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The Removal of Cobalt from Zinc Electrolyte by Cementation: A Critical Review

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The removal of cobalt from zinc electrolyte has been a focus of electrometallurgical research for over 20 years. This survey reviews the literature on cobalt cementation as well as zinc electrowinning and hydrogen evolution in the interest of characterizing the factors which are important in cobalt cementation by zinc dust and developing an improved purification process. The effect of speciation, the solubility of zinc hydroxide and zinc sulfate, temperature, pH, and the concentrations of reacting species, impurities, and catalytic agents are all investigated.

Keywords: Cementation; cobalt; zinc sulfate; additives

INTRODUCTION

Industrial Zinc Production

The roast-leach-electrowinning (RLE) process (Fig. 1) produces over 80% of the world's zinc. Zinc concentrate consists mainly of zinc sulfide, which is insoluble in dilute sulfuric acid; roasting converts the sulfide into soluble zinc oxide. Leaching the roasted concentrates with sulfuric acid liberates zinc ions as well as impurities such as iron,

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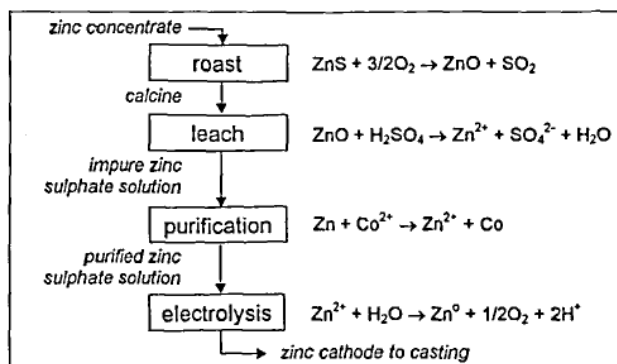


FIGURE 1 Roast-leach-electrowin process for zinc production.

copper, cadmium, cobalt and nickel; the leach solution must then be purified before becoming the feed to the electrolysis step from which metallic zinc is recovered.

The zinc electrowinning process is unusual from a thermodynamic point of view because zinc metal has a more negative reduction potential ($e^0 = -0.76$ V) than hydrogen ($e^0 = 0$ V); 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 has such a high overpotential on zinc metal [1]. In order to maintain this large overpotential, impurities in the leach solution must be completely removed [2]. Any remaining impurities act as catalysts for hydrogen evolution or codeposit with zinc, causing large drops in current efficiency (Fig. 2).

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 [4]. Remaining traces of impurities in the zinc electrolyte are subsequently removed in the main purification section of the process by zinc dust cementation [5].

In the process used at CEZinc., impurity removal by cementation is carried out continuously in three stages [6], as shown in Figure 3. Impure feed containing 1 g/l cadmium, 1 g/l copper, and 15 mg/l cobalt is treated in the first purification stage, consisting of two 150 m³ stirred-tank reactors in cascade. This stage removes copper, cadmium,

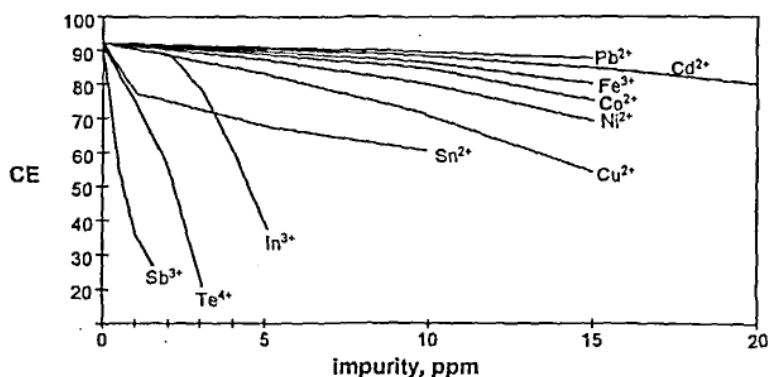


FIGURE 2 Effect of impurities on zinc electrowinning current efficiency [3].

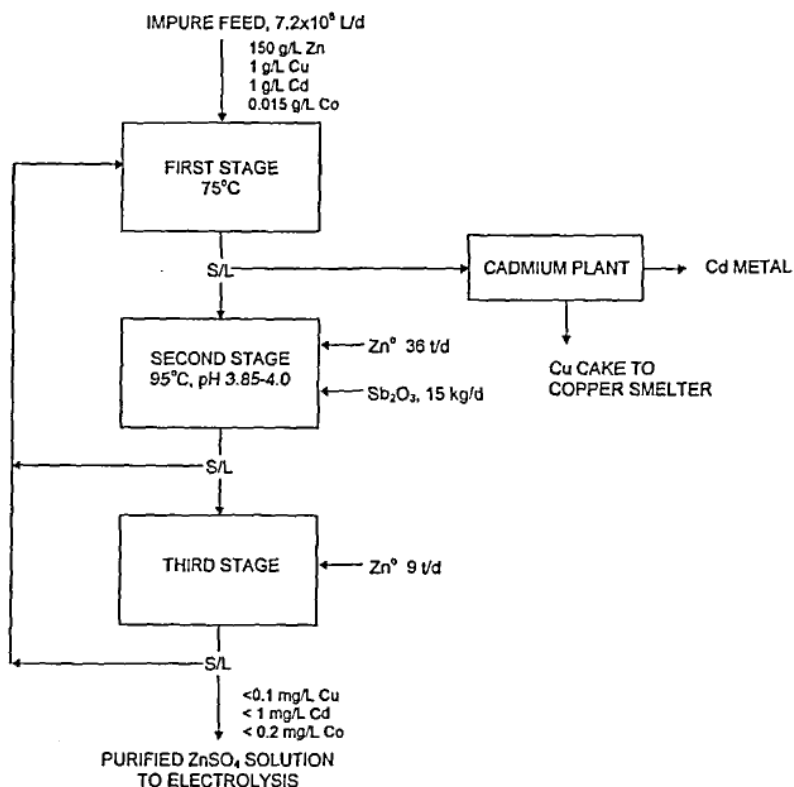


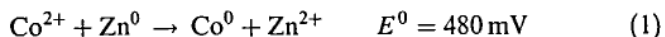
FIGURE 3 Three stage purification process (Canadian Electrolytic Zinc) [6].

and about 40% of the cobalt using purification residue recycled from the second and third stages. The solution temperature is about 75°C and the pH is 4.2–4.6. The second stage further reduces the level of cobalt. This stage uses 4–5 g/L of fresh zinc dust, as well as additions of antimony trioxide and copper sulfate, and operates at 95°C and pH 4.0. The last stage is a polishing stage to remove any redissolved cadmium, using a small amount of zinc dust (1–2 g/L).

Table I shows the maximum tolerable levels of some common impurities in the feed to the electrowinning operation. Cobalt is of particular concern because even low levels are harmful and it is 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.

