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NOVEL ACTIVATORS IN COBALT REMOVAL FROM ZINC ELECTROLYTE BY CEMENTATION

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ABSTRACT

In the electrolytic production of zinc, cobalt is removed from zinc electrolyte by cementation with zinc dust prior to electrowinning. Although the thermodynamics for this reaction are favourable, kinetic barriers to cobalt reduction render the method impractical unless activators such as antimony or arsenic in conjunction with copper are used. There is a large body of work studying the effect of these additives, yet the mechanism by which they act is still poorly understood. Moreover, regardless of the beneficial effect of the activators, from time to time the process fails to meet the target level of 0.1 mg/L cobalt in the purified electrolyte, with negative consequences in the electrowinning operation. Even when the target conditions are met, zinc dust consumption is excessively high: satisfactory operation requires up to 300 times the stoichiometric amount of zinc dust.

In the present work the role of the antimony/copper activators was investigated in a batch cementation process using synthetic electrolyte. The objectives were to study the fundamentals of cobalt cementation in zinc sulfate electrolyte with conventional additives, to clarify the action of additives and their role in cementation, and to identify and test novel additives.

The presence of zinc ions in solution inhibits cobalt cementation without activators. With activators cementation is rapid even in the presence of zinc ions. Small amounts of cadmium and chloride in addition to the activators increase the amount of cobalt removed beyond the level achieved with antimony and copper alone. Novel additives were evaluated in terms of cobalt reduction and zinc dust consumption. At least one element (tin) proved to be as effective as antimony in terms of cobalt reduction, and zinc dust consumption was greatly reduced in the presence of several other elements. The efficiency of activators for cobalt removal can be linked to hydrolysis. Combinations of additives were particularly effective in optimizing cobalt reduction while minimizing zinc dust consumption. Several combinations were identified with which the target level of cobalt is easily achieved and zinc dust consumption is negligible.

RÉSUMÉ

Dans la production électrolytique du zinc, le cobalt est extrait de la solution par cémentation avec de la poussière de zinc. Bien que la thermodynamique de cette réaction soit favorable, les barrières cinétiques à la réduction du cobalt rendent la méthode impraticable à moins que des activateurs tels que l'antimoine ou l'arsenic soient présents. Malgré le nombre important de travaux étudiant l'effet de ces additifs, le mécanisme par lequel ils agissent est encore mal compris. D'ailleurs, indépendamment de l'effet bénéfique de l'activateur, il arrive que le processus ne peut atteindre le niveau cible de 0,1 mg/L de cobalt dans l'électrolyte purifié. Même lorsque les conditions cibles sont atteintes, la consommation de la poussière de zinc est excessivement haute: jusqu'à 300 fois la quantité stoïchiométrique de poussière de zinc est nécessaire à une opération satisfaisante.

Dans le présent travail le rôle des activateurs (antimoine et cuivre) a été étudié pour le procédé de cémentation en lots utilisant un électrolyte synthétique. Les objectifs ont été d'étudier les principes fondamentaux de la cémentation du cobalt dans l'électrolyte de sulfate de zinc avec les additifs conventionnels, de clarifier leur action et leur rôle dans la cémentation, et d'identifier et de tester de nouveaux additifs.

La présence des ions de zinc en solution empêche la cémentation du cobalt sans activateur. Avec des activateurs la cémentation est rapide même en présence des ions de zinc. De petites quantités de cadmium et de chlorure, ajoutées aux activateurs, augmentent la quantité de cobalt retirée au delà du niveau réalisé avec de l'antimoine et du cuivre seuls. Des nouveaux additifs ont été évalués en termes de réduction du cobalt et de la consommation de poussière de zinc. Au moins un élément (étain) a été aussi efficace que l'antimoine en termes de réduction du cobalt. La présence de plusieurs autres éléments a énormément réduit la consommation de poussière de zinc. L'efficacité des activateurs dans l'extraction du cobalt peut être reliée à l'hydrolyse. La combinaison des additifs a été particulièrement efficace dans la réduction du cobalt tout en réduisant la consommation de poussière de zinc. Avec certaines de ces combinaisons le niveau cible de cobalt est facilement réalisé avec une consommation négligeable de poussière de zinc.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF TABLES

1. INTRODUCTION

1.1 INDUSTRIAL ZINC PRODUCTION

1.1.1 RLE process

The roast-leach-electrowinning (RLE) process (Figure 1.1) produces over 80% of the world's primary zinc. The feed material of the RLE process is zinc concentrate consisting mainly of zinc sulfide, which is insoluble in dilute sulfuric acid. Upon roasting, the zinc sulfide converts to zinc oxide, which is readily solubilized in dilute sulfuric acid solutions. However, leaching the roasted concentrates with sulfuric acid liberates not only zinc ions but also impurities such as iron, copper, cadmium, cobalt and nickel; the leach solution must therefore be purified before becoming the feed to the electrolysis step from which metallic zinc is recovered.

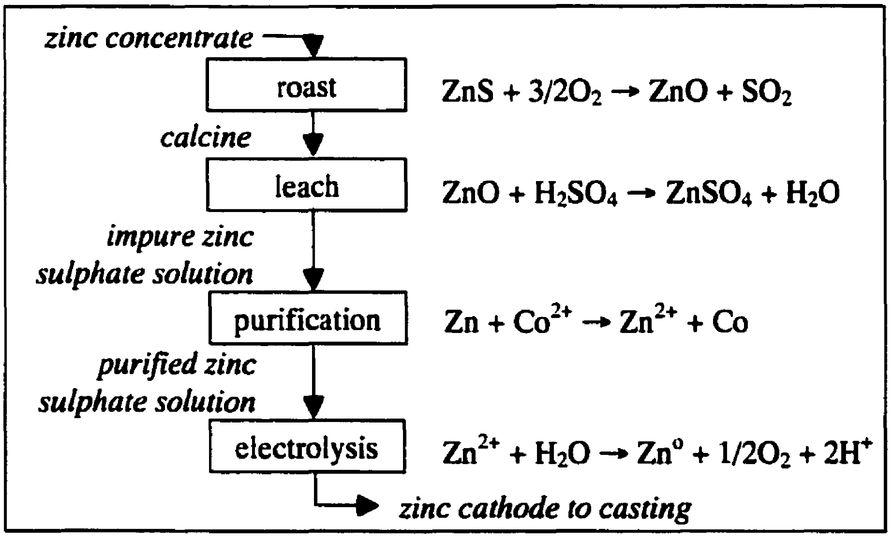

Figure 1.1: Roast-leach-electrowin process for zinc production.

1.1.2 Effect of impurities

The zinc electrowinning process is unusual from a thermodynamic point of view because zinc metal has a more negative reduction potential than hydrogen:

$$2H^{+} + 2e^{-} \rightarrow H_2 \qquad e^{o} = 0\ V \qquad (1.1)$$

$$Zn^{2+} + 2e^{-} \rightarrow Zn^{o} \qquad e^{o} = -0.76\ V \qquad (1.2)$$

One would therefore expect hydrogen gas to evolve at the expense of zinc deposition. However, zinc metal is electrowon economically from acidic zinc sulfate solution because hydrogen evolution has a high overpotential on zinc metal (Kita 1966). In order to maintain this large overpotential, almost all impurities in the leach solution must be completely removed (Tozawa *et al.* 1992). Any remaining impurities act as catalysts for hydrogen evolution or codeposit with zinc, causing large drops in current efficiency (C.E) (Figure 1.2).

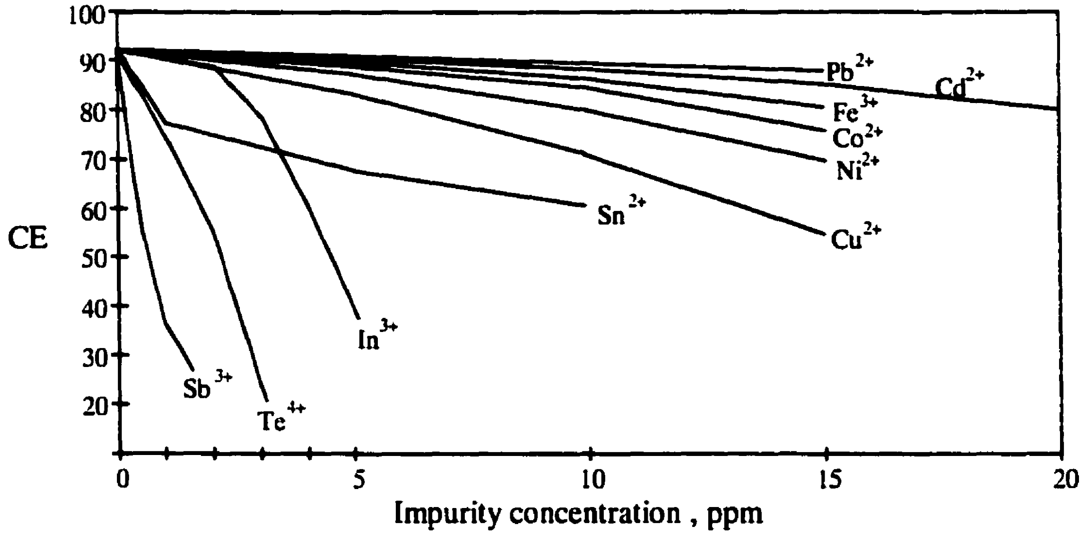

Figure 1.2: Effect of impurities on zinc electrowinning current efficiency (adapted from Duyvesteyn and van Weert 1993).

1.1.3 Purification

Primary impurity removal in the RLE process takes place towards the end of the neutral leach stage by the neutralization-precipitation of a ferric hydroxide phase that acts as a scavenger for impurities like arsenic, antimony, germanium and tin (Dutrizac 1987). Remaining traces of impurities in the zinc electrolyte are subsequently removed in the main purification section of the process by cementation with zinc dust (Figure 1.3).

1.2 CEMENTATION

Cementation is a heterogeneous reaction between two metals in which the less noble metal (Zn^0) displaces the ion of a more noble metal (Co^{2+}) from solution when placed in contact with it. Therefore cobalt ions deposit on the surface of the less noble zinc dust, which, in turn, progressively dissolves (Figure 1.3).

overall reaction: $Zn + Co^{2+} \rightarrow Zn^{2+} + Co$ (1.3)

anodic reaction: $Zn \rightarrow Zn^{2+} + 2e^-$ (1.4)

cathodic reaction: $Co^{2+} + 2e^- \rightarrow Co$ (1.5)

Due to the slow kinetics of this reaction, activators (elements acting as electrocatalysts) are used to improve the cementation process.

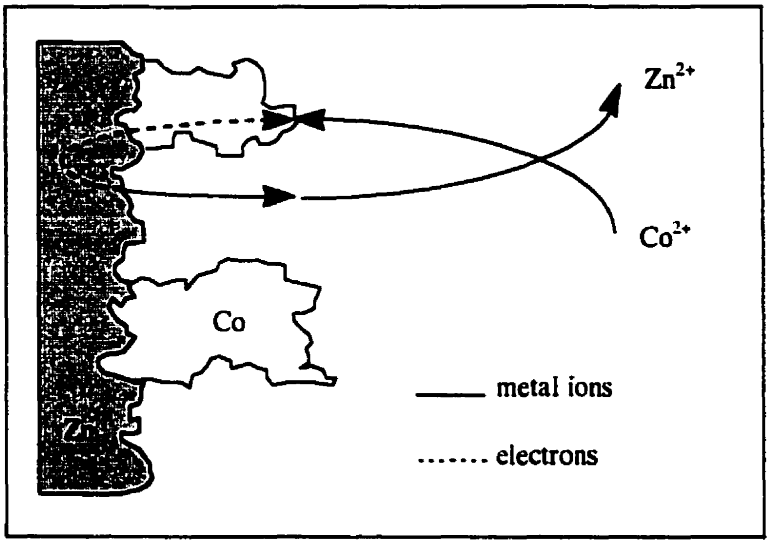

Figure 1.3: Cobalt cementation on zinc dust.

1.2.1 Industrial practice

Industry currently uses two activation methods to effect cobalt cementation: activation with arsenic/copper or with antimony/copper (Tozawa 1992, Ashman 1993). In the antimony/copper process used at CEZinc (Leroux, 1997), impurity removal by cementation is carried out continuously in two stages, as shown in Figure 1.4. Impure feed containing 0.5 g/L cadmium, 1 g/L copper, and 15 mg/L cobalt is treated in the first purification stage, which removes copper, cadmium, and about 40% of the cobalt. The solution temperature is about 75°C, the pH is 4.2-4.6, and 1.5 g/L zinc dust is added.

The second stage further reduces the level of cobalt in a series of four stirred-tank reactors. This stage uses 4-5 g/L of fresh zinc dust, as well as additions of antimony trioxide and copper sulfate, and operates at 90-95°C and pH 4.0.

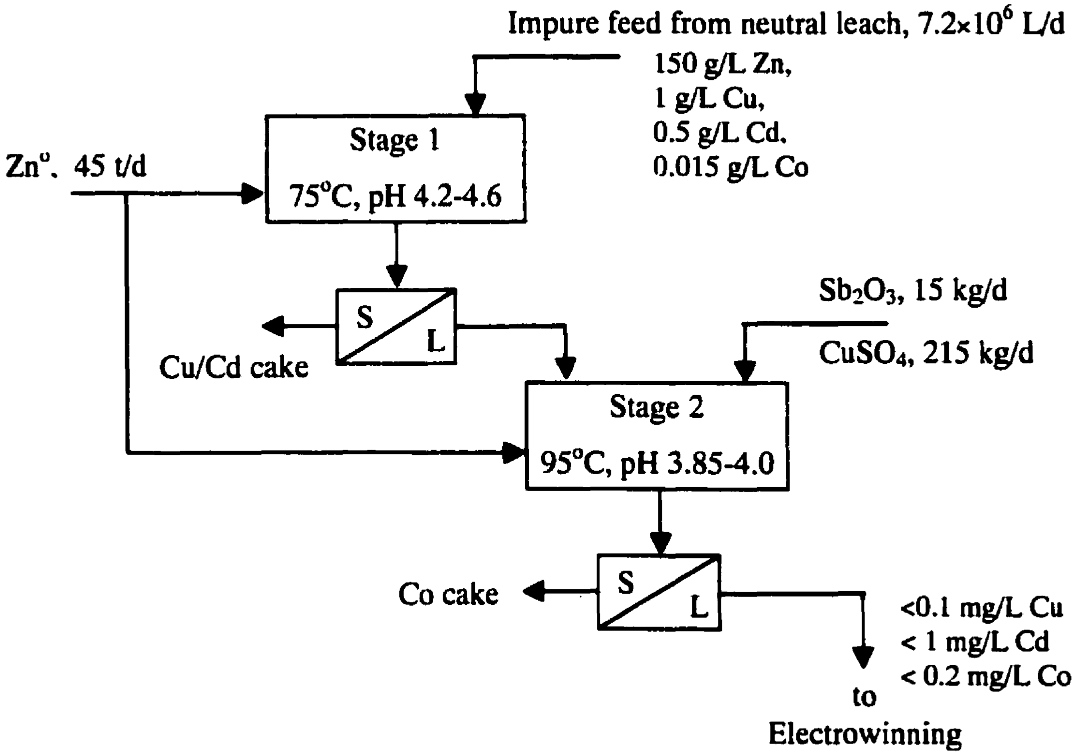

Figure 1.4: Two stage purification process (Canadian Electrolytic Zinc).

Table 1.1 shows the maximum tolerable levels of some common impurities in the feed to the electrowinning operation. Cobalt is of particular concern because even at low levels it is harmful and difficult to remove from the electrolyte:

- cobalt, which is more noble than zinc, codeposits with zinc, reducing the zinc quality and changing deposit structure and morphology.
- cobalt has a lower hydrogen overpotential than zinc; any codeposited cobalt catalyzes hydrogen evolution at the expense of zinc deposition, reducing current efficiency considerably.
- hydrogen evolution at the cathode creates a local increase in pH, which can lead to the formation of a passivating layer of zinc hydroxide or basic zinc sulfate on the cathode.

- cobalt interacts in a synergistic way with most other impurities, resulting in increased harmful effects.

Table1.1: Upper limits of common impurities in zinc electrowinning.

Impurity (mg/L)	CEZinc[a]	Cominco [b]	Hoboken-Overpelt[b]	Port Pirie[b]
Copper	0.1	-	0.2	0.15
Cadmium	1.0	0.3	1.0	0.35
Cobalt	0.2	0.3	1.0	0.05
Nickel	-	-	0.05	0.05
Arsenic	0.02	-	0.02	0.01
Antimony	-	0.03	0.02	0.025

a) Houlachi *et al.* 1990
b) Tozawa *et al.* 1992

1.2.3 Disadvantages

Cobalt is the one of the most difficult impurities to remove by cementation with zinc, despite favourable thermodynamics:

$$Co^{2+} + Zn^{o} \rightarrow Co^{o} + Zn^{2+} \qquad E^{o} = 480\ mV \qquad (1.6)$$

Lawson and Nhan (1981) calculated the ΔG^{o} of the above reaction to be -93 kJ/mol of cobalt at 25°C with an equilibrium constant of 2×10^{16}. An equilibrium constant of this magnitude suggests that metallic zinc should completely remove cobalt ions from aqueous solution, with essentially no back reaction occurring. In practice, however, cobalt cementation is very slow due to kinetic barriers and requires the use of activators to promote the rate of reaction and render the process useful. Even with activators, the process sometimes fails to meet the target level of cobalt in the electrolyte, with negative consequences for the electrowinning operation (Figure 1.2).

In addition to poor reaction kinetics, there are the following disadvantages to cobalt cementation:

- hydrogen evolution during cementation consumes much more zinc dust than that which would be required for cobalt reduction only, by a factor of 200-400. This gives a current efficiency of less than 1% for the process. Removing less than 40 tonnes of cobalt consumes approximately 1.6×10^4 tonnes of zinc dust (or 6-7% of cathode production) (Houlachi *et al.* 1990). The dissolved zinc dust must be reprocessed in the electrowinning step, clearly an inefficient process.

- the cementation process is sensitive to dissolved oxygen, which in practice is difficult to remove from the process.
- the electrolyte must be heated to 95°C in order to improve the reaction kinetics, and then must be cooled to 50°C for the electrowinning step.

1.3 RESEARCH OBJECTIVES

There is both a technical and economic incentive to investigate ways to improve the performance of the cobalt cementation system. The objectives of this work are three-fold:

1) to examine the parameters that affect the cementation process in order to better understand the activation mechanism;
2) to identify new additives that could lead to a more efficient purification process;
3) to test the new additives in synthetic electrolyte solutions.

Chapter 2 gives a summary of previous research on cobalt cementation. Chapter 3 explains the experimental design and procedures used to achieve the goals mentioned above, while Chapter 4 discusses the results. Chapter 5 offers some conclusions and suggestions for future work.

2. LITERATURE REVIEW

2.1 CEMENTATION

The removal of cobalt from zinc electrolyte by cementation has been the focus of research for over 20 years. Most of the published work focuses on optimizing operating parameters such as temperature and pH, characterizing additives such as copper, arsenic, and antimony, and studying the effect of chemicals present in the RLE process such as zinc itself and residual organics. The following pages systematically discuss the literature pertaining to the effect of these factors on the efficiency of the cementation process.

2.1.1 Zn(II)

In industry cementation occurs in a solution which typically contains 150 g/L Zn(II). In a solution containing no zinc ions, cobalt cementation on zinc particles proceeds rapidly, and has an activation energy of 13 kJ/mol, indicating a mass transfer controlled process (Fountoulakis 1983). However, even a small concentration of zinc ions in solution inhibits the rate of cementation severely (Tozawa *et al.* 1992). The activation energy increases (reported as 39 kJ/mol (Kim *et al.* 1992), 86.6 kJ/mol (Lew *et al.* 1993), and 65 kJ/mol (van der Pas and Dreisinger 1996)), indicating that the zinc ions interfere with the reaction step at the surface of the zinc dust. Xiong and Ritchie (1989) attributed zinc ion inhibition to a double layer effect: zinc cations adsorb on the surface of zinc dust, making the zeta potential of the metal more positive, which leads to a reduction in the surface concentration of the reacting species, Co(II). The same investigators confirmed by microscopic observation during electrolysis that zinc ion adsorption on the surface inhibits cobalt nucleation. In addition, the reaction between zinc ions and hydroxyls generated during the reduction of protons may form colloidal zinc hydroxide which acts as a secondary inhibitor by passivating the reaction surface. West-Sells *et al.* (1997) maintain that it is actually the $ZnOH^+$ species that adsorbs on the surface and prevents cobalt cementation, despite the relative scarcity of this hydrolysis product (see Section 2.1.1.1) . Tanabe *et al.* (1995) describe this as a hydroxide suppression mechanism in which iron group metal deposition is polarized (deposition overpotentials are increased) when deposition sites are occupied by adsorbed substances, i.e., zinc hydroxide.

