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A REVIEW OF METHODS FOR THE
ELIMINATION OF PRINCIPAL IMPURITIES
FROM ELECTROLYTES USED IN ZINC
ELECTROWINNING

BY
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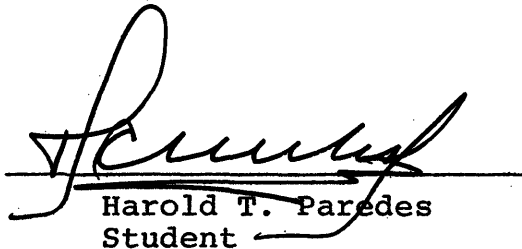
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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Metallurgical Engineering.

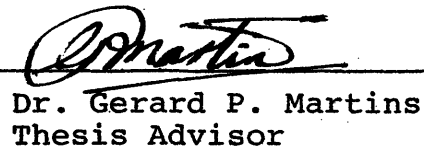
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ABSTRACT

A review of methods for the elimination of principal impurities from zinc sulphate electrolytes which are directly responsible for the electrowinning characteristics in these systems has been presented.

The basic principles embodied in the techniques employed to effect the solution purification are also discussed.

Emphasis has been placed on three types of treatment, which were subsequently investigated in the laboratory:

- i) Contact reduction (cementation) with zinc powder.
- ii) Contact reduction with zinc powder in the presence of arsenic to promote formation of arsenic inter-metallic compounds with Co, Cu and Ni.
- iii) Oxidation of impurities with KMnO_4 in the presence of arsenic to form arsenates and removal of excess arsenic by precipitation with zinc dust.

The laboratory tests using the above treatments were conducted with a synthetic solution containing Zn, Cd, Co, Cu, Fe, Ge, Ni, Sb, As, Se and Te. The composition was selected to conform approximately to that encountered in industrial plants.

The final concentrations of the low level impurities, Fe, Ge, Ni, Sb and Se, could not be determined because of

inadequate detection limits on the Atomic Absorption Spectrophotometric system (both flame and graphite furnace) used.

The contact reduction tests (i and ii) were run at 80°C and were found to offer the most promise for elimination of Co, Cd and Cu. Coreduction with arsenic (ii) appeared to be particularly effective for control of Co and Cu, in that, resolution of these species was prevented. Cadmium, however, presented problems of resolution which could be linked to contact reduction of excess arsenic by the cadmium already precipitated and/or dissolution of dislodged particles of cadmium.

The results of the arsenate precipitation were inconclusive because of the low temperature used, 60°C, and also because of the procedure employed. In any case coprecipitation of zinc arsenate may make this scheme unattractive.

It is felt that the results of the investigation can provide limits on the viability of the contact reduction technique for control of Co, Cu, Cd and As in zinc electrolytes.

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Chapter 1

INTRODUCTION

There are a number of processes for the production of zinc where hydrometallurgical flowsheet components are incorporated. In a typical flowsheet, zinc sulfide concentrate is roasted to produce zinc oxide which is leached with spent sulphate electrolyte. During leaching, zinc as well as other elements are solubilized. This solution is then purified to remove or control undesirable impurities after which it is circulated to electrolytic cells where a portion of the zinc in solution is cathodically deposited onto inert (Al or Ti) electrodes as zinc metal. This flowsheet is shown in Figure 1.1.

Metals such as arsenic, antimony, germanium, selenium, tellurium, copper, iron, etc., on which hydrogen ions are reduced to hydrogen at a higher rate than on zinc metal, can seriously reduce the current efficiency for zinc deposition. The mechanism by which an impurity produces these observed behaviors is not well understood and methods of counteracting its effect have not been successful. The effects of two

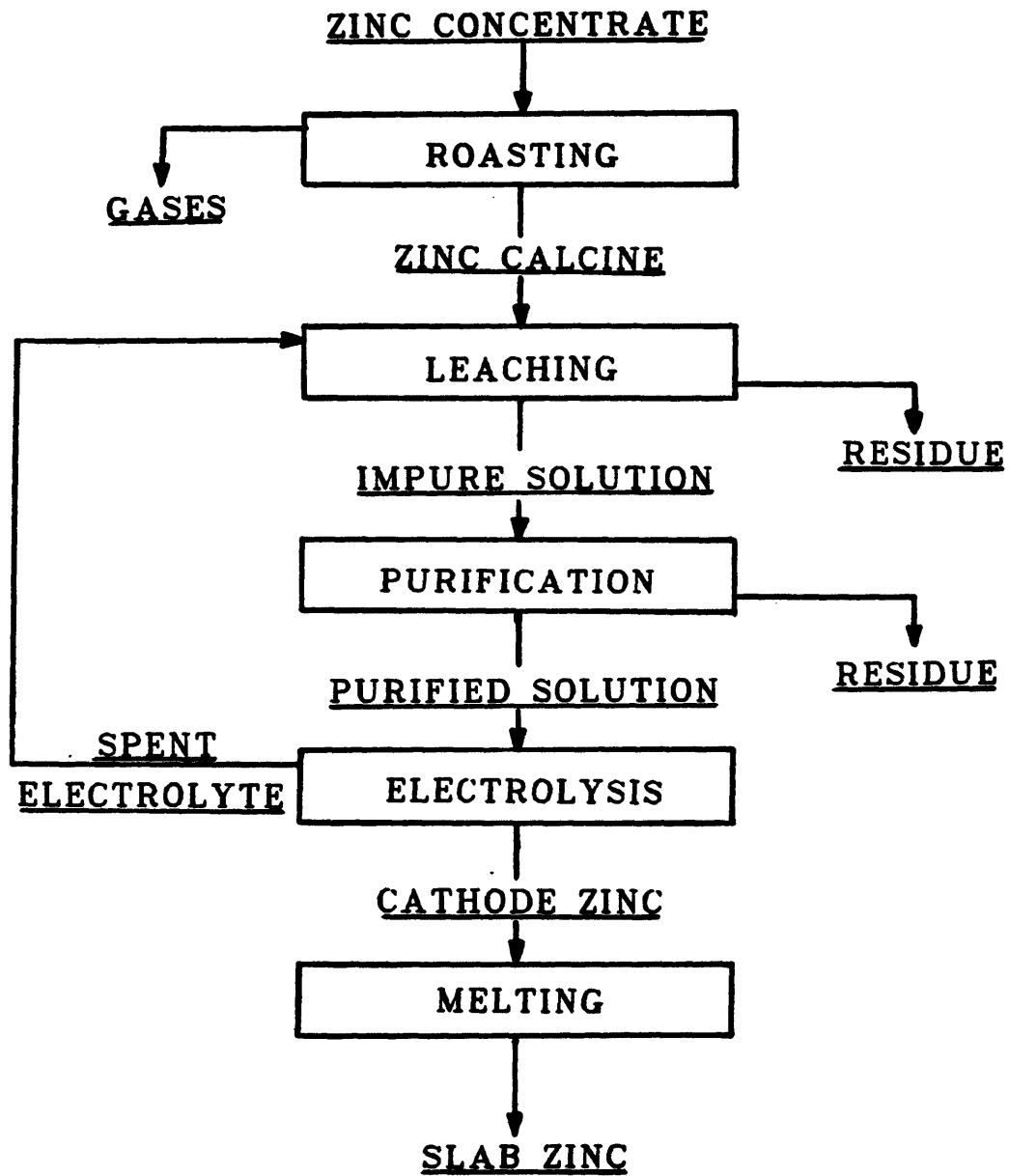


FIG 1.1 CONVENTIONAL ELECTROLYTE ZINC
PLANT FLOWSHEET

or more impurities in combination is an extremely complex problem, because of so-called "synergism" where the coupled electrochemical phenomena act to produce effects which are not predictable from the behavior when only a single impurity is present. In addition, it is not always possible to analyse and, therefore, detect chemical impurities which may be detrimental to the process, since analysis of "trace" impurities can be quite tedious and complex.

In this thesis a number of the various processes for reducing impurities from zinc electrolytes to concentration levels where their effects in subsequent electrowinning are only minimal is examined and tested under laboratory conditions. While it is recognized that in an industrial operation the mechanical shorts of the reactor quite often limit the achievement of results obtained in small-scale equipment used in the laboratory, the findings can represent the "best" that may be attainable. The mixing effects and filtration of residues are obviously another aspect of the problem which may need additional attention.

1.1 SCOPE

The purification of zinc electrolytes for the removal of metallic impurities which are detrimental in the electrolytic production of zinc has been generally accomplished by:

i) contact reduction with zinc dust (cementation) and

ii) formation of compounds of low solubility relative to conditions (pH, Eh) created within the solution. In both of the above techniques, adequate filtration of the precipitates is crucial to the success of the operation.

Solvent extraction has also been attempted as a method for purification, but unless the process stream contains a sufficiently high concentration of impurities (such as cobalt) this approach may not be economically feasible.

1.1.1 Contact Reduction (Cementation). Numerous studies on the cementation of copper onto iron have been documented in the literature.^(25, 30) Here, however, the primary objective is the recovery of the copper rather than purification of the solution.

Purification schemes where cementation is an

attractive procedure are those where the precipitant metal is the same as the major metal ion in solution. Examples are removal of copper from cobalt electrolytes with cobalt metal, and, as in the present study, removal of impurities which are more electronegative than zinc, with zinc powder for purification of zinc electrolytes. In purification processes it is the ultimate concentration of the impurity which is of importance rather than the recovery of the component.

The thermodynamics of cementation systems have been extensively studied in connection with predicting the probable equilibrium concentrations of the precipitate ions. However, equilibrium predictions are never realized in practice. As a result, the kinetics of these reaction systems have received a great deal of attention in recent years.^(25, 29, 30) The use of the rotating disc in these kinetic investigations became popular during this time. A limited number of studies^(4, 20, 31) using precipitant particles has been reported. Kinetics of particulate precipitants are, of course, relevant to many industrial processes where particulates are in fact employed.

High mass transfer rates due to turbulent eddies in mechanically agitated systems ⁽²⁰⁾ are unique to these operations.

A further consideration which is well documented in the literature but has received little fundamental attention is the co-reduction of arsenic (and antimony) together with metal ions such as copper, nickel and cobalt to form intermetallic compounds. These compounds appear to offer electrode kinetics which may be substantially different from when a "pure" metal is precipitated.

The physical properties of the precipitate on the precipitant metal have also received attention. The effects of temperature and initial concentration of precipitate ion on the morphology of the deposit have been noted. However, the relevance of these phenomena to particulate systems has not been determined.

Finally, the co-reduction of several ions, not withstanding the possibility of producing intermetallic compounds has not been addressed.

1.1.2 Low Solubility Compounds. Precipitation of oxides or hydroxides by pH adjustment and oxidation

with air and more recently ozonized air has been used in purification schemes. The nature of the resultant precipitate in these systems can quite often determine the success or failure of the procedure in relation to the subsequent filtration step.

Formation of arsenates (and antimonates) of the metal impurities by addition of arsenic (or antimony) and subsequent oxidation with potassium permanganate has been utilized. The use of ozonized air for the oxidation step in this treatment may be an attractive variation which as yet has not been reported in the available literature.

1.2 STATEMENT OF RESEARCH OBJECTIVES

After reviewing the scope of research associated with purification of zinc sulphate electrolytes, it was decided to investigate the features of a selected number of purification schemes which have been reported in the literature. The synthetic electrolyte composition was selected to conform approximately to that encountered in industrial plants. The major concern was that the principal impurities, which have been identified as being important to successful zinc electrowinning,

should be present. Thus arsenic, antimony, cadmium, cobalt, copper, germanium, iron, nickel, lead, selenium, and tellurium were included in the zinc electrolyte subsequently treated in laboratory tests.

The choice of research objectives was based on the need to examine an over-all purification scheme, with all the principal impurities present rather than individually. The profound influence of the initial morphology of cementation deposits on the reduction during the later stages when the concentration is low, was an important consideration. Also regardless of purification scheme the product of co-reduction or co-precipitation could have unique properties as related to subsequent resolution or dissolution.

The purification was to be carried out in a small laboratory reactor employing the following procedures:

i) Zinc powder as precipitant. A temperature of 80°C was selected based on results of previous investigations where temperature limits were established. (8,20) The use of higher temperatures can lead to significant solution loss or reflux due to evaporation.

ii) Zinc powder together with arsenic addition for intermetallic compound formation, in particular for cobalt removal. Multiple steps as related to residue

resolution and removal of excess arsenic.

iii) Formation of arsenates by addition of arsenic followed by oxidation with potassium permanganate. Multiple steps to control the precipitate dissolution and removal of excess reagents. Zinc powder also used in this treatment. A temperature of 60°C was selected so that the Eh of the solution could be monitored with the available redox electrode system (limit imposed by calomel reference electrode).

1.3 ORGANIZATION OF THE THESIS

The thesis consists of six chapters. Chapter 1 is an introduction which provides an examination of the scope of the problem and a statement specifying those aspects tackled in this investigation. In Chapter 2, a summary of available literature on purification of zinc sulphate solution from 1920 to the present is given with a discussion of results obtained as well as the principles of processes which have been effective. Chapter 3 covers theoretical aspects of predicting thermodynamic properties at elevated temperatures using Criss and Cobble's method, which were subsequently used to determine standard half-cell potentials. These were then used to estimate the equilibrium concentration

during the precipitation of impurities from zinc sulphate solutions onto zinc powder. Also thermodynamics of arsenate formation are examined to determine the equilibrium concentration of impurities possible, when these compounds are precipitated. Chapter 4 describes the experimental equipment, synthetic electrolyte used, reagents and procedures employed. Experimental results are presented and discussed in Chapter 5, and finally in Chapter 6, the investigation is concluded with a summary based on the findings of the work and suggestions of topics which warrant further study.

Chapter 2

LITERATURE SURVEY

The available literature covering purification of zinc sulphate solution is extensive. Therefore, this chapter reviews the literature covering the subjects of elimination of harmful impurities from zinc solutions. Cu, Cd, Ni and Co are major impurities⁽¹⁾ responsible for the deterioration of the zinc electrolysis process.

A brief history of the use of cementation is first presented. Behavior of the principal impurities in the hydro-metallurgical methods of producing zinc are then discussed, followed by a section on removal of the most critical impurities. Lastly, methods for the elimination by reduction and oxidation of ions in solution receive attention.

2.1 HISTORICAL ASPECTS OF ELIMINATION OF IMPURITIES FROM ZINC SOLUTIONS

One of the oldest methods of precipitating a metal in solution (metal ion) is by contact reduction with a solid metal which is less noble in the electrochemical

sense of having a lower electron affinity than that being precipitated. This process has been referred to as cementation and references to commercial production of copper by cementation date back to as early as 1500 A.D. ⁽²⁾ Reactions of this type have been used in industry for a long time, not only for the recovery of metal values (for example, the precipitation of copper from leach streams and mine waters with scrap iron is used extensively ⁽³⁾), but also for the purification of process streams. The removal of impurities such as arsenic, antimony, germanium, selenium, tellurium, nickel, copper, and cadmium ions from zinc sulphate electrolyte streams using zinc dust ⁽⁴⁾ is an example of this latter application.

Cobalt has been identified as an important impurity in zinc sulphate solution and maintaining its concentration at an appropriate low level is critical to the success of the electrometallurgy of zinc. There have been important practical studies regarding the effect of two or more impurities in combination. Kerby and Ingraham ⁽⁵⁾ presented an intensive investigation of the influence of single impurities and combinations of these on the current efficiency. The history of cobalt as a harmful impurity in the electrolytic deposition of

zinc dates back to sixty-two years ago. Great efforts have been made at developing processes to purify zinc sulphate solutions of harmful impurities especially where cobalt is present.

Field⁽⁷⁾ developed several methods for eliminating cobalt. His first experimental work⁽⁷⁾ involving the use of ozonized air to oxidize cobalt from Co^{++} to Co^{+++} might be considered as one of the first major studies carried out. In 1921, Field⁽⁸⁾ also proposed a method for the purification of zinc solutions, this time mercurous sulphate solutions and zinc powder were used at high temperature ($>100^{\circ}\text{C}$). In 1923⁽⁹⁾, he made a re-evaluation of these methods and suggested that the use of mercurous sulphate in combination with zinc dust offered significant advantages over the others.

Avery and Williams⁽¹⁰⁾, in an earlier patent, tried to precipitate cobalt from solutions with zinc powder and arsenic at temperatures above 50°C . This method is probably the first approach using a cementation reaction.

In 1924 the Canadian worker, Eldridge⁽¹¹⁾, used the strongly oxidizing properties of zinc hyposulphite to precipitate cobalt and other impurities such as nickel, iron, copper, lead, cadmium, etc., from zinc sulphate solutions.

Broken Hill Company of Australia⁽¹²⁾ realized that the main disadvantage in using a powerful oxidizer for the precipitation of cobalt, when an appreciable amount of manganese was also present in the impure solution, was the excessive oxidant consumption attributed to manganese oxidation.

Cambi, at the Tenth International Congress of Chemistry in Rome⁽¹³⁾, presented a discussion on two methods for cobalt removal from zinc sulphate solutions. These were an inorganic method, using copper sulphate and arsenic trioxide in a two-step treatment with zinc powder at a temperature above 75°C, and an organic method with alpha-nitroso-Beta Naphthol carried out at room temperature, where cobalt forms organic complexes which are then separated from the solution with benzene.

During 1940 to 1960, the research was more basic in nature. Chizhikov⁽¹⁴⁾ and Kreinzanz studied the kinetics of cobalt cementation onto zinc. They found that an increase in temperature resulted in higher cobalt extractions and that the "reaction rate constant" varied from 0.010 cm./sec. at 50°C to 0.053 at 96°C. They also studied the influence of nickel during cobalt precipitation and found that at a ratio of 1:20 of Co to Ni resulted in almost no cobalt extraction. These

authors also published another paper⁽¹⁵⁾ in which the effect of dissolved oxygen on impairing the cementation of cobalt by zinc and the use of sodium sulphite to counteract this effect were discussed.