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



Lawson and Nhan [7] calculated the ΔG^0 of the above reaction to be -93 kJ/mol of cobalt at 25°C with an equilibrium constant of

TABLE I Upper limits of common impurities in zinc electrowinning

Impurity (mg/L)	CE Zinc [6]	Cominco [2]	Hoboken-Overpelt [2]	Port Pirie [2]
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

$2 \cdot 10^{16}$. 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 (Fig. 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 $1.6 \cdot 10^4$ tonnes of zinc dust (or 6–7% of production) [6]. 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 90°C in order to improve the reaction kinetics, and then must be cooled to 50°C for the electrowinning step.

From the above it is apparent that there is much room for improvement in the cementation process. We have conducted the following literature survey in order to analyze the large amount of literature available on cementation and electrowinning, examine the parameters involved in the cementation reaction, particularly the effects of additives, and discern the mechanisms by which additives act.

REVIEW

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 residual organics.

Temperature

It is well known that increasing temperature has a beneficial effect on the rate of cobalt cementation [2, 8, 9, 10, 11]; indeed, some suggest that temperature is the most influential parameter on cementation [8]. While most studies simply state that cementation kinetics improve with increasing temperature, Lew *et al.* [10] showed a maximum increase in the rate of cementation of 80°C. A peak beyond which raising the temperature is no longer effective can be explained by the competing reaction, hydrogen evolution. The rate of hydrogen evolution increases at a greater rate with temperature than cobalt cementation does [10], hence beyond a certain point an increase in temperature does more to promote the parasitic reaction. The effect of temperature is logical for a process that is under chemical control, as is cobalt cementation in a zinc sulfate solution. The activation energy for cobalt cementation has variously been reported as 39 kJ/mol [9], 86.6 kJ/mol [10] and 65 kJ/mol [12], indicating a chemical or surface controlled process.

pH

The solution pH also affects the rate of cementation, although Blaser and O'Keefe suggested that this is the least influential parameter among temperature and reagent concentrations [8]. There is a window of optimum operating pH between 4.0 and 4.4 [10]: 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. Van der Pas and Dreisinger, however, argued that increasing the pH beyond the point where basic zinc compounds form does not inhibit the reduction of cobalt [12]. Borge and Ostvold found that the initial cementation rate is slightly higher for solutions at pH 4

(compared to 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 [11].

Presence of Zn(II)

There is a large amount of work studying the effect of zinc ions in solution on cobalt cementation. In industry cementation occurs in a solution which typically contains 150 g/L Zn(II) ions. In a solution containing no zinc ions, cobalt cementation proceeds rapidly, and has an activation energy of 13 kJ/mol, indicating a mass transfer controlled process [13]. However even a small amount of zinc ions in solution inhibits the rate of cementation severely [2]. The activation energy increases, indicating that the zinc ions interfere with the reaction step at the surface of the zinc dust. Xiong and Ritchie [14] 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.

Van der Pas and Dreisinger [12] 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 [15]. In a 1 molar solution of zinc and cobalt sulfate, if zinc constitutes less than 6% of the total, 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 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.*, 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 [16].

Oh [17] investigated the differential dissolution of a mixed cobalt-zinc metal disc. He looked at the effects of the concentration of reactants (hydrogen ions and oxygen), stirring speed, temperature, and disc composition on dissolution behaviour, and derived a rate expression for the dissolution of zinc from the mixed disc at constant pH. Theoretically, 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. The experiments confirm this expected behaviour. The dissolution rates decrease with increasing pH, and above pH 2.5 Oh shows that it is not possible to dissolve cobalt from mixed cobalt-zinc. The activation energies for cobalt and zinc from their pure discs are 16.3 and 22.0 kJ/mol respectively, and those for zinc from the mixed disc range from 22.6 to 23.0 kJ/mol.

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 (98°C) than arsenic (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 [11]. 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 cementation research.

An early study by DeBlander and Winand [18] 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, 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 no accelerating effect.

Lew *et al.*, observed that antimony alone activates cobalt reduction, but the final cobalt concentration is much higher than when antimony and copper are both present, and the rate of cementation is slower [10]. By observing the pH of the reaction solution with time, 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 their opinion this suggests that copper acts primarily as a substrate for cobalt cementation while antimony plays a role 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.

A fundamental study of the copper/antimony process by Van der Pas and Dreisinger [12] 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. 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. 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.

Polcaro *et al.*, studied the kinetics of cobalt cementation under the influence of additives and noted that the reduction of copper or antimony is a first order reaction and mass transfer controlled [19]. This work confirms that copper and antimony deposit before cobalt, and that cobalt reduction is also a first order reaction [2, 10, 12].

Wang and O'Keefe [20] looked at the effect of additives on zinc ion inhibition. The anomalous codeposition of zinc is sometimes explained as occurring due 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. Germanium additions nearly double the cobalt content.

Kim *et al.*, showed that the addition of antimony only enhances the cobalt cementation rate up to 5 ppm, after which cobalt redissolves [9]. Fontana and Winand noted that retention times of longer than one and a half hours in the second purification stage have the effect of putting cobalt back into solution [21]. They suspected that this was due to reoxidation of the cemented cobalt by dissolved oxygen.

Fontana and Winand also reported the effects of alternative additives to antimony, in particular lead, tin, arsenic, and bismuth, added as oxides or chlorides [21]. By comparing the removal rates 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 oxides in their experiments. Lead compares favourably to antimony as an additive, followed by tin, arsenic, and then bismuth, which had 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.

Jiang, Tseung *et al.*, contradict Fontana's conclusions about chlorides: their extensive study showed that the rate of cobalt deposition is significantly affected by anions in solution [22]. The rate of cobalt deposition increases correspondingly in the presence of the following anions: $\text{NO}_3^- < \text{CH}_3\text{COO}^- < \text{SO}_4^{2-} < \text{Cl}^-$. 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.*, also reported the catalytic effect of chloride and thiocyanate anions on the electrodeposition of iron-group metals [23]. They concluded that chloride has a depolarizing effect, in effect reducing the cobalt deposition overpotential.

Formation of 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.

Tozawa developed $M-As-H_2O$ and $M-Sb-H_2O$ potential-pH diagrams which show that metal arsenides and antimonides for Cu, Co and Ni are all more stable than the metals alone (see Fig. 4) [2]. 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 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 facts indicate that the mechanism of cobalt removal with antimony is different from that

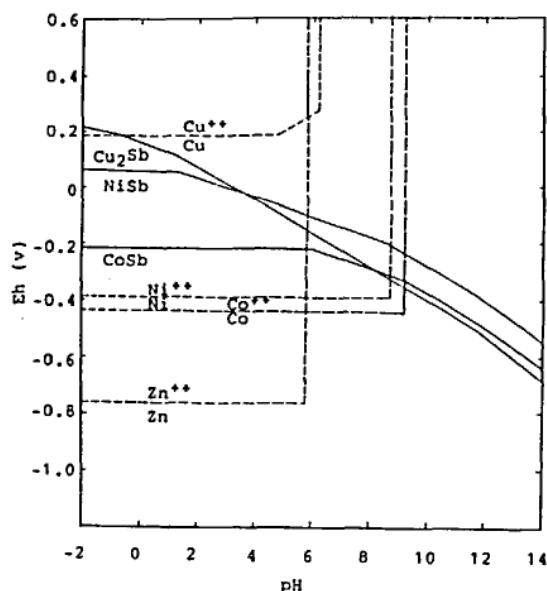
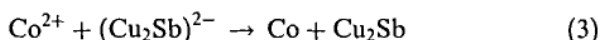
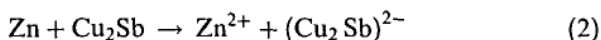


FIGURE 4 E_h -pH of $M-Sb-H_2O$ system. $[Cu] = [Ni] = [Co] = 10^{-5} M$, $[Zn] = 1 M^2$.