It is apparent from the above that zinc interferes with the cementation process in two possible ways, a double layer effect and surface passivation. In order to understand better the chances of either or both of these occurring, one should consider the properties of the zinc/cobalt/sulfate system, including speciation, solubility and surface properties.

2.1.1.1 Zinc speciation

Most studies of cobalt cementation and zinc electrowinning neglect to consider speciation altogether; not only does speciation play an important role in determining the concentration of the reacting species, cobalt, but also in that of zinc, which plays an important role in retarding the rate of cobalt cementation.

The following equilibrium constants describe the interaction of zinc ions with sulfate ions in an acidic medium, at ionic strength 3.0 and 25°C, without considering water molecules in the inner coordination sphere (Martell and Smith 1982):

$$Zn^{2+} + nSO_4^{2-} \rightarrow Zn(SO_4)_n^{(2-2n)+} \qquad K_1 = 5.01,\ K_2 = 5.01,\ K_3 = 7.94 \qquad (2.1)$$

Filippou *et al.* calculated Zn(II) sulfate speciation (Filippou *et al.* 1993, 1995), considering the effects of ionic strength and temperature. Figure 2.1 (calculated from Filippou *et al.* 1993) shows the speciation as a function of pH and total Zn(II) concentration. Clearly $ZnSO_4^0$ dominates in the solution. Figure 2.2 shows the effect of electrolyte temperature; over 99% of the Zn(II) species exists as $ZnSO_4^0$ in zinc electrolyte at 95°C.

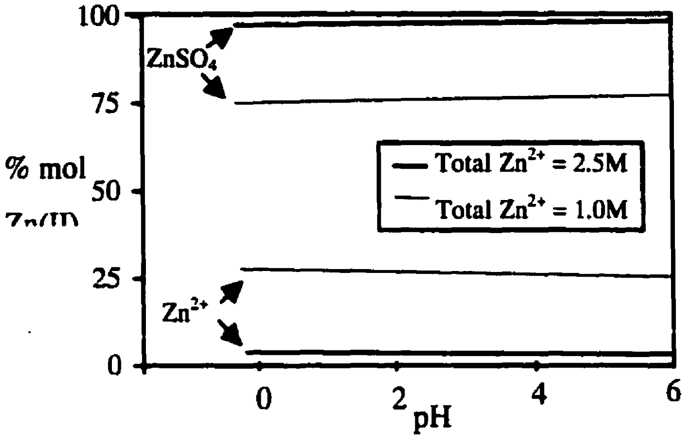

Figure 2.1: Zn(II) speciation as a function of pH; 25°C, total dissolved Zn(II) at 1.0 and 2.5 mol/L (calculated from Filippou et al. 1993).

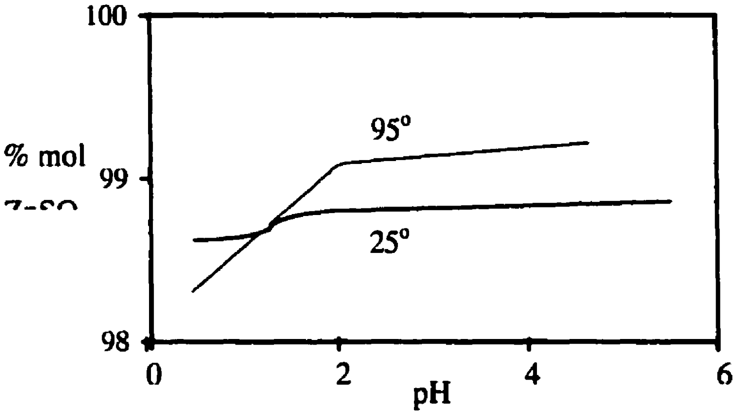

Figure 2.2: $ZnSO_4^0$ abundance as a function of pH at 25 and 95°C; total dissolved Zn(II) 2.5 mol/L (calculated from Filippou et al. 1993).

Co(II) ions can exist in the Co^{2+} and $CoSO_4^0$ forms with considerable hydration. The following describes Co(II) sulfate complexation at 25°C and ionic strength 3.0 (Martell and Smith 1982):

$$Co^{2+} + SO_4^{2-} \rightarrow CoSO_4^0 \qquad K_1 = 1.70 \qquad (2.2)$$

Co^{2+} (as opposed to $CoSO_4^0$) should dominate the Co-Zn-SO_4 system as Zn(II) consumes the SO_4^{2-} in solution. A sample calculation at 25 °C using the equilibrium constants from equations 2.1 and 2.2 and a charge balance show that the concentration of Co^{2+} is in fact twice as much as that of $CoSO_4^0$ (calculations are included in Appendix A).

The zinc ion hydrolyzes only sparingly to produce $ZnOH^+$ (Baes and Mesmer 1976):

$$Zn^{2+} + H_2O \rightarrow ZnOH^+ + H^+ \qquad \log K_1 = -9.17 \qquad (2.3)$$

The equilibrium constant is for 25°C and has been adjusted for ionic strength, and is so small as to be negligible. The value of $\log K_1$ decreases slightly with increasing temperature (Perrin 1962).

2.1.1.2 Zinc hydroxide/basic zinc sulfate solubility

DeBlander and Winand (1975) suggested that a less conductive zinc hydroxide or basic zinc sulfate forms on the surface of zinc dust; their general consensus was that this is the reason for slow cementation kinetics at high pH.

The solubility of zinc sulfate decreases with increasing sulfuric acid concentration, i.e., it is more soluble at high pH. At pH 4, insoluble zinc sulfate is not likely to passivate the zinc dust. However, the solubility of zinc sulfate does decrease again at temperatures greater than 90-100°C (Linke 1965). Zinc hydroxide is also soluble at pH 4 (Pourbaix 1974).

In the interfacial area between solid and liquid phases there is a much larger electric field and consequently a lower dielectric constant than in the bulk solution. Hence the formation constant for $Zn(OH)_2$ in the interfacial area (K_{sp}^s) is different from that in the bulk (K_{sp}) (James and Healy 1972), as illustrated in Figure 2.3. Furthermore, the zinc concentration in the interface is usually larger than in the bulk due to its adsorption on the zinc dust surface. These effects all suggest that surface precipitation is likely to occur well before bulk precipitation. It is probable that above pH 4 at the temperature of cementation zinc hydroxide/zinc sulfate precipitation is responsible at least in part for the slow cementation kinetics.

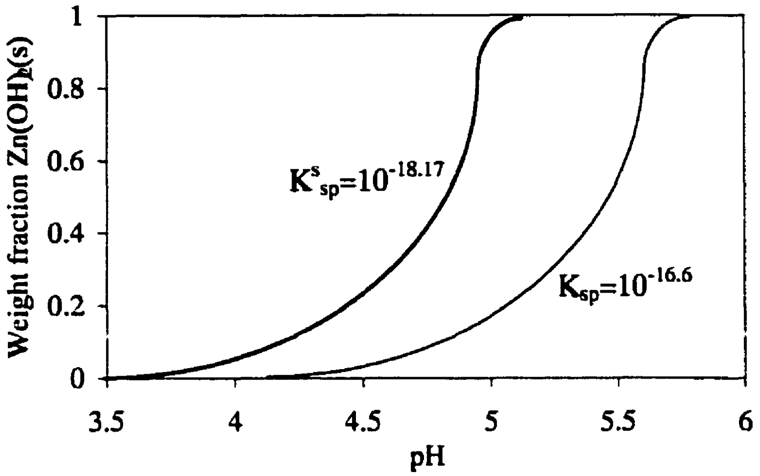

Figure 2.3: Surface vs. bulk precipitation of $Zn(OH)_2$ as a function of pH at 25°C (James and Healy 1972).

There are limited data on the formation of basic zinc sulfate, and no solubility data. Bear *et al.* (1995) identified the basic zinc sulfate formed in the cementation of lead on zinc as $ZnSO_4 \cdot 3Zn(OH)_2 \cdot 5H_2O$. They have determined a crystal structure and shown that the compound grows in large, flat, hexagonal platelets. The authors claim that, in lead cementation, these crystals do not cause passivation as ions can diffuse readily between the crystals and even through the crystal structure. Furthermore, they maintain that basic zinc sulfate plays an important role in the progress of the cementation process by keeping the cement agglomerates porous and allowing access of the solution to the precipitant pores.

2.1.1.3 Surface properties

Details of the surface charge of zinc particles are not certain (Bard 1970), but it is possible that SO_4^{2-} ions are specifically adsorbed in the inner Helmholtz plane (IHP), and subsequently zinc ions adsorb electrostatically in the outer Helmholtz plane (OHP). It is even more likely that a zinc ion complex simply adsorbs in the IHP, blocking electron transfer from the metal to cobalt ions and inhibiting the mass transfer of cobalt ion to the metal surface. The calculated speciation diagrams, Figure 2.4, suggest that most likely Zn^{2+} species in solution, not $ZnSO_4^o$, cause the problem, even though $ZnSO_4^o$ dominates in the solution (Figure 2.2). The y-axis values for line C in Figure 2.4 are read off the right hand side.

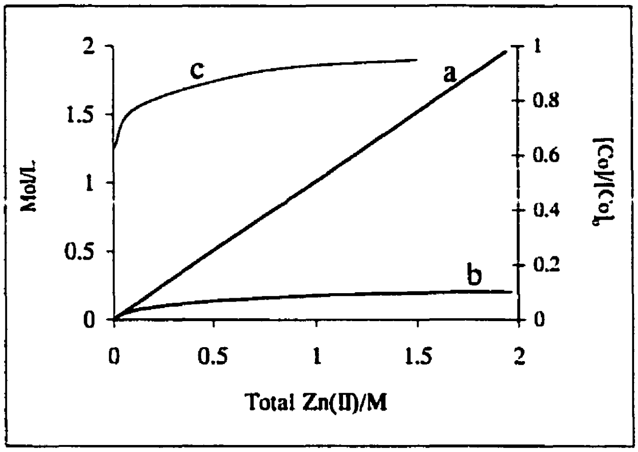

Figure 2.4: Comparison of Zn(II) speciation data: a) $ZnSO_4$ concentration (mol/L) as a function of total Zn(II) (90°C, pH 3.5) (Filippou et al. 1995); b) Zn^{2+} concentration (mol/L) as a function of total Zn(II) (90°C, pH 3.5) (Filippou et al. 1995); c) $[Co]_t/[Co]_o$ as a function of Zn(II) (90°C, pH 3.3-3.75) (Tozawa et al.1992).

2.1.1.4 Codeposition of zinc

Not only can zinc ions passivate the surface, but they can also be reduced by zinc dust. Van der Pas and Dreisinger (1996) showed that the cement from a solution containing zinc ions contains mainly zinc with very little cobalt (>98% Zn). In fact, zinc-free cobalt deposits cannot be obtained from sulfate solutions even when Zn^{2+} is present only in traces in the solution (Yunus *et al.* 1965). In a 1 molar solution of zinc and cobalt sulfate, if zinc constitutes less than 6% of the total metal concentration, then the proportion of zinc in the deposits is the same as that in the solution. Above 6% however, the proportion of zinc in the deposit is much higher than that in the solution. This phenomenon is known as anomalous co-deposition of zinc, anomalous because the less noble zinc deposits preferentially to the more noble cobalt, at a potential more positive than its reduction potential. Yamashita *et al.* (1997) reported that in electrolytic reduction of cobalt from a zinc sulfate solution, zinc is found in the deposit at potentials as large as -580 mV, whereas it is theoretically expected to deposit only at potentials lower than -768 mV. The difference between the potential at which deposition actually takes place and the theoretical reduction potential is proportional to the strength of adsorption of the metal on the substrate (Trassati 1995).

2.1.2 Temperature

It is often observed that increasing temperature has a beneficial effect on the rate of cobalt cementation (Tozawa *et al.* 1992, Blaser and O'Keefe 1983, Kim *et al.* 1992, Lew *et al.* 1993, Borve and Ostvold 1994); indeed, some authors have suggested that temperature is the most influential parameter on cementation (Blaser and O'Keefe 1983). While most studies simply state that cementation kinetics improve with increasing temperature, Lew *et al.* (1993) showed a maximum in the rate of cementation at 80°C. This peak can be understood by taking into consideration the parasitic reaction, hydrogen evolution. The rate of hydrogen evolution increases at a greater rate with temperature than cobalt cementation does, hence beyond a certain point an increase in temperature does more to promote the parasitic reaction. The beneficial effect of temperature is logical for a process that is under chemical control, as is cobalt cementation in a zinc sulfate solution.

Tanabe *et al.* (1992) interpreted the effect of temperature as reducing the deposition overpotential for iron-group metals such as cobalt and nickel. In a zinc-free solution, the deposition overpotential for cobalt is almost eliminated at elevated temperatures (80°C), and it follows that deposition might be promoted in the presence of zinc ions as well.

Figure 2.5 compares the effect of temperature on cementation rate obtained from different sources. As mentioned above, increasing the temperature not only promotes cobalt removal, but also increases the rate of hydrogen evolution and subsequent zinc dust consumption. The rate drop obtained from electrolytically reduced cobalt at constant current density on an antimony substrate at 90°C appears to be due to the elevated rate of hydrogen evolution at that temperature. The rate of cobalt removal drops because the current available remains constant in the electrolytic case, whereas in the cementation process excess zinc dust is available. It is also possible that at higher temperatures zinc underpotential deposition is inhibited, as the zinc content of cements obtained at higher temperatures is lower. Zinc ion adsorption in the double layer may change with temperature, with the desorption of zinc ions at higher temperatures resulting in easier cobalt deposition.

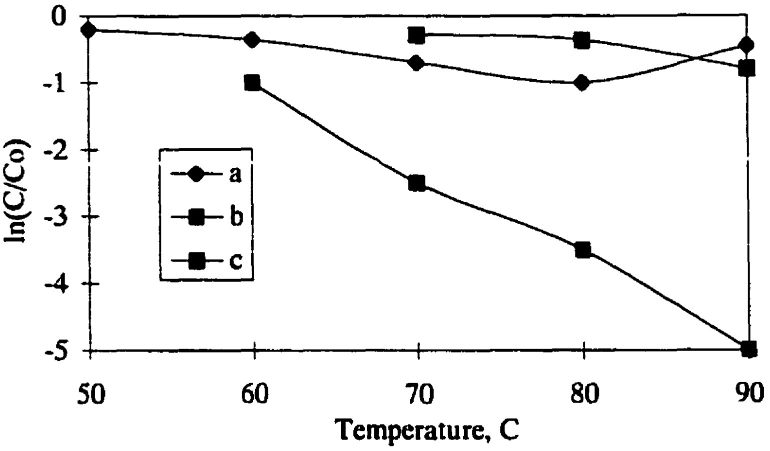

Figure 2.5: Effect of temperature on cobalt cementation: a) electrolytic reduction of cobalt on antimony substrate after 180 min; 30 A/m^2, [Co^{2+}]=30 mg/L, pH (init.)=4.0, total [Zn^{2+}]=155 g/L (van der Pas and Dreisinger 1996); b) cobalt cementation on zinc with additives after 60 min.(no pH control); [Co^{2+}]=26 mg/L, [Cu^{2+}]=46 mg/L, [Sb^{3+}]=1.5 mg/L, total [Zn^{2+}]=151 g/L (Lew et al. 1993); c) cobalt cementation with additives after 200 min; [Co^{2+}]=10 mg/L, [Cu^{2+}]=20 mg/L, [Sb^{3+}]=10 mg/L, total [Zn^{2+}]=150 g/L (Tozawa et al. 1992).

2.1.3 pH

The solution pH also affects the rate of cementation, although apparently it is the least influential parameter among temperature and reagent concentrations (Blaser and O'Keefe 1983). There is a window of optimum operating pH between 4.0 and 4.4 (Lew *et al.* 1993). Although it is important to maintain as high a pH as possible in order to decrease the hydrogen ion activity and minimize hydrogen evolution, if the pH is too high there is a risk of forming basic zinc sulfate or zinc hydroxide which slows the process by forming a passivating layer on the zinc dust surface. It has been argued that increasing the pH beyond the point where basic zinc compounds form does not inhibit the reduction of cobalt (van der Pas and Dreisinger 1996). Borve and Ostvold (1994) found that the initial cementation rate is slightly higher for solutions at pH 4 than at 4.7, but that the final cobalt concentration is independent of initial pH. Their results also indicate that hydrogen evolution, which can block sites for cobalt deposition, is more detrimental to the cementation process than the formation of zinc hydroxide. Van der Pas and Dreisinger (1996) also claimed that a low pH is more detrimental to cementation than a high pH.

Figure 2.6 summarizes the typical effects found in literature. Note that the cementation rate on antimony does not drop above pH 4 as it does with zinc dust cementation. Surface precipitation on zinc dust is facilitated by the adsorption of zinc ions in the double layer; this adsorption does not occur on antimony. By comparing the electrolytic data and the cementation data, we can infer that at high pH surface precipitation of zinc hydroxide or basic zinc sulfate retards cementation kinetics.

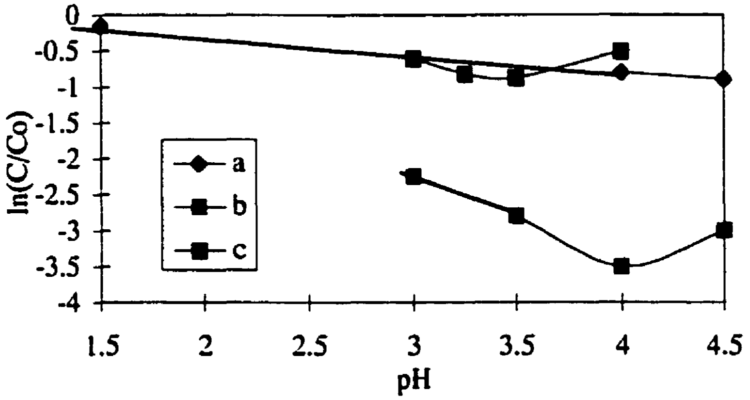

Figure 2.6: Effect of pH on cobalt cementation: a) electrolytic reduction of cobalt on antimony substrate after 180 min, 30 A/m^2, [Co^{2+}]=30 mg/L, 73°C, total [Zn^{2+}]=155 g/L (van der Pas and Dreisinger 1996); b) cobalt cementation on zinc with additives after 60 min; [Co^{2+}]=26 mg/L, [Cu^{2+}]=46 mg/L, [Sb^{3+}]=1.5 mg/L, 73°C, total [Zn^{2+}]=151 g/L (Lew et al. 1993); c) cobalt cementation with additives after 200 min; [Co^{2+}]=10 mg/L, [Cu^{2+}]=20 mg/L, [Sb^{3+}]=10 mg/L, 90°C, total [Zn^{2+}]=150 g/L (Tozawa et al. 1992).

2.1.4 Additives

Industry currently uses two methods to improve the kinetics of cobalt cementation: copper/antimony activation and copper/arsenic activation. These additives act as electrocatalysts to promote the rate of cobalt cementation. The antimony process typically operates at a higher temperature (80-95°C) than the arsenic process (70-75°C), but uses a smaller concentration of additive, as little as 2 mg/L compared to 50-100 mg/L for arsenic. The optimum concentration of antimony is reportedly 3-4 mg/L, and that of copper is 50-100 mg/L (Borve and Ostvold 1994). Little is known about the mechanism by which these additives work, particularly the way copper and antimony or arsenic work in conjunction; thus this has been the focus of the majority of research on cementation.

An early study by DeBlander and Winand (1975) showed that the formation of antimony, copper, and cobalt triple alloys accelerate cobalt deposition and inhibit hydrogen evolution. According to this study, copper has a greater accelerating effect on cementation, while antimony stabilizes the deposit. This is in direct contrast to many of the studies discussed below, which found that copper on its own has little or no accelerating effect.

Antimony alone activates cobalt reduction (Lew *et al.* 1993), but the final cobalt concentration is much higher than when antimony and copper are both present, and the rate of cementation is slower in the presence of antimony alone. By observing the pH of the reaction solution, the authors noted that antimony also suppresses hydrogen evolution (despite antimony having a much larger hydrogen exchange current density than zinc). Copper in solution alone also activates cobalt cementation but only very slightly, and it has no effect on hydrogen evolution. In the opinion of Lew *et al.* (1993) this suggests that copper acts primarily as a substrate for cobalt cementation while antimony plays roles in both maintaining a high overpotential for hydrogen evolution and in providing a substrate for cobalt deposition. Both additives cement out of solution within the first ten minutes to very low levels. There is no difference between tests performed with untreated zinc dust and tests with dust that had been pre-coated with copper and antimony.

The validity of the supposition that antimony acts to suppress hydrogen evolution is doubtful as both antimony and copper have a much higher hydrogen exchange current density than zinc; both should in fact catalyze hydrogen evolution. Lew *et al.* (1993) concluded that antimony suppressed hydrogen evolution, because the initial pH was lower in tests with antimony than in those without, indicating that hydrogen evolution was greater in the latter. Considering the total change in pH over the course of the 100 minute experiment, however, one can see that in reality the change in concentration of H^+ was more than two times greater in the experiment with antimony.