Klimenko⁽¹⁶⁾ developed a new method for cobalt precipitation using zinc powder and antimony salts. In order to prevent toxic effluents, because of the presence of the antimony compounds, Klimenko maintained a copper concentration in the solution fifty times greater than that of antimony, so as to produce insoluble copper antimonate.

Two years later, Pomosov⁽¹⁷⁾ studied the purification of zinc sulphate solutions of cobalt in the presence of antimony using an electrochemical corrosion technique. He found that Co extraction was possible because of "the depolarization of Co ions by antimony which promoted a sharp increase in the Co-Zn contact cells."

Fischer-Bartelk⁽¹⁸⁾ attempted to account for the difficulties encountered in removing Ni and Co from zinc sulphate solutions. They studied the effect of copper sulphate, arsenic trioxide and antimony trioxide on the precipitation of Co from zinc solution using zinc dust as precipitant. It was stated that the increase

in the rate of cobalt extraction in the presence of the above-mentioned reagents was a result of the formation of intermetallic compounds (CoAs) which provided a more positive potential to the concentration reaction.

MacKinnon⁽¹⁹⁾ investigated the kinetics of cobalt precipitation on zinc sheets, with respect to variables such as temperature, stirring velocity, acidity and the presence of other metallic ions. He considered that the cementation reaction was first order with respect to cobalt concentration during the first ten minutes. To account for the deviation from linearity after the initial period, he stated that the rate controlling mechanism changed to diffusion of zinc ions through the cemented cobalt.

Recently, Bonelli⁽²⁰⁾ investigated the behavior of copper and arsenic on contact co-reduction of cobalt from zinc sulphate solution with zinc powder at 80°C. Activation energies for the systems Co^{++}/Zn and $\text{Co}^{++}, \text{Cu}^{++}, \text{AsO}_2\text{H}/\text{Zn}$ were found to be 14 and 26 kcal/mole, respectively, indicating the possibility of electrochemically controlled reactions. However, the study was confined solely to cobalt and the final concentration of cobalt achieved (>1 ppm.) was greater than would be acceptable for industrial solutions.

2.2 BEHAVIOR OF THE PRINCIPAL IMPURITIES IN THE ELECTRO-METALLURGICAL PRODUCTION OF ZINC FROM AQUEOUS ELECTROLYTES

Once an impurity enters the electrowinning cell, it is virtually impossible to counteract its effect because the mechanism by which the impurity takes part in the subsequent electrodeposition is complex and not well understood. Certain impurities in the electrolyte are known to cause re-resolution of the deposited zinc⁽²¹⁾. Re-resolution usually occurs after a period of zinc deposition which has been referred to as an incubation period. Attempts have been made to establish relationships between process conditions and impurity concentrations with over-all current efficiency. Unfortunately most of the findings have been qualitative in nature, making it difficult, if not impossible, to apply to general situations.

The cation impurities⁽²²⁾ which seriously lower the zinc current efficiency can be classified into groups according to the nature of the reaction involved in reducing the efficiency. The presence of Ag, Cu, or Ni in the electrolyte produce preferential re-resolution of the deposits, while Ge, Se, or Sn result in evolution of H₂ over the entire electrode surface without localized corrosion of the zinc.

When the electrolyte contained Ni, there was little or no physical evidence of re-solution during the initial electrodeposition, corresponding to a certain elapsed time. Nickel was not detected in the pits or at re-solution areas so long as the current efficiency was high. The concentrations of Ge, Sb, and Sn which produced significant reduction in the current efficiency were lower by almost an order of magnitude, when compared to the critical levels for other impurities. Although the effects of these impurities were evident from the start of the deposition, they were never found on the electrode surface.

Except for Sn, impurities found at the re-solution sites (pitted areas) by means of X-ray spectrometry included Al, Co, Cr, Mn, Sb, and Ti on the Zn.

Two mechanisms⁽²³⁾ have been proposed to explain the reduction in the current efficiency due to the presence of impurities in the Zn electrolyte:

- i) preferential reduction of H^+ on co-deposited impurities as a result of the so-called hydrogen overpotential, combined with localized cell corrosion and
- ii) continuous co-deposition and evolution of H_2 on Zn without preferential areas of Zn corrosion.

Single impurity elements affecting the deposition

of zinc⁽²⁴⁾ can often be recognized by their effect on the deposit or their action in the cell. However, the effect of two or more impurities in combination is a more complex problem, because of the enormous number of combinations possible, both with respect to the elements present and their amounts. Usually a combination of detrimental elements is much more harmful than the same elements when present individually.

It is well known that the operating conditions within a particular plant vary from day to day and from month to month. The many factors involved, some of which may be unknown, result in the impossibility of making definitive statements regarding the effects of impurities under all conditions.

2.3 REMOVAL OF CRITICAL DETRIMENTAL IMPURITIES

Purification is vital to the successful electro-winning of zinc and it is usually accomplished by both oxidation and reduction methods. Removal of impurities by precipitation with zinc dust as the primary purifying agent in a neutral solution has been practiced to control cobalt, nickel and others. Control of cobalt in the system is very important especially if germanium is also present. Thermodynamic considerations indicate

that cobalt should be readily removed with zinc dust. "In practice, the removal is difficult as zinc sulphate appears to suppress completely the ionization of cobalt sulphate."⁽²⁴⁾ Presumably, this statement is in regard to formation of an uncharged sulphate complex because of the high free sulphate concentration present.

2.3.1 Elimination of Ions in Reduction Processes. The techniques used vary considerably, depending on the composition of the electrolyte and other factors, not the least of which is the subsequent recovery process. The oldest method for precipitating metals ions from a solution is by contact reduction with a less noble metal, traditionally referred to as cementation.⁽²⁵⁾

Cementation like electrolysis and gaseous reduction is an electrochemical reaction. Electrochemical reactions, unlike chemical redox reactions where charge transfer occurs at the same physical location, involve half-cell reactions which are separated by some finite distance. Consequently, the solid phase must be an electrical conductor.⁽²⁶⁾ The electron transfer occurs at the interface of the solid phase with the electrolyte. This particular aspect of the

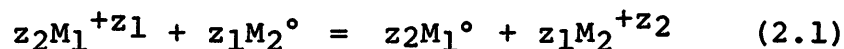
electrode process is called a charge transfer reaction.⁽²⁷⁾ Wadsworth has demonstrated that associated equilibrium and sequential chemical reactions may be involved in the total process and nonelectrochemical reactions may in fact be rate determining. Transport of ions by diffusion may also be rate determining. In addition, the interaction of the electrical field, associated with the electrical double layer at the electrode-electrolyte interface, can contribute to the overall transport of ions.

The influence of the electrical double layer is a fundamental feature of electrode reactions. It determines the activation energies of individual reactions depending upon the sign and magnitude of the charge of the reacting species and its position within the double layer.

i) Contact Reduction - The reduction of metal ions in solution, by precipitation onto metals which are more electropositive, may be viewed in terms of electrode processes as outlined above.

The theory of slow discharge has been used to explain cementation kinetics.⁽²⁷⁾ In general, contact reduction systems are first-order electrochemical processes which are usually diffusion controlled. In some systems, particularly at low temperatures and high ion concentration of the precipitate, the over-all rate cannot be described by a single rate controlling step and the intrinsic "surface" reaction and diffusion rates are then of the same magnitude.

The contact reduction of a particular ion may be represented by the over-all reaction:



Wadsworth complements the interpretation of these electrochemical reactions with a pictorial representation of an over-all reduction as shown in Figure 2.1.

Figure 2.1 depicts the flow of electrons from the anode to the cathode. The net current I is the sum of the partial currents $I_{(+)}$ and $I_{(-)}$.

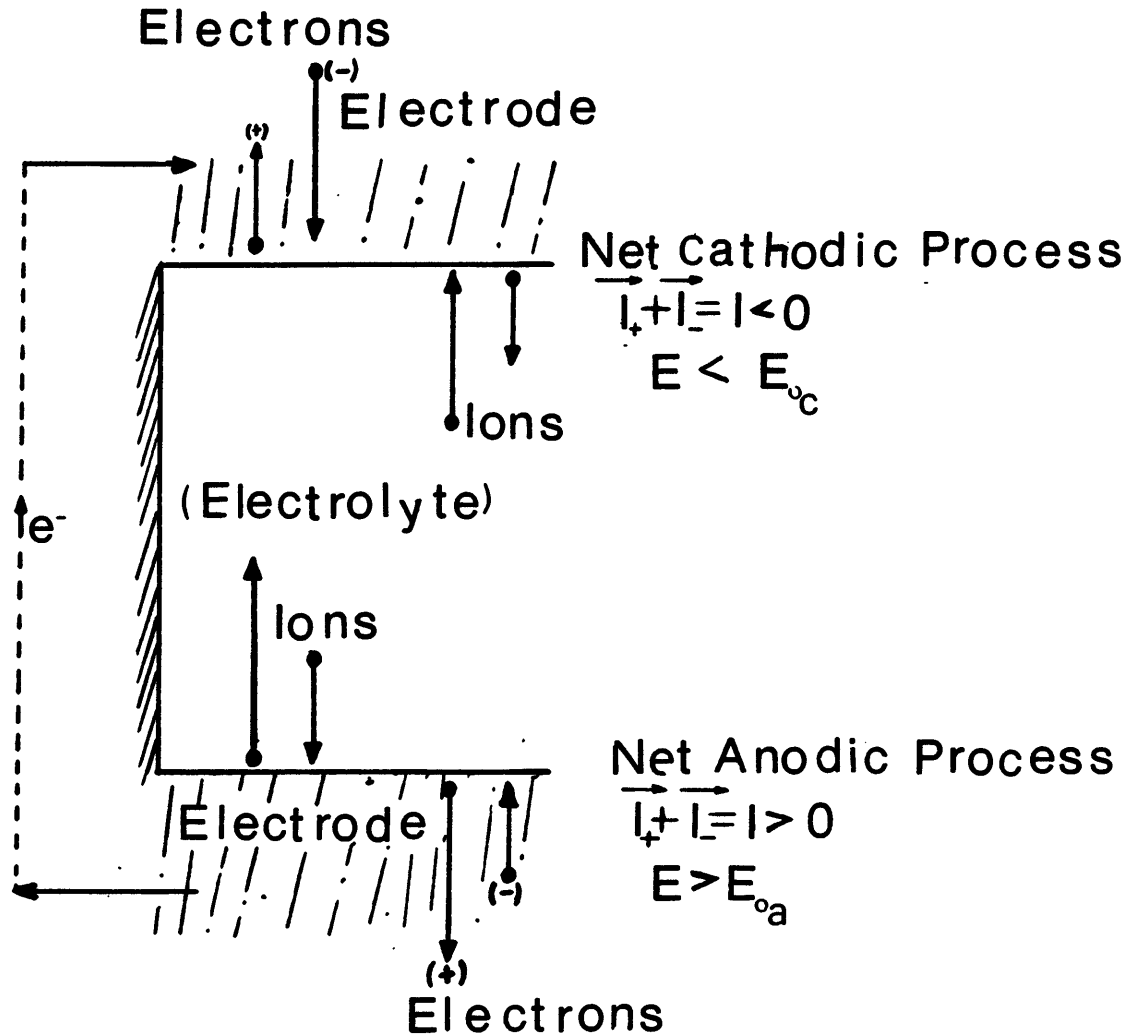


Figure 2.1: REACTION MODEL FOR OVERALL REDUCTION (ADAPTED FROM WADSWORTH). (+) and (-) on vectors for electrons indicate current flow due to oxidation and reduction of ions at the electrode surface, respectively; complimentary vectors for the current associated with the charge transfer from and to the ions are shown pointing away and towards the electrode surface, respectively.

The short circuited (common) electrode potential E will be less than the equilibrium potential for the cathodic electrode reaction E_{oC} and greater than the equilibrium E_{oA} of the anodic electrode reaction. For contact reduction of a single ion as shown in equation 2.1, the half cell reactions for the single cathodic and anodic processes are now E_{o1} and E_{o2} , the Nernst reduction potentials are given by:

$$E_{o1} = E_{o1}^{\circ} - \frac{RT}{z_1 F} \ln [M_1] \quad (2.4)$$

$$E_{o2} = E_{o2}^{\circ} - \frac{RT}{z_2 F} \ln [M_2] \quad (2.5)$$

for activity coefficients of unity.

Miller⁽²⁸⁾ and Strickland⁽²⁹⁾ have examined the thermodynamics of cementation system by calculating the equilibrium constants of the various reactions. The large values obtained indicate that at equilibrium the ratio of the precipitant ion activity is such that the equilibrium conversion will be essentially 100%. Moreover, if a

hypothetical cementation reaction between a pair of divalent ions and their respective metal electrodes, having a standard electrode potential difference of 0.1 volts is considered, it will be found that the equilibrium constant is of the order of 2500, which will result in an equilibrium conversion of 99%.

Cementation of ions from aqueous solution never produce the equilibrium concentration predicted. In a number of instances the precipitation is for most practical analytically complete. Research on systems where the noble metal ion has a more positive reduction potential than hydrogen ions indicate that at the pH investigated reduction of the metal ion is achieved in preference to hydrogen ions. On the other hand, when the more noble metal has a less positive standard electrode potential than hydrogen, then hydrogen ion reduction leading to hydrogen evolution becomes competitive. Examples of the latter which are of industrial importance are Cd^{++}/Zn and Co^{++}/Zn . At the same time the possibility of forming poisonous arsine or stibine should be considered when arsenic or antimony is present in the electrolyte.

2.4 KINETICS OF CONTACT REDUCTION OF METALS IN SOLUTION

Contact reduction of metals from solution has been used extensively in the minerals industry for recovery of metals values as well as for the purification of process streams. These processes have been in use for a considerable time.⁽³⁰⁾ Thermodynamic analyses indicate that equilibrium concentrations of the precipitate ion are extremely low, thus confirming the attractiveness of cementation systems. However, since actual yields and process efficiencies are determined by rate factors, a knowledge of the reaction kinetics is essential for the optimum utilization of the process.

The principal objectives of a kinetic research are:

i) to determine the relevant individual reaction steps which occur and result in the over-all reaction and

ii) to establish the relative contributions of the reaction steps to the over-all reaction rate.

In some cases a single reaction step can be rate controlling.

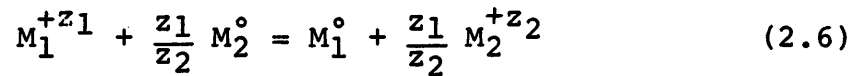
Intrinsic electrochemical reactions kinetics⁽²⁸⁾ can be analysed by considering the activation energy associated with the chemical process as well as that for the charge-transfer process. The latter arises because

The intrinsic electrochemical kinetics can be considered in terms of absolute reaction-rate theory, as demonstrated by Miller. This theory⁽²⁸⁾ considers the rate process by which the reactant species is transformed to the product species through an intermediate high-energy state. This high-energy or activated state is associated with an activated complex. Only a fraction of the reactant or product species acquired this energy at any instant and the activated complex cannot, in general, be isolated or observed directly by experimentation.

Thus, Miller was able to show how the Butler-Volmer equation can be derived from absolute reaction-rate theory. This was extended to the concept of a steady-state mixed potential for a cementation reaction, where the anodic and cathodic current (not current density) must be equal. (The diagram accompanying the related discussion in Miller's paper, in fact, shows current density, which would be true if the anodic and cathodic areas are equal--a condition which cannot be assumed a priori.) This was further complemented by discussion of the usefulness of Evan's diagrams, as employed in the analysis of corrosion reactions, for interpreting cementation reactions. Here, polarization curves for the two

a charge carrier (metal ion or electron) is transported through an electrical field developed in the region of the interface of the electrode as a result of a gradient in charge.

In its most elementary form, the over-all cementation reaction results in a net cathodic reaction with respect to the noble metal M_1 according to:



This can be represented by the two half-cell reactions and a conceptualization of the process is shown below:

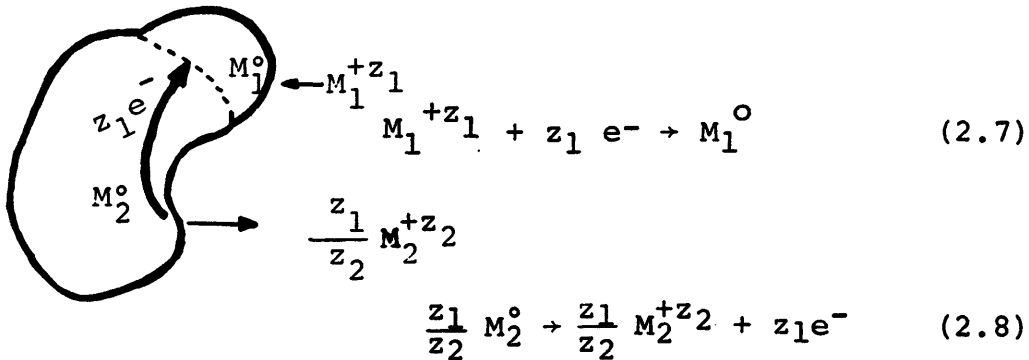


Figure 2.2.- Conceptualization of the Over-all Cementation Reaction.

electrodes of interest are used to obtain the mixed potential. Tafel equations for the anodic and cathodic half cells, at the mixed potential, lead to the establishment of criteria for electrochemical control and mass transfer control, based on the potential difference of the rest-potentials of the anode and cathode reactions. Using values which were "typical" of cementation systems, it was shown that:

$$\Delta E_0 < 0.06 \text{ V for electrochemical control and}$$

$$\Delta E_0 > 0.36 \text{ V for mass transfer control.}$$

It should be noted that at low concentrations of the precipitate ion the system will tend towards electrochemical control.

From these criteria it appears that the reaction kinetics of only a few systems should be controlled by an electrochemical reaction mechanism. Furthermore, the general irreversibility of these electrochemical reactions was established by Wadsworth⁽²²⁾ in which it was shown that if $Z_1 \Delta E^\circ$ is greater than 0.3 V, the back reaction kinetics should not be important.