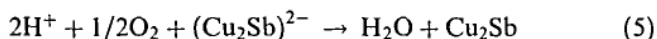
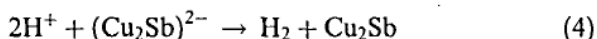
with arsenic. In these experiments, the deposition of cobalt arsenide was confirmed, in agreement with predictions from the potential-pH diagrams, but cobalt antimonide was not found by SEM investigation. In the arsenic tests, cobalt, arsenic, and copper deposited on the same site, while in the antimony tests copper and antimony co-existed with cobalt found around the copper-antimony deposit.

Fischer-Bartelk *et al.*, proposed thermal equilibrium diagrams for cobalt, nickel, and additives which show the possible constitution of new phases by electrochemical deposition [24]. 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.

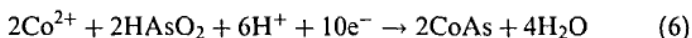
Kroleva [25] suggested the formation of a Cu_2Sb alloy which enhances deposition in the following way:



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

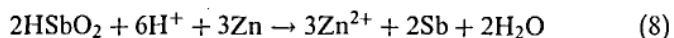


Yamashita *et al.* [16] proposed a mechanism for the accelerating effect of copper and arsenic on cobalt cementation: a galvanic cell forms between zinc dust and copper (which cements first), then the galvanic current reduces cobalt on copper as a Co-As alloy:



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 [21] concluded that the role of copper is to help solubilize antimony by the following reaction:



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.* [24]. Further study by Fontana *et al.* [26] 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 goes against the theory proposed by Fischer-Bartelk *et al.*

Lew *et al.*, on the other hand, identified no alloys in SEM micrographs of the cement [10]. Van der Pas and Dreisinger's work supports this finding [12]; 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.

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 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 (0.05–5wt%) increase the rate [27]. 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.

Zinc Dust

Lew *et al.*, stated that the optimal concentration of zinc dust for cobalt removal with the antimony-activated process is 4 g/L [10]; industry use ranges from 4 to 6 g/L. The size of the particles is important; smaller

dust gives faster initial kinetics and a lower final cobalt concentration [11]. This is likely a surface area effect, although there is no data on the effect of surface area.

Often the zinc dust from the second purification state is recycled to the first. 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 [28]. 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.

Residual 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 [6]. 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.* [6] showed that residual organics in zinc electrolyte at levels as low as 0.5 mg/l have a significant 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.* [10] confirmed the effect of residual organics, noting that the presence of 2 ppm animal glue, Percol 351, or lignin sulphonic acid greatly reduces the rate of cobalt cementation and the amount of cobalt removed.

Zinc Electrowinning

Evaluation of the effect of impurities and additives on zinc electrowinning performance is important in understanding the cobalt

cementation process because the mechanism of codeposition of zinc and cobalt and the subsequent effect on current efficiency are essentially the same in the two processes. In addition, the effect of additives used in the purification process on the subsequent electrowinning stage must be considered, since the purpose of removing the cobalt is to obtain a higher current efficiency and preferred deposit morphology in electrowinning. Some additives, if they remain in solution, may counteract this effect.

The presence of impurities in zinc electrolyte is problematic for the electrowinning operation. Small concentrations of impurities cause decreases in zinc current efficiency (Fig. 2) and changes in deposit morphology and cathodic polarization. Levels as low as parts per billion of some metals (Sb, Ge, As) and parts per million of others (Co) and organic agents greatly influence the reduction of zinc at the cathode.

Metal Contaminants

It is generally believed that the alkali and alkaline earth metals are not detrimental in the electrowinning of zinc [29]. In fact, Ault *et al.*, showed that the current efficiency increases slightly with the addition of high concentrations of sodium and potassium to the electrowinning solution (0.5 mol/L and 0.25 mol/L respectively) [30]. The authors suggested that such ions act by an adsorptive mechanism to inhibit the action of hydrogen on zinc deposition. However, there is also evidence that zinc ions inhibit the hydrogen evolution reaction rather than the reverse [31].

One can generally say that: ions of those metals with standard potentials more negative than zinc, such as Al, Mg, Ca and Na have little effect on current efficiency; ions of metals with standard potentials marginally more positive than zinc, such as Cd and Pb, tend to deposit at the cathode, decreasing its purity; ions of those metals with standard potentials much more positive than zinc and which are characterized by a high melting point and low hydrogen overpotential such as Pt, Ag, Au, Fe, Co, Ni, Cu decrease current efficiency [32]. Metals like Sb, As, Ge, Se, Te act in a more complex manner; they can form hydrides which serve as the cathodic reaction

for localized corrosion, making it possible for zinc to redissolve even while cathodically polarized. Additions of antimony cause a refinement of grain size and cause the deposit platelets to lie parallel to the surface, at the same time drastically reducing current efficiency. Antimony deposits with zinc significantly increasing the rate of hydrogen evolution, and the platelet edges are rounded indicating resolution of zinc (local cell corrosion) [32].

Ohoyama and Marioka evaluated the effects of impurities by measuring the volume of hydrogen gas evolved on cathode zinc, and classified them as follows [33]:

worst	worse	bad
Ge, Sb, Te, Se	As, Ni, Sn, Co, Fe, Ag	Ga, Bi, Tl, Cd, Hg, In, Pb

MacKinnon *et al.*, systematically studied the effects of many common metal impurities on current efficiency and deposit morphology. Lead impurity results in a higher zinc deposition overpotential [34, 35] and characteristic deposit morphologies and orientations, depending on the chemical form of the lead added and the presence of other impurities [34]. Cadmium, however, lowers the zinc deposition overpotential, while germanium in small quantities (~ 0.1 mg/L) rapidly lowers the current efficiency due to the formation of local Ge—Zn cells which promote hydrogen evolution and the redissolution of zinc [36]. Copper contamination as high as 50 mg/L does not affect the deposit current efficiency, but reduces the deposit grain size [37]. Antimony and copper together, however, cause a significant decrease in current efficiency and an increase in the copper content of the deposit. Tin concentrations of less than 2 mg/L considerably reduce the current efficiency, but the reduction levels off at greater concentrations. There are conflicting reports as to whether tin enhances or inhibits hydrogen evolution [38, 35]. While As (III) had no effect on the current efficiency and does not alter deposit morphology or orientation, the presence of small concentrations of As(V) (less than 5 mg/l) are detrimental, causing changes in morphology and orientation and a dramatic decrease in current efficiency [39]. The presence of either glue or antimony or both in solution further aggravates the effect of As (V). These additives also produce negative interactions with As(III) although the effects are

much less pronounced. Iron also has significant detrimental synergistic effects in combination with cobalt and arsenic [40].