A fundamental study of the copper/antimony process by van der Pas and Dreisinger (1996) confirmed that copper and antimony cement out of solution in the early stages of the process, before cobalt does, and that copper alone has very little effect on cementation. However, the effect of copper and antimony together is greater than the sum of the individual effects. The authors showed that the cobalt content of the cement is 10 times higher on an antimony substrate than on a copper substrate. They showed that the effect of copper on the other hand, is to deposit on the dust as a dendritic precipitate, increasing the surface area of the dust.

Comparing the available data in literature, it is apparent that copper improves the cementation rate only slightly (Figure 2.7a), but works in a synergistic way with antimony (Figures 2.7b and 2.7c).

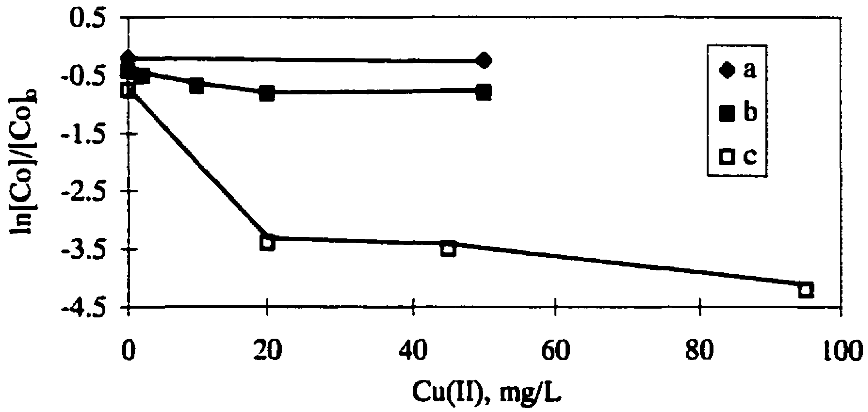

Figure 2.7: Effect of Cu(II) on cobalt cementation: a) Cobalt cementation after 90 min. ($[Co^{2+}]$=26 mg/L, natural pH, 73°C, $[Zn^{2+}]$=151g/L) (Lew et al. 1993); b) Cobalt cementation with antimony after 60 min. ($[Co^{2+}]$=26 mg/L, $[Sb^{3+}]$=1.5 mg/L, natural pH, 73°C, $[Zn^{2+}]$=151 g/L) (Lew et al. 1993); c) Cobalt cementation with antimony after 200 min. ($[Co^{2+}]$=10 mg/L, $[Sb^{3+}]$=10 mg/L, pH=3.3, 90°C, $[Zn^{2+}]$=150 g/L) (Tozawa et al. 1992).

It is probable that the additives form a substrate which is favourable for cobalt reduction, with copper forming a larger cathodic area and antimony increasing the amount of cobalt in the deposit. The beneficial effect of antimony on the rate of cobalt cementation with zinc dust may be attributed to the changing structure of the electrical double layer. There is significantly less adsorptive accumulation of Zn^{2+} on the antimony surface, permitting cobalt ions to reach the reaction surface. Figure 2.8 gives a schematic representation of the probable reaction mechanism.

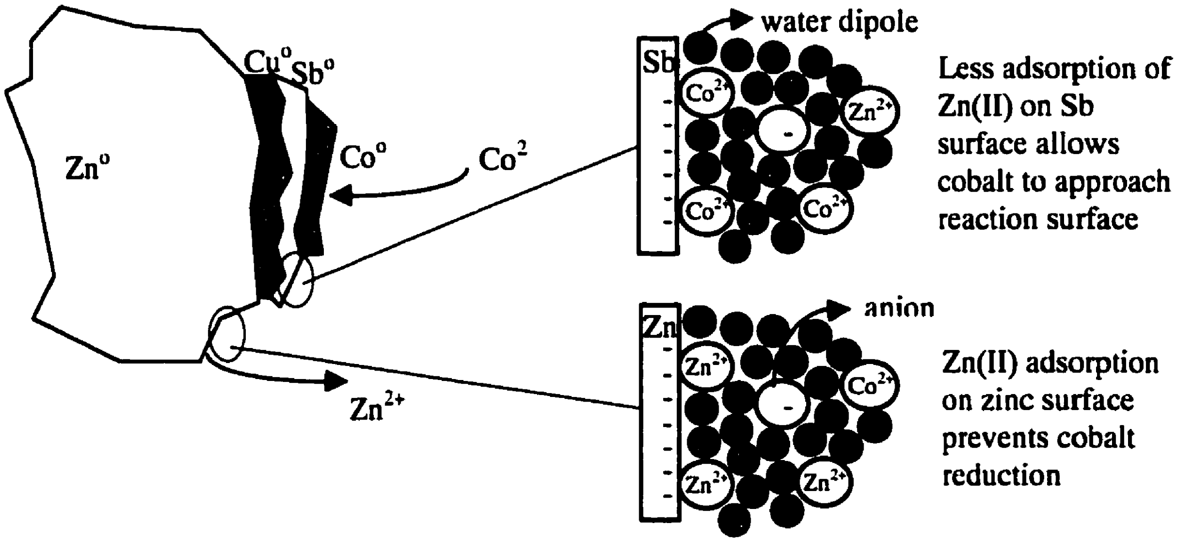

Figure 2.8: Schematic representation of the postulated activation role of antimony in cobalt cementation.

Wang and O'Keefe (1994) looked at the effect of additives on zinc ion inhibition. The anomalous codeposition of zinc is sometimes attributed to the formation and adsorption of a zinc hydroxide film which inhibits cobalt while favouring zinc reduction. The hydroxide forms when there is a pH rise in the area of the cathode due to hydrogen evolution. The authors postulated that antimony has the effect of disrupting the formation of the zinc hydroxide layer. They found that by adding 5 mg/l antimony they could increase the cobalt content of the deposit by a factor of 3. They also experimented with germanium as an additive; germanium additions nearly double the cobalt content.

Kim *et al.* (1992) showed that the addition of antimony only up to 5 mg/L enhances the cobalt cementation rate; at greater concentrations of antimony cobalt redissolves. Fontana and Winand (1971) noted that retention times of longer than one and a half hours in the second (i.e. cobalt) purification stage had the effect of putting cobalt back into solution. They suspected that this was due to reoxidation of the cemented cobalt by dissolved oxygen. In theory however, two metals in contact in an acid solution form a galvanic couple in which the dissolution rate of the component with the higher standard reduction potential is accelerated and that of the other retarded. Thus coupling zinc with cobalt, which has a more noble dissolution potential relative to zinc, results in a smaller dissolution rate of cobalt relative to that from pure cobalt, while accelerating that of zinc. Experiments confirmed this behaviour. Above pH 2.5 Oh (1995) showed that it is not possible to dissolve cobalt from mixed cobalt-zinc. Perhaps an excess amount of antimony results in the complete coverage of the zinc dust, at which point cobalt is no longer afforded cathodic protection by zinc.

Fontana *et al.* (1971) also reported the effects of alternative additives to antimony, in particular lead, tin, arsenic, and bismuth, added as oxides or chlorides. By comparing the removal rate of cobalt in the presence of both the oxides and the chlorides, they inferred that the chloride ion does not have a particularly beneficial effect, and as it is harmful to the electrowinning process, they chose to use the metal oxides in their experiments. Lead compares favourably to antimony as an additive, followed by tin, arsenic, and then bismuth, which has only a negligible effect. All the additives function better in the presence of copper or cadmium, or when two or more additives are used. The best combinations were Cu-Pb-Sb and Cu-Cd-As. The authors did not report the effect of additives on zinc dust consumption or hydrogen evolution.

2.1.5 Alloys

Many studies suggest that additives act by forming alloys with cobalt; these alloys may be more stable than cobalt alone or promote the rate of cementation. These theories and experimental results tend to contradict the previously discussed results which show that additives form a substrate upon which cobalt preferentially deposits.

M-As-H_2O and M-Sb-H_2O potential-pH diagrams show that metal arsenides and antimonides for Cu, Co, and Ni are all more stable than the metals alone (Figure 2.9) (Tozawa *et al.* 1992). From this one would presume that the removal of cobalt by cementation with either arsenic or antimony proceeds by the formation of cobalt arsenide or antimonide. However, Tozawa *et al.* (1992) found that the addition of copper ions contributed more to cobalt removal with arsenic trioxide in comparison to that with antimony trioxide, where its addition has a minimal effect. These findings indicate that the mechanism of cobalt removal with antimony is different from that with arsenic. In these experiments, the deposition of cobalt arsenide was confirmed, in agreement with predictions from the potential-pH diagrams, but cobalt antimonide was not found by SEM investigation. In the arsenic tests, cobalt, arsenic, and copper deposited on the same site, while in the antimony tests copper and antimony coexisted with cobalt found around the copper-antimony deposit.

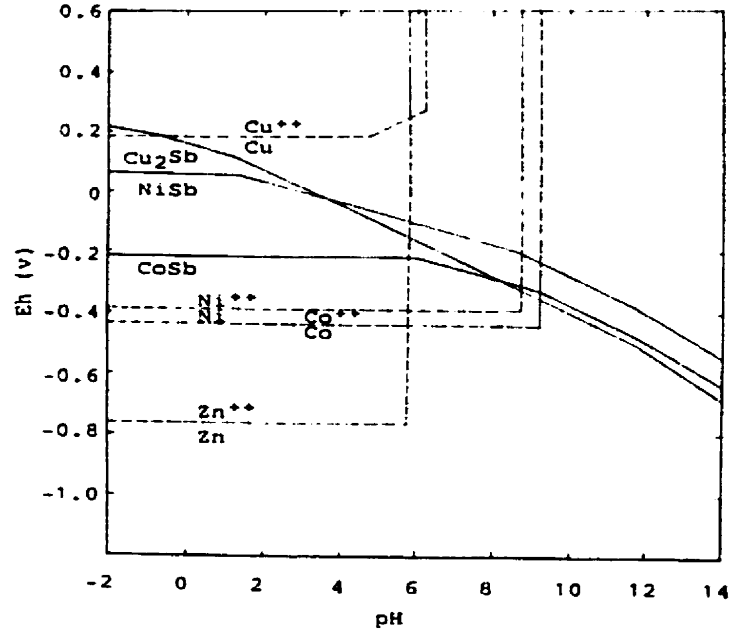

Figure 2.9: E_h-pH of M-Sb-H_2O system. [Cu] = [Ni] = [Co] = 10^{-5}M, [Zn] = 1 M (Tozawa et al. 1992).

Fischer-Bartelk *et al.* (1969) proposed thermal equilibrium diagrams for cobalt, nickel, and additives which show the possible constitution of new phases by electrochemical deposition. They postulated that the formation of strong intermetallic phases with cobalt and zinc imparts a more positive potential to the cementation reaction, compensating for the cobalt deposition overpotential. They identified alpha-brass and gamma-cobalt-zinc phases in the cement.

Kroleva (1980) suggested the formation of a Cu_2Sb alloy which enhances cobalt deposition by depolarizing the reaction:

$$Zn + Cu_2Sb \rightarrow Zn^{2+} + (Cu_2Sb)^{2-} \qquad (2.4)$$

$$Co^{2+} + (Cu_2Sb)^{2-} \rightarrow Co + Cu_2Sb \qquad (2.5)$$

However the author also suggested that a Cu_2Sb alloy depolarizes hydrogen evolution and dissolved oxygen reduction:

$$2H^+ + (Cu_2Sb)^{2-} \rightarrow H_2 + Cu_2Sb \qquad (2.6)$$

$$2H^+ + \tfrac{1}{2}O_2 + (Cu_2Sb)^{2-} \rightarrow H_2O + Cu_2Sb \qquad (2.7)$$

Yamashita *et al.*(1997) proposed a mechanism for the accelerating effect of copper and arsenic on cobalt cementation: a galvanic cell forms between zinc dust and copper (which cements first), then the galvanic current reduces cobalt on copper as a Co-As alloy:

$$2Co^{2+} + 2HAsO_2 + 6H^+ + 10e^- \rightarrow 2CoAs + 4H_2O \qquad (2.8)$$

The galvanic current is almost zero in zinc sulfate solution that contains no arsenic, but flows constantly when arsenic is present, maintaining a cathode potential of -500 mV.

Fontana and Winand (1971) concluded that the role of copper is to help solubilize antimony by the following reaction:

$$3Cu^{2+} + 2Sb + 4H_2O \rightarrow 2HSbO_2 + 6H^+ + 3Cu \qquad (2.9)$$

$$2HSbO_2 + 6H^+ + 3Zn \rightarrow 3Zn^{2+} + 2Sb + 2H_2O \qquad (2.10)$$

They also identified CoSb and $CoSb_2$ in the cement by X-ray diffraction; the characteristic peaks for antimony or cobalt alone are not observed. They concluded that antimony acts to diminish the cobalt reduction overpotential on zinc by forming definite alloys, as proposed by Fischer-Bartelk *et al.* (1969). Further study by Fontana *et al.* (1971) showed that lead, tin, and arsenic all improve cobalt cementation, leading the authors to believe that it is not possible to generalize the previous observation and say that the favourable action of additives is due to the formation of compounds or solid solutions. Lead is comparable to antimony in its effect on cobalt cementation, yet it does not form alloys with cobalt. This contradicts the theory proposed by Fischer-Bartelk *et al.* (1969).

Lew *et al.* (1993), on the other hand, identified no alloys in SEM micrographs of the cement. Van der Pas and Dreisinger's (1996) work supports this finding; it showed that the additives cement out of solution rapidly and form a substrate for cobalt reduction, rather than forming an alloy with cobalt that cements more rapidly.

2.1.6 Zinc dust concentration

Lew *et al.* (1993) stated that the optimal concentration of zinc dust for cobalt removal with the antimony-activated process is 4 g/L; this is the typical amount used in industry (van der Pas and Dreisinger 1996). The size of the particles is important; smaller dust (<24 micron diameter (Adams *et al.* 1995)) gives faster initial kinetics, a lower final cobalt concentration (Borve and Ostvold 1994), and is described as more reactive (Adams *et al.* 1995). The use of a finer dust also assists in stabilizing the cement (Adams *et al.* 1995). This is likely a surface area effect, although there are no measurements of surface area in either study. No studies mention the effect of zinc dust morphology either.

Assuming that the additives act once they have deposited on the dust as a metal, a zinc dust that is alloyed with the additive metal is potentially more effective than the pure metal. Kerby (1985) reported the influence of zinc alloys on cementation rates: while aluminum, antimony, arsenic, cobalt, tellurium, iron, and nickel alloys have a detrimental effect on cementation, lead alloys (0.05-5 % by weight) increase the rate. Copper alone has no benefit, but copper and lead together are more beneficial than lead alone. Cadmium, manganese and tin have only minor effects on the rate of cementation.

Often the zinc dust from the second (cobalt removal) purification stage is recycled to the first (cadmium removal). In an optimization study for the Electrolytic Zinc Plant at Debari in India, experiments showed that a 1:1 combination of recycled zinc dust and fresh dust gives better cobalt removal than fresh dust alone (Singh 1996). Not only is the initial reaction rate faster, but the final cobalt level achieved is lower. The increased activity of the recycled zinc dust is not explained. Implementation of this strategy in the plant resulted in a reduction of zinc dust consumption that had been as high as 85 kg/ton of zinc produced to 35-40 kg/ton zinc produced at the present time.

2.1.7 Organics

The RLE process uses organic reagents at several points in zinc production: flocculants such as Percol 156 are added in solid-liquid separation steps that use thickeners, and the electrowinning process uses glue to enhance deposit morphology, as well as agents such as saponin to eliminate acid-mist (Houlachi *et al.* 1990). As the spent electrolyte is recycled back to the leach operation, small amounts of residual organics may be present in the purification process.

Houlachi *et al.*(1990) showed that residual organics in zinc electrolyte at levels as low as 0.5 mg/l have a detrimental effect on cobalt cementation. They reported that increasing simultaneously the levels of zinc dust and antimony can overcome the detrimental effect, and that increasing the level of copper can partially reverse the detrimental effect.

Lew *et al.* (1993) confirmed the effect of residual organics, noting that the presence of 2 mg/L animal glue, Percol 351, or lignin sulphonic acid greatly reduces the rate of cobalt cementation and the amount of cobalt removed.

2.1.8 Chloride

As mentioned previously, Fontana *et al.* (1971) concluded that chloride had no effect on cementation. Jiang *et al.* (1990b) however, contradict the conclusions of Fontana *et al.* about chlorides: their extensive study showed that the rate of cobalt deposition is significantly affected by anions in solution. The rate of cobalt deposition increases correspondingly in the presence of the following anions: $NO_3^- < CH_3COO^- < SO_4^{2-} < Cl^-$. The presence of these ions causes the reduction potential of cobalt to shift more negatively, with the ions in this same sequence having a progressively greater effect. Shifts of the deposition potential to the more cathodic significantly increase the rate of cobalt electrodeposition. Tanabe *et al.* (1995) also reported the catalytic effect of chloride and thiocyanate anions on the electrodeposition of iron-group metals. They concluded that chloride has a depolarizing effect, in effect reducing the cobalt deposition overpotential

2.1.9 Oxygen

Oxygen solubility is temperature dependent: it is soluble to 8.5 mg/L at 25°C and 5 mg/L at 90°C (Perry and Green 1984) in pure water, and to 9.5 mg/L at 37°C in 2.15 M $ZnSO_4$ (Lide 1995). It is possible that oxygen inhibits cobalt reduction by the formation of oxides or hydroxides on the zinc dust surface, or it can cause the oxidation of zinc:

$$Zn + \tfrac{1}{2} O_2 + 2H^+ \rightarrow Zn^{2+} + H_2O \qquad (2.11)$$

Oxygen in solution also causes cobalt dissolution:

$$Co + \tfrac{1}{2} O_2 + 2H^+ \rightarrow Co^{2+} + H_2O \qquad (2.12)$$

Figure 2.10 shows the capacitance at the Co^{2+}/Zn interface to increase in the presence of oxygen: the rapid initial increase in capacitance in the presence of air indicates the formation of a layer of oxide or hydroxide on the surface of zinc, which may result in the passivation of the reaction surface (Xiong and Ritchie 1989). Bubbling nitrogen in the electrolyte is the most common way to deoxygenate, and also to increase the hydrogen overpotential on a cobalt electrode (by 100 mV) (Rojas *et al.* 1992). Typically deoxygenating with nitrogen is considered too expensive an option to implement industrially. Despite this, nitrogen blanketing was installed at Pasminco Metals-EZ for safety reasons, resulting in a savings of 5.3 kg zinc dust/t zinc produced (Adams *et al.* 1995).

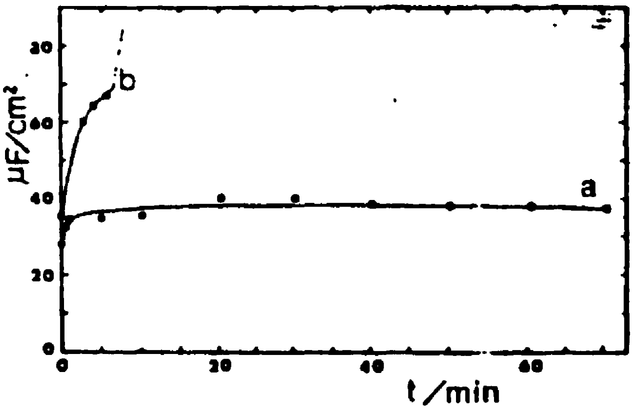

Figure 2.10: Variation of capacitance with time during cobalt cementation (pH 4.0, zinc disc rotation 700 rpm) (Xiong and Ritchie 1989): a) solution deoxygenated with argon; b) in the presence of air.

2.2 HYDROGEN EVOLUTION

2.2.1 Hydrogen exchange current density

It is apparent from the preceding sections on zinc dust cementation that hydrogen evolution is an important aspect of the process and integral to its success. It is necessary to inhibit hydrogen evolution in order to obtain fast cementation kinetics and low zinc dust consumption.

Hydrogen evolution is a complicated reaction composed of several steps (Scully 1990):

proton discharge: $H_3O^+ + e^- \rightarrow H_{ads} + H_2O$ (2.13)

atom combination: $H_{ads} + H_{ads} \rightarrow H_2$ (metal surface) (2.14)

secondary discharge: $H_3O^+ + H_{ads} \rightarrow H_2$ (metal surface) $+ H_2O$ (2.15)

Several metals are known to be good catalysts for hydrogen evolution, and there has been considerable investigation of alloys and composite materials as better electrocatalysts. Platinum is the best pure metal catalyst, and although there is some improvement in the hydrogen overpotential by modifying platinum with other metals, in most cases alloys lead to a higher evolution overpotential (Enyo 1983). Trassati (1972) has shown that the exchange current density of hydrogen evolution on the surface of a given metal can be related to the metal's work function. The exchange current density and work function (the energy with which electrons near the Fermi level are bound to the solid metal) are linearly related, regardless of the mechanism involved in the rate determining step.