Virtually all kinetic data for cementation reactions obey a first-order-rate law of the following form which can be attributed to mass transfer control:

$$\frac{dn_1}{dt} = -kAC_1 \quad (2.9)$$

The disappearance of the noble metal ion can be studied in a variety of experimental geometries--an important consideration due to the importance of mass transfer in these systems. The integrated rate expression then assumes the following common form, in terms of the noble metal ion concentration:

$$\ln \frac{C_1(t)}{C_1(o)} = \frac{-kAt}{V} \quad (2.10)$$

where:

$C_1(o)$ = initial concentration of noble metal ion

$C_1(t)$ = concentration at time t of noble metal ion

k = rate constant (cm/sec)

A = the surface area of the active metal

V = solution volume (cm³)

t = reaction time (sec)

The physical variables which may then be manipulated in order to effectively increase the rate will depend on the nature of the rate controlling step--should one exist. For example, increased agitation is effective in increasing the rate when the rate of fluid phase mass transfer is controlling. An increase in temperature will bring about an increase in rate, irrespective of the controlling mechanism; the magnitude

is much greater when the rate is chemically controlled. (29,32) Impurities may be present in practical situations in sufficient quantities to modify the kinetics of the principal reaction as well as the consumption of the precipitant metal. (33) The use of the activation energy as a means of deciding whether the rate controlling step is due to mass transport or a surface reaction rate can sometimes lead to incorrect conclusions because of the morphology of the deposited metal.

The extent of reaction is determined by the reaction rate rather than by the equilibrium thermodynamics and consequently, the information required for design and operation is that associated with these quantities rather than ultimate equilibrium conditions.

2.5 CEMENTATION KINETIC STUDIES

The cementation reaction, already given by equation 2.6, is heterogenous. The ions in solution are reduced to zero valence on a solid metallic surface. Strickand (33) has shown that provided the deposit is porous, the reaction can be considered as taking place via six steps which occur during the reaction.

Many investigators who have studied cementation have used flow system geometries in which the associated

fluid dynamics are either extremely difficult or impossible to analyse. As a result the data obtained can only be interpreted qualitatively and cannot be scaled or used in systems of different geometry. The work of Levich⁽³⁴⁾, on the fluid dynamics of the rotating disc, provides the basis of analysis for many investigators who have used this system geometry^(35,36) in studying cementation. Equally popular has been the rotating cylinder^(37,38) which is said to "...create more agitation and thus reduce the diffusion layer thickness more than in the case of rotating discs...."⁽³⁹⁾ Nevertheless, there is some question as to the validity of kinetic data obtained by rotating cylinder systems, since rate measurements are very much dependent on the relative system dimensions, unlike the rotating disc.⁽³³⁾ Therefore, in the interest of data reproducibility, it has been recommended that only rotating discs be used for work in cementation kinetics.

The unique aspect of the rotating disc is that it offers a uniformly accessible surface to mass transfer.⁽³³⁾ Levich derived equations which predict the mass transfer boundary layer thickness for a flat plate with parallel laminar fluid flow, and for a rotating disc which creates a radial flow pattern. The equations of interest are:

$$\delta_{\text{plate}} = 3D^{1/3}\gamma^{1/6}v^{-1/2}\chi^{1/2} \quad (2.12)$$

$$\delta_{\text{disc}} = 1.61 D^{1/3}\gamma^{1/6}\omega^{-1/2} \quad (2.13)$$

where:

D = Diffusion coefficient - cm^2/sec

γ = Kinematic viscosity - cm^2/sec

ω = Disc angular velocity - rad/sec

v = Bulk fluid velocity (plate) - cm/sec

χ = Distance from upstream plate edge - cm

δ = Mass transfer boundary layer thickness - cm

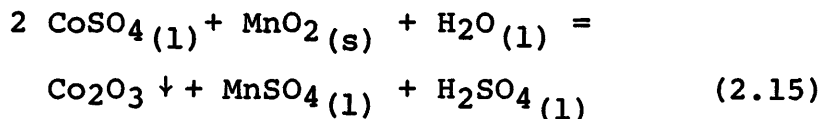
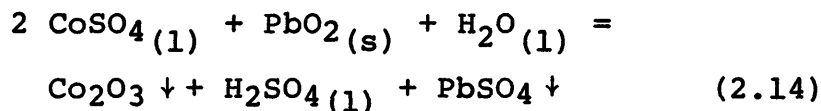
As can be seen from examination of equations (2.12) and (2.13) the diffusion boundary layer thickness is uniform (and independent of radius) for the rotating disc, but not for the flat plate. It is, therefore, apparent that of the three available geometries only the rotating disc produces a uniform boundary layer thickness and, hence, a uniformly accessible area. This is, however, not true for the flat plate or rotating cylinder, where it is possible to have different controlling mechanisms and reaction rates over their surfaces. When more than one rate mechanism is present at different positions of the same surface, the apparent system behavior will, in general, be influenced by all of the mechanisms. This obviously makes the analysis of the reaction kinetics extremely difficult to elucidate. It is for these reasons that the use of rotating discs is preferred.

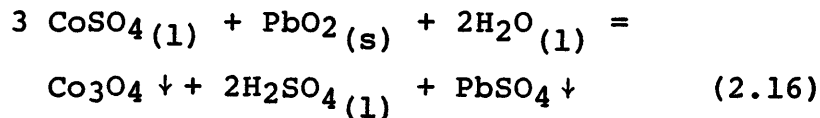
2.6 OTHER METHODS OF IMPURITY ION ELIMINATION

Control of Co in the ZnSO_4 electrolyte is very important especially if Fe, As, Sb, Ge, Se and Te are also present. Simple thermodynamic consideration indicates that cobalt should be readily removed with zinc dust. In practice, as mentioned previously, this is never achieved. (24)

Several methods have been developed to control the amount of cobalt. In general, most of the impurities of zinc solutions are eliminated by one of two general methods, oxidation and reduction. Cobalt may be removed in both ways.

2.6.1 Lead and Manganese Dioxides Process. Precipitation of cobalt was first and for a long time very successfully effected by boiling the cobaltiferous liquor with lead dioxide, manganese dioxide or the mixed oxides constituting cell mud. The following reactions have been suggested to explain the behavior: (9)





This method reduced the cobalt in the liquors to about 5 ppm.. Other oxidizing agents such as sodium hypochlorite and bleaching powder were available but these introduced chloride into the liquors and were rigidly avoided. However, chloride can be removed by treating the acidified solution with silver sulphate. The precipitated silver chloride is then processed with sulphuric acid and zinc dust to recover the silver.

2.6.2 Antimony and Arsenic Trioxides Process. The addition of potassium antimony tartrate or antimony trioxide as a dry solid during zinc dust purification can remove as much as 2 mgpl. Co from the solution. The addition of excess antimony will not increase the amount of cobalt removed and concentrations below 0.5 mg/l are not attainable by this method. ⁽²⁴⁾ In addition antimony may carry over into the electrowinning cells with detrimental effect. Arsenic compounds react in a similar manner. Furthermore, the possibility of forming poisonous arsine or stibine should be considered when using either of these compounds.

2.6.3 Cobalt and Nickel Removal by Solvent Extraction

and Precipitation. Alpha-Nitroso-Beta-Naphtol, Beta-Nitroso-Alpha-Naphtol, 1,2,-cyclohexane dione dioxime (nioxime), di-2-pyridyl ketone oxime and dimethylglyoxime in a separate solution will remove cobalt from solution in quite large amounts. Their chemical structures are shown in Figure 2.3. The use of Alpha-Nitroso-Beta-Naphtol and Beta-Nitroso-Alpha-Naphtol⁽⁴⁰⁾ in various diluents, pH and reagent concentrations show that both reagents primarily remove cobalt and that extraction is greater than 99% of the cobalt at a pH of 3.5 in the diluent kerosine-isodecanol. A maximum of 4% zinc is coextracted. To be completely effective iron and copper must be removed prior to this step.⁽²⁴⁾ The primary difficulty in using either of these reagents is that the cobalt cannot be stripped from the organic phase because it is oxidized to trivalent cobalt. Cobalt removal is due to formation of cobalt-nitrosonaphthate, which is very stable and does not release the cobalt during the stripping stage.

When 1,2,cyclohexane dione dioxime (nioxime)⁽³¹⁾ was used greater than 99% of the

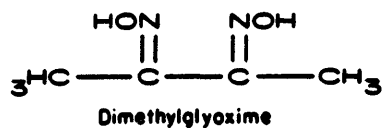
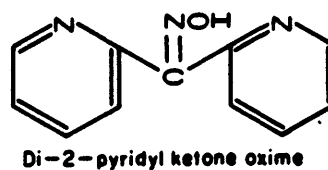
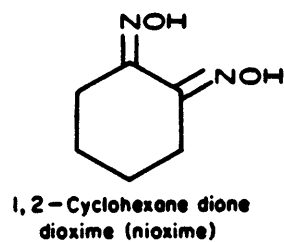
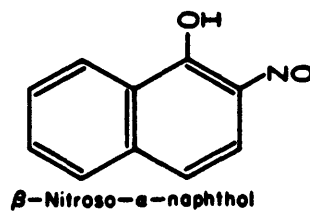
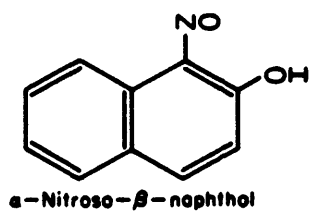


Figure 2.3.- Chemical structures of complexing reagents used to remove cobalt and/or nickel from ZnSO_4 solution (40).

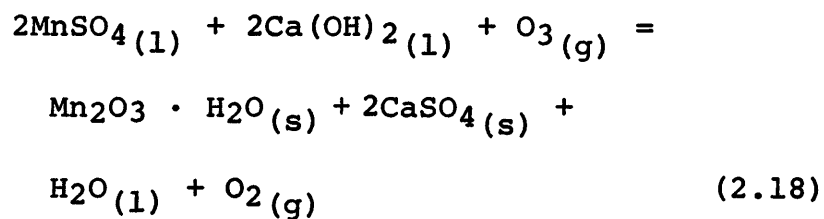
nickel and 75% to 80% of the cobalt were extracted at a pH 5.2 in the diluents toluene-isodecanol and kerosine-isodecanol. A pH less than 3.2 resulted in 99% extraction of nickel without the extraction of cobalt. Thus by adjustment of pH both nickel and cobalt may be extracted by a single complexing reagent. Although stripping the complexed metals from the loaded nioxime was possible, the functional groups could not be regenerated.

As a final comment it was stated that "the relatively inexpensive nature of the reagents makes their use feasible."

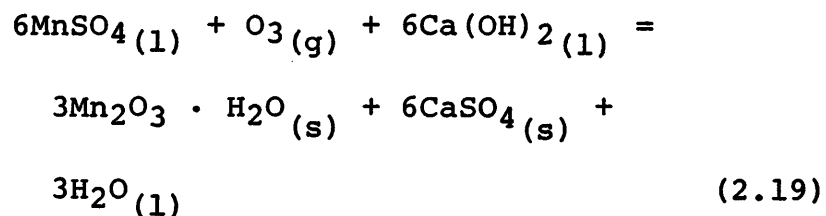
Alpha-Nitroso-Beta-Naphtol in the form of sodium naphthenate and sodium nitrate) has also been used to precipitate cobalt from zinc sulphate solutions commercially.⁽⁴⁰⁾ Zinc electrolytic plants in Australia⁽¹²⁾ make use of this technique. The precipitated cobalt-nitrosonaphthate is recovered and oxidized at elevated temperatures to a cobalt oxide.

2.6.4 Ozone Process. Ozone or ozonized air is known to be a powerful oxidizing agent. Patent rights have been granted in several countries covering the use of ozone or ozonized air. The particular

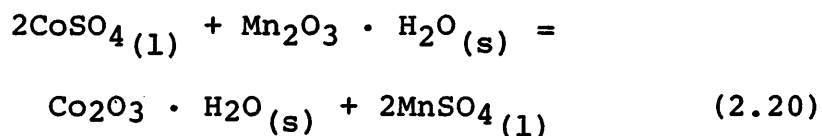
impurities removed are those which are susceptible to oxidation such as iron, cobalt, arsenic, antimony, germanium, selenium and tellurium. "Ozonized air is easily and cheaply produced, readily distributed and combines both functions of purification and stirring agent."⁽⁹⁾ It may be pointed out here that oxidized manganese compounds are very effective in the removal of iron from zinc liquors. Normally the impure zinc solutions contain manganese in the divalent form. Even in neutral solution, ozonized air precipitates manganic compounds in the presence of small amounts of lime which precipitates the manganese in a form readily susceptible to oxidation. This is effected by ozone⁽⁹⁾ according to:



or



In the presence of arsenic and antimony, iron is precipitated as a basic ferric arsenate or antimonate. With cobalt compounds the oxidation appears to proceed according to the following reaction:



The cobalt is precipitated as a higher oxide while the manganese, in the absence of alkali or alkali carbonate, would be reverted to sulphate. Manganese compounds thus act as a chemical intermediate and only manganous compounds need be added. Ozonized air is used at an elevated temperature (60°C) and is most effective in the elimination of cobalt.

Use of ozone to precipitate cobaltic hydroxide makes it possible to implement the process without introducing extraneous ions into the solution.⁽⁴¹⁾ However, the hydroxide produced is finely-dispersed and is not readily filtered. The structure of a precipitate depends upon the conditions of precipitation. The degree of supersaturation of the solutions from which the precipitate crystallizes is important in determining

the average size of the crystals. The ozone concentration in the air, it was stated, was in the range "28 - 30 mg/dm³."

2.6.5 Hot Copper-Arsenic-Zinc Process. This process is effective in removing cobalt, nickel, antimony and germanium. ⁽²⁴⁾ The purification is usually made on a clarified solution and utilizes copper sulphate solution or metallic copper, arsenic trioxide dissolved in a caustic solution, and metallic zinc dust. Once the cobalt has been reduced to <10 ppm., the nickel is then assumed to be lower than this value. Further purification by filtering, followed by the addition of a fine zinc dust (-325 mesh) to the solution and filtration, after cooling, removes cadmium. ⁽⁵⁴⁾ The two filter cakes are both processable products, the first for its copper content, the second for its cadmium content, with the cobalt and nickel residues being discarded to the tailings.

Fugleberg ⁽⁴²⁾ found that in tests where Co and Ni were present in solution with high content that both Co and Ni were precipitated with Cu. However, X-ray diffraction of the cementation residue could only identify metallic Cu and Cu₃As,

Co or Ni compounds could not be observed. Further examination by X-ray microprobe, in order to locate Co and Ni in the Cu_3As , revealed that Co and Ni were not occluded with the Cu compounds to any great extent, but were rather present as definite compounds with As which were substantially free of Cu. He concluded that Co and Ni are precipitated as pure As compounds which proved to be CoAs and NiAs (or quite close to these intermetallic compounds). Further, these compounds could be precipitated without copper being present in the impure zinc sulphate solution.

Chapter 3

THEORETICAL

This chapter covers the application of data for the estimation of equilibrium concentrations of impurities based on the principal cementation reactions occurring in the zinc sulphate solution, when zinc dust is used as a reductant. Since the reactions take place at temperatures above 298°K extrapolation of free energy data is carried out using Criss and Coble's method. In addition, qualitative and semi-quantitative assessment of the behavior of the reaction kinetics of cementation are also examined.

Calculations are also carried out for relative assessment of the equilibria, under conditions when intermetallic compounds of arsenic are formed.

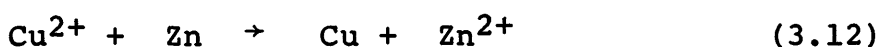
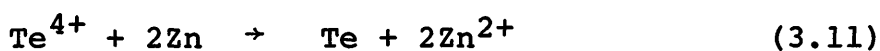
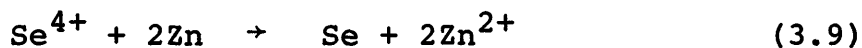
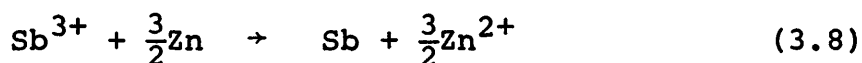
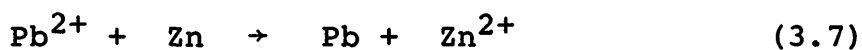
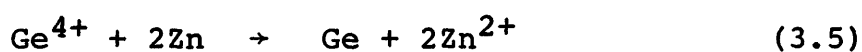
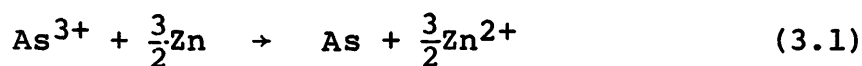
Finally, the equilibria of arsenate formation are examined.

3.1 THERMODYNAMIC ASPECTS OF FREE ENERGY EXTRAPOLATION TO HIGH TEMPERATURES

The application of chemical thermodynamic functions for the extrapolation of free energy data pertinent to

the cementation reactions of interest in this study are presented here. The temperature of interest was 80°C; however, extrapolation up to 150°C was carried out.

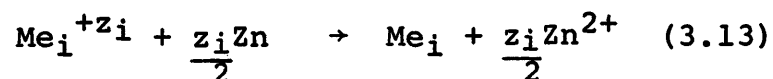
The principal reactions considered in the impure ZnSO₄ solution are:



Although Pb and Sn were not studied experimentally, they were examined for completeness.

3.1.1 Calculation of the Gibbs Free Energy Above 298°K.

The over-all contact reduction may be represented by the general equation:



where Me_i is a specific impurity present in the impure ZnSO₄ solution.

