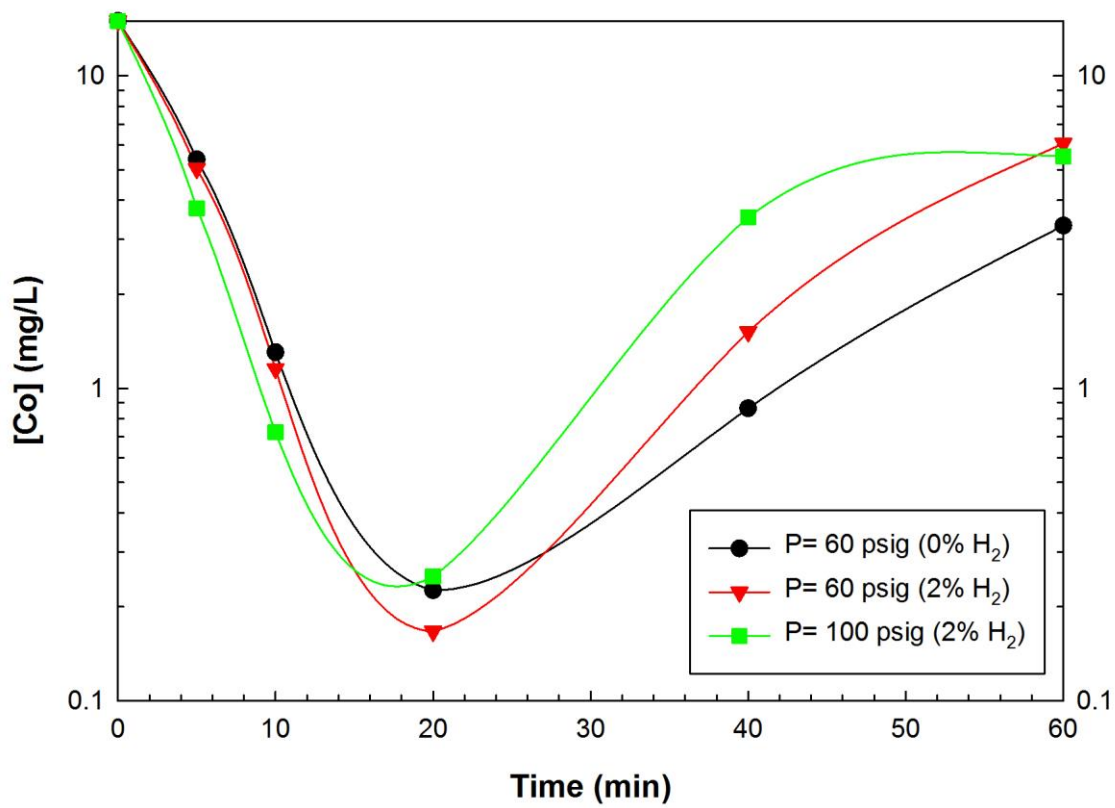


Figure 5-11. Effect of H<sub>2</sub> gas on cobalt cementation (125°C, 145 g/L Zn<sup>2+</sup>, 45 mg/L Cu<sup>2+</sup>, 2.5 mg/L Sb<sup>3+</sup>, 3.5 g/L J.T.Baker zinc dust, P(80) = 108 μm).



## 6 Conclusions

The aim of this research was to study the effect of different variables on the cobalt cementation process at high temperature (100-150°C) and high pressure (0-100 psig) conditions.

The results obtained from this study can be summarized as follows:

1. pH control during the cobalt cementation process was not necessary. The tests conducted at 85°C (and at atmospheric condition) showed that the absence of pH control leads to a higher initial cobalt removal rate. However, minor cement redissolution was observed in the tests performed without pH control.
2. Conducting the cobalt cementation tests at high temperatures (100-150°C) showed a significant improvement in the rate of cobalt removal. The optimum temperature was found to be 125°C - temperature at which the target level of cobalt removal (meeting the cobalt concentration of 0.1 mg/L) could be reached in 20 min. This is one-third of the required retention time for the process when it is practiced at the typical LT/LP condition. Carrying out the cobalt cementation tests at HT/HP also significantly increased the rate of cobalt cement redissolution.
3. At 125°C and in the presence of 2.5 mg/L Sb and 45 mg/L Cu, 3.5 g/L zinc dust was found to be the optimum zinc dust addition to lower cobalt concentration from the initial level of 15 mg/L to below 0.1 mg/L. Decreasing zinc dust dosage (below 3.5 g/L) not only caused the target level of cobalt not to be met, but also increased the cobalt cement redissolution.
4. Smaller zinc dust particles gave better results in terms of the rate and extent of cobalt removal. However, the cobalt cement redissolution occurred more quickly with smaller particles compared to larger particles.

5. Sb (2.5 mg/L) had a more substantial effect than Cu (45 mg/L) on the cobalt cementation.

At 125°C, with addition of Sb to the solution (and without Cu addition), the cobalt concentration could be lowered to 0.27 mg/L in 60 min. However, the best result for cobalt removal (in terms of the extent and rate of removal) was obtained when both of the activators were present in the solution simultaneously.

6. As expected, increasing the overhead pressure of N<sub>2</sub> (tested at 85°C) did not alter the cobalt removal profile remarkably. Also, the effect of increasing the partial pressure of H<sub>2</sub> (tested at 125°C) on cobalt removal was negligible.