2.2.2 Dependence on particle morphology

The type of metal surface and the electrolyte composition can affect the reaction through one or more of the above steps. For example, a study of hydrogen evolution on vanadium, chromium, manganese and cobalt in sulfuric acid sulfate solutions revealed that hydrogen evolution on vanadium and manganese proceeds by proton discharge (equation 2.13), whereas on cobalt and chromium it occurs by the radical ion mechanism (equation 2.15) (Belanger and Vijh 1992). Table 2.1 summarizes the data for cobalt.

Table 2.1: Hydrogen evolution data for cobalt electrodes (Belanger and Vijh 1992).

Parameters	Values	Comments
Tafel slope (25°C)	115 mV/decade	in 1*N* H_2SO_4+2*N* Na_2SO_4, pH=0.7
Exchange current density(25°C)	6.25×10^{-7} A/cm^2	
Corrosion potential	-114 mV	
Corrosion current	5.4×10^{-6} A/cm^2	open circuit potential in 1*N* H_2SO_4 + 2*N* Na_2SO_4

The morphology of the metal surface can also affect hydrogen discharge. Hydrogen evolution on carbon electrodes with different structures demonstrates the significance of the electrode surface condition on hydrogen evolution (Brennan and Brown 1972). The activity of hydrogen ion on various types of surfaces can be partially correlated to surface area, but not entirely. In general, very rough or porous surfaces are more active for hydrogen evolution (Los *et al.* 1991). Also, the active surface area can be reduced by the formation of hydrogen gas in pores and crevices in the electrode (Brennan and Brown 1972).

Impurities in the metal also have a significant effect on hydrogen evolution. In zinc, for example, most impurities (Fe, Mn, Cu, Hg) lower the hydrogen overpotential without changing the mechanism for hydrogen discharge. Savadogo and co-workers (Ndzebet and Savadogo 1994, Savadogo and Ndzebet 1992, 1993, Savadogo *et al.* 1992, Savadogo and Allard 1991) systematically investigated the catalytic behaviour of nickel with a variety of additives. The main conclusions of interest are:

1. the electrocatalytic parameters (exchange current density i_o and hydrogen overpotential η) are improved by adding Cu(II) to the electrolyte;
2. nickel deposited with Co(II) in solution was a better catalyst for hydrogen discharge than nickel alone, due to the formation of Ni-Co alloys;
3. any improvement in catalytic activity for hydrogen evolution corresponds to an increase in i_o and a decrease in η, while the value of the Tafel slope, b, remains constant for different electrodes, indicating that those additives do not change the discharge mechanism.

However, other reports (Millenbach *et al.* 1983) showed that impurities in solution (such as arsenic) do change the Tafel slope and thus also the discharge mechanism.

The presence of oxygen in solution can affect the hydrogen overpotential by the participation of oxygen in the reduction reaction (Cui *et al.* 1992, Jiang and Tseung 1990a and 1990b). Cobalt oxides and hydroxides (CoOOH, Co_3O_4, CoO) formed during oxygen reduction are further reduced to Co, which results in a more porous electrode, and a lower hydrogen overpotential. Bubbling nitrogen, conversely, results in a considerable increase in the hydrogen overpotential, due to the dense surface layer of cobalt deposited with bubbled nitrogen.

2.3 CONCLUSIONS

From the wealth of information collected above and the various theories of cobalt cementation put forth, it seems safe only to conclude that zinc ion adsorption on the zinc dust surface is responsible for the slow rate of reaction (whether by physically or electrically blocking the reacting surface or by subsequent formation of a passivating precipitate). Antimony and copper deposition on the zinc substrate seems to change the surface properties and prevent zinc ion adsorption, thus facilitating cobalt reduction. The activation mechanism is unclear; however, the evidence for antimony depositing before cobalt and forming a preferable substrate for cementation is more convincing than for the formation of a Co-Sb alloy with a reduced cobalt deposition overpotential. By looking at a broad range of additives, this author hopes to elucidate the characteristics of efficient activators, and in doing so perhaps shed some light on the underlying mechanism.

3. EXPERIMENTAL

3.1 CHEMICALS

Analytical grade chemicals were used in all the experiments, and all solutions were prepared with de-ionized water. The synthetic electrolyte contained 150 g/L zinc prepared by the dissolution of a suitable amount of zinc sulfate heptahydrate and 30 mg/L of cobalt (from the dissolution of cobalt sulfate pentahydrate). The additives and concentrations used in the experiments are listed in Table 3.1, unless otherwise stated in the text.

Table 3.1: Chemicals used in experimental work.

Element	Compound	Typical concentration of cation
Antimony	Sb_2O_3	2 mg/L
Copper	$CuSO_4{\cdot}5H_2O$	30 mg/L
Cadmium	$3CdSO_4{\cdot}8H_2O$	30 mg/L
Lead	PbO	30 mg/L
Mercury	HgO	30 mg/L
Indium	$In_2(SO_4)_3$	30 mg/L
Tellurium	$TeCl_4$	30 mg/L
Selenium	SeO_2	30 mg/L
Silver	$AgNO_3$	30 mg/L
Bismuth	Bi_2O_3	30 mg/L
Germanium	$GeCl_4$	30 mg/L
Arsenic	As_2O_3	30 mg/L

3.2 ZINC DUSTS

Five grams of zinc dust per litre of solution were used in each test. Two zinc dusts were used: a commercial dust from Zincorp (Philadelphia, Pennsylvania, USA), and a water atomized dust from CEZinc (Valleyfield, Quebec, Canada). Table 3.2 gives the characteristics of each dust. The zinc dust surface area was measured with a BET analyzer. SEM photos of the two dusts follow in Figure 3.1.

Table 3.2: Zinc dust characteristics

	average particle size	surface area	composition
Zincorp	7 µm (90% -15 µm)	0.533 m^2/g	0.15% lead, 3.1% zinc oxide
CEZinc	50-75 µm	1.741 m^2/g	0.7-1% lead

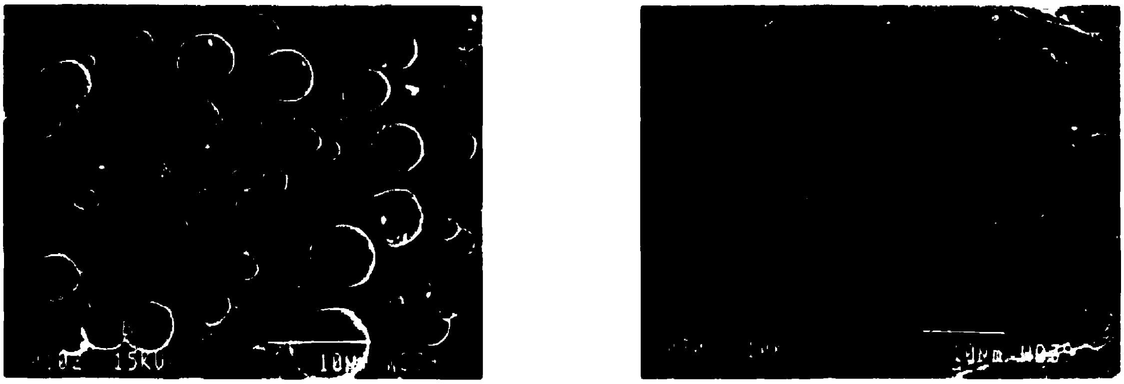

Figure 3.1 Zincorp dust (left) and CEZinc dust (right). Note that CEZinc dust fills entire frame of photo (no background is visible).

3.3 EXPERIMENTAL SETUP

Batch cementation tests were performed in a one litre, double-walled reactor fitted with a stainless steel lid to prevent solution loss by evaporation (Figure 3.3). Water at 98 °C passing through the walls maintained the temperature of the solution at 95°C ± 0.5 (or at the selected test temperature), and the pH was manually adjusted to the desired pH throughout each test by adding concentrated solutions of sodium hydroxide or sulfuric acid. The pH was measured with an Orion pH meter model 720A and a combination electrode with a silver/silver chloride reference element, accurate to ±0.05 pH units over its entire temperature range (-5 to 100°C). The meter was calibrated at the beginning of each test. An axial-mixing type impeller, with 6 flat blades inclined at 45°, agitated the solution at 1000 rpm. The inside of the lid, impeller, baffles, and all other exposed steel parts were coated with Teflon to prevent any corrosion or cementation on them.

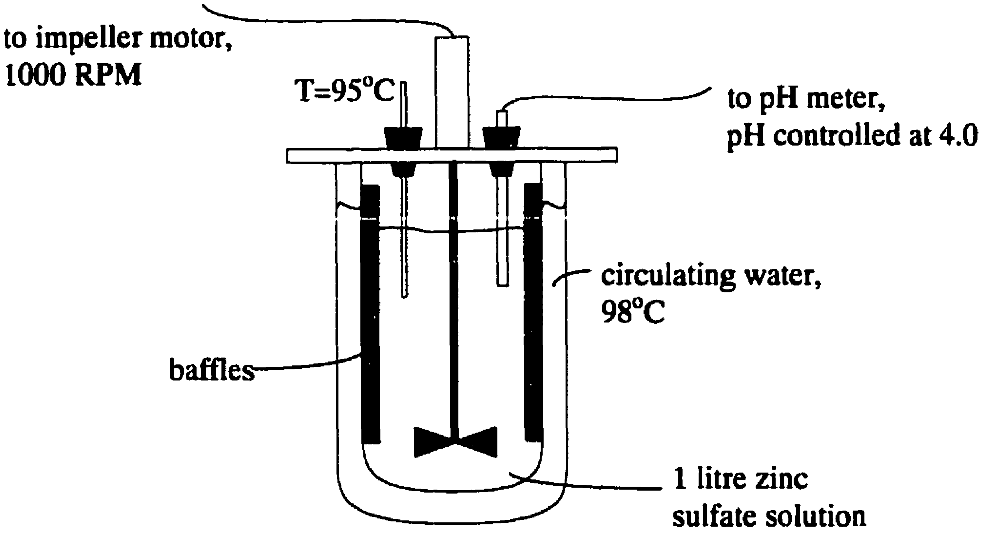

Figure 3.2: Experimental setup.

3.4 EXPERIMENTAL PROCEDURE

In a typical test, the zinc electrolyte was brought to temperature in the reactor, and then the appropriate additives were added in the form of aqueous stock solutions. The pH was adjusted to 4.0, and then 5 g/L zinc dust was added to start the experiment. The pH was maintained at 4.0 during the course of each test, except where noted. The tests ran for 2 hours, and samples were taken before the zinc dust addition and at intervals 5, 15, 30, 45, 60, 90, 120 minutes after. Each 5 mL sample was diluted with 5 mL of a 5% HNO_3 solution to prevent precipitation of salts on cooling. At the end of the test the remaining solids were filtered, washed with deionized water, air-dried at room temperature (to prevent any oxidation that might occur at the elevated temperatures in an oven), weighed, and collected for further analysis. Zinc dust consumption was determined by subtracting the weight of the remaining dust from the weight of the initial amount used in the test.

3.5 ANALYTICAL PROCEDURE

In the first part of the research (cementation fundamentals), samples were analyzed for cobalt and additives by atomic absorption spectroscopy (AA). In the second part (novel activators and combinations of additives), samples were analyzed by inductively coupled plasma spectroscopy (ICP), mainly for the lower detection limits afforded by this technique.

3.5.1 Atomic absorption spectroscopy

The cobalt content in solution was determined with a Perkin Elmer model 3100 atomic absorption spectrophotometer. The linear range of measurement for cobalt is between 0 and 7 mg/L; the machine was calibrated using 1, 3.5, and 7 mg/L standards prepared from 1000 mg/L certified cobalt standard. The standards were prepared to match the background matrix of the samples (i.e., the standards had the same zinc concentration). The detection limit for cobalt by AA is 0.1 mg/L under the best conditions (no background matrix), and for the comparison of some results, this proved to be inadequate.

3.5.2 Inductively coupled plasma spectroscopy

ICP offers several advantages over measurement with AA:

- lower detection limits (some typical detection limits for ICP-MS are listed in Table 3.3)
- lower inter-element interferences due to higher flame temperature
- determination of element over several decades of concentration (compared to 1 or 2 for AA)
- one set of conditions gives good spectra for most elements, permitting the determination of several elements simultaneously.

Table 3.3: Typical detection limits for relevant analytes.

Element	Detection limit, ppt[a]
Cd	0.1-1
Co	0.1-1
Cu	0.01-0.1
Pb	0.1-1
Sb	0.1-1
Sn	0.1-1
Zn	0.1-1

a) Montaser 1998

The ICP analysis of cobalt and additive concentrations was performed by the Department of Chemistry at McGill University on a Thermo Jarrell Ash ICP-MS model POEMS II. The machine was calibrated using 1, 10, and 100 μg/L cobalt standards prepared from certified 1000 mg/L solutions. The standards were prepared with the appropriate background matrix of zinc sulfate.

3.5.3 Scanning electron microscope

The morphology of the unreacted zinc dust and the samples collected at the end of each test were determined by scanning electron microscope (SEM), on a JEOL 840A machine. Polished cross sections of the dust as well as whole dust particles were examined, and elemental mapping of the cross sections was also performed to assess the composition and structure of the deposits.

4. RESULTS AND DISCUSSION

4.1 CONVENTIONAL CEMENTATION PARAMETERS

The object of the first part of the research was to confirm results found in literature and explore the fundamentals of cobalt cementation with conventional additives, antimony and copper. The main parameters considered were: temperature, pH, Zn(II) concentration, the effect of additives (Sb/Cu), the presence of oxygen, the presence of some chemicals commonly found in zinc electrolyte (chloride and cadmium), and the type of zinc dust. Initially zinc dust from Zincorp was used in these tests, but as a supply of zinc dust became available from CEZinc that dust was used for the remainder of the tests. In this section each test was performed only once, unless the results differed significantly from those found in literature (or unless no literature results were available for comparison).

4.1.1 Temperature

The range of temperatures tested (75-95°C) match those used in industry in different cobalt cementation processes. The initial cobalt concentration was 30 mg/L, and there were no additives. The pH, initially 4.0, was not controlled in order to observe the effect of temperature alone.

The effect of temperature is shown in Figure 4.1. The left hand y-axis shows the fraction of cobalt remaining in solution (cobalt concentration at time *t* divided by the initial cobalt concentration). The pH values are read off the right-hand axis, with the profile shown by the dotted line. The pH profile was nearly identical at each temperature so an average of the three values at each time is shown.

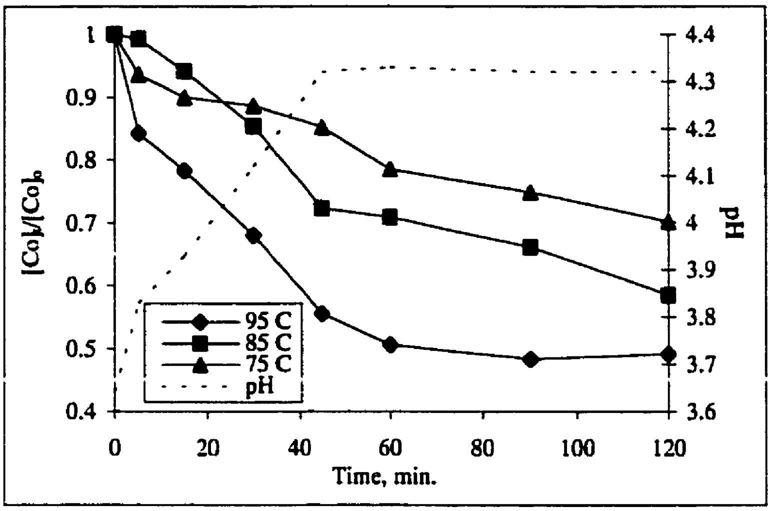

Figure 4.1: Effect of temperature on cobalt cementation (natural pH, 150 g/L $ZnSO_4$, 5 g/L Zincorp dust, no activators).

Without activators, cobalt removal was slow, with less than 50% percent removed over 2 hours. As expected from the literature (Lew *et al.* 1993), removal rates improved with increasing temperature. This behaviour is typical of a chemically controlled process (indicated by large activation energies, Section 2.1.1).

4.1.2 pH

The CEZinc cobalt removal process operates at pH 4.0. There is a narrow operating window around this pH; much above this value zinc salts will precipitate, passivating the zinc dust, and below this value the activity of H^+ increases and zinc dust consumption accelerates.

To confirm this behaviour, the process was tested at pH 3.8, 4.0, and 4.2 (constant temperature of 95^0C, no additives). The data are difficult to interpret as there is not a significant difference between the three sets of data (Figure 4.2). However, it appears that after an hour at the highest pH, the remaining cobalt in solution levels off, indicating passivation of the zinc dust. There is insufficient difference between the cobalt removal at pH 4.0 and pH 3.8 to determine which is more effective.

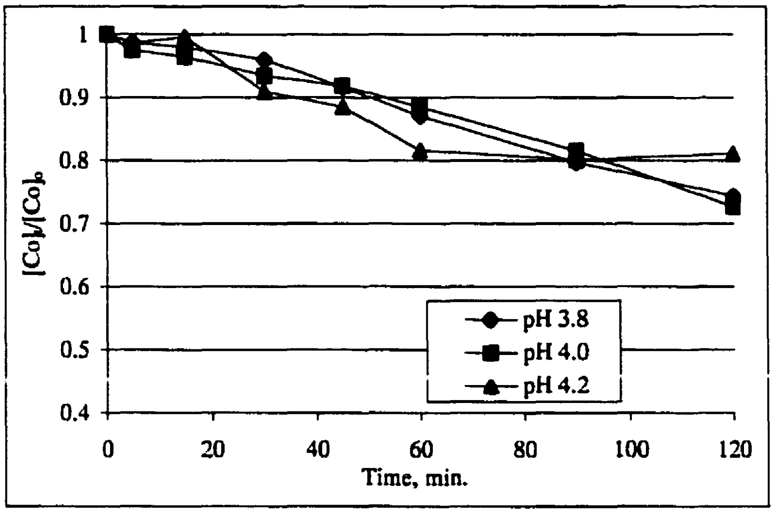

Figure 4.2: Effect of pH on cobalt removal (95°C, 150 g/L $ZnSO_4$, 5 g/L Zincorp dust, no activators).

The amount of zinc dust consumed follows the expected trend: 96% at pH 3.8, 45% at pH 4.0, and less at pH 4.2. The exact amount consumed at 4.2 is undetermined due to the large amounts of precipitate formed.

4.1.3 Additives

Once the baseline temperature and pH were confirmed, the additives used at CEZinc (Sb_2O_3 and $CuSO_4$) were tested individually and together. Figure 4.3 summarizes the results from tests using antimony and copper as activators. As expected, copper alone only marginally improves cobalt removal, and the deposit is not stable (redissolution of cobalt is observed). Antimony greatly improves the rate and extent of reaction, while copper and antimony together give the best removal rate. The deposit obtained with antimony is very stable over the remainder of the test. Analysis of the electrolyte shows that copper and antimony both cement out of solution in the first 5 minutes and remain at undetectable levels throughout the remainder of the test. This suggests that they form a substrate for cobalt deposition, as van der Pas and Dreisinger (1996) have suggested. An attempt was made to obtain elemental maps of polished cross sections of the zinc dust with the cement, with the hope that this would show such stratification in the deposit. However, this was impossible for two reasons. The polishing procedure seems to partially destroy the cement layer, which is not firmly fixed to the zinc dust. In addition, the thickness of the deposit layer is on the order of one micron, which is close to the level of resolution of the X-ray beam used to image the sample. Therefore any data obtained are noisy and inaccurate.

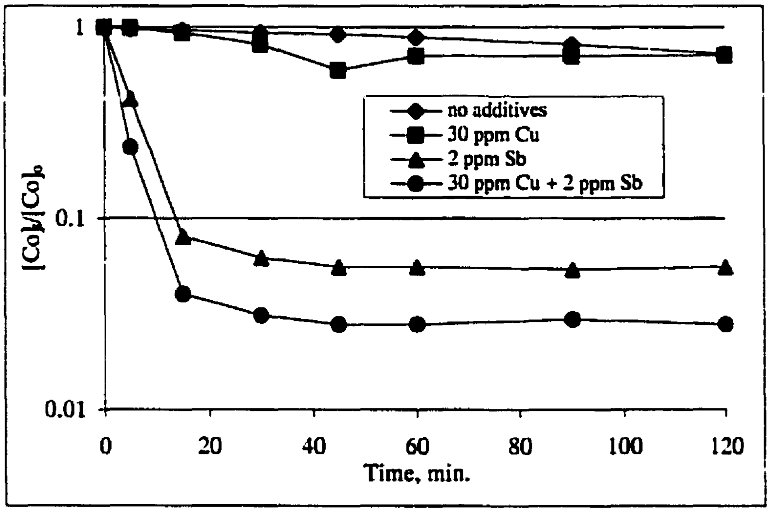

Figure 4.3: The effect of copper and antimony on cobalt cementation (95°C, pH 4.0, 150 g/L $ZnSO_4$, 5 g/L Zincorp dust).