Fosnacht and O'Keefe studied the mechanism of cobalt and germanium interaction in zinc electrolytes using cyclic voltammetry [31]. The CV tests show that germanium and cobalt behave similarly at the working electrode, except that the germanium interaction becomes apparent at concentration levels twenty times smaller than for cobalt. Interestingly, the ratio of exchange current densities for hydrogen discharge on germanium and cobalt is equal to 21. The authors interpreted this to mean that the interaction of the impurity is dependent on its ability to act as a site for hydrogen discharge. They proposed that initially the impurities codeposit in a manner proportional to their concentration, leading to the formation of local cells on the electrode surface. This enhances hydrogen evolution on zinc dissolution, which, with time, causes the net cathode deposition process to deteriorate. Conventionally, germanium and antimony are thought to behave in a similar manner, but when the authors compared their work with previous research on antimony [41], they found substantial variations in behaviour.

Organic Impurities

Organic additives (such as animal glue) are used in zinc electrowinning to promote smooth cathode deposit growth, to control the negative effect of impurities such as antimony and cobalt on the current efficiency, and to prevent the formation of acid mist over the cells. It is difficult to generalize about the role of organics, but experience shows that while a few additives such as gum arabic and animal glue can be beneficial, most other organics are harmful to zinc deposition.

Glue additions can increase the cathode polarization as much as 30 mV at low current densities [32]. It also causes refinement of grain size and causes the deposit platelets to align perpendicularly to the substrate. Current efficiency decreases moderately and linearly with glue addition due to hydrogen evolution at the glue deposits. At these sites hydrogen evolves freely with concurrent zinc deposition, rather than zinc local cell corrosion which occurs at antimony deposit sites (this results in zinc deposits with rounded edges).

Kerby *et al.*, examined the effect of organic agents of zinc electrowinning and developed a cyclic voltammetry technique to give a rapid quantitative evaluation of the effectiveness of organic additives in minimizing the detrimental effects of impurities in electrowinning [41]. Additives (such as glue [42]) which increase the activation overpotential of zinc deposition are the most effective in controlling impurities. Animal glues prove to be more effective than several gums, enzymes, and amino acids that the authors tested, the best glues having average molecular weights of 25,000 to 30,000.

MacKinnon looked at the effect of foaming agents, alone or in combination with antimony, magnesium, and manganese [43]. Both Dowfroth and Saponin decrease the zinc deposition current efficiency and change the deposit morphology and orientation. The addition of antimony and/or manganese sulphate moderates the effects of these agents, such that certain combinations maximize the current efficiency and improve the deposit morphology. The addition of MgSO_4 has no effect. The addition of MnSO_4 to synthetic electrolyte containing foaming agents and antimony results in deposit morphologies similar to those obtained with industrial electrolyte containing similar reagent concentrations.

Cachet *et al.*, reported the influence of another additive, triethylbenzylammonium chloride (TEBA) on zinc deposition in a sulfate electrolyte containing nickel as an impurity [44]. The authors concluded that TEBA adsorption on the cathode inhibits both the nucleation and growth of zinc deposits and hydrogen evolution; TEBA adsorption competes with nickel and zinc adsorption and reduces zinc redissolution.

Fosnacht and O'Keefe [45] examined the effects of germanium, antimony, arsenic, cobalt, glue, temperature, and acid concentration, alone and in combination, on zinc electrowinning current efficiency. They found acid content to be the most critical factor, followed by cobalt, temperature, antimony, germanium, and arsenic levels. Cobalt and acid act in a significantly detrimental synergistic manner, as well as cobalt and arsenic. The combination of glue and antimony appears to lessen the detrimental effects of other impurities, but in the absence of glue, antimony has a detrimental synergistic interaction with cobalt. The proper combinations of glue and impurity optimize the current efficiency.

MacKinnon and Brannen also found that while glue increases zinc deposition overpotential germanium decreases it [42]. They suggested that the opposing influences of antimony and glue (or germanium and glue) counteract each other resulting in a preferred morphology. This effect is confirmed by others [46, 47]. Robinson and O'Keefe reported 0.08 mg/L Sb and 30 mg/L as the optimum combination of glue and antimony to maximize current efficiency [32].

Physical Parameters

Physical parameters such as temperature and the smoothness of the cathode can have an important effect on the action of impurities in electrowinning. Fosnacht and O'Keefe investigated the effects zinc and acid concentration, temperature, and surface roughness on electrolyte solutions with germanium and cobalt impurities [31]. They found that increased temperature, surface roughness, acid concentration and decreased zinc concentration increase the deleterious effects of the impurities on electrowinning.

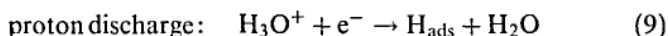
Impurities such as nickel and antimony have a more pronounced effect when the cathode surface is rough. For a very smooth cathode surface, impurities have an almost negligible deleterious effect, particularly nickel [48].

Increasing zinc concentration increases the current efficiency and lowers the energy consumption, due to the increasing reaction rate with zinc concentration. Increasing acidity decreases the current efficiency, due to increased proton activity and thus hydrogen evolution, resulting in decreased zinc deposition (due to competing reactions). However, the cell voltage drops due to the high mobility of protons, offsetting the decreasing current efficiency and leading to an overall drop in energy consumption. Increasing cell temperature increases the current efficiency in pure electrolyte, due to the decreasing voltage with increasing temperature. In an impure solution, increased temperature is detrimental as it increases the activity of the impurities. Current efficiency is independent of current density, but the voltage goes up due to increased IR drop. The optimum operating conditions for zinc electrowinning are 60–70 g/l zinc, 160 g/l acid, 40–45°C, 350–450 A/m² [49].

Hydrogen Evolution

It is apparent from the preceding sections of zinc dust cementation and zinc electrowinning that hydrogen evolution is an important aspect of both processes and integral to the success of either. In terms of cementation, it is of interest to inhibit hydrogen evolution in order to obtain fast cementation kinetics and low zinc consumption.

Hydrogen evolution is a complicated reaction composed of several steps [50]:



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 [51]. Trassati 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 [52].

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 9), whereas on cobalt and chromium it occurs by the radical ion mechanism (equation 11) [53]. Table II summarizes the data for cobalt.

The morphology of the metal surface can also affect hydrogen discharge. Hydrogen evolution on carbon electrodes with different

TABLE II Hydrogen evolution data for cobalt electrodes [53]

Parameters	Values	Comments
Tafel slope (25°C)	115 mV/decade	in 1N H ₂ SO ₄ + 2N Na ₂ SO ₄ , pH = 0.7
Exchange current density (25°C)	$6.25 \cdot 10^{-7}$ A/cm ²	
Corrosion potential	-114 mV	open circuit potential in 1N H ₂ SO ₄ + 2N Na ₂ SO ₄
Corrosion current	$5.4 \cdot 10^{-6}$ A/cm ²	

structures demonstrates the significance of the electrode surface condition on hydrogen evolution [54]. The activity of hydrogen ion on various types of surfaces can be partially correlated to surface area, but not entirely. The reaction order also changes with the type of surface. This is confirmed in other reports [55, 56].