## 7 Recommendations for Future Work

A synthetic zinc electrolyte was used in all the experiments carried out in this work. There are evidences reporting that cobalt removal from industrial zinc electrolyte can be slightly different compared to the condition where synthetic zinc electrolyte is used (Industrial zinc electrolyte contains different components that may interfere in the cobalt cementation process). Therefore, it is critical that a future study focuses on reproducing the results obtained in this work using an industrial zinc electrolyte.

This research showed that conducting the cobalt cementation process at HT/HP condition not only enhances the rate of cobalt removal, but also accelerates the rate of cobalt cement redissolution. Redissolution of cobalt cement is totally undesirable and future work in this area may focus on better understanding the causes of this issue at HT/HP condition. For instance, it is believed that a noticeable portion of the redissolution is related to pH change in the surface of zinc dust where the reactions take place, so developing a technique to monitor pH at the zinc dust surface can provide valuable insight on the reason of the cobalt cement redissolution.

The separate effect of the activators (45 mg/L Cu and 2.5 mg/L Sb) on cobalt cementation at 125°C was studied in this research. It was shown that the influence of Sb is more substantial than Cu, and the best cobalt removal (in terms of rate and extent) is achieved when both of the activators are present in the solution simultaneously. It would be interesting if a future work would focus on optimizing the concentrations of the added activators to the solution at 125°C. HT/HP cobalt cementation, because of the increased rate of cobalt removal, may require lower amounts of the activators compared to the LT/LP conditions.

This work focused on studying the effect of different parameters at HT/HP condition on the kinetics of cobalt removal, and no investigation was performed to study the influence of the

variables on the morphology and composition of the cement products formed on zinc dust. Previous studies have reported that using zinc dust to study the cement products usually is not successful. For example, it is very difficult to cut zinc dust and analyze a cross section. Conducting the HT/HP cobalt cementation experiments in an electrochemical cell where the reduction reactions take place on a substrate (e.g. on a rotating zinc disc) can be an alternative for studying the cement products. Such study will also provide a better understanding of the mechanism of cobalt cementation at HT/HP condition.

## References

### References

- Asselin, E. 2013. "Advanced Hydrometallurgy (MTRL 559) Course Notes."
- Blander, F. and R. Winand. 1975. *Electrochimica Acta* 20:839-852.
- Blaser, M. S. and T. J. O'Keefe. 1983. "Screening Design Test for Cobalt Cementation from Zinc Electrolyte." *Metallurgical Transactions B* 14(3):495-497.
- Bøckman, Oluf and Terje Østvold. 2000a. "The Influence of Tartrate on Cobalt Cementation on a Rotating Zinc Disc in Zinc Sulphate." *Hydrometallurgy* 55(1):107-112.
- , 2000b. "Products Formed during Cobalt Cementation on Zinc in Zinc Sulfate Electrolytes." *Hydrometallurgy* 54(2-3):65-78.
- Bøckman, Oluf, Terje Østvold, George A. Voyiatzis and George N. Papatheodorou. 2000. "Raman Spectroscopy of Cemented Cobalt on Zinc Substrates." *Hydrometallurgy* 55(1):93-105.
- Boyanov, B., V. Konareva and N. Kolev. 2004a. "Purification of Zinc Sulfate Solutions from Cobalt and Nickel through Activated Cementation." *Hydrometallurgy* 73:163-168.
- , 2004b. "Removal of Cobalt and Nickel from Zinc Sulfate Solutions using Activated Cementation." *J. Min. Metall.* 40B(1):41-55.

- Brove, K. and T. Ostvold. 1994. "Norzink Removal of Cobalt from Zinc Sulphate Electrolytes.":563-577.
- Cao, Yang and Paul Duby. 2001. "Cobalt Cementation with Ferromanganese." *Hydrometallurgy* 61(3):195-205.
- Dib, A. and L. Makhoulfi. 2006. "Mass Transfer Correlation of Simultaneous Removal by Cementation of Nickel and Cobalt from Sulphate Industrial Solution Containing Copper: Part II: Onto Zinc Powder." *Chemical Engineering Journal* 123(1–2):53-58.
- , 2007. "Mass Transfer Correlation of Simultaneous Removal by Cementation of Nickel and Cobalt from Sulfate Industrial Solution Containing Copper: Part I: Onto Rotating Zinc Electrode Disc." *Chemical Engineering Journal* 130(1):39-44.
- Dreher, Trina M., Amy Nelson, George P. Demopoulos and Dimitrios Filippou. 2001. "The Kinetics of Cobalt Removal by Cementation from an Industrial Zinc Electrolyte in the Presence of Cu, Cd, Pb, Sb and Sn Additives." *Hydrometallurgy* 60(2):105-116.
- Esna-Ashari, M. F., H. 1983. "Purification of Zinc Solutions for the Tankhouse." 184:83-84,85.
- Friedrich, B., J. Kruger and M. B. Graciela. 2001. "Alternative Solution Purification in the Hydrometallurgical Zinc Production.".
- Fugleberg, S., A. Jarvinen and V. Sipila. 1980. "Solution Purification at the Kokkola Zinc Plant.".

Habashi, F. 1997. "Zinc." Pp. 641-679 in *Handbook of extractive metallurgy.*, edited by F.

Habashi.

Harlamovs, J. and S. Sharpe. 2014. "UBC Hydrometallurgy Research Chair Yearly Meeting."

Houlachi, G. 2012. "Zinc Electrowinning; Purification and Electrolysis."

Houlachi, G., F. Belanger and F. Principe. 1990. "International Symposium of Electrometallurgy  
Plant Practice.":177.

Houlachi, G., G. Leroux and J. P. Saint-Onge. 1995. "Process for the Removal of Cobalt  
Impurities from Zinc Sulfate Solutions."