SEM photos of the deposits with and without additives give an idea of the relative amount of deposit (Figure 4.4).

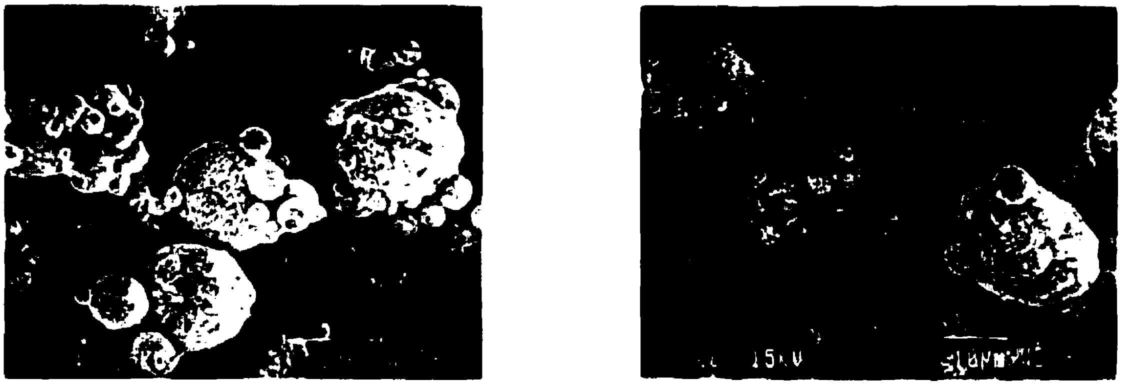

Figure 4.4: SEM photos of cobalt cemented in the absence (left) and presence (right) of additives (Zincorp dust, pH 4.0, 95°C).

In the test with no additives, the smooth dust (compare with photo of unreacted dust in Section 3.2) is now covered with small ridges of deposit. With additives, the deposit is much more evident, granular and needle-like; the reaction has obviously proceeded to a much greater extent.

4.1.4 Zinc(II) concentration

Without zinc ions in solution cobalt cements out rapidly to a low level (Figure 4.5); this suggests that the zinc sulfate electrolyte itself interferes severely with cobalt cementation, possibly by Zn^{2+} adsorbing on the surface of the zinc dust, in effect passivating it. This test confirms previous work which shows inhibition of cobalt reduction by specific adsorption of $ZnOH^+$ on zinc dust (Tanabe *et al.* 1995, West-Sells 1997).

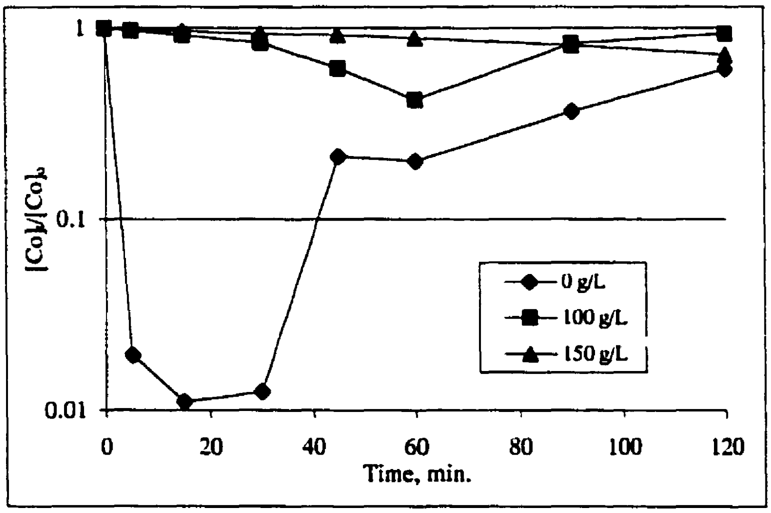

Figure 4.5: The effect of zinc sulfate loading on cobalt cementation (95°C, pH 4.0, 5 g/L Zincorp dust, no activators).

The test results show complete redissolution of the cobalt deposit in the absence of $ZnSO_4$; without the buffering capacity of large amounts of sulfate, a great deal of acid must be added in order to maintain the pH at 4.0. This results in the complete dissolution of the zinc dust in less than 30 minutes, after which the cobalt deposit itself dissolves. Zinc in effect provides cathodic protection for cobalt; when the two metals are in contact it is possible only to dissolve the zinc (Oh 1995).

4.1.5 pH control

In the course of an experiment the pH rises due to consumption of H^+ in the hydrogen evolution reaction. Usually the pH is maintained close to 4.0 to prevent precipitation of zinc salts, but a few tests were run without pH control to get an idea of the range of the pH rise and to see its effect on cobalt reduction.

The first test was run without additives (Figure 4.6). The pH profile is shown by the dotted line (right-hand axis): it appears to be self-regulating after reaching a plateau around 4.3. The lack of pH control has a substantial positive effect on cementation, likely due to the smaller number of protons competing for reaction sites at the zinc surface, and the larger surface area of zinc dust available due to lower consumption.

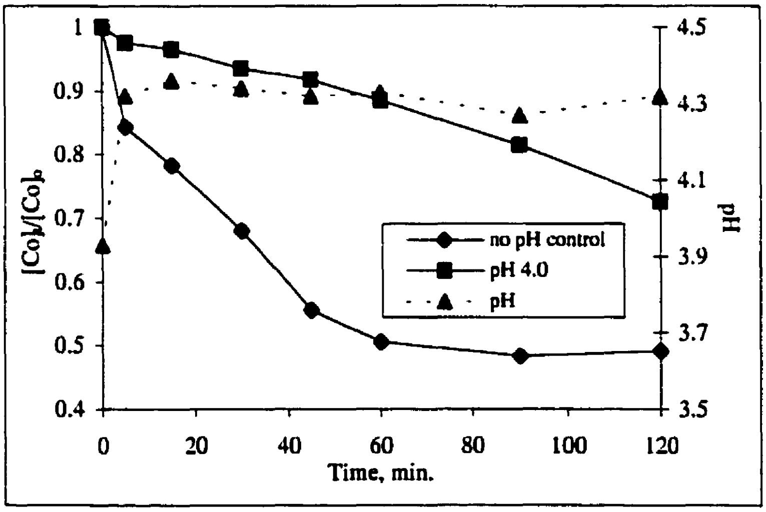

Figure 4.6: Cobalt cementation with and without controlled pH in the absence of activators (95°C, 150 g/L $ZnSO_4$, 5 g/L Zincorp dust). Dashed line shows pH profile, values on right-hand axis.

The second test was run in the presence of additives. The beneficial effect here is less pronounced but still present (Figure 4.7 -- note that left-hand y-axis is on a log scale). Again the pH reaches a plateau near 4.3 and appears to be self-regulating. Evidently the catalytic effect of additives is large enough to render the decrease in competing reaction almost negligible in comparison. Cobalt cementation is slightly enhanced, once again due to a reduction in the rate of the competing reaction. There was significant formation of precipitates in the test with no pH control, evident both in the colour of the reaction solution (noticeably more white) and in the solids filtered at the end of the test. Since in the presence of additives cementation is quite rapid, and the formation of precipitates seems to be quite slow (solution colour remained unchanged for first 60 minutes of experiment), most likely the zinc dust surface does not become passivated until well after cementation is complete. At this point passivation by precipitates may in fact be beneficial, preventing oxidation or dissolution of the deposit. There are no data from literature studying the effect of leaving the pH uncontrolled, although Borve and Ostvold (1994) and Van der Pas and Dreisinger (1996) both concluded that an elevated pH is less detrimental to cementation than a reduced one. From an industrial point of view, the solids become difficult to handle due to the formation of amorphous precipitates, though this could be avoided by lowering the pH just prior to filtration.

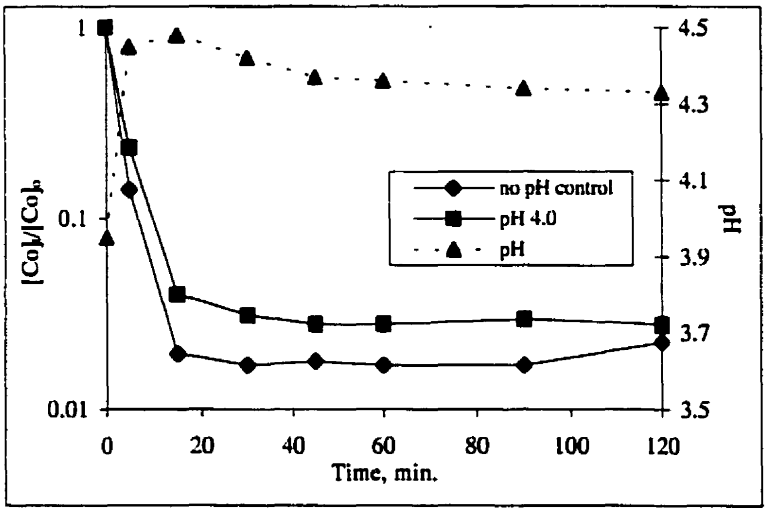

Figure 4.7: Cobalt cementation with and without controlled pH in the presence of activators (95°C, 150 g/L $ZnSO_4$, 5 g/L CEZinc dust, 30 mg/L Cu^{2+}, 2 mg/L Sb^{3+}). Dashed line is pH profile, values on right-hand axis.

4.1.6 Cadmium

Zinc electrolyte contains many chemicals and impurities: organics added at other stages of the RLE process, cadmium, which may be carried over from the first cementation stage, chloride, and oxygen. The effect of organics is a broad field of study and has been researched extensively (Houlachi *et al.* 1990, Lew *et al.* 1993), and so was not included in the present work. The effects of cadmium and chloride ions on the other hand are not well understood; preliminary tests showed that the presence of these elements affects cobalt cementation significantly.

At this point in the research, a supply of zinc dust from CEZinc was made available. This dust was used in the remainder of the tests to better approximate industrial conditions. A comparison of the two zinc dusts is made later (Section 4.1.9); for the next three sections only tests using the same dust are compared.

Cadmium in small quantities has a beneficial effect on the final cobalt concentration, but has little effect on the initial kinetics (Figure 4.8). The dashed line across the graph indicates the desired final cobalt concentration (0.1 mg/L).

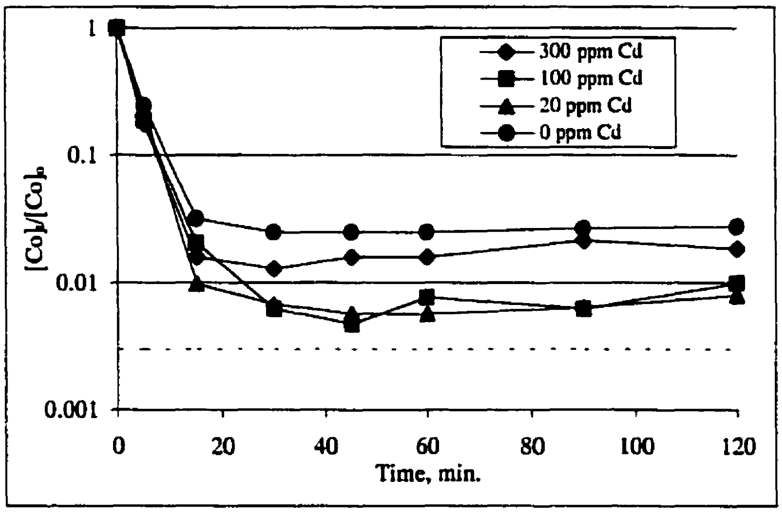

Figure 4.8: Effect of cadmium on cobalt removal (95°C, pH 4.0, 30 mg/L Cu^{2+}, 2 mg/L Sb^{3+}, 150 g/L $ZnSO_4$, 5 g/L CEZinc dust).

The addition of up to 100 mg/L Cd^{2+} acts synergistically with Sb/Cu, bringing the final cobalt concentration even lower than the levels obtained with Sb/Cu alone. Although a small amount has a positive effect, increasing the Cd^{2+} concentration results in progressively higher final cobalt concentrations.

Figure 4.9 shows more clearly that a small amount of cadmium is beneficial in terms of the final cobalt concentration, but that increasing amounts gradually reverse this effect. This is an important consideration in purification circuits that remove cadmium completely prior to cobalt cementation (i.e. by filter-pressing the cadmium cementate): in this case it might be judicious to regard cadmium as an activator and add it at the cobalt cementation stage. In all cases it would be prudent to monitor the amount of cadmium entering the second cementation stage.

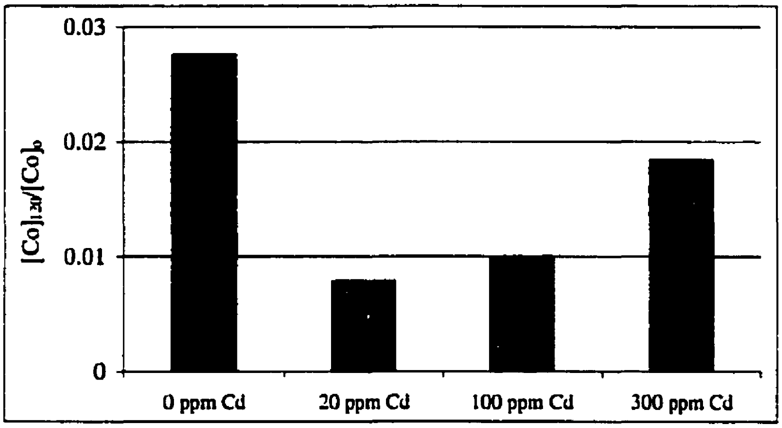

Figure4.9: Cobalt removal as a function of cadmium concentration (120 min., 95°C, pH 4.0, 30 mg/L Cu^{2+}, 2 mg/L Sb^{3+}, 150 g/L $ZnSO_4$, 5 g/L CEZinc dust).

A small amount of cadmium, without copper, improves cementation with antimony, similar to the way a small amount of copper with antimony is more effective than antimony alone (Figure 4.10).

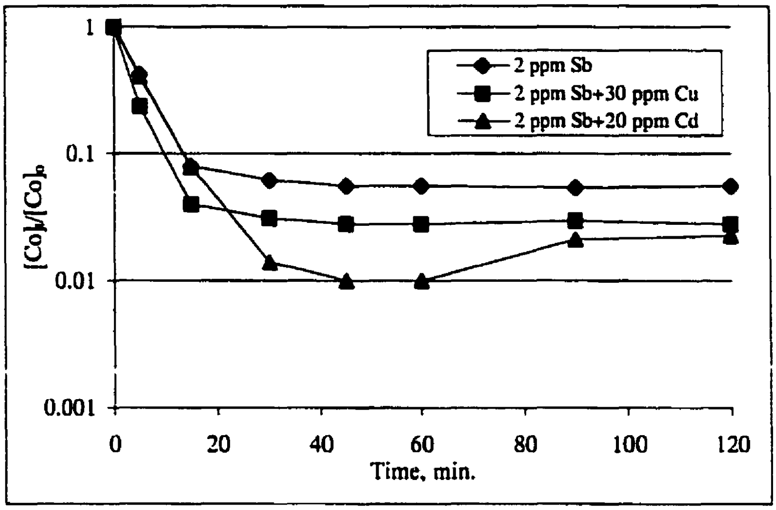

Figure4.10: Comparison of the effects of Sb, Sb/Cu, and Sb/Cd on cobalt removal (95°C, pH 4.0, 150 g/L $ZnSO_4$, 5 g/L CEZinc dust).

Cadmium might affect cobalt removal in a similar way to copper, which increases the surface area available for cementation by forming a dendritic deposit (van der Pas and Dreisinger 1996). SEM photos do not bear this supposition out, however. The deposit with cadmium is much smoother than the dendritic form of deposit obtained with copper (Figure 4.11). Comparison of the specific surface area of the dusts with cadmium or copper deposit was not possible due to the small amount of dust remaining at the end of the test.

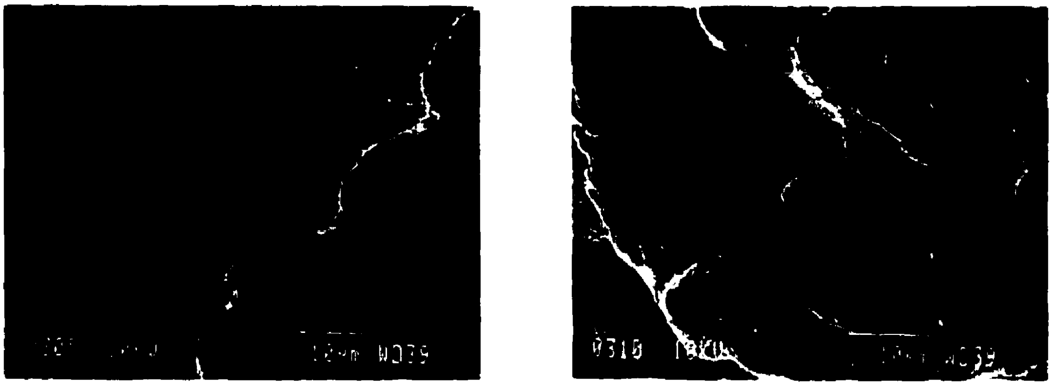

Figure 4.11: SEM photos of cobalt cemented with Sb/Cu (left) and with Sb/Cd (no Cu) (right) (CEZinc dust, 30 mg/L Cu or Cd, 2 mg/L Sb).

4.1.7 Chloride

The presence of large amounts of chloride improves cobalt cementation; Tanabe *et al.* (1995) describe chloride as having a catalytic effect on cobalt cementation. However these investigators worked with 2, 4, and 6 molar solutions, quantities which are unacceptable in zinc electrowinning. In this work smaller amounts of chloride were added and the results are shown in Figure 4.12. It is apparent that even the addition of a few hundred mg/L Cl^- has a positive effect on the final cobalt concentration, although it has no effect on the kinetics except for a considerable increase at 600 mg/L. Typically zinc electrolyte contains 150-250 mg/L Cl^-, which is close to the upper tolerance limit for the electrowinning process. Hence further addition of Cl^- to capitalize on its catalytic effect does not seem feasible.

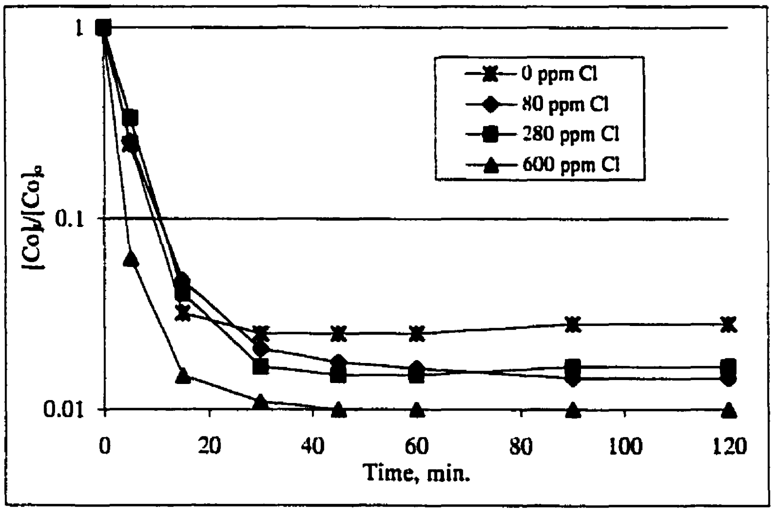

Figure 4.12: Effect of chloride ions on cobalt removal (95°C, pH 4.0, 30 mg/L Cu^{2+}, 2 mg/L Sb^{3+}, 150 g/L $ZnSO_4$, 5 g/L CEZinc dust).