The standard potential of the reaction is obtained from:

$$\Delta E_T^\circ = \frac{-\Delta G_T^\circ}{z_i F}$$

where ΔG_T° is the standard free energy of the reaction at temperature T . ΔG_T° is calculated by use of the equation:

$$\Delta G_{T_2}^\circ = \Delta H_{T_2}^\circ - T_2 \Delta S_{T_2}^\circ \quad (3.16)$$

where $\Delta H_{T_2}^\circ$ and $\Delta S_{T_2}^\circ$ are the standard enthalpy and standard entropy changes, respectively, at absolute temperature T_2 , and are calculated thus:

$$\Delta H_{T_2}^\circ = \Delta H_{T_1}^\circ + \int_{T_1}^{T_2} \Delta C_p^\circ dT \quad (3.17)$$

$$\Delta S_{T_2}^\circ = \Delta S_{T_1}^\circ + \int_{T_1}^{T_2} \frac{\Delta C_p^\circ}{T} dT \quad (3.18)$$

By introducing $\overline{\Delta C_p^\circ} \Big|_{T_1}^{T_2}$ -- the average value of the change in standard partial molal heat capacities, ΔC_p° between the two temperatures considered-- these relationships lead to:

$$\Delta G_{T_2}^\circ = \Delta G_{T_1}^\circ - \Delta S_{T_1}^\circ (T_2 - T_1) + \overline{\Delta C_p^\circ} \Big|_{T_1}^{T_2} (T_2 - T_1) - T_2 \overline{\Delta C_p^\circ} \Big|_{T_1}^{T_2} \ln \frac{T_2}{T_1} \quad (3.19)$$

T_1 , being the standard temperature, conventionally taken as 298°K.

3.1.2 Criss and Cobble's Method for Determining Standard Redox Potential at Elevated Temperature.

It was shown in the previous section that in order to obtain free energy estimates at temperatures greater than 298°K account must be taken of the variation of enthalpy and entropy with temperature. This is the basic principle incorporated into several methods which have been developed.⁽⁴³⁾ The Gibbs free energy values calculated by Criss and Cobble's method⁽⁴⁴⁾ and Khodakovsky's method^(45,46) are both in good agreement with experimental data and it would appear that either method may be employed up to 300°C. This has been substantiated in a number of cases. One of these is shown in Figure 3.1. It was decided to use the method proposed by Criss and Cobble in this study.

This principle^(44,47,48) states that if a standard state is properly chosen by fixing the entropy of $H^+(aq)$ at each temperature, the partial molal ionic entropies at that temperature are linearly related to their corresponding entropies at the same reference temperature. Their choice of standard state at 298°K corresponds to an entropy for the hydrogen ion of $-5.0 \text{ cal mole}^{-1} \text{ } ^\circ\text{K}^{-1}$ in

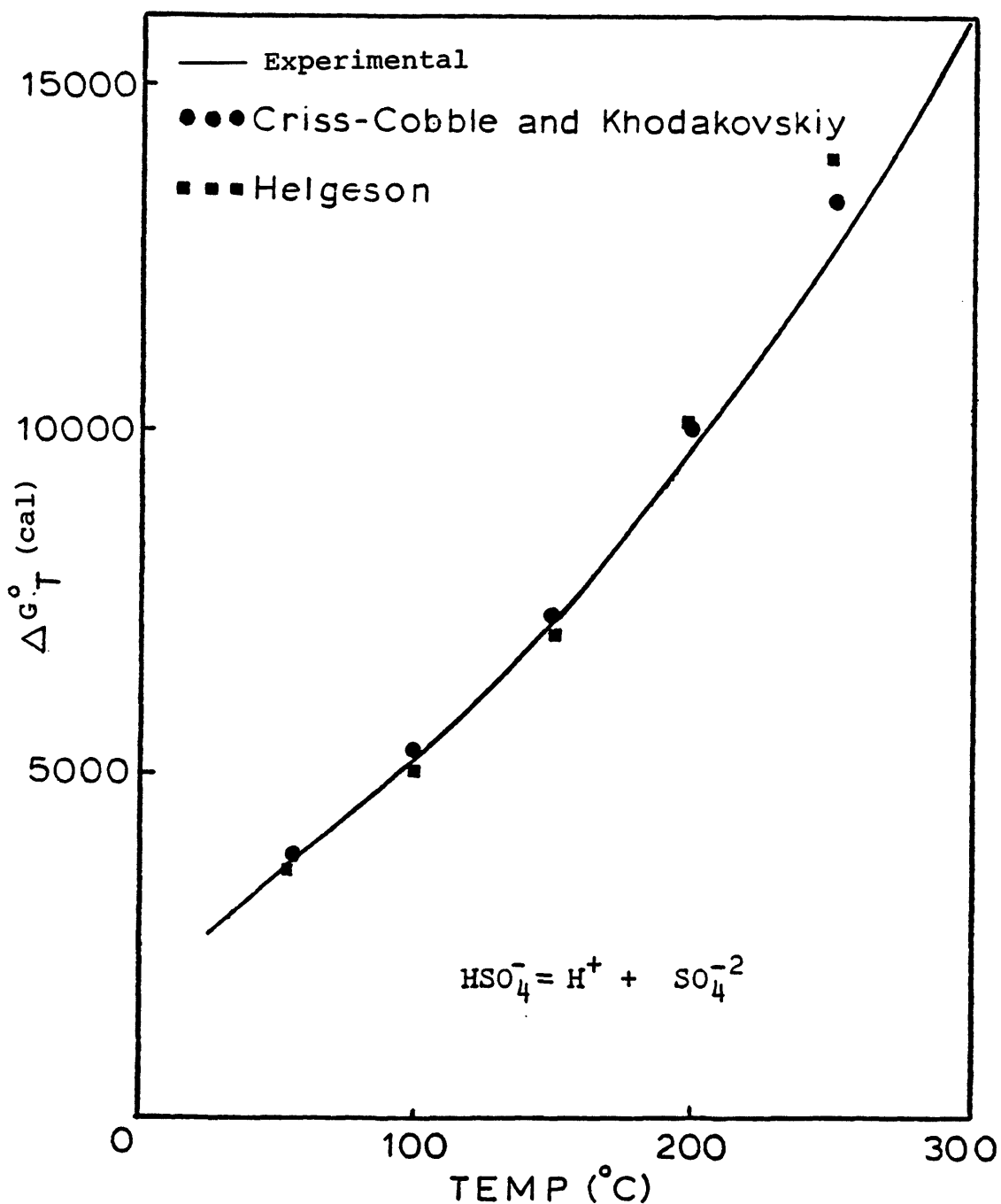


FIG. 3.1. A COMPARISON OF EXPERIMENTAL ΔG°_T WITH VALUES CALCULATED BY DIFFERENT METHODS (Adapted from the literature, (40))

agreement with the value for the "absolute" ionic entropy of $H^+(ag)$ suggested by other authors.

The correspondence principle leads to the following general relationship:

$$\overline{S}_{T_2}^{\circ}(abs) = a_{T_2} + b_{T_2} \cdot S_{298}^{\circ}(abs) \quad (3.20)$$

where a_{T_2} and b_{T_2} are parameters dependent on the class of ions (cations, anions, oxyanions) and on the temperature considered. Table A-1.2 presents the entropy for equation 3.20. $\overline{S}_{298}^{\circ}(abs)$ refers to the ionic partial molal entropies on an "absolute" scale which is not, in fact, absolute, considering the above-mentioned standard state at 298°K.

$$\overline{S}_{298}^{\circ}(abs) = \overline{S}_{298}^{\circ}(conventional) - 5.0z \quad (3.21)$$

where z is the ionic charge.

Applying these considerations to the average value of the partial molal heat capacity between 298°K and temperature T_2 it follows that:

$$\overline{C_p}^{\circ} \Big|_{298}^{T_2} = \frac{\overline{S}_{T_2}^{\circ}(abs) - \overline{S}_{298}^{\circ}(abs)}{\ln \frac{T_2}{298}} \quad (3.22)$$

and from Equation 3.20,

$$\overline{C_p}]_{298}^{T_2} = \alpha_{T_2} - \beta_{T_2} \overline{S}_{298}^{\circ} \text{ (abs)} \quad (3.23)$$

where α_{T_2} and β_{T_2} are parameters, related to a_{T_2} and b_{T_2} introduced previously. These are listed in Table A-1.3.

The standard free energies and standard redox potentials at elevated temperature are calculated by a computer program using standard free energies⁽⁴⁹⁾ and entropies⁽⁵⁰⁾ at 25°C, as well as values of α_{T_2} and β_{T_2} from Table A-1.2. The results are tabulated in Appendix A-1.4. These results are shown in Figures 3.2, 3.3, 3.4 and 3.5.

3.1.3 Standard Reaction Gibbs Free Energies and Reaction Potentials for Cementation with Zinc Dust at 80°C.

The standard Gibbs free energies and standard potentials of the reactions 3.1 to 3.12 were calculated from the data computed in the previous section. These are tabulated in Table 3.1. The large negative values indicate that low equilibrium values of the precipitate ion would be expected. These are confirmed in the section which follows.

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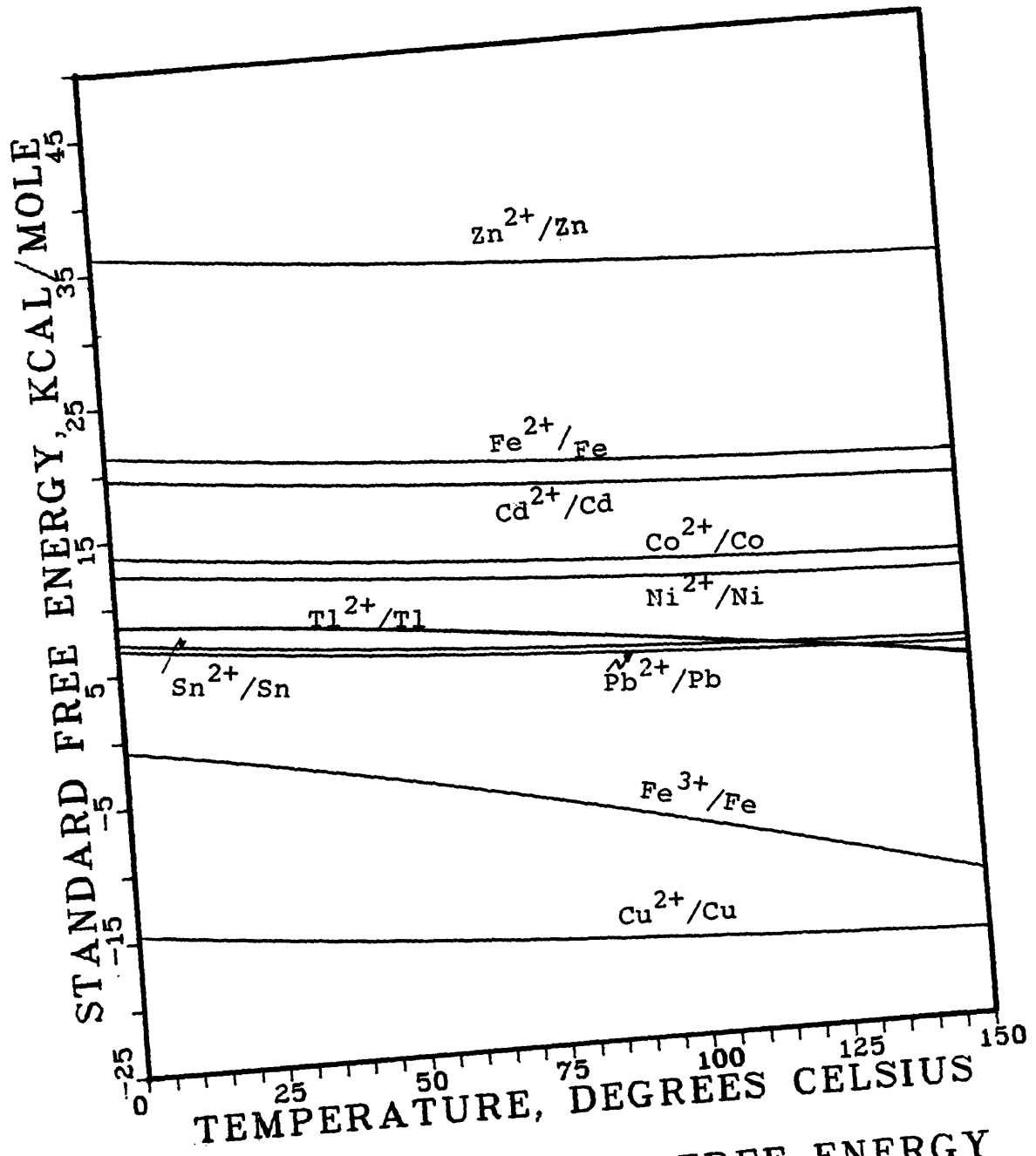


FIG. 3.2 THE STANDARD FREE ENERGY OF HALF-CELL REACTION

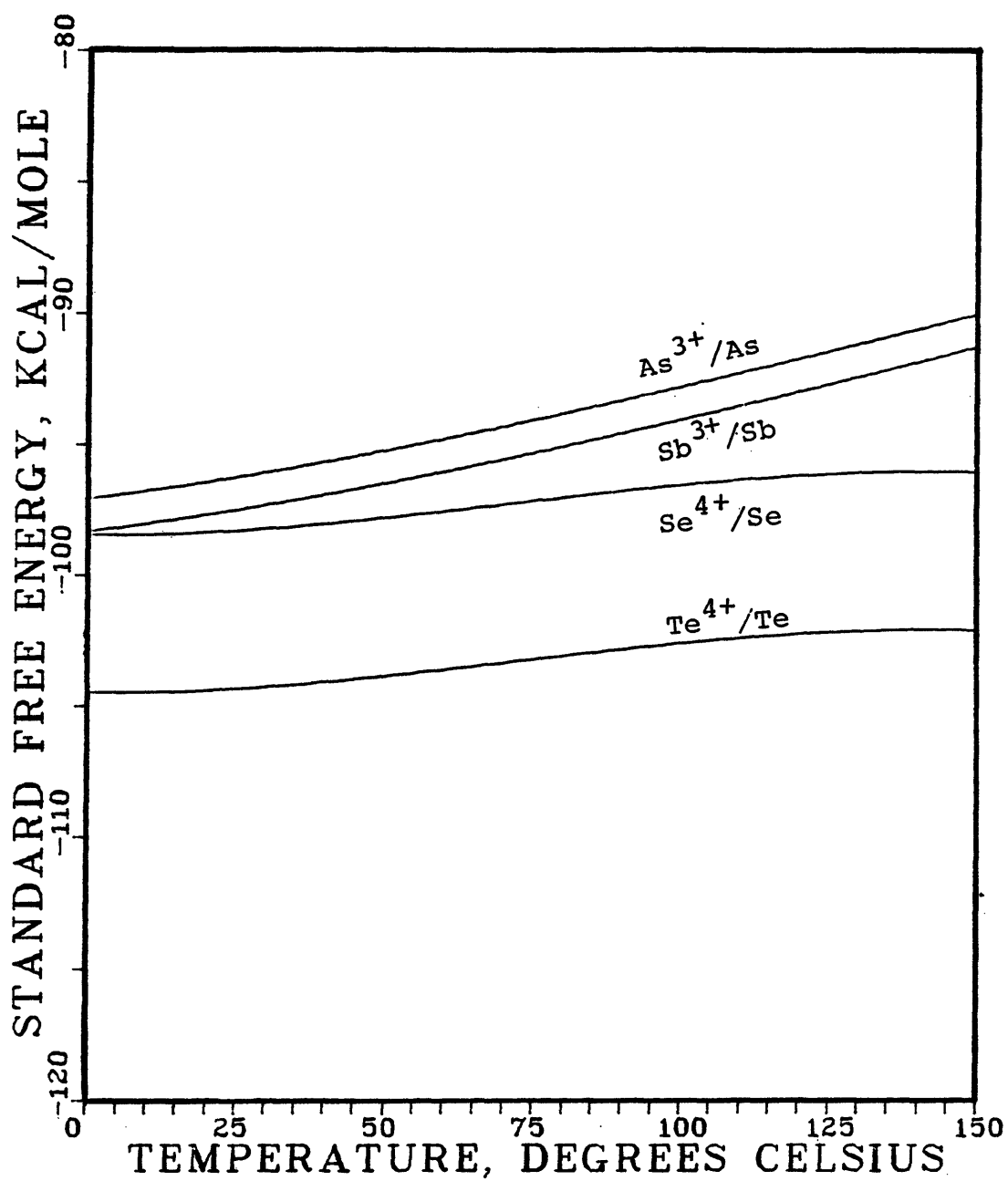


FIG. 3.3 THE STANDARD FREE ENERGY OF HALF-CELL REACTION

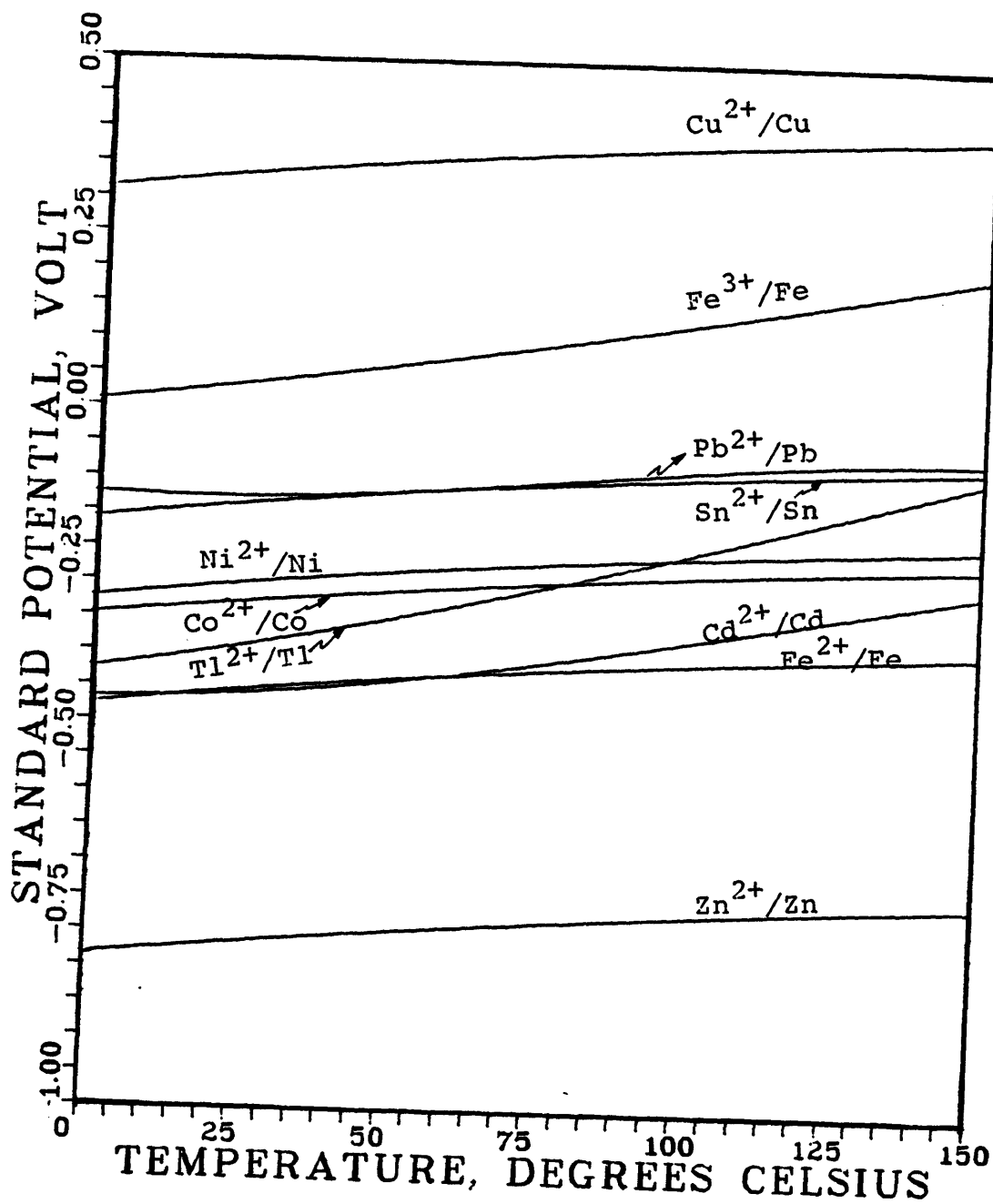


FIG. 3.4 THE STANDARD HALF-CELL POTENTIAL AT HIGH TEMP.