Huggare, T. L., A. Ojanen and A. Kuivala. 1973. "How Zinc Concentrates are Processed at the  
Outokumpu Zinc Plant in Kokkola.":771-805.

Jiang, K., H. Wang and L. Li. 2014. "Hydrometallurgical Developments in the Zinc Industry in  
China." 1:17-31.

Jun, D., W. De-quan, J. Lan and J. Man. 2002. "Removal of Cobalt from Zinc Sulphate Solution  
using Rude Antimony Trioxide as Additive." *Trans. Nonferrous Met. Soc. China*  
12(6):1172-1175.

Karavasteva, M. 2001. "The Effect of Certain Surfactants on the Cementation of Cobalt from  
Zinc Sulphate Solutions by Suspended Zinc Particles in the Presence of Copper Or  
Antimony." *Canadian Metallurgical Quarterly* 40:179-184.

- Kayin, P. B. 2003. "Removal of Cobalt from Zinc Sulphate Solution by Cementation Prior to Zinc Electrowinning.", The Middle East Technical University, .
- Lew, R. W. 1994. "The Removal of Cobalt from Zinc Sulphate Electrolytes using the Copper-Antimony Process."
- Lu, Jianming and D. B. Dreisinger. 2014. "Cobalt Removal from Zinc Sulfate Solution with Zinc Dust- a New Understanding."
- Lu, Jianming, D. B. Dreisinger and W. C. Cooper. 1997. "Cobalt Precipitation by Reduction with Sodium Borohydride." *Hydrometallurgy* 45(3):305-322.
- Mackinnon, D. J., R. M. Morrison and J. M. Brannen. 1986. "The Effect of Nickel and Cobalt and their Interaction with Antimony on Zinc Electrowinning from Industrial Acid Sulphate Electrolyte." *Journal of Applied Electrochemistry* 16:53-61.
- Maja, M. and P. Spinelli. 1971. "Detection of Metallic Impurities in Acid Zinc Plating Baths." *Journal of the Electrochemical Society* 118(9):1538-1540.
- Morrison, R. M., D. J. Mackinnon, D. A. Uceda, P. E. Warren and J. E. Mouland. 1992. "The Effect of some Trace Metal Impurities on the Electrowinning of Zinc from Kidd Creek Electrolyte." *Hydrometallurgy* 29:413-430.
- Mureşan, Liana, G. Maurin, L. Oniciu and Delia Gaga. 1996. "Influence of Metallic Impurities on Zinc Electrowinning from Sulphate Electrolyte." *Hydrometallurgy* 43(1–3):345-354.



- Musadaidzwa, J. M. and E. I. Tshiningayamwe. 2009. "Skorpion Zinc Solvent Extraction: The Upset Conditions." *The Journal of the South African Institute of Mining and Metallurgy* 109:691-695.
- Nelson, A., G. P. Demopoulos and G. Houlachi. 2000. "The Effect of Solution Constituents and Novel Activators on Cobalt Cementation." *Canadian Metallurgical Quarterly* 39(2):175-186.
- Nelson, A., W. Wang, G. P. Demopoulos and G. Houlachi. 2000. "The Removal of Cobalt from Zinc Electrolyte by Cementation: A Critical Review." *Mineral Processing and Extractive Metallurgy Review* 20(4-6):325-356.
- Nelson, A. 1998. "Novel Activators in Cobalt Removal from Zinc Electrolyte by Cementation.".
- Omar Zahir, K. and H. Keshtkar. 1998. "A Colorimetric Method for Trace Level Determination of Cobalt in Natural and Waste Water Samples." *International Journal of Environmental Analytical Chemistry* 72(2):151-162.
- Outokumpu. "HSC Chemistry 5.11.".
- Owusu, George. 1998. "Oxidation–precipitation of Co from Zn–Cd–Co–Ni Sulphate Solution using Caro's Acid." *Hydrometallurgy* 48(1):91-99.
- Painter, L. A. 1980. "The Electrolytic Zinc Plant of Jersey Miniere Zinc Company at Clarksville, Tennessee.":124-143.

- Polcaro, Anna M., S. Palmas and S. Dernini. 1995. "Kinetics of Cobalt Cementation on Zinc Powder." *Ind. Eng. Chem. Res.* 34(9):3090-3095.
- Raghavan, R., P. K. Mohanan and S. K. Verma. 1999. "Modified Zinc Sulphate Solution Purification Technique to Obtain Low Levels of Cobalt for the Zinc Electrowinning Process." *Hydrometallurgy* 51(2):187-206.
- Rodier, D. D. 1980. "The Canadian Electrolytic Zinc Sulphate Solution Purification Process and Operating Practice.":144-157.
- Safarzadeh, Mohammad S., Nikhil Dhawan, Mustafa Birinci and Davood Moradkhani. 2011. "Reductive Leaching of Cobalt from Zinc Plant Purification Residues." *Hydrometallurgy* 106(1–2):51-57.
- Salin, A. A. 1964. *Tsvetn Metals (in Russian)* 37:46-51.
- Sandberg, R. G. and T. L. Hebble. 1978. "Cobalt and Nickel Removal from Zinc Sulphate Electrolyte by Solvent Extraction and Precipitation Techniques.":1-17.
- Sinclair, Roderick J. 2005. *The Extractive Metallurgy of Zinc*. Australia: AusIMM.
- Singh, Vakil. 1996. "Technological Innovation in the Zinc Electrolyte Purification Process of a Hydrometallurgical Zinc Plant through Reduction in Zinc Dust Consumption." *Hydrometallurgy* 40(1–2):247-262.