4.1.8 Oxygen

The presence of oxygen in the cementation system will cause the following reactions to occur:

$$Zn + 2H^+ + \tfrac{1}{2}O_2 \rightarrow Zn^{2+} + H_2O \qquad (4.1)$$

$$Co + 2H^+ + \tfrac{1}{2}O_2 \rightarrow Co^{2+} + H_2O \qquad (4.2)$$

Even though the solubility of oxygen at 95°C in zinc electrolyte is less than 9 mg/L (Perry and Green 1984), the effect on deposit stability and zinc dust consumption can be significant. Pasminco Metals found that employing a nitrogen blanket in the cementation stage resulted in zinc dust savings of 5.3 kg/ton of zinc produced (Adams *et al.* 1995). Nitrogen blanketing is commonly considered too expensive to be viable on an industrial scale. Wishing to find a more economical way to deoxygenate the electrolyte, the possibility of adding sodium sulfite at the level of parts per million to consume the oxygen was investigated:

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \qquad (4.3)$$

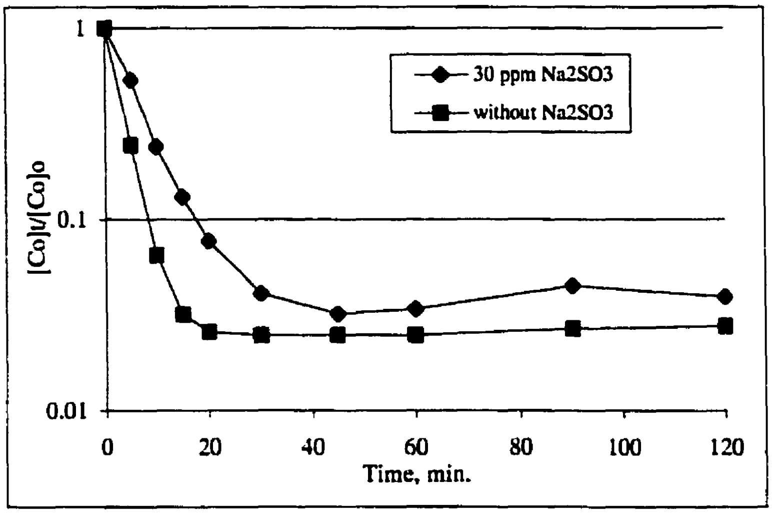

Figure 4.13: Effect of Na_2SO_3 on cobalt removal (95°C, pH 4.0, 30 mg/L Cu^{2+}, 2 mg/L Sb^{3+}, 150 g/L $ZnSO_4$, 5 g/L CEZinc dust).

Instead sulfite was reduced completely to elemental sulfur, which adhered to the zinc dust surface forming a passivating layer:

$$SO_3^{2-} + 2Zn + 6H^+ \rightarrow 2Zn^{2+} + S + 3H_2O \qquad (4.4)$$

This not only increased the final concentration of cobalt remaining in solution (Figure 4.13), but also slowed the initial reaction kinetics. However, the zinc dust consumption was much less than usual (by about 20%) due to the protection this passivating layer affords the zinc dust from acid attack. The use of small amounts of sodium sulfite cannot, however, be disregarded as it may be added to the solution just prior to filtration, thus reducing zinc dust losses in this part of the circuit.

4.1.9 Zinc dust

Towards the end of these preliminary tests, zinc dust from CEZinc was obtained to run the tests in conditions that more closely resembled those used at CEZinc. Both zinc dusts were tested in standard cementation tests (95°C, pH 4.0, 30 mg/L Co^{2+}, 30 mg/L Cu^{2+}, and 2 mg/L Sb^{3+}) to determine if they were comparable. At this point the analytical procedure was changed as well. The cobalt concentrations achieved with additives were at or below the detection limits of AA, and so ICP became the analytical method for the remaining tests.

Zinc dust source has quite a large effect (Figure 4.14) that would not have been apparent with AA. The dotted line across the graph indicates the desired final concentration for cobalt (0.1 mg/L), which was not reached with the CEZinc dust in tests with synthetic zinc sulfate electrolyte.

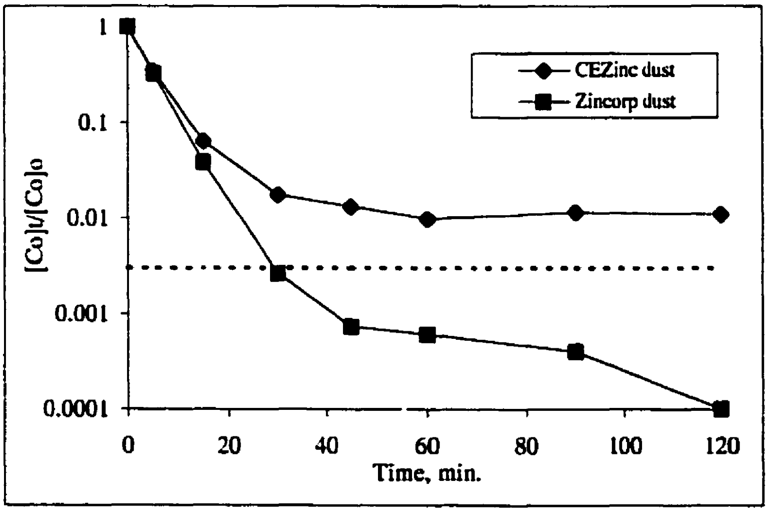

Figure 4.14: The effect of zinc dust type on cobalt cementation (95°C, pH 4.0, 30 mg/L Cu^{2+}, 2 mg/L Sb^{3+}, 150 g/L $ZnSO_4$, 5 g/L dust).

One possible explanation for this behaviour is the dust morphology: the active surface area of the dust can be reduced by the formation of hydrogen bubbles in its pores and crevices (Brennan and Brown 1972). This problem is compounded by the increased activity for hydrogen evolution on very rough or porous surfaces (Los *et al.* 1991). The effect is not believed to be due to surface area as the Zincorp dust has a smaller specific area than CEZinc dust (refer to Section 3.2). Despite the above results, CEZinc dust was used in all the subsequent experiments to approximate plant conditions as closely as possible.

4.2 TESTS WITH NEW ADDITIVES

Elements to be tested as a replacement for antimony as an activator were selected on the basis of the following considerations and observations:

1) Sb(III) itself is more harmful than cobalt in its effect on the current efficiency of the zinc electrowinning process (Figure 1.2).
2) Sb(III) undergoes rapid reduction by zinc:

$$2Sb^{3+} + 3Zn \rightarrow 2Sb + 3Zn^{2+} \qquad E^{o} = 0.152\text{-}(-0.76) = 0.91\ \text{V} \qquad (4.5)$$

3) The antimony deposit forms a favourable substrate for cobalt deposition (van der Pas and Dreisinger 1996).
4) Prior reduction and removal of the additive from the solution is a prerequisite to application since otherwise any escape of the activator into the zinc electrowinning plant will cause catastrophic loss of current efficiency.

The following elements were selected on the basis of the thermodynamic driving force for reduction by zinc: As(III), Sn(II), Te(IV), In(III), Bi(III), Pb(II), Hg(II), Se(IV), Ge(IV), and Ag(I). For this initial survey 30 mg/L of each additive was used. Copper was also used in each test (30 mg/L) as it appears to have little effect on cementation but probably plays a role in increasing surface area for cobalt cementation. This also allowed a better comparison between the tests with new additives and the standard Sb/Cu test. Other conditions remained standard: 95°C, pH 4.0, 120 minutes, 5 g/L CEZinc dust. Two replicates of each test were performed to be sure the results were reproducible.

4.2.1 Cobalt removal

The fraction of cobalt remaining at the end of the test for each additive is presented in Figure 4.15.

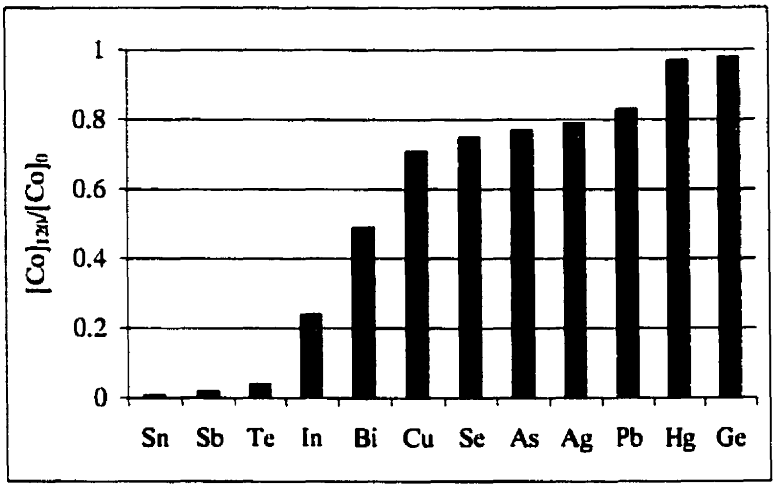

Figure 4.15: Cobalt remaining in solution as fraction of initial concentration (95°C, pH 4.0, 120 min., 30 mg/L Cu^{2+}, 150 g/L $ZnSO_4$, 5 g/L CEZinc dust).

Tin and tellurium (as well as antimony) were the most effective, while germanium, mercury, lead, silver, arsenic, selenium and copper had little or no effect. The average value for the final cobalt concentration with tin was 0.28 mg/L and for antimony was 0.66 mg/L. These numbers are not statistically different however, due to a large variation among the replicates (for these two elements three replicates were performed). It is possible that a difference between the averages exists, but a larger number of replicates is needed to show it.

The poor result for arsenic was not expected. Arsenic is used industrially as an alternative to antimony as an activator (Tozawa *et al.* 1992, Ashman 1993). However, usually a much larger amount of arsenic is required (>50 mg/L), and the reaction temperature is much lower, 70-75°C. These factors may explain the unusual result.

Cobalt removal as a function of time is shown in Figure 4.16 for the most successful additives. Interestingly, while antimony and tin initially give a rapid rate of removal but reach a plateau after 20 minutes, tellurium, indium and bismuth initially give a slower rate of cementation but do not reach a plateau in the two hour experiment. Thus tellurium might prove to be a better activator than antimony in that, even though the kinetics are slower, the final value of cobalt reached might be smaller given enough time.

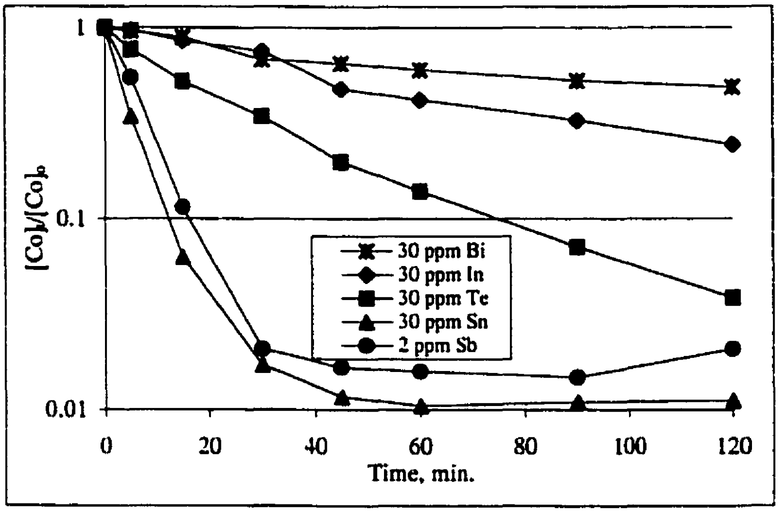

Figure 4.16: Effect of novel activators on cobalt cementation (95°C, pH 4.0, 30 mg/L Cu^{2+},150 g/L $ZnSO_4$, 5 g/L CEZinc dust).

As mentioned earlier, it is imperative that any activator used must be completely removed from solution during cementation, as many of these additives have a more harmful effect on electrowinning than cobalt itself (Figure 1.2). All samples were tested by ICP for the activator used as well as for cobalt. All activators were removed to undetectable limits (0.1-1 part per trillion) within 40 minutes, and most within less than 20 minutes. Figure 4.17 shows typical removal rates for some of the more interesting additives.

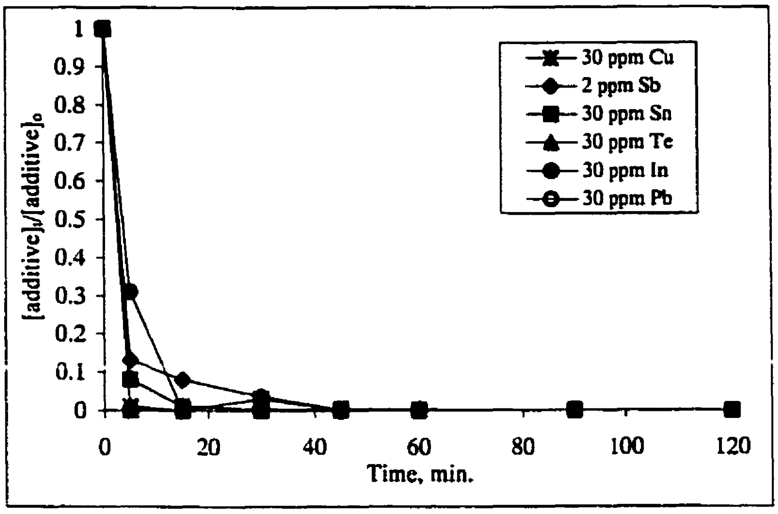

Figure 4.17: Removal of activator as a function of time (95°C, pH 4.0, 150 g/L $ZnSO_4$, 5 g/L CEZinc dust).

These results corroborate the previously discussed theory that additives cement out of solution first, forming a substrate on the zinc dust which is more active for cobalt cementation.

4.2.2 Activation mechanism

Characteristics of metal ions have been used in a few cases to predict certain activities or effects of the metal: for instance several ion characteristics related to metal affinities for ligands have been correlated with the metals' relative toxicity (McCloskey *et al.* 1996), and the rate of hydrogen evolution on the surface of a metal has been shown to correlate with the work function of the metal (Trassati 1972). This type of structure-activity relationship is used frequently in the fields of organic chemistry and biology for predicting activity, but rarely in inorganic chemistry. The cementation of cobalt by zinc dust is an excellent example of where this method might be applied. The mechanism by which activators function is complex and poorly understood, making it difficult to suggest novel activators. However, the effectiveness or activity of the activator can be related to characteristics of the metal ion; the metal characteristic which correlates with activation may give some indication of the underlying activation mechanism.

To quantify the efficiency of each activator, a scale was created based on the slope of the line for cobalt removal over two hours, with tin the standard (assigned a value of 100) against which the others are compared (calculations are in Appendix B). Using a linear slope value takes into account not only the final cobalt concentration reached, but also the initial kinetics. Using the data from the eleven elements studied as activators, the cobalt removal efficiency of the activator was correlated with the various metal characteristics shown in Table 4.1.

Table 4.1: Additive characteristics used in study of structure-activity relationship.

	Activity for cobalt removal	Atom. weight	-log K_{OH}[a,b]	e^{o}_{red},[c] V	-log $i_{o,H}$,[d] A/cm^2	Work function eV[c]	Atomic radius in metal[c], Å	First ionization potential[c], eV	Electro-negativity[e]	Atomic electron affinity[c] eV
Sn	100	118.7	2.7	-0.14	10.0	4.35	1.51	7.34	1.96	1.11
Sb	99.18	121.8	-1.41	0.152	8.6	4.56	1.45	8.64	2.05	1.05
Te	88.52	127.6	1.98	0.593	10.1	4.95	1.42	9.01	2.1	1.97
In	61.48	114.8	5.39	-0.34	11.3	4.08	1.67	5.79	1.78	0.3
Bi	43.44	209.0	6.09	0.32	10.4	4.36	1.56	7.29	2.02	0.95
Se	29.51	79.0	9.16	0.74		5.9	1.16	9.75	2.55	2.02
As	43.44	74.9	4.33	0.248	14.2	3.75	1.25	9.82	2.18	0.81
Ag	17.21	107.9	12.0	0.799	7.9	4.64		8.99	1.93	1.30
Pb	27.05	207.2	7.06	-0.13	11.4	4.18	1.75	7.42	2.33	0.36
Hg	50.00	200.6	6.87	0.796	12.3	4.5	1.51	10.44	2.0	n. s.[f]
Ge	15.57	72.6	10.0	-0.13		5.0		7.90	2.01	1.23

[a] Values have been corrected for ionic strength
[b] Hydrolysis constants (Baes and Mesmer 1976)
[c] standard reduction potentials (Lide 1995)
[d] Hydrogen exchange current densities (Trassati 1972)
[e] (Allred 1961)
[f] Not stable, refers to negative ion

The best correlation was with the log of the hydrolysis constant (pK_{OH}) for the predominant hydrolysis product at pH 4.0. A metal may form several hydrolysis products (i.e. $Hg(OH)^{+}$, $Hg(OH)_2^{0}$), and the likelihood of any one particular product forming varies with pH. The predominant hydrolysis product at a given pH can be found from charts like the one shown in Figure 4.18:

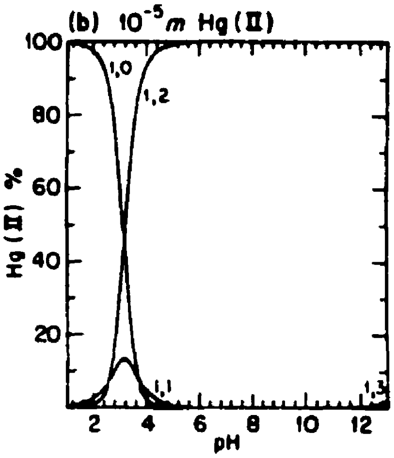

Figure 4.18: Distribution of Hg(II) hydrolysis products with pH (Baes and Mesmer 1976).

The hydrolysis constant for the predominant hydrolysis product of each metal at pH 4.0 was used in the model (Figure 4.19). A small value for log K_{OH} indicates that at equilibrium relatively little of the hydrolysis product is formed. The squared correlation coefficient (R^2) for this model was 0.83, indicating that 83% of the variation among additives in cobalt removal rate can be explained by their log K_{OH} values.

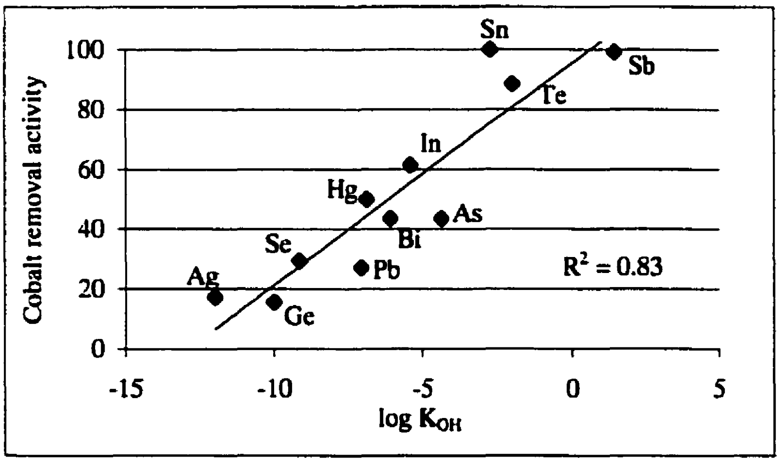

Figure 4.19: Cobalt removal activity correlated with log K_{OH}.

Cobalt removal efficiency increases with K_{OH}, which corresponds well with the theory that zinc monohydroxide ($ZnOH^+$) inhibits cobalt cementation. The inhibition of cobalt cementation by $ZnOH^+$ adsorption on the zinc dust surface (Tanabe *et al.* 1995, West

Sells 1997), and the correlation between hydrolysis and activator efficiency suggests that partial hydrolysis is a precursor to adsorption on the surface of zinc dust. With zinc, this adsorption leads to a passivation of the zinc dust, and also to the underpotential deposition of zinc (Tanabe *et al.* 1995). Additives form a hydrolyzed species which is adsorbed in the place of $ZnOH^+$. Once adsorbed, metals more noble than zinc are reduced to the elemental state. These metals then form substrate on which zinc hydroxide does not adsorb, allowing cobalt to reach the surface and discharge. Metals that have a large hydrolysis constant compete better for adsorption sites with zinc, which forms relatively little hydrolysis product ($\log K_{OH} = -8.96$).

This hypothesis (that hydrolysis is a precursor to adsorption) is supported by a study of the adsorption of metal ions at an oxide-water interface by James and Healy (1972). They found many cases of indirect evidence showing that adsorption or adsorption related phenomena are linked to hydrolysis or the formation of hydrolysis products. They went on to develop a mathematical model of metal adsorption at a solid-liquid interface which describes a barrier formed by ion-solvent interactions, preventing highly charged ions from approaching the interface. When the ionic charge is lowered by hydrolysis, the energy barrier is decreased, allowing the ions to approach the interface, resulting in adsorption.

4.2.3 Zinc dust consumption

In this previous section, solids were filtered at the end of the test, washed with deionized water, dried at room temperature overnight, and weighed. Often there was a white precipitate along with the remaining zinc dust, making it impossible to compare zinc dust consumption for different tests. It was apparent however that the amount of zinc dust remaining at the end of a test varied a great deal. In order to better compare zinc dust consumption with different activators, a new procedure was used in which the solution pH was lowered to 3.5 just before filtration. The dried zinc dusts were always clean, with no visible precipitates. The procedure was not completely successful, because some of the final samples weighed more than the initial amount of zinc dust used, but never by more than 2%. To minimize the amount of zinc dust consumed, the dusts were exposed to this low pH for less than 30 seconds.

Interestingly, the zinc dust consumption varied significantly among activators (Figure 4.20).