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 *et al.* [57–61] systematically investigated the catalytic behaviour of nickel with a variety of additives. The main conclusions of interest are: the electrocatalytic parameters (exchange current density i_o and hydrogen overpotential η) are improved by adding Cu(II) to the electrolyte; 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; and 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 [62] showed that impurities in solution (such as arsenic) do change the Tafel slope and thus also the discharge mechanism.

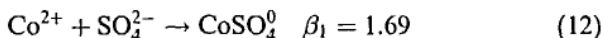
The presence of oxygen in solution can affect the hydrogen overpotential by the participation of oxygen in the reduction reaction [22, 63, 64]. Cobalt oxides and hydroxides (CoOOH, Co₃O₄, CoO) formed during oxygen reduction are further reduced to Co, which results in a more porous electrode, and a lower 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.

DISCUSSION

Speciation

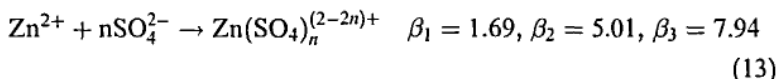
Most studies of cobalt cementation and zinc electrowinning neglect to consider speciation altogether; not only does speciation play an important role in determining the concentration of the reacting species cobalt, but also of zinc, which plays an important role in retarding the rate of cobalt cementation.

Co(II) ions can exist in the Co^{2+} and CoSO_4^0 forms with considerable hydration. The following describes Co(II) sulfato complexation [65]:



The smaller constants are neglected since the cobalt concentration is negligible compared to the zinc concentration. Co^{2+} should dominate the Co—Zn— SO_4 system as Zn(II) consumes the SO_4^{2-} in solution.

The following describes the interaction of zinc ions with sulfate ions in an acidic medium without considering water molecules in the inner coordination sphere [65]:



Filippou *et al.*, calculated Zn(II) sulfato speciation [66,67], considering the effects of ionic strength and temperature. Figure 5 shows the speciation as function of pH and total Zn(II) concentration. Clearly ZnSO_4^0 dominates the solution. Figure 6 shows the effect of electrolyte temperature; over 99% of the Zn(II) species exists as ZnSO_4^0 in zinc electrolyte at 95°C.

Solubility

DeBlander and Winand [18] suggested that a less conductive zinc hydroxide or basic zinc sulfate ($\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) forms on the surface of zinc dust; the general consensus is that this is the reason for slow cementation kinetics at high pH. Although there is some data for

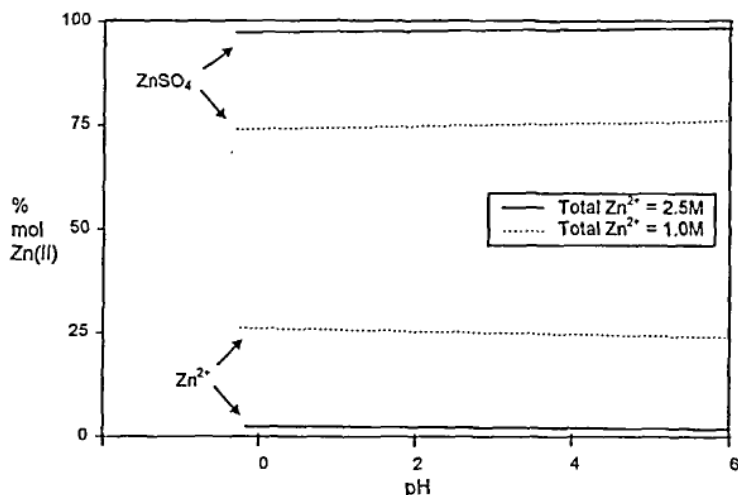


FIGURE 5 Zn(II) speciation as a function of pH; 298 K, total dissolved Zn(II) at 1.0 and 2.5 M.

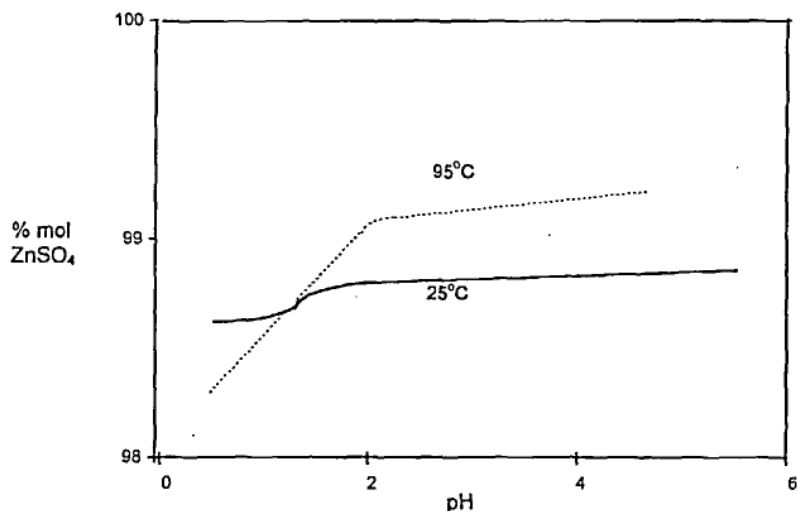


FIGURE 6 ZnSO₄ abundance as a function of pH at 25 and 95°C; total dissolved Zn(II) 2.5 M.

the formation of this compound [68], there is no solubility data. 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.

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 K_{sp} for $Zn(OH)_2$ in the interfacial area is different from that in the bulk, as illustrated in Figure 7. 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 zinc hydroxide/basic zinc sulfate precipitation is responsible at least in part for the slow cementation kinetics.

Zn(II) Ions

Cobalt cementation from solutions containing no zinc ions is a mass transfer controlled process, but in a zinc sulfate solution becomes a chemical/surface controlled process. Obviously zinc ions are impairing cobalt deposition in some way. The possibility of surface passivation by solid formation has been discussed; alternatively zinc is adsorbed in the double layer of the zinc dust particles obstructing cobalt reduction at the surface. Details of the surface charge of zinc particles are not certain [69], but it is possible that SO_4^{2-} ions are specifically adsorbed

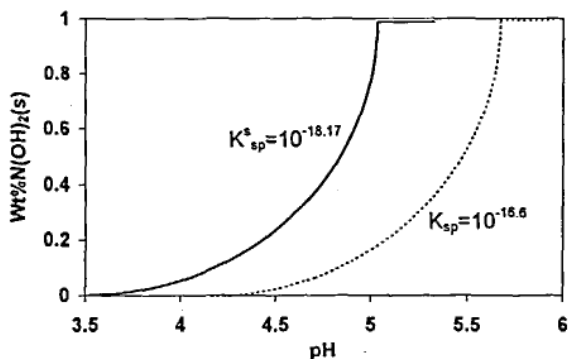


FIGURE 7 Surface vs. bulk precipitation of $Zn(OH)_2$ as a function of pH at 298 K.

in the inner Helmholtz plane (IHP), and subsequently zinc ions adsorb electrostatically in the outer Helmholtz plane (OHP). It is even more likely that zinc ions simply adsorb 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 (Fig. 4) suggest that most likely Zn^{2+} species in solution, not ZnSO_4 , cause the problem, even though ZnSO_4 dominates in the solution.