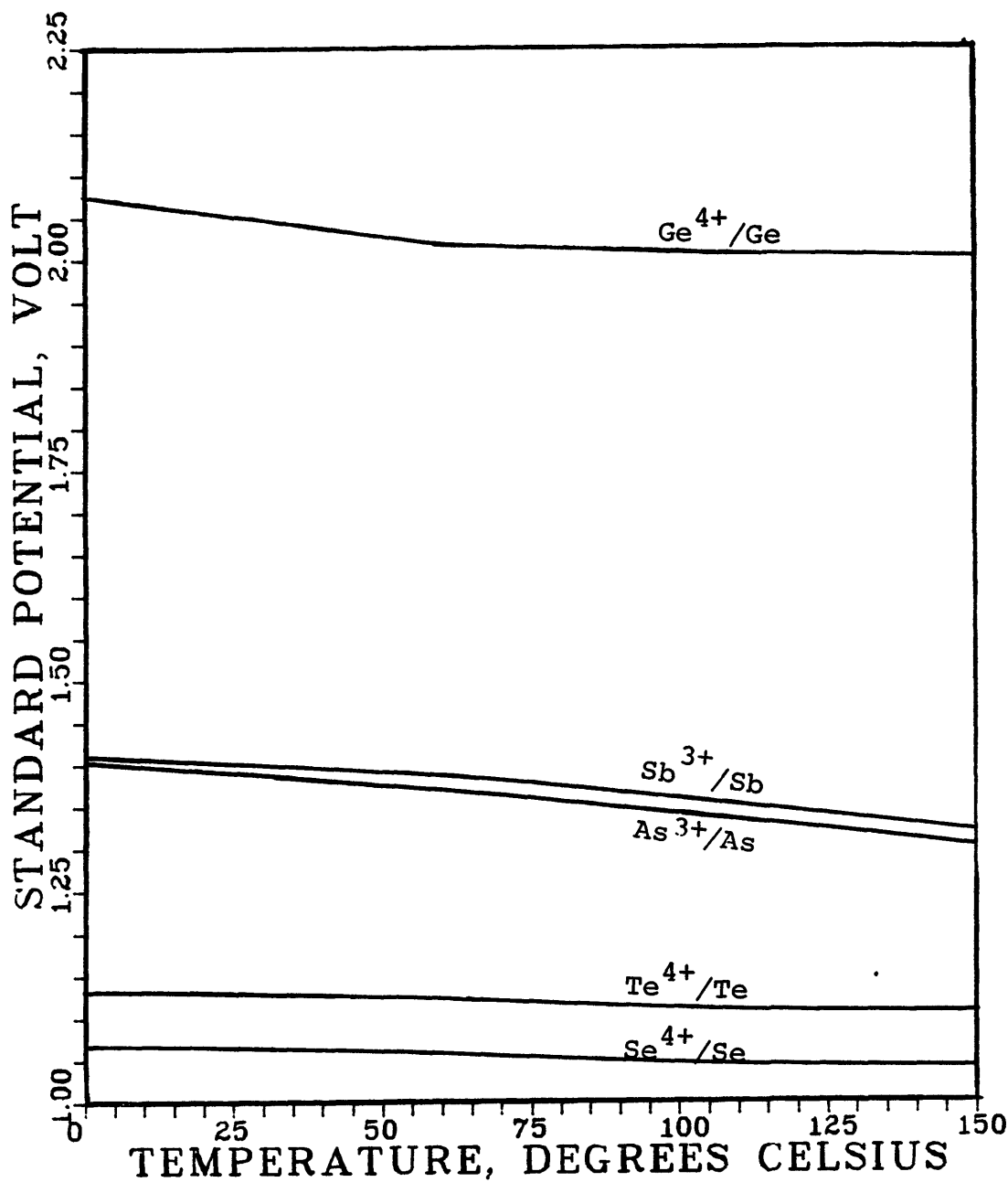


FIG. 3.5 THE STANDARD HALF-CELL POTENTIAL AT HIGH TEMP.

Table 3.1

DATA FOR CEMENTATION REACTIONS IN THE PURIFICATION OF
ZnSO₄ SOLUTION WITH ZINC POWDER AT 80°C

<u>Equation No./</u> <u>System</u>	<u>Standard Potential,</u> <u>ΔE (Volt)</u>	<u>Standard Free</u> <u>Energy ΔG°</u> <u>(kcal./mole)</u>
3.1, As ³⁺ /Zn	2.096	-145.00
3.2, Cd ²⁺ /Zn	0.360	- 16.60
3.3, Co ²⁺ /Zn	0.493	- 22.74
3.4, Cu ²⁺ /Zn	1.083	- 49.95
3.5, Fe ²⁺ /Zn	0.323	- 14.90
3.6, Ge ⁴⁺ /Zn	2.743	-253.00
3.7, Ni ²⁺ /Zn	0.523	- 24.12
3.8, Pb ²⁺ /Zn	0.623	- 28.73
3.9, Sb ³⁺ /Zn	2.110	-146.00
3.10, Se ⁴⁺ /Zn	1.789	-165.00
3.11, Sn ²⁺ /Zn	0.613	- 28.12
3.12, Te ⁴⁺ /Zn	1.854	-171.00

3.2 EQUILIBRIUM CONCENTRATIONS OF IMPURITIES IN ZnSO₄ SOLUTIONS IN CONTACT WITH ZINC DUST

The equilibrium constant for Equation 3.13 can be calculated from:

$$\ln K_T + \frac{-\Delta G^\circ}{RT} = \frac{z_i F \Delta E^\circ}{RT} \quad (3.24)$$

where $\Delta E^\circ = E_c^\circ - E_a^\circ$ and E_c and E_a are the reversible standard reduction potentials for the metal impurity and zinc metal, respectively. (48)

$$K_T = \frac{\{ \text{Me}_i \} \{ \text{Zn}^{2+} \}^{\frac{z_i}{2}}}{\{ \text{Me}_i^{+z_i} \} \{ \text{Zn} \}^{\frac{z_i}{2}}} \quad (3.25)$$

The quantities { } are the activities of products and reactants. If there is no solid solubility of the reduced metal impurity, the solid phases may be considered as single component phases of unit activity. Also, if the ion considered is of about the same size and the same valency as zinc, then the activity coefficients of zinc and impurity ions may be considered to be equal. Thus,

$$\ln \frac{[\text{Me}_i^{+z_i}]}{[\text{Zn}^{2+}]} = \frac{-z_i F \Delta E^\circ}{RT} \quad (3.26)$$

Therefore, for a zinc concentration of 140 gpl., that is 2.15 M. Equation 3.26 may be rearranged to give the following expression for the equilibrium concentration of the impurity ion:

$$[M_e^{+z_i}] = 2.15 \exp \left(\frac{-z_i F \Delta E^\circ}{RT} \right) \quad (3.27)$$

where $\Delta E^\circ = E_c^\circ - E_a^\circ$ (volt) at temperature T

$$R = 0.001987 \text{ (kcal mole}^{-1} \text{ }^\circ\text{K}^{-1}\text{)}$$

$$T = 353^\circ\text{K}$$

$$F = 23.06 \text{ (kcal volt}^{-1} \text{ . equivalent}^{-1}\text{)}$$

z_i = electrons transferred in the reaction
(equivalent . mole⁻¹)

For the trivalent ions, such as arsenic, the activity coefficients do not cancel. Then the activity of this ion would appear on the left side of Equation 3.27. This was set equal to unity for the purpose of the calculations.

Using the values of ΔE° tabulated in Table 3.1, the equilibrium concentrations of the impurities at 80°C were calculated and are listed in Table 3.2 where the observed concentrations achieved in an industrial operation are also noted. The very low equilibrium concentrations shown in some instances have little physical meaning-- for example, in the case of copper (2.55×10^{-28} mgpl.), it corresponds to less than one ion per liter of solution! These values can only imply that the reactions are stoichiometrically complete at equilibrium. The marked differences between the predicted equilibrium concentrations and those observed at Centromin-Peru⁽⁴⁸⁾ are at once apparent. At this plant the purification step is stopped when cadmium is reduced below 0.5 mgpl. and, thus, high

Table 3.2

EQUILIBRIUM AND OBSERVED CONCENTRATIONS IN (mg/l)
FOR PRECIPITATION OF IMPURITIES BY ZINC
AT CONTROMIN-PERU (48)

<u>Metal Precipitated</u>	<u>Equilibrium Concentration</u>	<u>Concentration Before Purifi- cation by Zinc</u>	<u>Concentration After Purifi- cation by Zinc</u>
Tellurium	3.67×10^{-57}	1.2×10^{-1}	8.0×10^{-2}
Antimony	3.63×10^{-49}	1.3	2.0×10^{-2}
Arsenic	1.35×10^{-48}	5.0×10^{-1}	2.5×10^{-2}
Selenium	3.62×10^{-47}	8.0×10^{-2}	4.0×10^{-2}
Copper	2.55×10^{-28}	1.7×10^{-2}	3.0×10^{-1}
Germanium	9.46×10^{-26}	$<5.0 \times 10^{-2}$	$<5.0 \times 10^{-2}$
Tin	6.72×10^{-15}	-	-
Lead	3.48×10^{-15}	-	-
Nickel	2.50×10^{-12}	6.5×10^{-1}	$<1.0 \times 10^{-1}$
Cobalt	1.80×10^{-11}	10.0	4.0
Cadmium	1.13×10^{-7}	1.9×10^2	5.0×10^{-1}
Iron	1.28×10^{-6}	2.0	2.0

concentrations of some impurities may not be unexpected. However, increasing the contact time leads to the formation of hydroxides and oxidation of the precipitated metals with air with no measurable improvements in the final concentrations. The lack of reduction in the concentration levels of Co, Ni and Fe is particularly noticeable.

3.3 RATE PHENOMENA IN CONTACT REDUCTION OF METALS FROM SOLUTION

The general contact-reduction reaction for removal of impurities in solution by zinc has already been given in Equation 3.13. The mechanisms responsible for the reaction may be attributed to numerous micro-cells, ⁽²⁶⁾ one of which is depicted below.

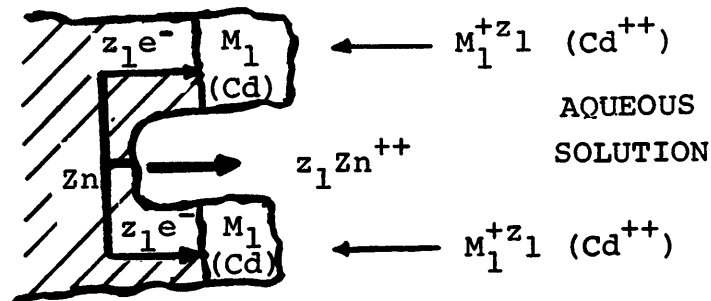


Figure 3.6 Electrochemical Micro-cell in Contact Reduction of Metal Ion $M_1^{+z_1}$ by zinc.

These short-circuited electrolytic micro-cells can be analysed in terms of their respective electrode reactions:



The reaction is termed electrochemical, as distinct from a chemical redox reaction, in the sense that the electrons are not exchanged at the same site but rather the electrode reactions are separated by an arbitrary, but finite, distance which necessitates that the solid phase be a conductor or semiconductor. In addition, contact reduction should be distinguished from electrolytic deposition where the electrons are supplied from an external source, rather than by the ionization of the less noble metal.

In cementation systems the anode and cathode are short-circuited and the rate of the reaction (or current) is most frequently determined by the transport of the discharging metal ions at cathodic sites, due to diffusional processes. In electrolysis this limiting current is not often achieved.

The reaction rate of the precipitate ion, which is related to the current, is the response most frequently used by researchers to characterize a given contact

reduction system. A detailed analysis of cementation reactions in terms of electrochemical theory has been given by Wadsworth. (27) The expression obtained for the rate of cementation is in fact a recast of the Butler-Volmer equation:

$$\frac{dn_1}{dt} = C_1 k_0 \left(1 - \frac{C_2^{z_1/z_2}}{C_1} \exp \left[\frac{-z_1 (E_2^0 - E_1^0) F}{RT} \right] \right) \quad (3.30)$$

where:

- C_1 is the concentration of the noble metal ion $M_1^{+z_1}$ (Cd), at time t ,
- C_2 is the concentration of the active metal ion $M_2^{+z_2}$ (Zn) at time t ,
- z_1 is the charge of the noble metal ion,
- z_2 is the charge of the active metal ion,
- E_1^0 is the standard half-cell potential for M_1 ,
- E_2^0 is the standard half-cell potential for M_2 ,
- k_0 is the rate constant, which may be function of anodic and cathodic overpotentials, the double layer potential, diffusion coefficient, and diffusion distance.

The back-reaction rate is represented by the second term in Equation 3.30 and affects the rate by less than 1% when:

$$\frac{C_2^{z_1/z_2}}{C_1} \exp \left[\frac{-z_1 (E_2^0 - E_1^0) F}{RT} \right] \gtrsim 10^{-2} \quad (3.31)$$

In most systems, and for typical values of $\frac{C_2^{z_1/z_2}}{C_1}$, this condition is not achieved and consequently the back reaction would not be expected to be important in determining the net reaction rate. Miller⁽²⁶⁾ says "Only when $(E_2^\circ - E_1^\circ)$ is of the order of 0.5 volts will the back reaction be worthy of consideration in defining the kinetics of a system."

This is, indeed, the case for the present study as can be seen in Table 3.3. The values shown were calculated from information in Table 3.1 on standard reaction potentials for the system and in Table 3.2 using the values of the impurity ions which are observed in practice. In general, however, small values of $(E_2^\circ - E_1^\circ)$ can lead to other complicating factors where competing reactions and surface adsorption become important.

Table 3.3

DATA FOR BACK REACTION KINETICS
IN CEMENTATION REACTIONS OF THE
PURIFICATION OF ZnSO₄ SOLUTION WITH
ZINC POWDER AT 80°C OF TEMPERATURE

<u>Systems</u>	<u>(E₂-E₁)</u> <u>Volt</u>	Values of Back-Reaction Parameter (Eq. 3.31)
Fe ²⁺ /Zn	0.323	3.574 x 10 ⁻⁵
Cd ²⁺ /Zn	0.360	2.526 x 10 ⁻⁵
Co ²⁺ /Zn	0.493	3.766 x 10 ⁻¹⁰
Ni ²⁺ /Zn	0.523	1.464 x 10 ⁻⁹
Ge ²⁺ /Zn	0.993	1.369 x 10 ⁻²²
Cu ²⁺ /Zn	1.083	5.376 x 10 ⁻²⁶
Se ²⁺ /Zn	1.743	7.122 x 10 ⁻⁴⁴
As ²⁺ /Zn	1.793	4.039 x 10 ⁻⁴⁵
Sb ³⁺ /Zn	1.813	2.202 x 10 ⁻⁴⁵
Te ²⁺ /Zn	2.093	5.828 x 10 ⁻⁵⁴

3.3.1 Factors Affecting the Contact Reduction Reaction.

Most contact reduction systems appear to be first-order process with respect to $M_1^{+Z_1}$ and can be represented by the first-order rate equation:

$$\frac{dn_1}{dt} = kAC_1 \quad (3.32)$$

where A is the contact area between the solution and precipitant metal. The rate of cementation, as in any heterogenous reaction, is affected by the labile area on which the noble metal ion is to be reduced. The area that controls experimentally observed reaction rates is determined by the nature of the surface deposit. In cementation reactions, the reaction product (deposited metal) usually does not impede the reaction progress and frequently enhances the reaction kinetics, due to the electrochemical nature of the reaction and the morphology of the surface deposit.