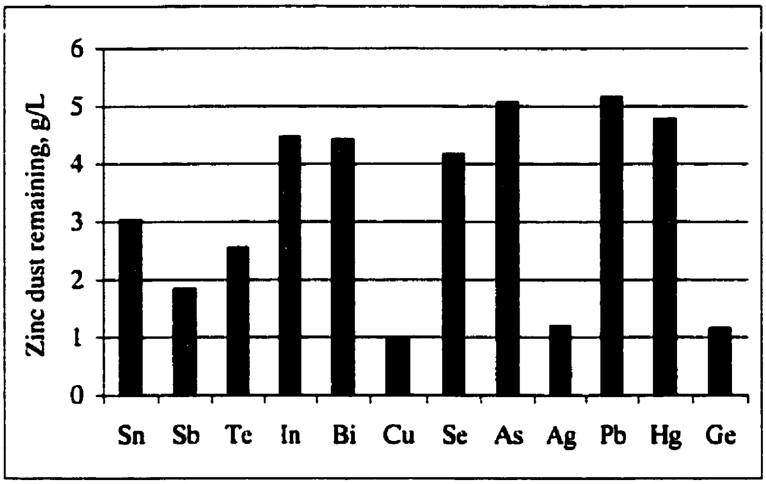

Figure 4.20: Zinc dust remaining at 120 min. (initial 5 g/L).

There is no apparent connection between zinc dust consumption and cobalt reduction, although in general those additives which perform better for cementation (including copper) are among the worst in terms of zinc dust consumption.

Metals with large hydrogen exchange current densities (Table 4.2) in effect act as catalysts for hydrogen evolution. As all the metals selected for testing are more noble than zinc, when in contact with zinc they form a galvanic couple from which zinc is preferentially dissolved (as it is with cobalt, Section 2.1.4). Zinc dust with deposits of a metal that is catalytic for hydrogen evolution might therefore be expected to dissolve more rapidly than dust without such deposits.

Table 4.2: Hydrogen exchange current densities and remaining zinc dust for the metals tested.

	remaining zinc dust, g/L	-log $i_{O,H}$, A/cm^2 (Trassati 1972)
Cu	0.99	7.8
Ag	1.2	7.9
Sb	1.85	8.6
Sn	3.04	10.0
Te	2.56	10.1
Bi	4.43	10.4
In	4.48	11.3
Pb	5.17	11.4
Hg	4.79	12.3
As	5.07	14.2
Se	4.18	n/a
Ge	1.17	n/a

Unfortunately, $i_{O,H}$ values were not available for selenium and germanium. A correlation of all the zinc dust values versus -log $i_{O,H}$, shown in Figure 4.21, gives a very good correlation, with R^2 equal to 0.81.

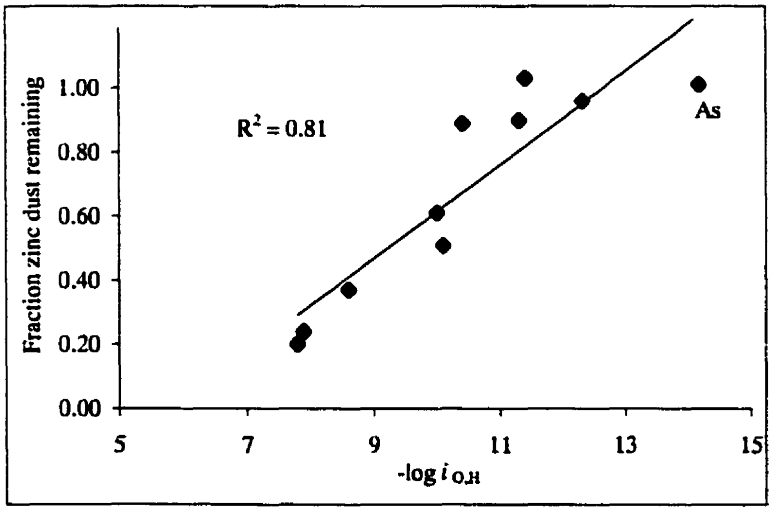

Figure 4.21: Remaining zinc dust as a fraction of initial loading (5 g/L) as a function of the hydrogen exchange current density.

Arsenic stands out a little from the regression as it has a very low hydrogen exchange current density, but cannot have more than one hundred percent zinc dust remaining. Without arsenic, the squared correlation coefficient is 0.90.

4.3 TESTS WITH ADDITIVE COMBINATIONS

The previous section established that, in addition to antimony and copper, other additives play a catalytic role in the cementation of cobalt, and that in general those additives that performed well in terms of cobalt removal performed poorly in terms of zinc dust consumption. As the goal of the present research is to optimize cobalt cementation in terms of both of those criteria, it seemed appropriate and interesting to test combinations of additives in order to get both desired effects.

From the survey of novel additives, there were three areas of interest in terms of combinations:

- cobalt removal: antimony versus tin
- secondary additives: cadmium versus copper
- zinc dust consumption: of the several elements that prevent zinc dust consumption, lead was chosen, as it is already often used in plants as an alloying agent in zinc dust.

A series of tests were performed to determine the most promising combinations from among the areas of interest mentioned above. A block of experiments was designed for a complete 3-way factorial test. The three factors were:

- the presence of antimony, tin, or both (3 levels)
- the presence of copper, cadmium, or both (3 levels)
- the presence or absence of lead (2 levels)

The concentration of each additive in any test was 30 mg/L, with the exception of antimony, of which 2 mg/L were added. The tests were all carried out at the standard cementation conditions employed in the previous sections: pH 4.0, 95°C, 5 g/L zinc dust and 150 g/L Zn^{2+}.

The factorial design tests each possible combination of these factors, a total of 18 tests (a complete list of all the test performed and some results follows in Appendix C). Three replicates of each test were performed, and the tests were randomized. The means for the replicates are given below in Tables 4.3 and 4.4. In general, the combinations were very successful in combining good cobalt removal with reduced zinc dust consumption.

Table 4.3: Cobalt in solution as a fraction of initial loading (30 mg/L) at 120 min. for each combination.

	Cu		Cd		Cu+Cd	
	-Pb	+Pb	-Pb	+Pb	-Pb	+Pb
Sn	0.01	0.00	0.24	0.09	0.00	0.00
Sb	**0.02**	0.1	0.37	0.07	0.00	0.00
Sn+Sb	0.22	0.03	0.2	0.07	0.00	0.00

Table 4.4: Zinc dust remaining (g/L) at 120 min. for each combination (initial loading 5 g/L).

	Cu		Cd		Cu+Cd	
	-Pb	+Pb	-Pb	+Pb	-Pb	+Pb
Sn	3.04	4.00	4.38	4.66	4.64	3.98
Sb	**1.85**	4.45	5.07	4.80	4.83	4.53
Sn+Sb	1.26	1.68	4.05	3.85	4.32	3.63

The results for the standard test (2 mg/L Sb^{3+}, 30 mg/L Cu^{2+}) are highlighted in each table. This combination gives one of the worst overall results, having not only a high final cobalt value, but also one of the highest amounts of zinc dust consumption. It is immediately apparent that the best results for cobalt removal occur when cadmium and copper are both present, regardless whether tin or antimony is used as the primary activator, or whether lead is present.

In terms of zinc dust consumption, the trends are not so easily recognizable, but will be discussed more in depth in the next section. The combinations that overlap with the best cobalt removal are Sb-Cu-Cd, Sb-Pb-Cu-Cd, and Sn-Cu-Cd. Statistically, there is no difference in the average values for zinc dust consumption for these three combinations.

A plot of cobalt removal over time for the six best combinations reveals interesting observations about the kinetics (Figure 4.22).

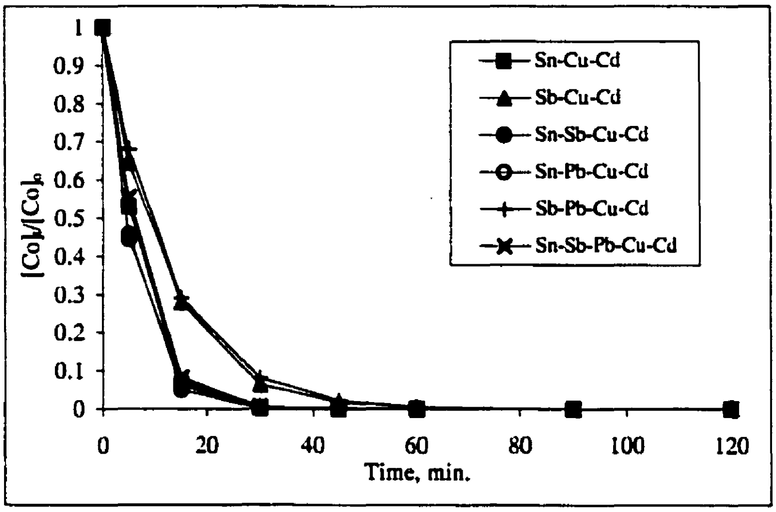

Figure 4.22: Fraction of cobalt remaining in solution as a function of time for 6 combinations that combine optimum cobalt removal with low zinc dust consumption.

Even though all the combinations reach the same final concentration (< 0.001 mg/L), all the combinations that include tin show much faster initial removal rates. This could be significant in terms of reducing the required residence time for the process, which would also reduce the amount of zinc dust consumed and reduce the risk of cobalt redissolution.

Once again, the additive concentrations as well as that of cobalt were measured during each test to ensure that the additives are completely removed from solution. All additives were removed to below detection limits (<one part per billion) in less than 30 minutes (Figure 4.23).

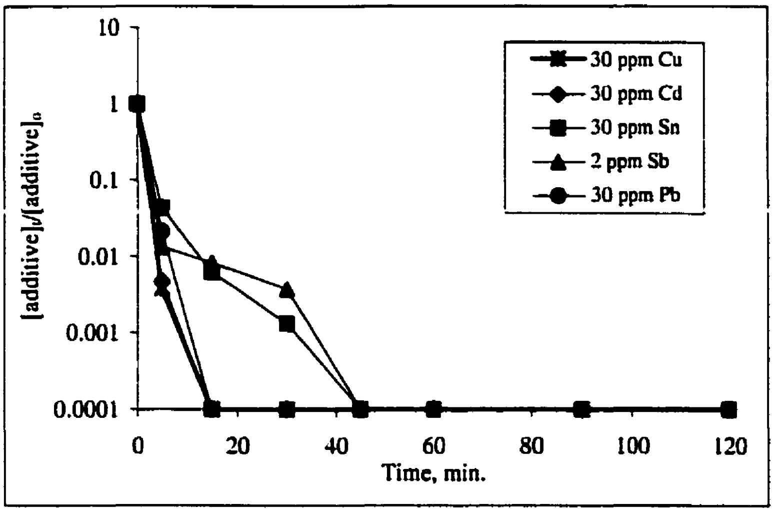

Figure 4.23: Removal of activators (95°C, pH 4.0, 150 g/L $ZnSO_4$, 5 g/L CEZinc dust).

4.3.1 Statistical analysis

The 3-way factorial design permits us not only to see the effects of each individual factor (main effect), but also to see the effects of interactions among the factors (i.e., whether the presence of lead changes the effect of the tin-antimony factor). The ability to see significant effects depends on the power of the analysis (if the power is low an effect might be incorrectly assessed as insignificant) (Zar 1992). The power largely depends on having enough replicates to be able to distinguish between signal and noise (variance). In this case the replicates for cobalt removal were largely too variable to detect effects, with a few exceptions. The power for the insignificant effects was very low, however, and with more replicates effects might be detected. The zinc dust measurements were much less variable; all main effects and interactions were significant.

4.3.1.1 Cobalt removal

The significant effects found among the three factors and their P values (the probability that such an effect would be observed simply by random sampling of a population where no such effect exists) are listed in Table 4.5.

Table 4.5: Significant effects and P-values found in a 3-way analysis of variance (ANOVA) of cobalt removal results.

Effect	P-value
Cu-Cd	0.000
Pb	0.009
Cu-Cd by Pb	0.019

The main effect of lead is best illustrated by a bar graph (Figure 4.24). The presence of lead results in consistently lower cobalt values with only one exception in the case of antimony-copper-lead. The combined means (the average of all test results in a given group, i.e., tests with lead) for the fraction of cobalt remaining is 0.12 for tests without lead and 0.04 for test with lead. Ashman (1993) suggested that additions of lead in the solution stabilize the deposit and prevent redissolution of cemented cobalt. The results presented here confirm this finding.

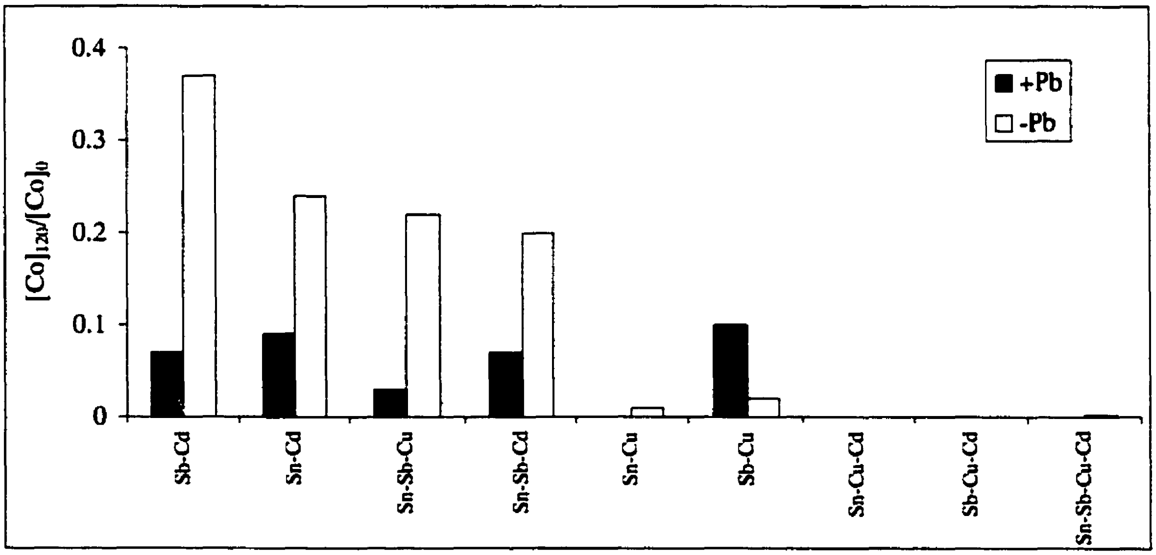

Figure 4.24: Fraction of cobalt remaining in solution for combinations with and without lead.

The copper-cadmium effect is graphed in Figure 4.25. The values for Cu-Cd together are all less than 0.00 and do not appear on the chart. There is no apparent trend for the action of copper or cadmium alone, but in combination they consistently produce the lowest fraction remaining cobalt, i.e., cadmium acts synergistically with copper in helping the primary additive (whether Sn or Sb) in eliminating cobalt from the solution.

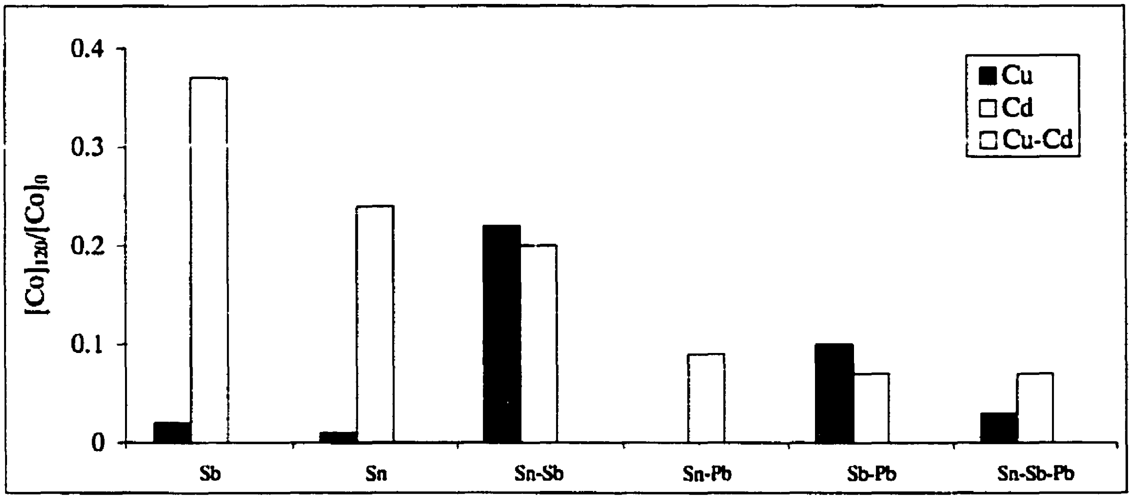

Figure 4.25: Fraction of cobalt remaining in solution for combinations with copper, cadmium, or both.

The interaction between lead and copper-cadmium is also apparent in Figure 4.25. The presence of lead significantly reduces the combined mean for cadmium, but the combined mean for copper remains approximately the same with or without lead. In the presence of lead, the combined mean for cadmium is reduced to approximately the same level as that of copper in the presence or absence of lead (Figure 4.26). The combined mean for copper-cadmium together also remains the same in the presence or absence of lead (although it is impossible to determine if the presence of lead affects the copper-cadmium combination as these values are all zero).

Figure 4.26: Interaction of lead and copper-cadmium on the fraction of remaining cobalt.

In summary, lead has an important beneficial effect when cadmium is used in conjunction with tin or antimony, and it has a slight beneficial effect when copper is used with tin or antimony. However, copper and cadmium together have a much greater main effect on cobalt reduction (either with tin or with antimony), and this combination does not seem to be affected by the presence of lead.

4.3.1.2 Zinc dust consumption

For zinc dust consumption all the effects were significant. Not only do the three factors have significant main effects, but there are interactions among them all as well. The effects and the P values are listed in Table 4.6:

Table 4.6: Significant effects and P-values found in 3-way ANOVA of zinc dust consumption results.

Effect	P-value
Cu-Cd	0.000
Pb	0.009
Sn-Sb	0.000
Cu-Cd by Pb	0.000
Cu-Cd by Sn-Sb	0.000
Pb by Sn-Sb	0.001
Cu-Cd by Pb by Sn-Sb	0.000

The effect of copper-cadmium is shown in Figure 4.27. The remaining zinc dust values are consistently lower for copper than those for cadmium or copper and cadmium together. This effect can at least in part be explained by the low hydrogen exchange current density on cadmium, preventing excessive zinc dust dissolution even in the presence of copper, which has the highest hydrogen exchange current density of all the metals tested (refer to Table 4.2). The combined mean for copper (2.71 g) is significantly lower for either that of cadmium (4.47 g) or copper-cadmium (4.43 g).

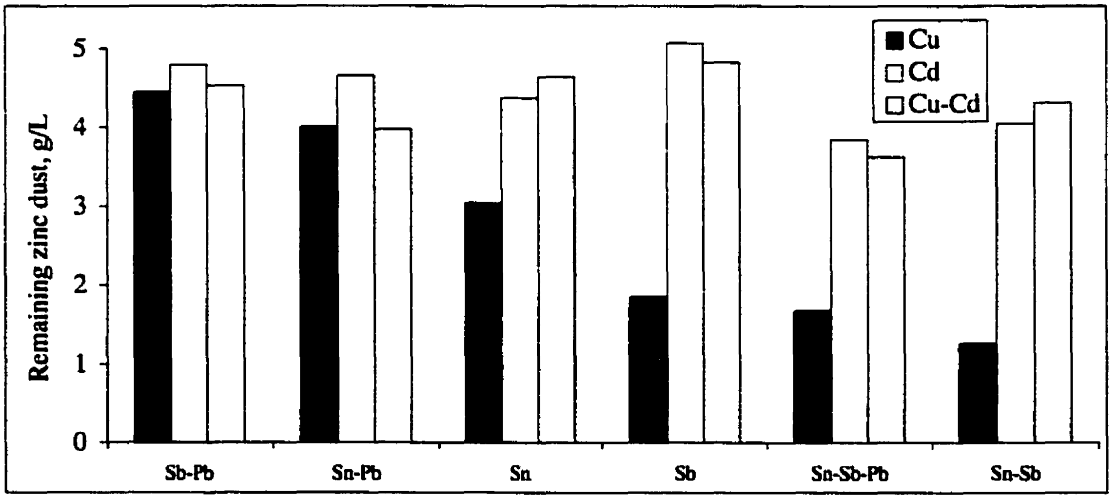

Figure 4.27: Residual concentration of zinc dust solids for combinations with copper, cadmium, or both (initially 5 g/L zinc dust).

The effect of lead is not so obvious but does exist (Figure 4.28). The combined mean without lead is 3.72 g and with lead is 3.95 g. In many of the combinations tested, the remaining zinc dust appears lower in the test with lead, but these differences may not be significant.