Temperature

Figure 8 compares the effect of temperature on cementation rate obtained from different sources. Although increasing the temperature promotes the cobalt removal rate, it 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 as the current available remains constant, whereas in the cementation process excess zinc dust is available. It is

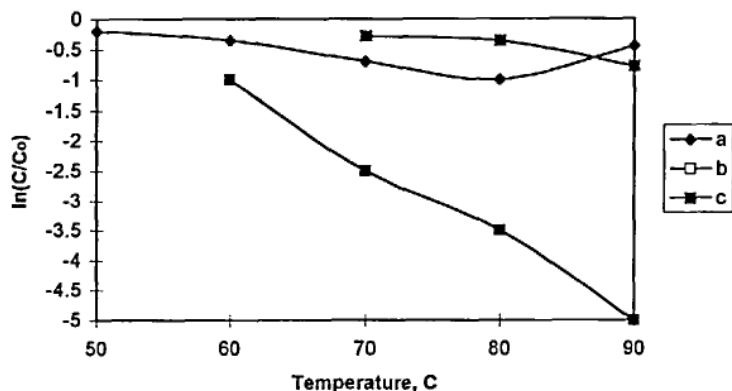


FIGURE 8 Effect of temperature on cobalt cementation: (a) electrolytic reduction of cobalt on antimony substrate after 180 min; 30 A/m^2 , $[\text{Co}^{2+}] = 30 \text{ ppm}$, $\text{pH}(\text{init}) = 4.0$, total $[\text{Zn}^{2+}] = 155 \text{ g/L}^{12}$. (b) cobalt cementation of zinc with additives after 60 min. (no pH control); $[\text{Co}^{2+}] = 26 \text{ ppm}$, $[\text{Cu}^{2+}] = 46 \text{ ppm}$, $[\text{Sb}^{3+}] = 1.5 \text{ ppm}$, total $[\text{Zn}^{2+}] = 151 \text{ g/L}^{10}$. (c) cobalt cementation with additives after 200 min; $[\text{Co}^{2+}] = 10 \text{ ppm}$, $[\text{Cu}^{2+}] = 20 \text{ ppm}$, $[\text{Sb}^{3+}] = 10 \text{ ppm}$, total $[\text{Zn}^{2+}] = 150 \text{ g/L}^2$.

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.

pH

The optimum operating pH must balance reducing the hydrogen ion activity (by raising the pH) and reducing the chance of forming solid precipitates (by lowering the pH). Van der Pas and Dreisinger claimed that a low pH is more detrimental to cementation than a high pH [12]. Figure 9 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 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 deduce that at high pH surface precipitation of zinc hydroxide or basic zinc sulfate retards cementation kinetics (see Fig. 10).

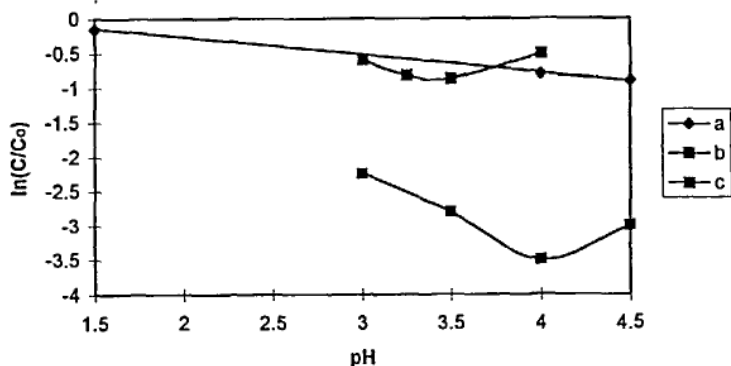


FIGURE 9 Effect of pH on cobalt cementation: (a) electrolytic reduction of cobalt on antimony substrate after 180 min; 30 A/m², [Co²⁺] = 30 ppm, 73°C, total [Zn²⁺] = 155 g/L¹². (b) cobalt cementation of zinc with additives after 60 min. [Co²⁺] = 26 ppm. [Cu²⁺] = 46 ppm. [Sb³⁺] = 1.5 ppm, 73°C, total [Zn²⁺] = 151 g/L¹⁰. (c) cobalt cementation with additives after 200 min; [Co²⁺] = 10 ppm, [Cu²⁺] = 20 ppm, [Sb³⁺] = 10 ppm, 90°C, total [Zn²⁺] = 150 g/L².

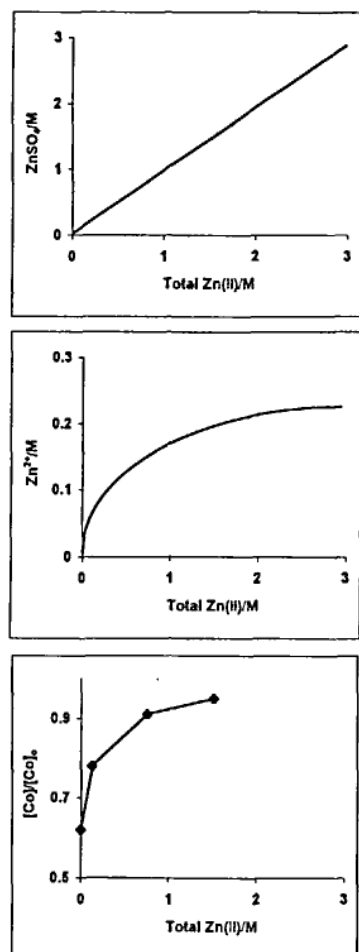
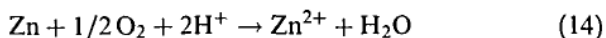


FIGURE 10 Comparison of Zn(II) speciation data: (a) ZnSO₄ concentration as a function of total Zn(II) [66] (363 K, pH 3.5). (b) Zn²⁺ concentration as a function of total Zn(II) [66] (363 K, pH 3.5). (c) Effect of Zn(II) on cobalt removal [2] (363 K and pH 3.3–3.75).

Dissolved Oxygen

Oxygen solubility is temperature dependent: it is soluble to 8.5 ppm at 25°C and 5 ppm at 90°C [70] in pure water, and to 9.5 ppm at 37°C in 2.15 M ZnSO₄ [71]. 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:



Oxygen in solution also causes cobalt dissolution:

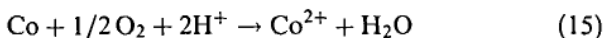


Figure 11 shows the capacitance at the Co^{2+}/Zn interface to increase in the presence of oxygen: the rapid initial increase in capacitance in the presence of air indicates the formation of a layer of oxide or hydroxide on the surface of zinc, which may result in the passivation of the reaction surface [14]. Bubbling nitrogen in the electrolyte is the most common way to deoxygenate, and also increase the hydrogen overpotential on a cobalt electrode (by 100 mV) [72].