- Stanojević, D., B. Nikolić and M. Todorović. 2000. "Evaluation of Cobalt from Cobaltic Waste Products from the Production of Electrolytic Zinc and Cadmium." *Hydrometallurgy* 54(2–3):151-160.
- Tanabe, K., T. Ohgai, T. Akiyama and H. Fukushima. 1995. "Characteristic Behavior of Iron-Group Metals in the Purification Process using Zinc Dust.":303-309.
- Tozawa, K., T. Nishimura, M. Akahori and Miguel A. Malaga. 1992. "Comparison between Purification Processes for Zinc Leach Solutions with Arsenic and Antimony Trioxides." *Hydrometallurgy* 30(1–3):445-461.
- U.S. Geological Survey. 2012. "2011 minerals yearbook." Pp. 84.1-84.12 in "2011 minerals yearbook."
- van der Pas, V. 1995. "A Fundamental Study of Cobalt Cementation with Zinc Dust in the Presence of Copper and Antimony Activators."
- van der Pas, V. and D. B. Dreisinger. 1996. "A Fundamental Study of Cobalt Cementation by Zinc Dust in the Presence of Copper and Antimony Additives." *Hydrometallurgy* 43(1–3):187-205.
- Van Tonder, G. J., P. J. Cilliers, E. H. O. Meyer, N. M. Vegter, R. Klue, S. R. Izatt and R. L. Bruening. 2002. "Cobalt and Nickel Removal from Zincor Impure Electrolyte by Molecular Recognition Technology (MRT)- Pilot Plant Demonstration." *The Journal of the South African Institute of Mining and Metallurgy*:11-17.

- West-Sells, P. G. 1996. "Fundamental Studies of the Deposition of Cobalt from Electrolytes Containing Zinc." Doctor of Philosophy dissertation, the university of British Columbia, .
- Xu, Z., Q. Jiang and C. Wang. 2013. "Atmospheric Oxygen-Rich Direct Leaching Behavior of Zinc Sulphide Concentrate." *Trans. Nonferrous Met. Soc. China* 23:3780-3787.
- Yamashita, S., K. Hata and S. Goto. 1997. "Electropurification of Zinc Leaching Solution.":163.
- Yamashita, S., M. Okubo, S. Goto and K. Hata. 1997. "Purification of Zinc Leaching Solution - Mechanism of Removal of Cobalt by Zinc Dust with Arsenious Oxide and Copper Ion." *Metallurgical Review of MMIJ* 14(1):37-52.
- Yang, Dajin, Gang Xie, Guisheng Zeng, Jikun Wang and Rong-xing Li. 2006. "Mechanism of Cobalt Removal from Zinc Sulfate Solutions in the Presence of Cadmium." *Hydrometallurgy* 81(1):62-66.
- Yunus, M., C. Capel-Boute and C. Decroly. 1965. "Inhibition Effect of Zinc on the Cathodic Deposition of cobalt—I. Electrochemical and Structural Observations in Sulphate Solutions." *Electrochimica Acta* 10(9):885-900.
- Zeng, G. S., M. J. Li and Y. Xie. 2012. "Influencing Factors and Mechanism of Cobalt Redissolution from Zinc Sulphate Solution." *Advanced Materials Research* 402:12-16.

## Appendices

### Appendix A: SEM Photographs of the Zinc Dusts

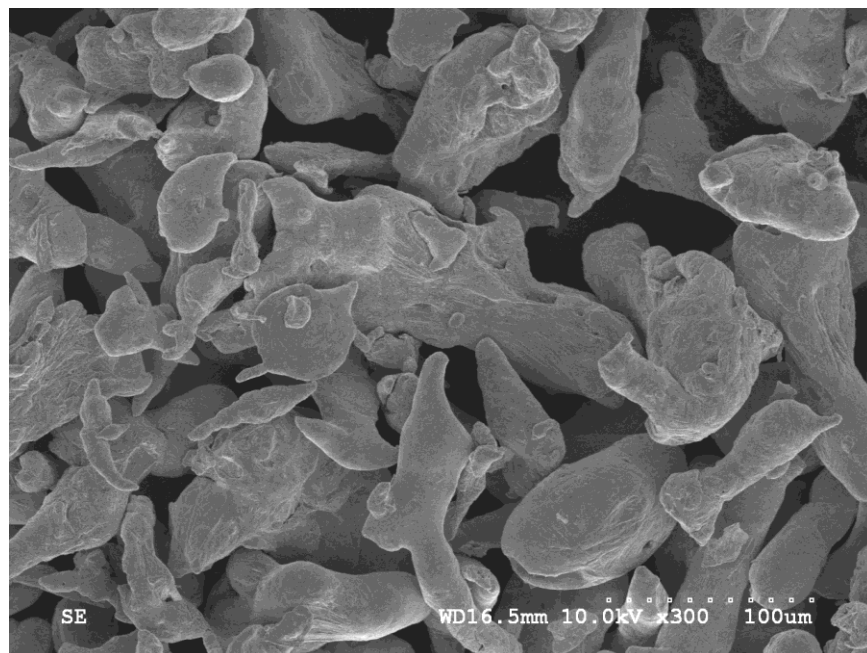


Figure A-1. CEZinc zinc dust before cementation.