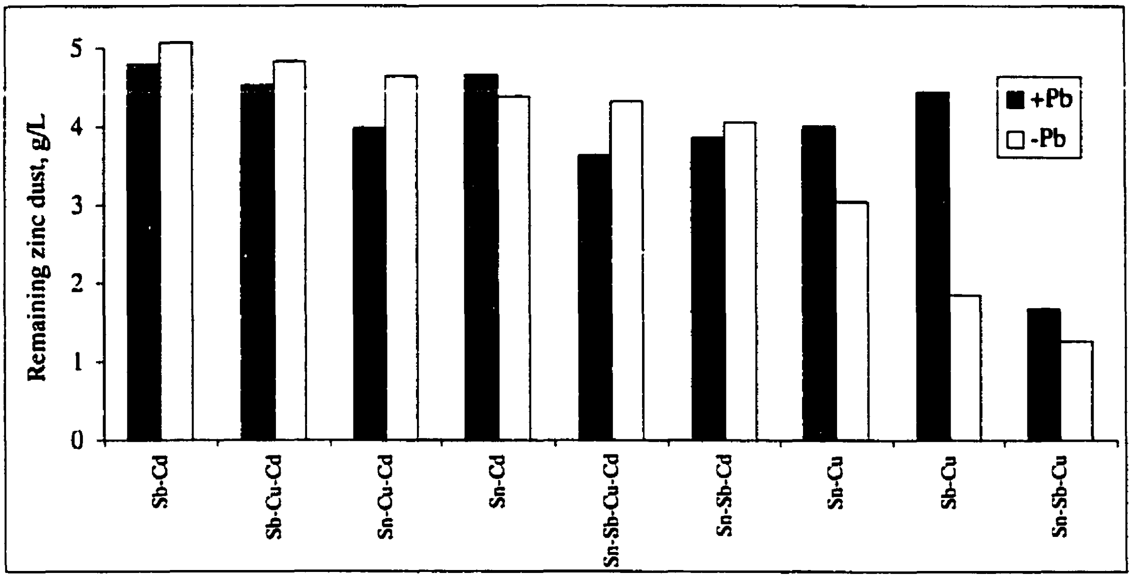

Figure 4.28: Residual concentration of zinc dust solids for combinations with and without lead.

More apparent from this chart is the interaction between lead and copper-cadmium. In the absence of cadmium, the advantage of having lead in the solution is obvious. In effect, lead takes the place of cadmium in its absence by preventing zinc dust dissolution. This interaction is presented more clearly in Figure 4.29. When cadmium is present the addition of lead is unnecessary, and might have a negative effect in the presence of copper and cadmium together.

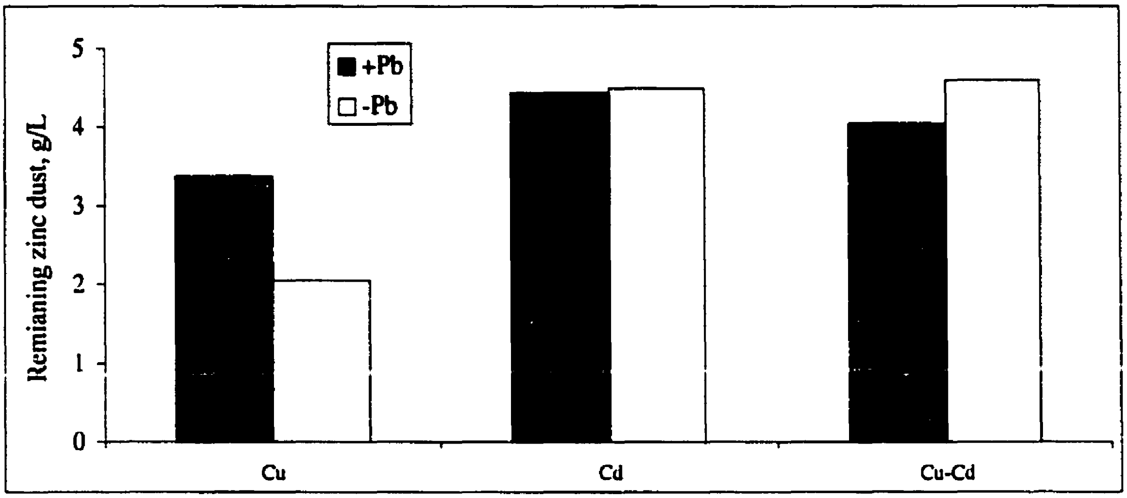

Figure 4.29: Interaction of lead and copper-cadmium on concentration of remaining zinc dust.

The main effect of the antimony-tin factor is shown in Figure 4.30. Antimony gives consistently better zinc consumption results than tin, although only slightly (the combined averages are 4.25 and. 4.12 g/L, respectively). Both antimony and tin individually, however, are significantly better than the two together (combined average of 3.13 g/L).

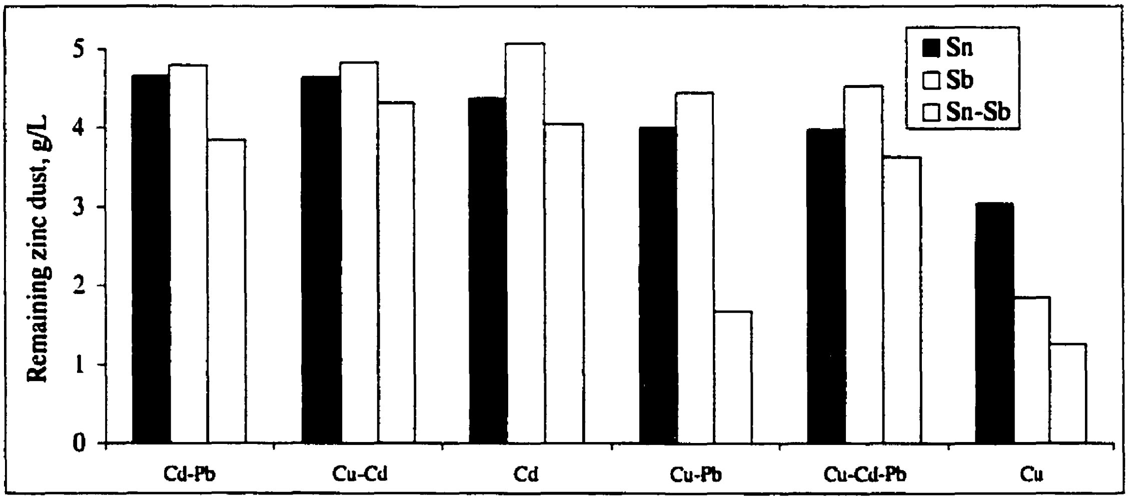

Figure 4.30: Residual concentration of zinc dust solids for combinations with tin, antimony, or both.

The interaction between antimony-tin and copper-cadmium is also apparent on this chart. The trend for the relative effects of antimony, tin, and both are very consistent except in the presence of copper alone. The same trend can be seen with the combined averages in Figure 4.31. Copper and antimony together seem to have a negative effect on zinc dust consumption that is counteracted by the presence of cadmium. The same can be said for the combination of antimony, tin, and copper. Tin and copper may also have a negative synergistic effect, but it is much less than that of copper and antimony.

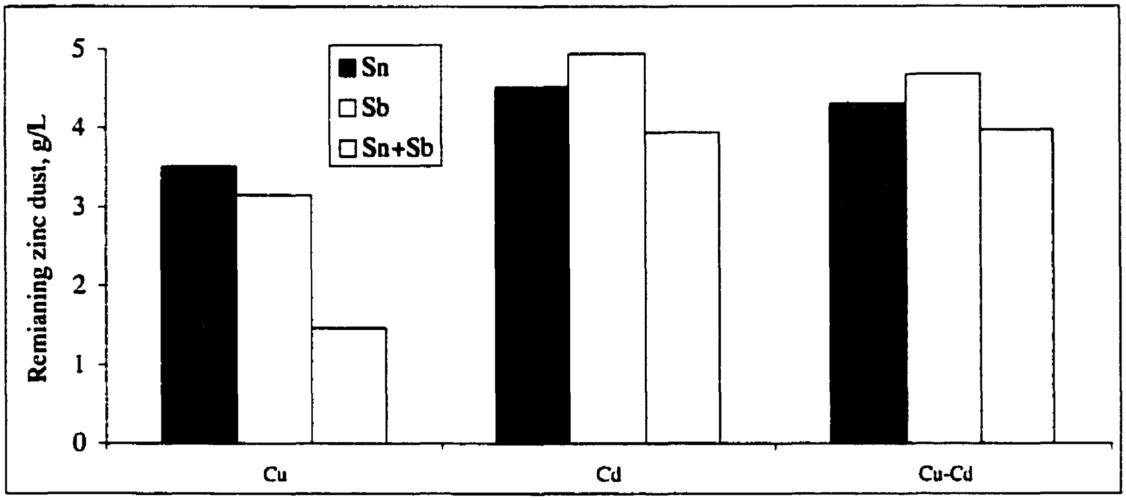

Figure 4.31: Interaction of tin-antimony and copper-cadmium on concentration of remaining zinc dust.

This effect also makes sense in terms of hydrogen exchange current densities (Table 4.2): the low hydrogen exchange current density on cadmium counteracts the large ones on antimony, tin, and copper, but in the absence of cadmium the large hydrogen exchange current densities on these last three act synergistically, particularly in the case of copper and antimony, which have the lowest exchange current densities of all the elements tested.

In summary, in terms of reducing the amount of zinc dust consumption, the most important factor is the presence of cadmium. It is important to have cadmium present, whether tin or antimony is used, and whether copper is present or not. In the absence of cadmium, lead can take its place, but is still not quite as effective. The use of tin or antimony makes little difference in the presence of cadmium.

4.3.2 Optimum additive concentrations

From the preceding analysis of the combinations in terms of cobalt removal and zinc dust consumption, the two combinations that best meet the criteria were chosen. Table 4.7 lists the fraction of cobalt remaining in solution and the residual zinc dust concentration, as well as the initial rate of cobalt removal. The removal rates were calculated from the data obtained in the first 45 minutes of the test (after this point the reaction is complete, no further removal occurs). The reactions are first order (a plot of $\ln([Co^{2+}]_o/[Co^{2+}])$ vs. time gives a straight line) and the rate constant was determined by taking the slope of that line.

Table 4.7: Optimum combinations for eliminating cobalt from zinc electrolyte and minimizing zinc dust consumption.

No.	Combination	Fraction of cobalt remaining in solution	Concentration of remaining zinc dust, g/L	Rate of removal
1	Sb-Cu-Cd	0.0	4.8	$r = 0.09[Co^{2+}]$
2	Sn-Cu-Cd	0.0	4.6	$r = 0.23[Co^{2+}]$

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The goal of this research was to study the fundamentals of cobalt cementation in zinc sulfate electrolyte with conventional additives (antimony and copper), to clarify the action of additives and their role in cementation, and to study novel additives. The objective was not only to improve cobalt removal (meeting a target concentration of <0.1 mg/L), but also to reduce zinc dust consumption. From the results in Section 4, the following conclusions can be drawn:

Cobalt cementation fundamentals

- zinc ions or a zinc complex inhibit cobalt cementation, which proceeds rapidly in the absence of zinc sulfate.
- by manipulating operating parameters such as temperature, pH and the addition of activators, cobalt removal can be optimized. However, the target of 0.1 mg/L in solution was not met (in synthetic electrolyte).
- in the presence of additives, pH control is not necessary and may contribute to excessive zinc dust consumption.
- cadmium and chloride ions in limited amounts are both beneficial to cobalt cementation.
- the type of zinc dust used has a significant effect on the amount of cobalt removed; by changing the type used it is possible to meet the target cobalt concentration.

Novel activators and activation mechanism

- among novel activators tested, tin is equally as effective as antimony in removing cobalt
- the initial kinetics of cobalt cementation with tin are faster than with antimony. This could shorten the necessary residence time for the process.
- zinc dust consumption varies widely among the additives tested. Tests with tin and antimony had some of the highest levels of zinc dust consumption.

- activator efficiency can be linked to the hydrolysis constant of the activator.
- zinc dust consumption can be linked to the hydrogen exchange current density for each activator.

Combinations of additives

- combinations of additives are highly effective at reducing cobalt to well below the target level and reducing zinc dust consumption to almost negligible amounts.
- among the factors tested in the combinations, the most important are:
    - the presence of copper and cadmium together for the best cobalt removal, (regardless of whether tin or antimony is used as the primary activator).
    - the presence of cadmium (or lead in the absence of cadmium) to minimize zinc dust consumption.

5.2 RECOMMENDATIONS FOR FURTHER WORK

Further studies should focus on showing that the results obtained, particularly those with combinations of additives, are reproducible in industrial electrolyte. Once that is shown, the optimal operating conditions (temperature, pH, additive concentrations, zinc dust concentration) for such a system should be studied. This work is being carried out at McGill University by Trina Dreher in the Department of Metallurgy. In addition, the results should be tested in a continuous reactor setup and compared with plant data.

One of the more interesting findings of this research that was not pursued was the effect of the type of zinc dust (or the effect of zinc dust morphology). There is no published research in this area (although there are some brief comments on the effect of particle morphology on hydrogen evolution), yet the type of zinc dust seems to have a large effect on cobalt cementation. There are many parameters that could be addressed by such a study: surface area, surface roughness, alloying elements, surface oxidation, particle size.

Systematic electrochemical investigation is recommended since the mechanism is electrochemical.

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APPENDIX A

Calculation of free sulfate and $CoSO_4^0$ concentrations in a zinc sulfate solution at 25°C and ionic strength 3.0.

Known concentrations:

$$\left[Co^{2+}\right] = \frac{0.03\ g/L}{58.93\ g/mol} = 0.00051\ mol/L$$

$$\left[Zn^{2+}\right] = \frac{150\ g/L}{65.39\ g/mol} = 2.294\ mol/L$$

$$\left[H^{+}\right] = 0.0001\ mol/L \quad (\text{pH} = 4.0)$$

Equilibrium constants (Martell and Smith 1982):

$$Co^{2+} + SO_4^{2-} \leftrightarrow CoSO_4^o \quad K_1=1.70$$

$$Zn^{2+} + SO_4^{2-} \leftrightarrow ZnSO_4^o \quad K_2=5.01$$

$$Zn^{2+} + 2SO_4^{2-} \leftrightarrow Zn(SO_4)_2^{2-} \quad K_3=5.01$$

$$Zn^{2+} + 3SO_4^{2-} \leftrightarrow Zn(SO_4)_3^{4-} \quad K_4=7.94$$

$$H^{+} + HSO_4^{-} \leftrightarrow H_2SO_4 \quad K_5=8.13$$

$H^{+} + SO_4^{2-} \leftrightarrow HSO_4^{-}$ $K_6=6.83\times10^{-7}$ (Filippou *et al.* 1993)

Charge balance:

$$2\left[Co^{2+}\right]+2\left[Zn^{2+}\right]+\left[H^{+}\right]=2\left[SO_4^{2-}\right]+\left[HSO_4^{-}\right]+2\left[Zn(SO_4)_2^{2-}\right]+4\left[Zn(SO_4)_3^{4-}\right]$$

Solving 6 equations with 6 unknowns:

$$72.86\left(\left[SO_4^{2-}\right]\right)^3+22.99\left(\left[SO_4^{2-}\right]\right)^2+2.00\left(\left[SO_4^{2-}\right]\right)-4.59=0$$

$$\left[SO_4^{-}\right]=0.2987\ mol/L \qquad \left[CoSO_4^o\right]=0.00026\ mol/L$$

APPENDIX B

Calculation of cobalt removal activity scale

In order to perform regressions of cobalt removal activity with additive characteristics it was necessary to characterize the graphs of cobalt removal as a function of time as a single number for each novel additive. This was difficult as the lines are not straight, in which case the slope of the line would have provided a convenient characterization of the removal efficiency. Nor could the lines be characterized by a single exponential value, or by a logarithmic value. In the end it seemed appropriate to approximate the curved cobalt removal line with a straight line, as this not only took into account the initial kinetics, but also the final cobalt concentration reached. Essentially the slope of the line represents the mean cobalt concentration over the course of the experiment. The slope is by no means an accurate representation of cobalt removal, and is only meant as a convenient and simple method to rank the additives for cobalt removal activity. The following figure shows the cementation curves for tin and bismuth, as well as the linear regression lines and their slopes.

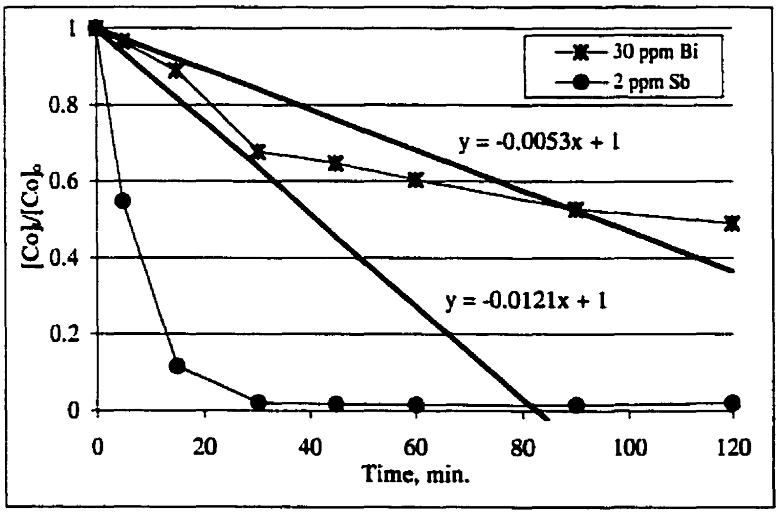

Figure B.1: Cobalt removal as a function of time for antimony and bismuth.

Tin had the largest slope and that number was multiplied by a factor to give tin a removal activity of 100. The rest of the slopes were multiplied by the same factor to create a scale of cobalt removal activity, shown in the following table:

Table B.1: Slope of line approximating cobalt removal curve for each additive and corresponding cobalt removal activity index.

Additive	Slope	slope × (-8196.72)
As	-.0053	43.44
Sb	-.0121	99.18
Sn	-.0122	100
Pb	-.0033	27.05
Bi	-.0053	43.44
Se	-.0036	29.51
Te	-.0108	88.52
In	-.0075	61.48
Hg	-.0061	50.00
Ag	-.0021	17.21
Ge	-.0019	15.57

APPENDIX C

Table C.1: Experiments included in 3-way factorial design to test combinations of additives (all tests: 120 min, pH 4.0, 95°C, 150 g/L Zn^{2+}, 5 g/L zinc dust). Each test was repeated 3 times, final cobalt values and residual zinc dust concentrations are given for each replicate.

Test no.	Sb^{3+}, 2 mg/L	Sn^{2+}, 30 mg/L	Cu^{2+}, 30 mg/L	Cd^{2+}, 30 mg/L	Pb^{2+}, 30 mg/L	Final cobalt conc., mg/L	Residual zinc dust, g/L
1	x		x			1. 0.47 2. 0.81 3. 0.69	1. 2.26 2. 1.93 3. 1.36
2	x			x		1. 10.52 2. 24.61 3. 0.52	1. 5.14 2. 5.38 3. 4.68
3	x		x	x		1. 0.00 2. 0.00 3. 0.00	1. 4.97 2. 4.88 3. 4.83
4		x	x			1. 0.52 2. 0.19 3. 0.14	1. 3.47 2. 2.59 3. 3.07
5		x		x		1. 8.4 2. 9.12 3. 7.36	1. 4.14 2. 4.40 3. 4.60
6		x	x	x		1. 0.00 2. 0.00 3. 0.00	1. 4.48 2. 4.78 3. 4.67
7	x	x	x			1. 6.82 2. 6.04 3. 5.08	1. 1.18 2. 1.54 3. 1.05
8	x	x		x		1. 5.91 2. 6.82 3. 5.09	1. 4.32 2. 4.24 3. 3.59
9	x	x	x	x		1. 0.00 2. 0.05 3. 0.12	1. 4.41 2. 4.19 3. 4.36
10	x		x		x	1. 6.80 2. 0.00 3. 0.19	1. 4.31 2. 4.38 3. 4.67
11	x			x	x	1. 0.63 2. 3.36 3. 2.11	1. 4.67 2. 4.84 3. 4.88
12	x		x	x	x	1. 0.00 2. 0.02 3. 0.00	1. 4.42 2. 4.28 3. 4.90
13		x	x		x	1. 0.00 2. 0.04 3. 0.00	1. 4.14 2. 4.19 3. 3.66

continued on next page

Test no.	Sb^{3+}, 2 mg/L	Sn^{2+}, 30 mg/L	Cu^{2+}, 30 mg/L	Cd^{2+}, 30 mg/L	Pb^{2+}, 30 mg/L	Final cobalt conc., mg/L	Residual zinc dust, g/L
14		x		x	x	1. 2.96 2. 2.30 3. 2.64	1. 4.19 2. 5.28 3. 4.50
15		x	x	x	x	1. 0.00 2. 0.00 3. 0.00	1. 3.94 2. 4.24 3. 3.77
16	x	x	x		x	1. 0.54 2. 0.53 3. 1.62	1. 1.90 2. 1.72 3. 1.42
17	x	x		x	x	1. 5.17 2. 0.85 3. 0.80	1. 4.47 2. 3.61 3. 3.48
18	x	x	x	x	x	1. 0.00 2. 0.00 3. 0.00	1. 3.65 2. 3.60 3. 3.63