Additives

Copper itself improves the cementation rate only slightly (Fig. 12a), but works in synergistic way with antimony (Figs. 12b and 12c). 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

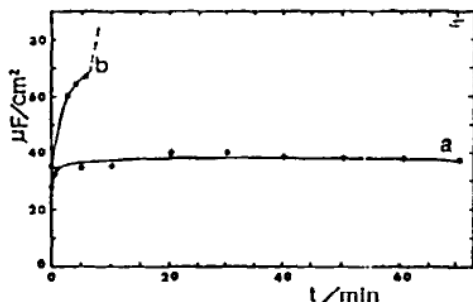


FIGURE 11 Variation of capacitance with time during cobalt cementation (pH 4.0, zinc disc rotation 700 rpm) [14]: (a) solution deoxygenated with argon; (b) in the presence of air.

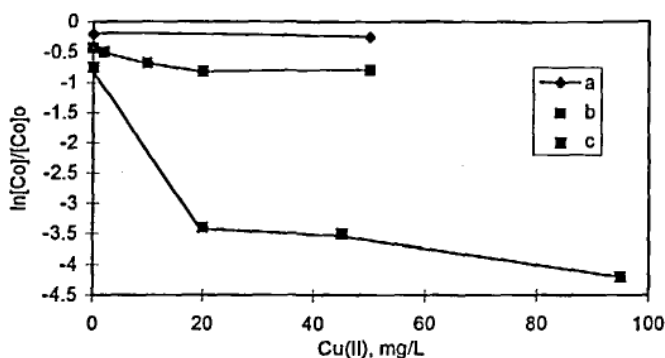


FIGURE 12 Effect of Cu(II) on cobalt cementation: (a) Cobalt cementation after 90 min. [10] ([Co] = 26 mg/L, natural pH, 73°C, [Zn] = 151 g/L). (b) Cobalt cementation with antimony after 60 min. [10] ([Co] = 26 mg/L, [Sb] = 1.5 mg/L, natural pH, 73°C, [Zn] = 151 g/L). (c) Cobalt cementation with antimony after 200 min. [2] ([Co] = 10 mg/L, [Sb] = 10 mg/L, pH = 3.3, 90°C, [Zn] = 150 g/L).

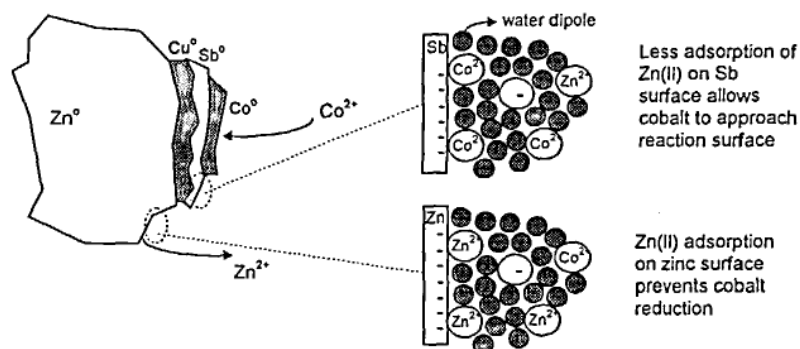


FIGURE 13 Schematic representation of the postulated activation role of antimony in cobalt cementation.

significantly less adsorptive accumulation of Zn^{2+} on the antimony surface, permitting cobalt ions to reach the reaction surface. Figure 13 gives a schematic representation of this postulated mechanism.

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 deposition on copper substrate seems to prevent zinc ion adsorption thus facilitating cobalt reduction. Experimental investigations are required to substantiate this conclusion.

References

- [1] Kita, H. (1966). *Journal of the Electrochemical Society*, **113**, 1095.
- [2] Tozawa, K., Nishimura, T., Akahori, M. and Malaga, M. A. (1992). *Hydrometallurgy*, **30**, 445.
- [3] Duyvesteyn, W. P. C. and van Weert, G. (1993). 'Hydrometallurgie', Technische Universiteit Delft.
- [4] Dutrizac, J. (1987). 'Crystallization and Precipitation' (Eds: Strathdee, G. L., Klein M. O. and Melis, L. A.), Pergamon Press, New York, p. 259.
- [5] Ashman, D. W. (1993). "Hydrometallurgy: Fundamentals, Technology, and innovation" (Eds: Hiskey and Warren), AIME, Littleton CO, p. 63.
- [6] Houlachi, G., Belanger, F. and Principe, F. (1989). *Proceedings, International Symposium of Electrometallurgy Plant Practice* (Eds: Claessens, R. and Harris, G. B.), Pergamon Press, New York, p. 177.
- [7] Lawson, F. and Nhan, I. T. (1981). Hydrometallurgy '81, *Proceedings of the Society of the Chemical Industry Symposium*, G4/1-10.
- [8] Blaser, M. S. and O'Keefe, T. J. (1983). *Metall. Transactions B*, **14B**, 495.
- [9] Kim, B. G., Lee, S. W. and Dzo, H. (1992). *Hang'guk Chawon Konghak Hoechi* (Korean), **29**, 46.
- [10] Lew, R. W., Dreisinger, D. B. and Gonzalez-Dominguez, J. A. (1993). *International Symposium World Zinc '93*, Hobart, October, p. 227.
- [11] Borve, K. and Ostvold, T. (1994). 'Hydrometallurgy '94', Cambridge, England, Chapman and Hall, London, p. 563.
- [12] van der Pas, V. and Dreisinger, D. B. (1996). *Hydrometallurgy*, **43**, 187.
- [13] Fountoulakis, S. G. (1983). *Ph.D. Thesis*, Columbia University.
- [14] Xiong, J. and Ritchie, I. M. (1989). *Proceedings of the First International Conference on Hydrometallurgy* (Eds: Yulin and Jiong), Pergamon Press, New York, p. 632.
- [15] Yunus, M., Capel-Boute, C. and DeCroly, C. (1965). *Electrochim. Acta*, **10**, 885.
- [16] Yamashita, S., Hata, K. and Goto, S. (1997). 'Aqueous Electrotechnologies: Progress in Theory and Practice' (Edited by Dreisinger, D. B.), The Minerals, Metals and Materials Society, p. 163.
- [17] Oh, Y. (1995). *Hydrometallurgy*, **37**, 59.
- [18] DeBlander, F. and Winand, R. (1975). *Electrochim. Acta*, **20**, 839.
- [19] Polcaro, A. M., Palmas, S. and Dernini, S. (1995). *Ind. Eng. Chem. Res.*, **34**, 3090.
- [20] Wang, H. M. and O'Keefe, T. J. (1994). *J. Appl. Electrochem.*, **24**, 900.
- [21] Fontana, A. and Winand, R. (1971). *Metallurgie XI*, **3**, 162.
- [22] Jiang, S. P. and Tseung, A. C. C. (1990). *J. Electrochem. Soc.*, **137**, 3387.
- [23] Tanabe, K., Ohgai, T., Akiyama, T. and Fukushima, H. (1995). *Zinc and Lead '95* (Eds: Azakami, Masuko, Dutrizac and Ozberk), MMIJ, Japan, p. 303.
- [24] Fischer-Bartelk, C., Lange, A. and Schwabe, K. (1969). *Electrochim. Acta*, **14**, 829.