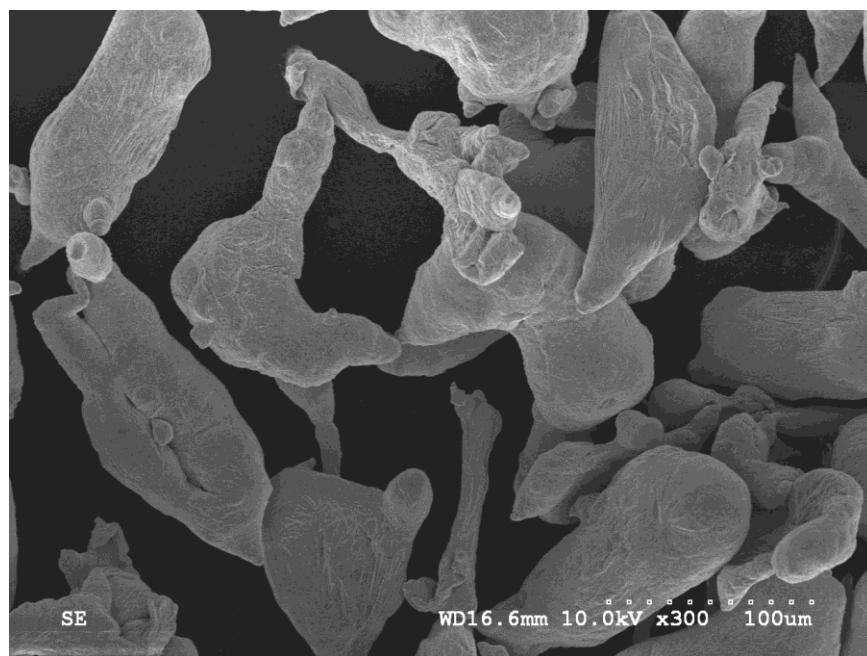


Figure A-2. J.T.Baker zinc dust before cementation.

## Appendix B: Energy-Dispersive X-ray (EDX) Spectroscopy of the Zinc Dusts

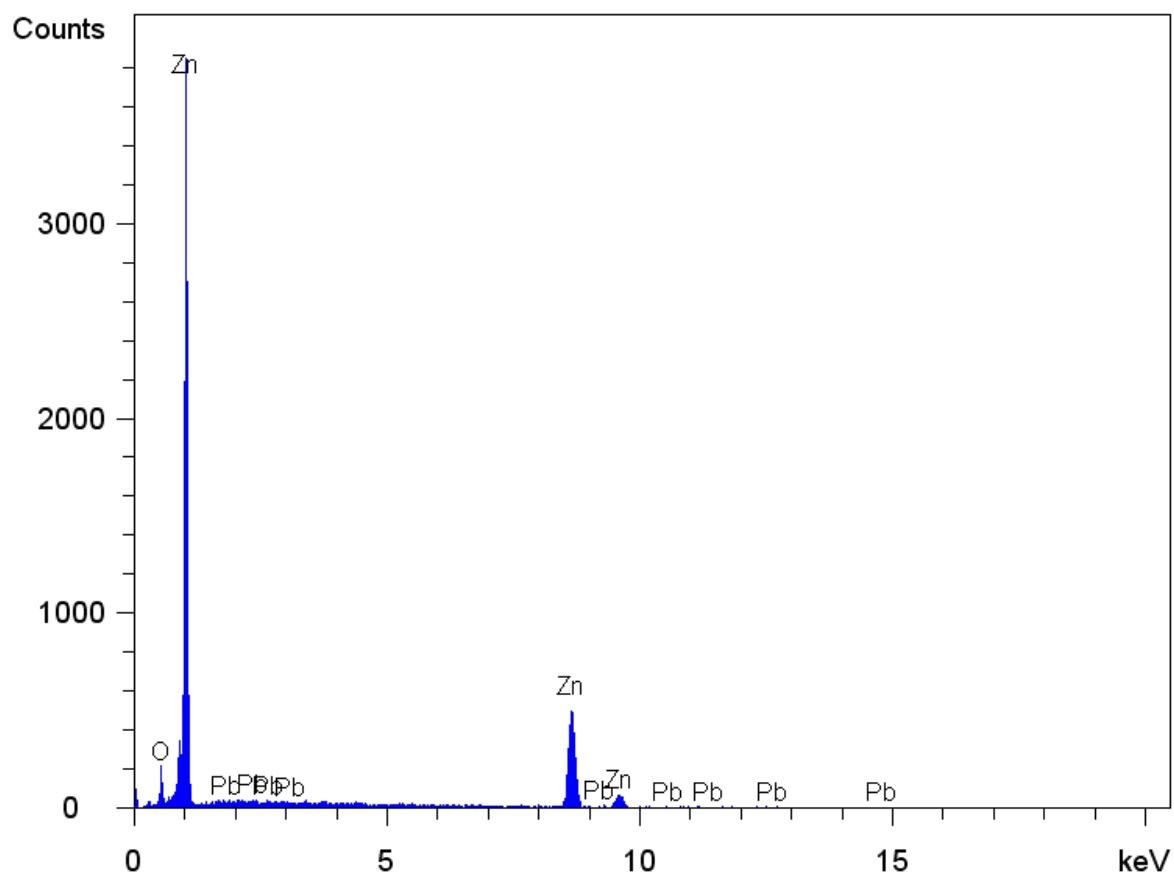


Figure B-1. EDX spectrum of J.T.Baker Chemical Co. zinc dust before cementation.