Surface deposits formed in cementation systems are quite similar to electrolytic deposits because of the electrochemical nature of the reaction. In cementation systems the current density is not an independent variable and, consequently, the surface-deposit effects observed are not predictable. The significance of the

surface deposit resulting rate behavior can be discussed in terms of hydrodynamics, concentration, temperature and particle - particle interaction effects.

Regarding hydrodynamics, this is an important variable which controls the type of deposit obtained in electrolytic cells and can be extended to cementation systems. The results from such a study⁽⁵²⁾ indicate that fluid flow not only determines the extent of surface deposited removal by shear forces on a macroscopic basis, but can also determine the basic character and structure of the surface deposit at the microscopic level as well.

Concentration effects on contact reduction reaction kinetics have been observed in rotating disc.⁽²⁹⁾ Two stages of reaction are apparent. The initial stage of reaction corresponds to deposition on a relatively smooth surface where the deposit structure and thickness have not significantly changed. During the second stage of reaction an increased rate of reaction is observed due to the development of a structured surface deposit, which increases the surface area available for reaction.

In addition, micro-turbulence produced by the rotating surface can also be a contributing factor.

The concentration of noble metal ion, and the ionic strength in general, can influence cementation reaction kinetics indirectly as they relate to the structure and porous nature of the surface deposited. While directly, they influence the diffusion coefficient and activity of diffusing species. Thus, the value of the initial concentration can produce anomalous behavior of the reaction rate constant. Sometimes an increase in the initial concentration results in an increased reaction rate constant. Frequently, such a response occurs in dilute solutions of the noble metal ion where an increased concentration produces a deposit which is more porous. In more concentrated solutions, and in the same system, the apparent reaction rate constant can decrease with an increase in the initial concentration, as a result of increased ionic strength.

The temperature dependence of the contact reduction reaction rate constant can be used to determine the apparent activation energy, E_A , using the Arrhenius equation:

$$k \propto \exp(-E_A/RT) \quad (3.33)$$

A plot of $\log k$ versus $1/T$ frequently results in a straight line from which E_A is determined. For reactions controlled by diffusion in a liquid phase, E_A is generally between 2 and 6 kcal/mol; whereas for a process controlled by a chemical reaction E_A is greater than 10 kcal/mol. Most contact reduction systems at high temperatures are diffusion-controlled reactions. A few systems, however, exhibit rather large activation energies at low temperatures. This has been interpreted as being a change from a diffusion-controlled process at high temperature to a surface-reaction-controlled process, or a pore diffusion process at low temperature. Beckstead⁽⁵³⁾ suggests that these results are a consequence of the temperature sensitivity of the surface deposit, i.e., the observed activation energies at low temperatures are high, either because the nature of the surface deposit inhibits the anodic reaction or because of a change in the effective cathodic area.

Particle - particle interaction can play an important role in the behavior of contact reduction systems. This can lead to rate enhancement, since the conducting particles act to extend the cathodic

surface area and promote noble metal deposition, even though the noble metal ion may never contact the active metal. This has been described as a fluidized cathode mechanism where an effective increase in cathodic area provides good particle - particle contact for electron conduction. It has been shown⁽²⁸⁾ that enhancement is directly related to the concentration of particulate conductors up to some saturation point. In other words, the rate enhancement should be proportional to the number of conductive particles, the collision rate, and time of contact.

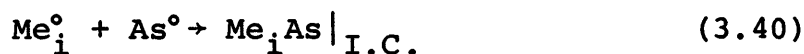
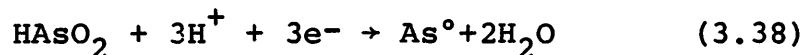
While the various kinetic aspects discussed previously can all play a role in a particular cementation system, it is nevertheless difficult to apply these quantitatively to complex systems where several ions are being co-precipitated and particles are used as precipitant. Turbulent eddies can significantly increase the mass transfer to particles which are small (less than the micro-scale of turbulence) due to perturbative unsteady mass transport. Thus, in particulate systems mass transport may not be a rate determining factor. Furthermore, when zinc metal is used, the competitive

hydrogen ion reduction rate can be a significant effect in reducing the rate of removal of a given impurity ion. It should be remembered that the hydrogen ion discharge can occur on the precipitate metal deposited which may not have a high overvoltage for hydrogen. pH control can only partially alleviate this problem. In this regard, co-precipitation where intermetallic compound may be formed can offer benefits in terms of its electrode kinetics as well as standard potential. Another consequence of co-precipitation is that at a later stage in the precipitation process resolution can occur because of complete dissolution of zinc or blinding of the zinc particle. Metals already deposited, which are less noble than others which are still present in solution, will now precipitate these ions and thus reappear in solution.

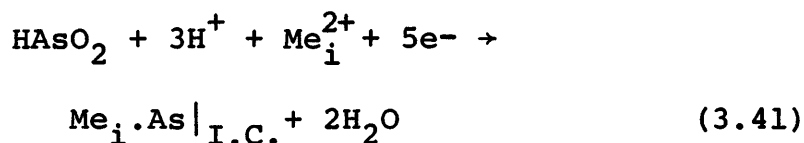
3.4 THERMODYNAMICS OF INTERMETALLIC COMPOUND FORMATION WITH ARSENIC

Copper, nickel and cobalt are capable of forming intermetallic compounds with arsenic and antimony. These intermetallic compounds, which can be produced during co-reduction, have been cited as being responsible for improvements in impurity removal. (20,42)

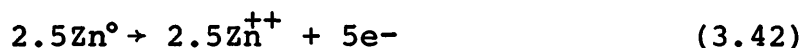
For the general case the following reactions can be written when arsenic is used:



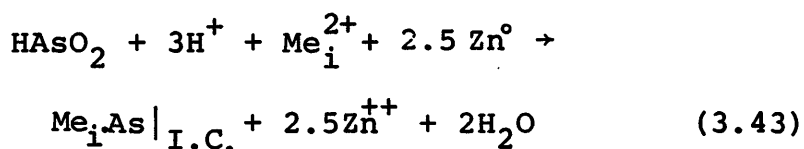
where Me_i may be Co^{2+} , Ni^{2+} or Cu^{2+} . These reactions determine the following over-all cathodic reaction:



The anodic reaction is:



Then, the over-all reaction becomes:



The equilibrium constants and the corresponding equilibrium concentrations of cobalt and nickel concentration were estimated from the thermodynamic data at 25°C, listed in Table A-2.1. The calculations are presented in Appendix 2. Data for copper was not found in the literature examined.

i) Cobalt

$$K_{25^{\circ}\text{C}} = 3.77 \times 10^{81}$$

$$[\text{Co}^{++}] = 7.95 \times 10^{-62} \text{ mole/liter}$$

ii) Nickel

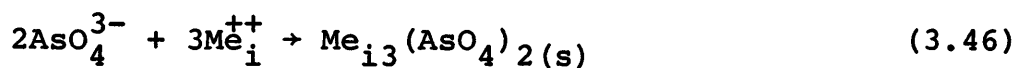
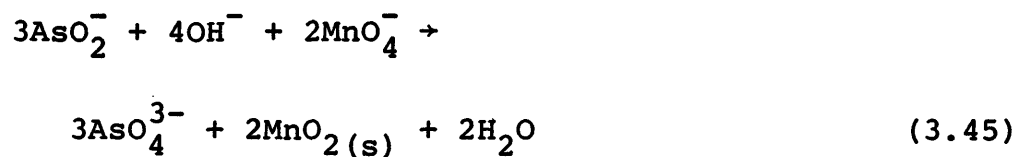
$$K_{25^{\circ}\text{C}} = 3.07 \times 10^{80}$$

$$[\text{Ni}^{++}] = 9.75 \times 10^{-61} \text{ mole/liter}$$

The values of equilibrium cobalt concentration and equilibrium nickel concentration in the system Co^{++} , HAsO_2/Zn and Ni^{++} , HAsO_2/Zn at 25°C , respectively, are lower than the values of equilibrium concentration of cobalt and nickel obtained in the system Co^{++}/Zn and Ni^{++}/Zn . On a relative basis, the reaction with inter-metallic compound formation appears to be more effective in removing cobalt and nickel. However, in the final analysis the electrode kinetics of the deposit will determine how the impurity removal is affected.

3.5 THERMODYNAMICS OF ARSENATE FORMATION

The following chemical reactions may be used to demonstrate the formation of arsenates with the principal impurities (Co, Ni, Cd, or Cu) present in the impure zinc sulphate solution. Potassium permanganate is used as oxidant at a pH $_{25^{\circ}\text{C}}$ of about 5.



The manganate ion thus oxidizes the trivalent arsenic to the pentavalent arsenate ion. This, then, reacts to form the arsenate compound. The solubility products for a selected number of arsenates are presented in Table A-1.5. The values are extremely small, indicating that with excess arsenic, it is probable that low concentrations of the impurities could be obtained.

Chapter 4

EXPERIMENTAL

This chapter provides details of the experimental equipment and procedures used in the work reported in this thesis.

The various experimental equipment are presented in the first section. Included are a photograph and sketch of the laboratory reactor system. Chemical reagents and other materials used in the tests and the procedures carried out to effect the removal of the impurities conclude the chapter.

4.1 EQUIPMENT

The tests were carried out in a water jacketed pyrex glass reactor with a cover but vented to the atmosphere. The liquid capacity of the reaction chamber was 135 cm^3 and four longitudinal indentations in the sides acted as baffles. This arrangement eliminated the formation of a vortex. The cover contained three holes. Two were used to insert platinum and saturated calomel electrodes for Redox measurements and the other contained a thermocouple for temperature measurement of the zinc sulphate solution.

The reactor was placed over a magnetic stirrer (Corning Glass Works, Model PC-353), which provided rotation of a Teflon covered magnetic impeller located in the solution at the bottom of the reactor. The rotational speed of the magnetic impeller was measured with a General Radio Model A531-AB Strobatac. It was found that a speed of 500 RPM was adequate for suspension of zinc particles. The water jacket was connected to a constant temperature circulating system (Lab-line Instruments, Inc., Model 3052), and provided thermostating of the reactor.

The temperature was measured using a stainless steel sheathed type K (Chromel-Alumel) thermocouple. The thermocouple output relative to a melting ice junction was recorded using a potentiometric strip chart recorder (Honeywell, Electronic 196).

The pH of solutions at the ambient temperature in the laboratory (25°C) was measured using a digital pH meter (Radiometer, Model pH M62) with a Radiometer, Model GK2301C glass/calomel combination pH electrode. Corning Cat. No. 476060 platinum electrode and Radiometer Model K401 calomel electrode was also used with the pH meter for Redox measurements. The salient features of the set-up are shown in Figures 4.1 and 4.2.

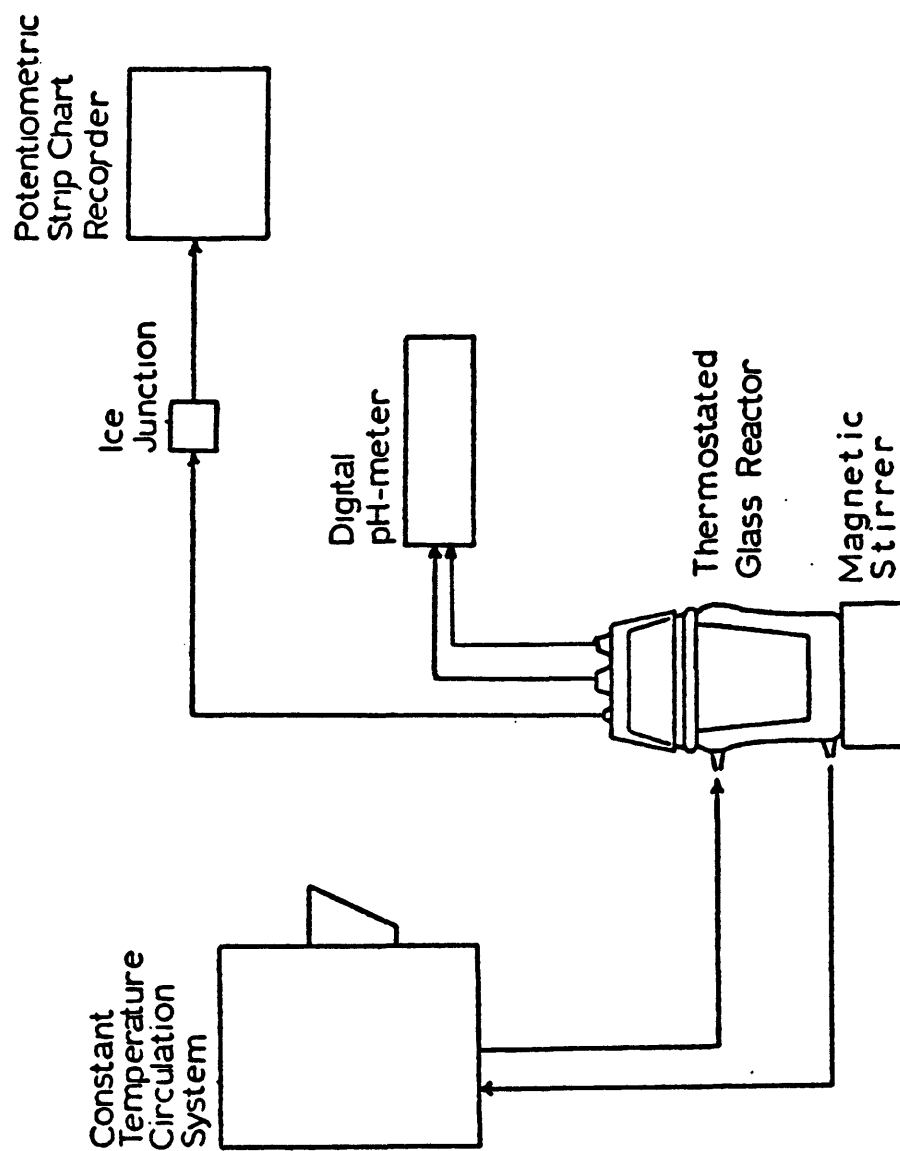


Figure 4.1 Schematic of the experimental set-up.

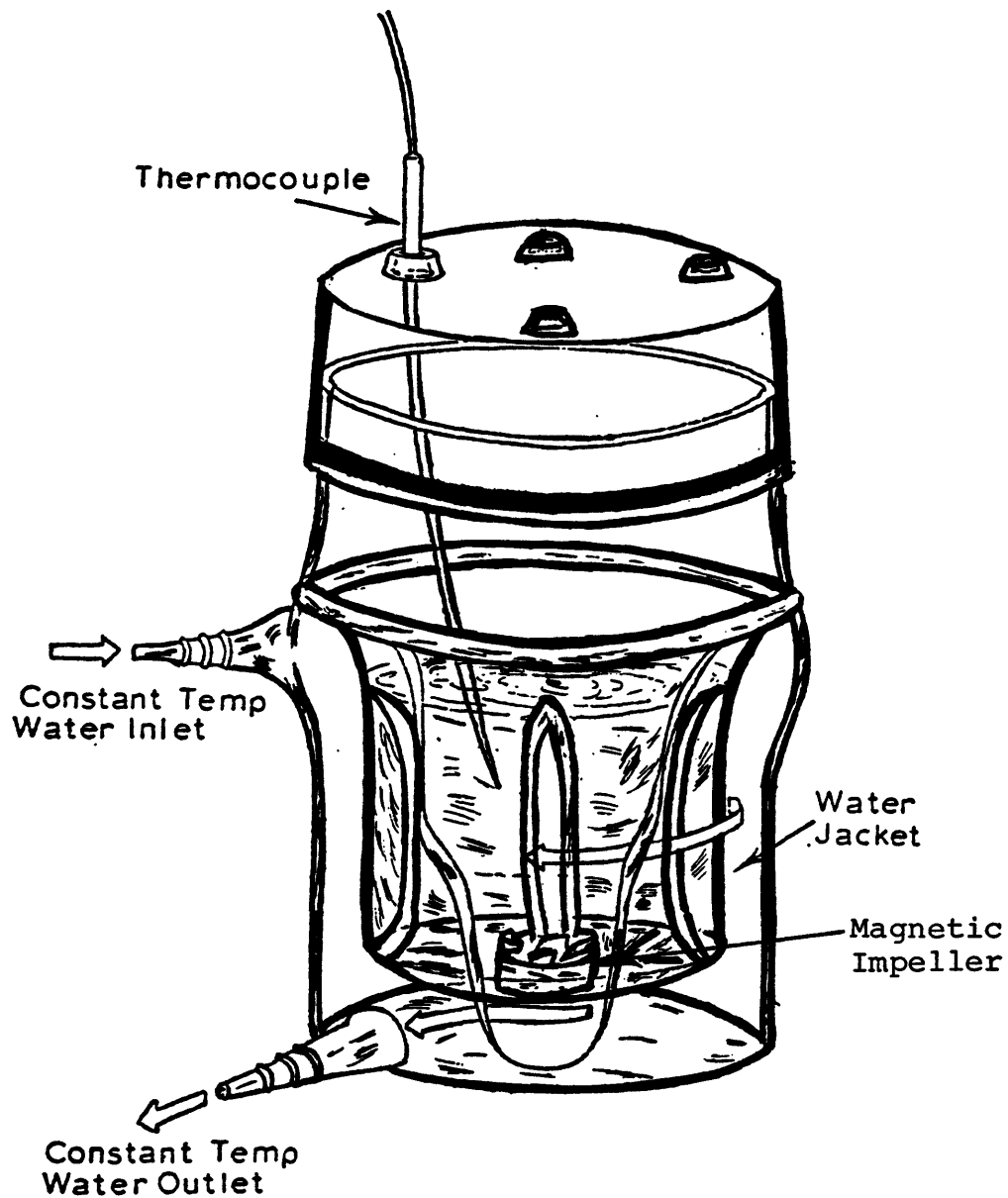


Figure 4.2: View of the thermostated glass reactor.