- [25] Kroleva, V. (1980). *Metallurgiya Sofia*.
- [26] Fontana, A., Martin, J., van Severen, J. and Winand, R. (1971). *Metallurgie XI*, 3, 168.
- [27] Kerby, R. C. (1985). *Proceedings, Annual AIME Meeting*, Warrendale, p. 229.
- [28] Singh, V. (1996). *Hydrometallurgy*, 40, 247.
- [29] Wever, G. T. (1959) *J. Metals*, 11, 130.
- [30] Ault, A. R., Frazer, E. J. and Smith, G. D. J. (1988). *J. Appl. Electrochem.*, 18, 32.
- [31] Fosnacht, D. R. and O'Keefe, T. J. (1980). *J. Appl. Electrochem.*, 10, 495.
- [32] Robinson, D. J. and O'Keefe, T. J. (1976). *J. Appl. Electrochem.*, 6, 1.
- [33] Ohoyama, S. and Mrioka, S. (1985). *Zinc '85* (Ed: Tozawa, K.), MMII Tokyo, Japan, p. 219.
- [34] MacKinnon, D. J., Brannen, J. M. and Kerby, R. C. (1979). *J. Appl. Electrochem.*, 9, 55.
- [35] Justinijanovic, I. N., Jovicevic, J. N. and Despic, A. R. (1973). *J. Appl. Electrochem.*, 3, 193.
- [36] MacKinnon, D. J., Brannen, J. M. and Kerby, R. C. (1979). *J. Appl. Electrochem.*, 9, 71.
- [37] MacKinnon, D. J. (1985). *J. Appl. Electrochem.*, 15, 952.
- [38] MacKinnon, D. J. and Fenn, P. L. (1984). *J. Appl. Electrochem.*, 14, 701.
- [39] MacKinnon, D. J., Brannen, J. M. and Fenn, P. L. (1986). *J. Appl. Electrochem.*, 16, 899.
- [40] Morrison, R. M., MacKinnon, D. J., Uceda, D. A., Warren, P. E. and Moulard, J. E. (1994). *Hydrometallurgy*, 35, 413.
- [41] Kerby, R. C., O'Keefe, T. J. and Wang, Y. M. (1977). *Metall. Transactions B*, 8B, 661.
- [42] MacKinnon, D. J. and Brannen, J. M. (1977). *J. Appl. Electrochem.*, 7, 451.
- [43] MacKinnon, D. J. (1994). *Hydrometallurgy*, 35, 11.
- [44] Cachet, C., Wiart, R., Ivanov, I., Stefanov, Y. and Rashkov, S. (1994). *J. Appl. Electrochem.*, 24, 713.
- [45] Fosnacht, D. R. and O'Keefe, T. J. (1983). *Metall. Transactions B*, 14B, 644.
- [46] MacKinnon, D. J., Morrison, R. M., Moulard, J. E. and Warren, P. E. (1990). *J. Appl. Electrochem.*, 20, 728.
- [47] MacKinnon, D. J., Morrison, R. M., Moulard, J. E. and Warren, P. E. (1990). *J. Appl. Electrochem.*, 20, 955.
- [48] Aros, H. M. and O'Keefe, T. J. (1993). *Can. Metall. Quarterly*, 32, 295.
- [49] Scott, A. C., Pitblado, R. M. and Barton, G. W. (1988). *J. Appl. Electrochem.*, 18, 120.
- [50] Scully, J. C. (1990). *The Fundamentals of Corrosion*, Pergamon Press, New York.
- [51] Enyo, M. (1983). *Comprehensive Treatise of Electrochemistry* (Edited by Conway, Bockris, Yeager, Khan and White), Vol. 7, Plenum Press, New York.
- [52] Trassati, S. (1972). *J. Electroanal. Chem.*, 39, 163.
- [53] Belanger, A. and Vijh, A. K. (1992). *J. Electrochem. Soc.*, 121, 225.
- [54] Brennan, M. P. J. and Brown, O. R. (1972). *J. Appl. Electrochem.*, 2, 43.
- [55] Chen, L. and Lasia, A. (1992). *J. Electrochem. Soc.*, 139, 3214.
- [56] Los, P., Rami, A. and Lasia, A. (1991). *J. Appl. Electrochem.*, 21, 135.
- [57] Savadogo, O. and Ndzebet, E. (1993). *J. Appl. Electrochem.*, 23, 915.
- [58] Savadogo, O. and Allard, C. (1991). *J. Appl. Electrochem.*, 21, 73.
- [59] Savadogo, O. and Ndzebet, E. (1992). *Inter. J. Hydrogen Energy*, 17, 751.
- [60] Ndzebet, E. and Savadogo, O. (1994). *Inter. J. Hydrogen Energy*, 19, 687.
- [61] Savadogo, O., Levesque, S., Ndzebet, E., Martel, A. and Lessard, J. (1992). *Inter. J. Hydrogen Energy*, 17, 101.
- [62] Millenbach, P., Givon, M. and Aladjem, A. (1983). *J. Appl. Electrochem.*, 13, 169.
- [63] Jiang, S. P. and Tseung, A. C. C. (1990). *J. Electrochem. Soc.*, 137, 3381.
- [64] Cui, Q., Jiang, S. P. and Tseung, A. C. C. (1992). *J. Electrochem. Soc.*, 139, 60.

- [65] Martell, A. E. and Smith, R. M. (1982). 'Critical Stability Constants', First Supplement, Vol. 5.
- [66] Filippou, D., Demopoulos, G. P. and Papangelakis, V. G. (1995). *AIChE Journal*, **41**, 171.
- [67] Filippou, D., Papangelakis, V. G. and Demopoulos, G. P. (1993). "Hydrometallurgy: Fundamentals, Technology and Innovation" (Eds: Hiskey and Warren), AIME, Littleton CO, p. 23.
- [68] Bear, I. J., Grey, L. E. and Woods, R. (1995). *Zinc and Lead '95* (Eds: Azakami, Masuko, Dutrizac and Ozberk), MMIJ, Japan, p. 191.
- [69] Bard, A. J. (1970). *Encyclopedia of Electrochemistry of the Elements*, **3**, Marcel Dekker Inc., New York.
- [70] Perry, R. H. and Green, D. W. (Eds.), "Perry's Chemical Engineers' Handbook", McGraw Hill Inc., New York, pp. 3-103.
- [71] Lide, D. R. (Ed.) (1995). "CRC Handbook of Chemistry of Physics", CRC, Boca Raton.
- [72] Rojas, M., Fan, C. L., Miao, H. J. and Piron, D. L. (1992). *J. Appl. Electrochem.*, **22**, 1135.