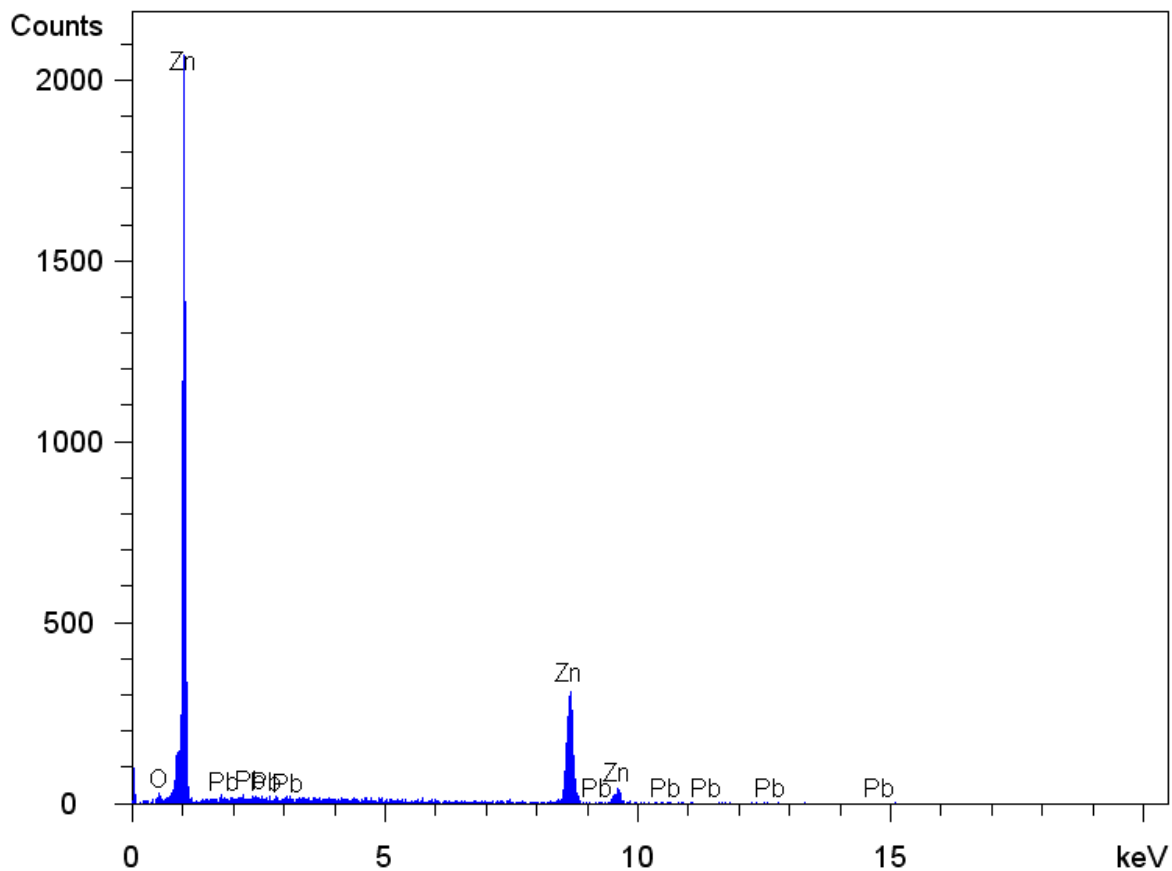


Figure B-2. EDX spectrum of CEZinc zinc dust before cementation.

Noting the above figures, the following compositions were obtained for the surface of the zinc dusts (It should be noted that the EDX analysis provided information regarding the surface composition of the samples, and these compositions cannot be generalized to the bulk of the samples):

Table B-1. Surface composition of the zinc dusts used in the experiments.

	<b>J.T.Baker zinc dust</b>	<b>CEZinc dust</b>
<b>Zinc</b>	85.39 wt%	95.35 wt%
<b>Oxygen</b>	14.59 wt%	3.49 wt%
<b>Lead</b>	0.03 wt%	1.16 wt%

## **Appendix C: Economical Study on Electrowinning the Added Zinc Dust to the Cementation Stages**

The data provided in Table C-1 show how the excess zinc dust addition to the cementation stages can cause significant additional cost for zinc electrowinning. All the data provided in this section are derived from (Houlachi 2012). The following assumptions have been made in the calculations:

1. The initial concentrations of the impurities are 1g/L, 1 g/L, and 20 mg/L, respectively for Cu, Cd, and Co.
2. All the added zinc dust is dissolved in the electrolyte and eventually gets recovered from the electrolyte at EW stage.
3. The energy required for zinc electrowinning is 3.3 KWh/Kg. Energy costs 0.04 \$/KWh.

Noting Table C-1, it can be inferred that electrowinning of the excess zinc dust added to the cementation stages costs 1.95 million dollars per year. Almost 1million dollars of this cost arises from the excess zinc dust used in the cobalt cementation stage.



Table C-1. Effect of excess zinc dust addition to the cementation stages on the cost of zinc electrowinning.

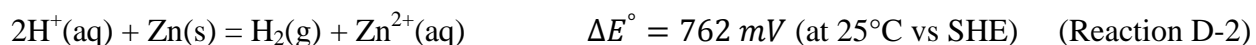
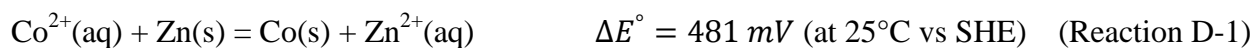
<b>Impurities</b>	<b>Concentration of impurities (g/L)</b>	<b>Stoichiometrically required zinc dust (g/L)</b>	<b>Stoichiometrically required zinc dust (t/d)<sup>1</sup></b>	<b>Real added zinc dust (g/L)</b>	<b>Real added zinc dust (t/d)</b>	<b>EW cost for the stoichiometrically zinc dust addition (\$M/y)</b>	<b>EW cost for the real zinc dust addition (\$M/y)</b>
<b>Cu</b>	1.00	1.03	9.6	3.50 <sup>2</sup>	32.55	0.46	1.56
<b>Cd</b>	1.00	0.58	5.5			0.26	
<b>Co</b>	0.020	0.022	0.2	2.50	23.25	0.01	1.12
<b>Total</b>		1.63	15.3	6.00	55.80	<b>0.74</b>	<b>2.68</b>

<sup>1</sup> This is calculated with multiplying the stoichiometrically-required zinc dust (g/L) by the rate of purified electrolyte.