4.2 CHEMICAL REAGENTS AND MATERIALS

The synthetic impure zinc sulphate solution was formulated to include the principal harmful impurities. The chemical reagents used were of the following specifications:

- Antimony Trioxide (Powder) from "Baker Analyzed" Reagent.
- Arsenic Trioxide (Powder) from Mallinckrodt Chemical Works.
- Cadmium Oxide (Powder) from Fisher Scientific Company.
- Cobalt Sulphate (Crystal $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) from Mallinckrodt Chemical Works.
- Copper (ic) Sulphate (Powder $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) from Sargent-Welch.
- Germanium Dioxide (Powder) from Goldsmith Chemical and Metal Corporation.
- Iron (Powder) from "Baker Analyzed" Reagent.
- Nickelous Sulphate (Crystal $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) from "Baker Analyzed" Reagent.
- Selenium Dioxide (Powder) from Sargent-Welch.
- Tellurium Dioxide (Powder) from Sargent-Welch.
- Zinc Sulphate (Granular $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) from Mallinckrodt Chemical Works.
- Sodium Hydroxide (Solution 50%) from Mallinckrodt Chemical Works.
- Zinc Metallic (Powder-325 Mesh) from ASARCO.
- Potassium Permanganate (Granular, KMnO_4) from "Baker Analyzed" Reagent.

The residue was separated from the treated ZnSO_4 solution by filtration using polycarbonate membranes 47 mm. diameter with 1.0 μm openings (Nuclepore Corporation).

4.3 PROCEDURE

Details of the preparation of the synthetic zinc sulphate solution and the various purification methods investigated are presented in the following two sections:

4.3.1 Preparation of Solutions. The zinc sulphate was prepared by dissolving $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water. In addition ZnO and sulphuric acid were used to obtain 15 liters of solution of the desired zinc concentrations.

Stock solutions were prepared by dissolving cobaltous sulphate, copper sulphate, nickelous sulphate in distilled water. Cadmium oxide, germanium dioxide, iron, selenium dioxide and tellurium dioxide were prepared in 1 N. sulphuric acid, while arsenic trioxide and antimony trioxide were prepared in 50% sodium hydroxide. The concentration of each of these was adjusted to 1 gpl. except for cadmium and copper which were 10 gpl..

Volumes of 100 ml. were prepared in each case. Calculated volumes of each impurity were added to the zinc sulphate solution to obtain the desired impurity concentration. The impure zinc sulphate solution was finally adjusted to $\text{pH}_{25^{\circ}\text{C}}$ 4.85 by addition of sodium hydroxide solution. This solution was stored in a 20-liter glass bottle and subsequently analysed by flame and/or graphite furnace atomic absorption spectrophotometry for all the elements. The analysis is shown in Table 4.1.

Table 4.1

ANALYSIS OF THE SYNTHETIC IMPURE $ZnSO_4$ SOLUTION

<u>Element</u>	<u>Concentration (mgpl)</u>
Zn	107.0 gpl.
Cd	137.0
Cu	107.0
Co	3.3
Sb	2.0
Ge	1.0
As	0.5
Te	0.5
Se	0.5
Ni	0.2
Fe	0.1

4.3.2 Methods for Precipitating Impurities. The methods of precipitating the impurities were investigated in order to assess their effectiveness.

In each test approximately 130 cm³ of impure solution was treated. Approximately 10 cm³ were lost during a run due to evaporation. This solution was brought up to the working temperature (60 or 80°C) by connecting up the water jacket to the water bath. The time required was typically five minutes. The initiation of a run was marked when zinc dust or KMnO₄ (with arsenic already present) was introduced into the solution. At the end of the run the reactor was disconnected from the water bath and connected to the cold water tap to quench the reaction in about a minute.

i) The first set of experiments was carried out with the objective of precipitating the impurities by contact-reduction with zinc dust. Once the solution attained the run temperature of 80°C, under constant agitation, the required amount of zinc powder for the particular run was added. Reaction times of 5, 10, 30, 45 and 60 minutes with a fixed amount of zinc dust addition were investigated. A number of runs were also

carried out at a fixed time of reaction but with different amounts of zinc dust addition.

ii) The second set of experiments was conducted in a similar manner to the first set. The tests were again carried out at 80°C. However, arsenic trioxide dissolved in sodium hydroxide (10 gpl. As) and neutralized with H_2SO_4 , was used as a reagent in the treatment. The objective now was to promote the formation of intermetallic compounds of arsenic, in particular with cobalt. Furthermore, the "stock" impure solution was doped with cobalt to increase the concentration by 10 ppm. Arsenic was added at the start of the run, simultaneously with the zinc dust, to the impure solution. In addition, a similar treatment was carried out as the second step of a two-step procedure where the first step corresponded to the treatment as in Set No. 1, where arsenic was not added initially.

iii) In the third set of experiments the treatment temperature was 60°C. Also the "stock" impure solution was doped with additional 10 ppm. of cobalt. Trivalent arsenic was added to the solution in preparation to the addition of 0.5 M $KMnO_4$ solution for precipitation of impurities as

arsenates. The KMnO_4 solution was added until the $\text{Eh}_{60^\circ\text{C}}^*$ attained a value of 1.0 volt. After a reaction time of 15 minutes, zinc dust was added (without removal of the precipitate) to eliminate excess arsenic by contact-reduction. Two different reaction times were used for this second step in two separate runs.

A variation of the previous procedure was used in a subsequent series of runs where the residue was eliminated before the second treatment step. Finally, a series of runs where the impure solution was first treated with zinc dust, as in Set No. 1, for 45 minutes, after which trivalent arsenic was added (based on residual impurities), followed by KMnO_4 solution addition to produce an $\text{Eh}_{60^\circ\text{C}}$ of 1.0 volt. The reaction time for this second step was 45 minutes. A third and last step consisted of adding zinc dust to remove excess arsenic. Reaction times of 15 and 30 minutes were investigated.

A schedule of these procedures is provided in Table 4.2.

$$*\text{Eh}_{60^\circ\text{C}} = E_{\text{Pt-Cal}_{60^\circ\text{C}}} - E_{\text{Cal-H}_{260^\circ\text{C}}} = (E_{\text{Pt-Cal}_{60^\circ\text{C}}} + 220) \text{ mV}$$

where $E_{\text{Pt-Cal}}$ is the measured potential using the Redox system described previously.

Table 4.2
SCHEDULE OF TREATMENT PROCEDURES

Treatment Carried Out at 80°C					
Set No.	No. of Steps	Chemical Details	Run No.	Treatment Conditions and Procedure	Fig. No.
1	1	-Impure ZnSO ₄ sol. -Zinc dust ¹	1,2,7A 5,9	-Stoich. amount of zinc dust ¹ varied for each run -Reaction time: 60 min.	5.1
			3,4,6,7 8	-Variable reaction time -3 times stoich. amount of zinc ¹	5.2
2	2	-Impure ZnSO ₄ sol. -First addition of zinc dust ¹ -As ₂ O ₃ *with Second Addition of zinc dust ³ †doped with 10ppm Co.	10,11 12,13	-3 times stoich. zinc dust ¹ -The residue was eliminated. First step, reaction time: 45 min. -Stoich. amount of arsenic ² varied for each run -3 times stoich. amount of zinc dust ³ -Second step reaction time: 45 min.	5.3
			14,15 16,17 18	-3 times stoich. zinc dust ¹ -The residue was eliminated. First step, reaction time: 45 min. -3 times stoich. amount of arsenic ^{2†} -3 times stoich. amount of zinc dust ³ -Variable reaction times for second step	5,4

*As₂O₃ dissolved in NaOH sol. pH adjusted to 4.5 with H₂SO₄.

1. Stoich. amount of Zn dust with respect to all impurities.
2. Stoich. amount of As with respect to cobalt in solution.
3. Stoich. amount of Zn dust with respect to excess arsenic.

Table 4.2
(Continued)

Treatment Carried Out at 80°C					
Set No.	No. of Steps	Chemical Details	Run No.	Treatment Conditions and Procedure	Fig. No.
2	2	-Impure ZnSO ₄ sol. -First addition of zinc dust ² -Co: 10 ppm + As ₂ O ₃ * with second addition of zinc dust ³	19,20	-3 times stoich. zinc dust ¹ -Residue not eliminated -First reaction time: 45 min. -Stoich. amount of As ₂ varied for each run -3 times stoich. amount of zinc dust ³ -Second step reaction time: 45 min.	5.5
			21,22		
2	2	-Impure ZnSO ₄ sol. + Co: 10 ppm + As ₂ O ₃ * -First addition of zinc dust ¹ -Second addition of zinc dust ³	23,24	-3 times stoich. zinc dust ² -Residue not eliminated -First step reaction time: 45 min. -3 times stoich. of arsenic -3 times stoich. of zinc dust ³ -Variable reaction times for second step	5.6
			25,26 27		
	2	-Impure ZnSO ₄ sol. + Co: 10 ppm + As ₂ O ₃ * -First addition of zinc dust ¹ -Second addition of zinc dust ³	28 29	-3 times stoich. amount of arsenic ² -3 times stoich. amount of zinc dust ¹ -First step reaction time: 45 min. -In Run #28 residue not eliminated -In Run #29 residue eliminated -3 Times stoich. amount of zinc dust ³ -Second reaction time: 45 min.	Table No. 5.2

Table 4.2
(Continued)

Treatment Carried Out at 60°C					
Set No.	No. of Steps	Chemical Details	Run No.	Treatment Conditions and Procedures	Fig. No.
	2	-Impure ZnSO ₄ sol. + Co: 10 ppm + KMnO ₄ for first step -Zinc dust ¹ for second step	32, 38	-3 times stoich. arsenic with respect to all impurities -KMnO ₄ addition until Eh (60°C): 1.0 volt -Reaction time 15 min. precipitate not eliminated -3 times stoich. amount of zinc dust ¹ -Two different reaction times for second step	5.7
3			33, 34 37	-2 times stoich. arsenic with respect to all impurities -KMnO ₄ addition until Eh (60°C): 1.0 volt -First step reaction time: 45 min. -Precipitate eliminated -3 times stoich. zinc dust ¹ -Second step reduction times: 0, 30, 45 min.	5.8
	3	-Impure ZnSO ₄ sol. + zinc dust ¹ for first step -Co: 10 ppm + As ₂ O ₃ * + KMnO ₄ for second step -Zinc dust ³ for third step	35, 36	-3 times stoich. amount of zinc dust ¹ -First reaction time: 45 min. -Residue eliminated (Soln. from Run No. 9) -3 times stoich. amount of arsenic ² -KMnO ₄ addition until Eh (60°C): 1.0 volt Second reaction time: 15 min. -3 times stoich. amount of zinc dust ³ -Two different reaction times for third step	5.9

Chapter 5

RESULTS

Two sets of contact reduction runs were performed as set forth in the schedule presented under Table 4.2. Set No. 1 was carried out to investigate the behavior of impurity removal when zinc dust alone was used. In Set No. 2 the role of arsenic as a reagent with regard to intermetallic compound formation during co-reduction with other ions by zinc was investigated. A third set of runs was carried out to investigate impurity removal by arsenate formation. The initial concentrations of the ten impurity elements were presented in the previous chapter under Table 4.1. The contact reduction procedures in Set Nos. 1 and 2 were carried out at 80°C and the procedures involving arsenate formation were run at 60°C.

Set No. 1 consisted of ten runs where the behavior of cadmium, cobalt and copper were observed in relation to the amount of zinc dust addition and the reaction time.

In Set No. 2 twenty runs were carried out to investigate:

- a) The role of arsenic as a reagent for removal of cobalt to low levels (<0.1 ppm.). This was

investigated with regard to the amount of arsenic used and the time of reaction.

- b) The effect of carrying out the treatment in two steps where the first step residue was eliminated.

In Set No. 3 there were seven runs. The principle of the treatment was the formation of arsenates by arsenic addition and oxidation with KMnO_4 . These tests examined:

- a) The effect of multiple steps in the treatment. Elimination of excess arsenic with zinc dust after arsenate precipitation with and without removal of the precipitate.
- b) Primary contact reduction with zinc dust alone, followed by arsenate formation and precipitate removal, and a third and final step where excess arsenic was removed by contact reduction with zinc.

In all of the sets, some runs were carried out where the solutions were doped with additional cobalt (10 ppm.) to increase the cobalt content of these solutions. The chemical analyses for all the runs are presented in Table 6.1 of Appendix 6. Stoichiometric calculations pertaining to these tests are provided in Appendices 3, 4, and 5.

5.1 CONTACT REDUCTION WITH ZINC DUST ALONE - SET NO. 1

The behavior of cadmium, copper and cobalt in the solution after treatment with zinc powder for 60 minutes and for different stoichiometric amounts of zinc dust are presented in Figure 5.1. These results indicate that as the stoichiometric amount of zinc dust is increased to the maximum amount studied (5 times), cadmium and cobalt concentrations are continuously decreased in the solution, and attain a value of 0.1 to 0.3 ppm. at the previously mentioned limit. However, in the case of copper a plateau is reached at around 0.1 ppm. once the stoichiometric amount of zinc is doubled. This behavior can be attributed to the cathodic area available for copper reduction attaining a maximum value. It is brought about by agglomeration of the zinc dust particles as a result of the cementation process where the deposited metal serves to bond clusters together.

Figure 5.2 shows the behavior of cadmium, cobalt and copper as a function of the time of reaction with three times the stoichiometric amount of zinc dust. Cadmium and copper attain a value of less than 0.1 ppm. at the end of twenty-five minutes after which re-solution appears to take place. Similarly, cobalt is reduced to about 0.2 ppm. at about forty minutes. Beyond this time

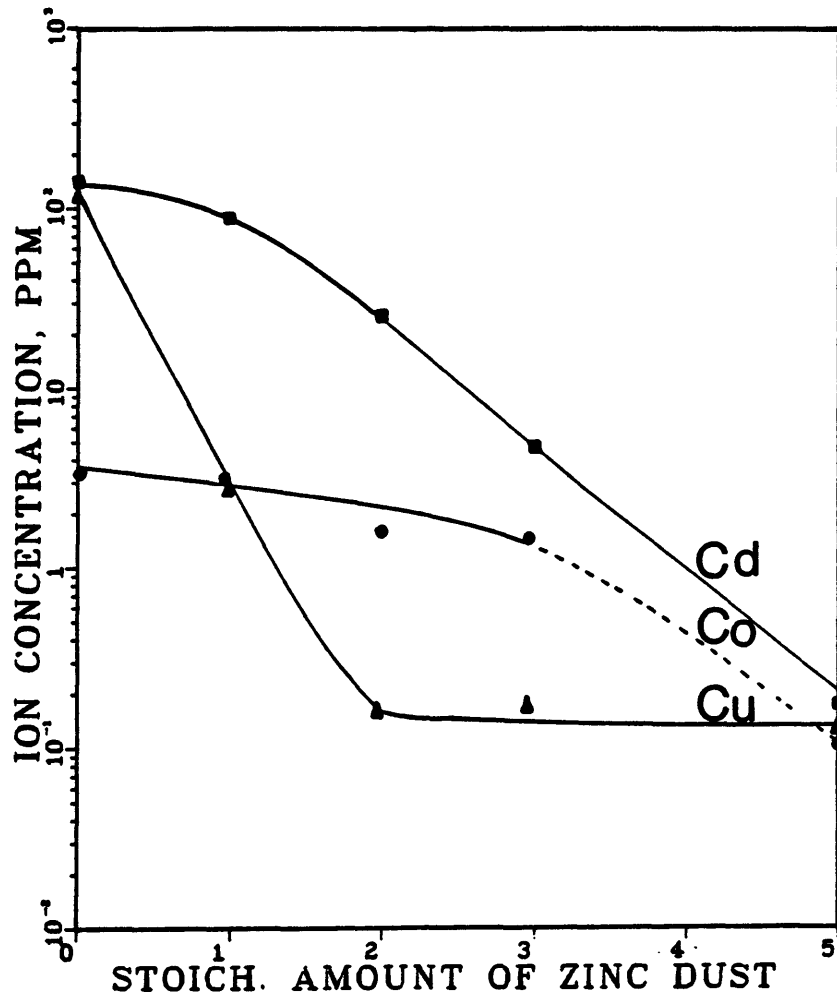


Figure 5.1 -- Effect of stoichiometric amount of zinc dust on the precipitation of cobalt, copper, and cadmium. Run Nos. 1,2,7A,5,9. Set No. 1. See Table 4.2.