<sup>2</sup> This value is the total amount of zinc dust that is added to the Cu-Cd cementation stage.

## Appendix D: Thermodynamic Studies

Cobalt cementation and hydrogen evolution on zinc dust are usually described with Reaction D-1 and Reaction D-2. It was discussed in section 2.1 that Reaction D-1 is not an ideal representative for the cobalt cementation reaction since cobalt cements on zinc dust not as pure cobalt, but as cobalt-zinc alloy. Moreover, a noticeable portion of the cobalt is removed from the solution with precipitation on zinc dust as cobalt basic salt. However, because no reaction mechanism has been proposed so far for the formation of the Co-Zn alloys and cobalt basic salts, Reaction D-1 is assumed to be the cobalt cementation reaction in this study.



The  $\Delta E^{\circ}$  values presented in the above reactions give a rough estimate on the driving forces for the cobalt cementation and hydrogen evolution on zinc dust. For instance, they show that  $\text{H}^{+}$  reduction on Zn has a significantly higher electromotive driving force compared to  $\text{Co}^{2+}$  reduction. However, these values are not an accurate representative for thermodynamics of the cobalt cementation and hydrogen evolution reactions occurring during the cobalt purification stage. Two main considerations should be taken into account to convert the  $\Delta E^{\circ}$  values presented in the above reactions to  $\Delta E$  values which are based on the condition of the cobalt cementation process:

### **1. Activities of the species should be included in the thermodynamic calculations**

This is done by the Nernst equation, which is presented by Equation D-1 and Equation D-2, respectively for Reaction D-1 and Reaction D-2.

$$\Delta E = \Delta E^\circ - \frac{2.303RT}{nF} \log \frac{a_{Zn^{2+}} \cdot a_{Co}}{a_{Co^{2+}} \cdot a_{Zn}} \quad (\text{Equation D-1})$$

$$\Delta E = \Delta E^\circ - \frac{2.303RT}{nF} \log \frac{a_{Zn^{2+}} \cdot a_{H_2}}{a_{H^+}^2 \cdot a_{Zn}} \quad (\text{Equation D-2})$$

Based on the solution constituents in this work (145 g/L  $Zn^{2+}$ , 15 mg/L  $Co^{2+}$ , 45 mg/L  $Cu^{2+}$ , and 2.5 mg/L  $Sb^{3+}$ ):

- $a_{Zn^{2+}} = 2.28$  and  $a_{Co^{2+}} = 0.26 \times 10^{-3}$  (activities of ionic species are assumed to be equal to their molal concentrations)
- $a_{H^+} = 10^{-4}$  (pH of the solution at 85°C is 4)
- $a_{Co} = a_{Zn} = 1$  (activity of pure solid species is assumed to be equal to 1)
- $a_{H_2} = 0.56$ <sup>1</sup> (activity of gaseous species is assumed to be equal to their partial pressure in atm)

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<sup>1</sup> Lu (Lu and Dreisinger 2014) reported that in a solution containing 150 g/L  $Zn^{2+}$ , 16 mg/L  $Co^{2+}$ , 35 mg/L  $Cu^{2+}$ , 2.5 mg/L  $Sb^{3+}$ , and 3.5 g/L zinc dust, at 85°C, 19 mmol/L  $H_2$  evolves during the cementation process. Since the experimental condition of Lu's work is almost the same as the experimental conditions of this work, the same value can be assumed for hydrogen gas evolution for this work. If the evolved  $H_2$  gas is assumed to be an ideal gas, then its partial pressure can be calculated as below (the autoclave had a 2 L volume, 1 L of which was the solution, so the remaining volume for the gas phase was 1 L):

$$19 \text{ mmol } H_2 \times 8.314 \frac{J}{\text{mol} \cdot K} \times (273.15 + 85)K \times \frac{1}{10^{-3}m^3} \times \frac{1 \text{ atm}}{101.3 \text{ KPa}} = 0.56 \text{ atm } H_2$$

By assuming that any zinc dust which is not used for the cobalt cementation reaction (Reaction D-1), is consumed by the hydrogen evolution reaction (Reaction D-2), the maximum amount of  $H_2$  gas that can evolve during the process can be calculated as below:

$$\left\{ 3.5 \frac{g \text{ Zn}}{L} - \left[ 15 \frac{mg \text{ Co}^{2+}}{L} \times \frac{1 \text{ mol } Co^{2+}}{58.93 \text{ g } Co^{2+}} \times \frac{1 \text{ mol Zn}}{1 \text{ mol } Co^{2+}} \times \frac{65.39 \text{ g Zn}}{1 \text{ mol Zn}} \right] \right\} \times \frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} \times \frac{1 \text{ mol } H_2}{1 \text{ mol Zn}} = 53.3 \frac{\text{mmol } H_2}{L}$$

According to the following calculation, 53.3 mmol  $H_2$  corresponds to 1.57 atm.

$$53.3 \text{ mmol } H_2 \times 8.314 \frac{J}{\text{mol} \cdot K} \times (273.15 + 85)K \times \frac{1}{10^{-3}m^3} \times \frac{1 \text{ atm}}{101.3 \text{ KPa}} = 1.57 \text{ atm } H_2$$

By inserting the above mentioned activity values in Equation D-1 and Equation D-2, 364 and 523 mV (at 25°C vs SHE) are obtained as the electromotive driving forces ( $\Delta E$ ), respectively for Reaction D-1 and Reaction D-2. (in all these calculations it is assumed that activities are independent of temperature).

## **2. Effect of higher temperatures should be included in the thermodynamic calculations**

Changing temperature affects the free energy of species and subsequently the  $\Delta E^\circ$  value of reaction. Noting that  $\Delta E^\circ = -\frac{\Delta G^\circ}{nF}$ , to obtain a  $\Delta E^\circ$  value for a reaction at a specific temperature, first of all,  $\Delta G^\circ$  of the reaction should be calculated at that temperature. For the temperature range studied in this work (85-150°C), the free energy of the species was calculated as follows:

$$G_T^\circ = G_{298}^\circ + C_P|_{298}^T \theta - (T - 298)S_{298}^\circ \quad (\text{Equation D-3})$$

where:

$$\theta = T - 298 - T \ln \frac{T}{298} \quad (\text{Equation D-4})$$

and  $C_P|_{298}^T$  is calculated as below:

### **For ionic species (Criss-Cobble method):**

$$C_P|_{298}^T = \alpha_T + \beta_T \bar{S}_{298}^\circ \quad (\text{Equation D-5})$$

where:

$$\bar{S}_{298}^\circ = S_{298}^\circ + z\bar{S}_{298}^\circ(H^+) \quad (\text{Equation D-6})$$

In the above equations,  $\alpha_T$ ,  $\beta_T$ , and  $\bar{S}_{298}^\circ(H^+)$  are extracted from the table below, and z is the number of valance electrons for simple cations.

Table D-1. Criss-Cobble constants (Asselin 2013).

<b>T(°C)</b>	<b><math>\bar{S}^{\circ}(H^{+})</math></b>	<b><math>C_P _{298}^T(H^{+})</math></b>	<b><math>\alpha_T</math> (for simple cations)</b>	<b><math>\beta_T</math> (for simple cations)</b>
<b>25</b>	-20.9	-	-	-
<b>60</b>	-10.5	94.2	147	-0.405
<b>100</b>	8.4	131	192	-0.553
<b>150</b>	27.2	137	194	-0.594

**For elements and compounds (Kelley equation):**

$$C_P|_{298}^T = a + \frac{b \times 10^{-3}}{T} (T + 298) + \frac{c \times 10^5}{298T} + \frac{d \times 10^{-6}}{3} (T^2 + 298T + 298^2) \quad (\text{Equation D-7})$$

a, b, c, and d values for the species involved in Reaction D-1 and Reaction D-2 are presented in Table D-2.

Table D-2. Kelley equation parameters (Outokumpu).

<b>Species</b>	<b>a</b>	<b>b</b>	<b>c</b>	<b>d</b>
<b>Zn</b>	23.827	8.331	-0.516	-3.816
<b>Co</b>	27.685	-4.386	-2.065	13.71
<b>H<sub>2</sub></b>	25.855	4.837	1.584	-0.372

Knowing the free energy of the species at each temperature, the Gibbs free energy of the cobalt cementation and hydrogen evolution reaction is obtained from the following equations. The results for the temperature range of 85-150°C are given in Table D-3.

$$\Delta G_{Co-Zn}^{\circ} = G_T^{\circ}(Zn^{2+}) + G_T^{\circ}(Co) - G_T^{\circ}(Co^{2+}) - G_T^{\circ}(Zn) \quad (\text{Equation D-8})$$

$$\Delta G_{H_2-Zn}^{\circ} = G_T^{\circ}(Zn^{2+}) + G_T^{\circ}(H_2) - 2G_T^{\circ}(H^+) - G_T^{\circ}(Zn) \quad (\text{Equation D-9})$$

Table D-3. Effect of temperature on Gibbs free energy of the cobalt cementation and hydrogen evolution reaction.

Reactions	$\Delta G^{\circ}$ (KJ/mol)				
	85°C	110°C	125°C	135°C	150°C
$Co^{2+}(aq) + Zn(s) = Co(s) + Zn^{2+}(aq)$	-92.3	-92.1	-91.9	-91.8	-91.7
$2H^+(aq) + Zn(s) = H_2(g) + Zn^{2+}(aq)$	-146.2	-145.8	-145.5	-145.4	-145.1

Now knowing  $\Delta G^{\circ}$  ( $\Delta E^{\circ}$ ) for the cobalt cementation and hydrogen evolution reaction at each tested temperature, and noting the activity values discussed above, the driving force ( $\Delta E$ ) for these reactions is calculated according to Equation D-1 and Equation D-2. The results are provided in Table D-4.

Table D-4. Effect of temperature on electrochemical driving forces of the cobalt cementation and hydrogen evolution reaction.

Reactions	$\Delta E$ (mV)				
	85°C	110°C	125°C	135°C	150°C
$Co^{2+}(aq) + Zn(s) = Co(s) + Zn^{2+}(aq)$	338	327	321	316	310
$2H^+(aq) + Zn(s) = H_2(g) + Zn^{2+}(aq)$	469	447	434	425	412