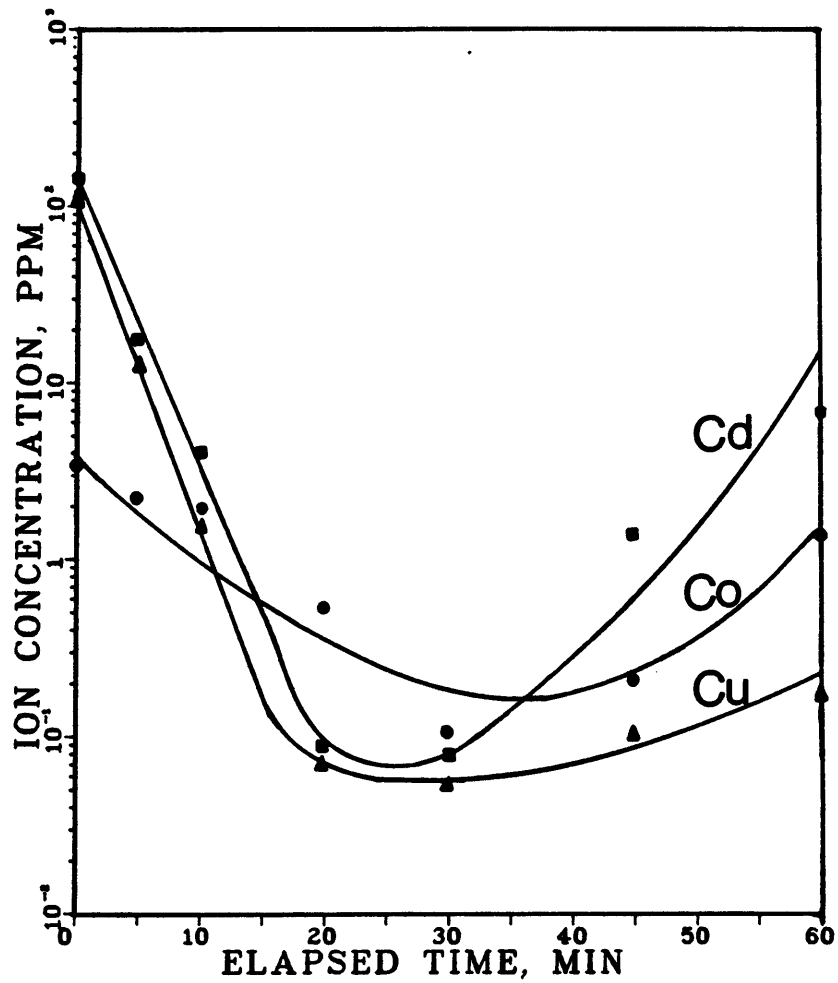


Figure 5.2 -- Variation of impurity concentration of cobalt, copper, and cadmium as a function of time. Three times stoichiometric zinc dust initial pH = 4.85 final pH: 5.3-5.8. Test Nos. 3,4,6,7,8. Set No. 1. See Table 4.2

resolution also takes place. It should be noted that the minima at twenty-five minutes and forty minutes cannot really be discriminated as being different, because of the lack of data points for cobalt. There are two plausible explanations for this behavior:

i) The components re-oxidize in the reactor after the zinc has been "used up."

ii) The components re-oxidize during the filtration step when the solution is decanted at the end of the run.

The zinc consumption and possible exhaustion should be considered in light of hydrogen co-reduction (the arsenic was not high enough for arsine formation), observed as bubbles during the runs.

5.2 CONTACT REDUCTION WITH ZINC DUST AND ARSENIC ADDITION - SET NO. 2

This set of experiments investigated the cementation of cobalt, copper and cadmium when trivalent arsenic solution (present as HAsO_2) was added simultaneously with zinc dust. In general there were two steps in the procedure. The arsenic was usually added in the second step after prepurification with zinc dust alone. The runs may be classified into those where the residue was not eliminated prior to the second step and those where it was.

The final runs were carried out where arsenic was added in the first step.

5.2.1. Arsenic Added to the Second Step. In all but two runs, this procedure was adopted. The residue was eliminated prior to the arsenic addition in runs 10 to 18, and was left in the prepurified solution during runs 19 to 27.

A) Residue Eliminated. In runs 10 to 13 the solution was first treated with zinc dust alone (3 times the stoichiometric amount with respect to all impurities present in the solution) for 45 minutes, after which the residue was eliminated by filtration and this prepurified solution was now treated a second time using arsenic and zinc dust. The results of using different amounts of arsenic in this second step are shown in Figure 5.3. The cobalt concentration appears to be unaffected by this treatment and the arsenic concentration increases as the arsenic addition increases.

The behavior may be attributed to two reasons:

i) At small amounts of arsenic, residual cadmium (see Figure 5.2) was not used in calculating the zinc dust requirements and the

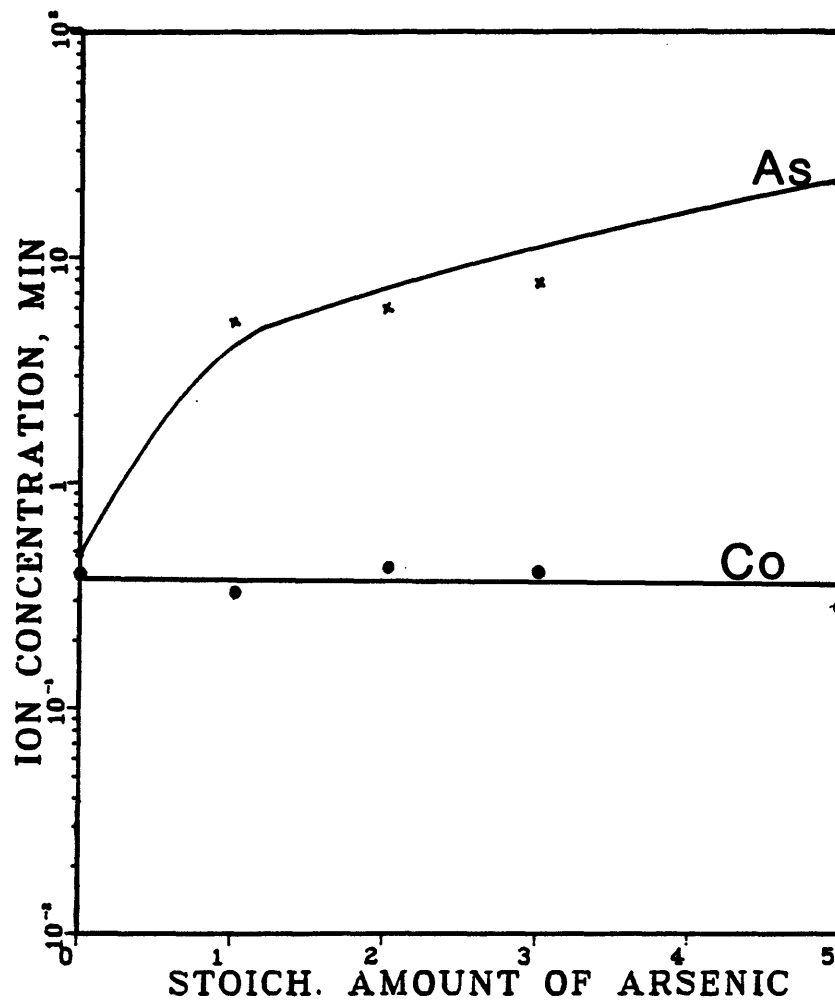


Figure 5.3 -- Effect of stoichiometric amount of arsenic for the second step after elimination of the residue of the first step. Set No.2. Run Nos. 11-13. See Table 4.2.

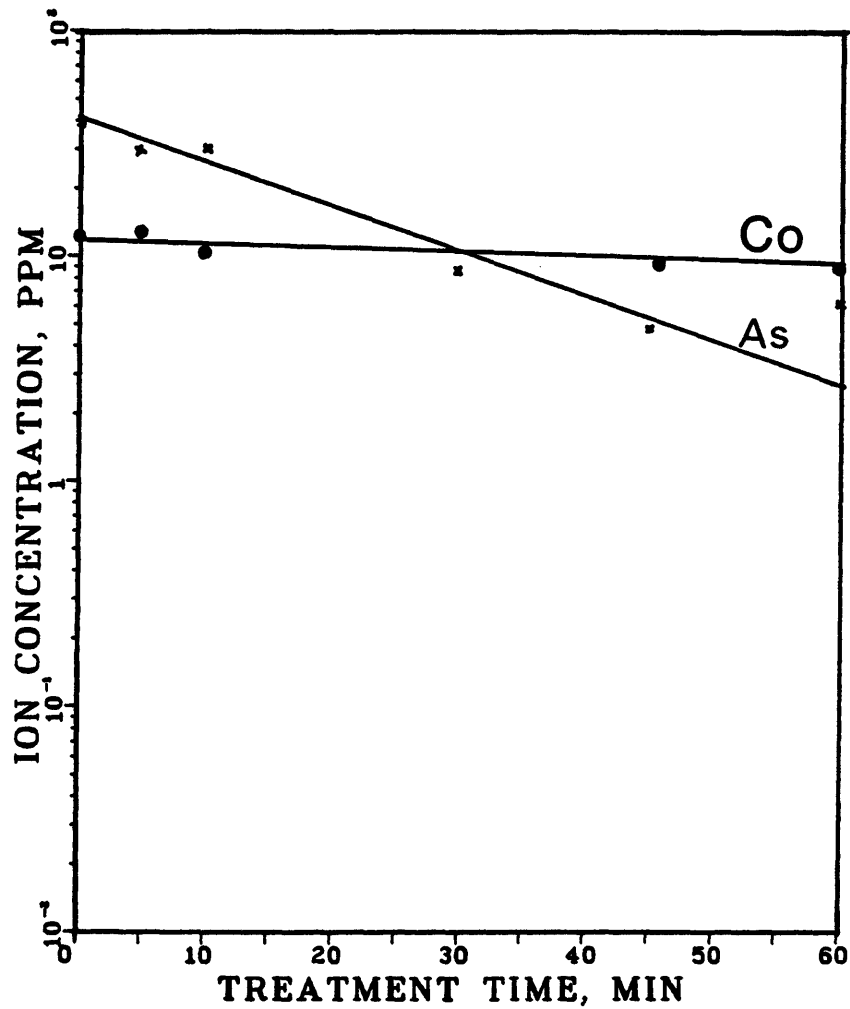


Figure 5.4 -- Variation of cobalt and arsenic concentrations as a function of treatment time for the second step in the two-step process of Set. No. 2 Tests. Run Nos. 14-18. See Table 4.2.

zinc may have been "used up" in precipitating this element together with arsenic.

ii) At higher amounts of arsenic, the arsenic deposit may completely cover the zinc dust and prevent further cementation.

The variations of Co and As are shown in Figure 5.4 for this second step treatment when three times the stoichiometric amount of arsenic was used. The prepurified solution in the runs was doped with 10 ppm. Co to give an initially higher concentration of cobalt. The cobalt concentration is unaffected by the treatment time; however, the arsenic added as a reagent is seen to decrease over the 60 minutes run time. This procedure was not pursued further since it was realized that a significant amount of zinc was still present in the eliminated residue, and could be effectively utilized by leaving it in place during the second step.

- B) Residue not Eliminated. Figures 5.5 and 5.6 present the behavior when the residue was not eliminated prior to arsenic addition. In these tests the prepurified solution of the first step was doped with 10 ppm. Co prior to the second step treatment.

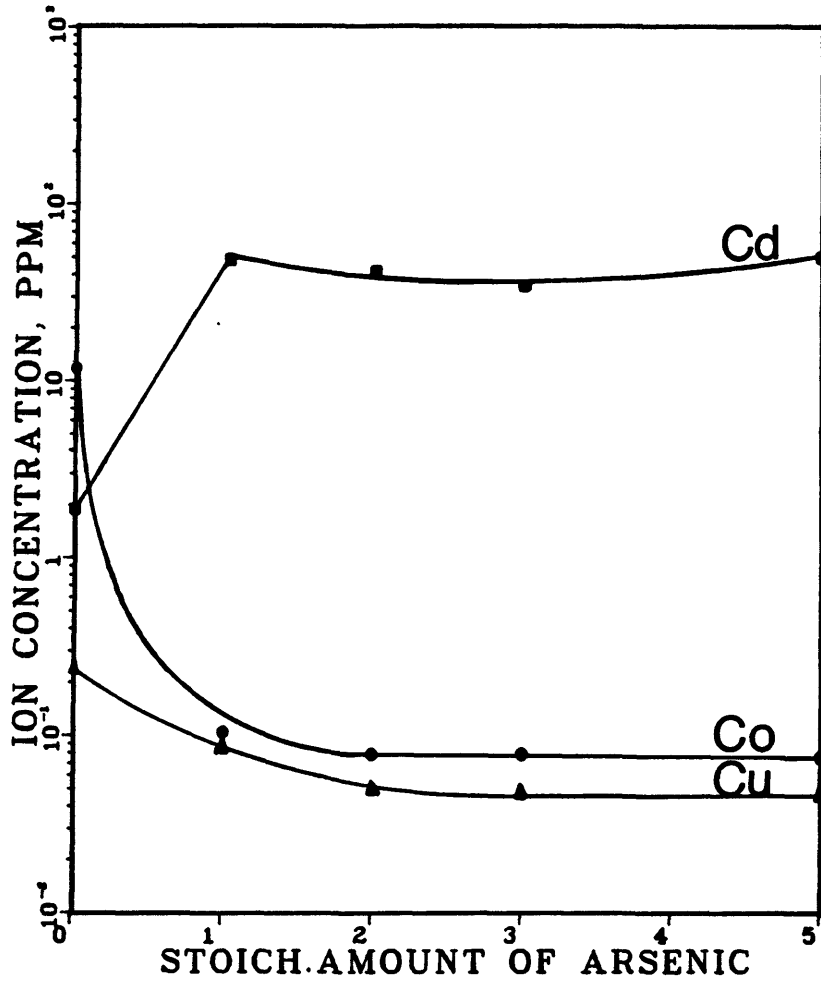


Figure 5.5 -- Effect of stoichiometric amount of arsenic on the precipitation of cobalt, copper, and cadmium when the residue is not eliminated. Set No. 2. Run Nos. 19-22. See Table 4.2.

The effect of arsenic addition in the second step treatment is shown in Figure 5.5 when the treatment time was set at 45 minutes. The cobalt and copper concentrations are not reduced any further once the arsenic addition exceeds twice the stoichiometric amount. This probably occurs as a result of "complete" arsenic elimination (<0.5 ppm.) during the time of treatment and no further elimination of either cobalt or copper as intermetallic compounds occurs at these low levels (approximately 0.1 ppm.). In addition, the high cadmium level (60 ppm.) cannot then be explained as being due to contact reduction of arsenic (by cadmium) and instead can only be attributed to cadmium re-solution with air in the reactor. The fixed treatment time may be the reason why the cadmium concentration is unaffected, if the average rate of the resolution is considered constant in each of these tests.

The effect of the treatment time on this second step is shown in Figure 5.6. The pre-purified solution was doped with 10 ppm. Co and three times the stoichiometric amount of

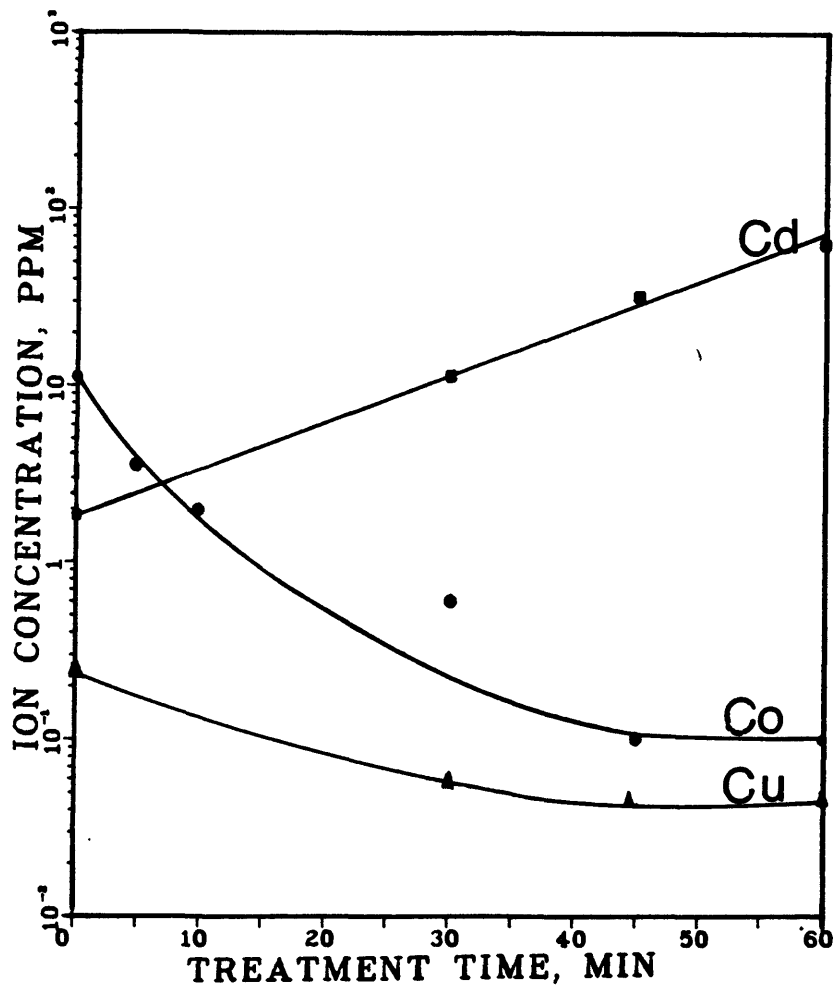


Figure 5.6 -- Variation of cadmium, cobalt, copper concentrations as a function of treatment time for the second step in the two-step process of Set No. 2. Run Nos. 23-27. See Table 4.2.

arsenic with respect to cobalt was used. Copper and cobalt are reduced to about 0.1 ppm. at the end of 45 minutes and no further reduction is obtained at 60 minutes. There is a continuous re-solution of cadmium where the reaction rate appears to be first order. This re-solution as stated previously, occurs as a result of oxidation of the deposited cadmium (some of which may become dislodged from the zinc dust) by oxidation with air in the reactor. The stability of cobalt and copper (when compared to the behavior in Figure 5.2) is probably due to these metals being co-reduced with arsenic to form intermetallic compounds which are not as readily oxidized.

5.2.2 Arsenic Added to the First Step. Two runs were carried out where the initial cobalt concentration of the impure zinc sulphate solution was increased by 10 ppm., and three times the stoichiometric amount of arsenic with respect to the total cobalt was then used. The amount of zinc dust added was based on all the impurities, including the additional cobalt and arsenic introduced into the solution. In the first step the reaction time was 45 minutes. In the second step the residue was

Table 5.1

FINAL CONCENTRATIONS OF Co, Cd, Cu AND As
AND pH - SET NO. 2

<u>Measurement</u>	<u>Residue Eliminated Run No. 29</u>	<u>Residue Not Eliminated No. No. 28</u>
Final pH	5.53	5.54
Cd	34.6 mgpl.	24.6 mgpl.
Cu	<0.01 mgpl.	0.01 mgpl.
Co	0.9 mgpl.	0.2 mgpl.
As	<0.5 mgpl.	<0.5 mgpl.

eliminated in one run and left in place in the other. Zinc dust used in this second step was based on "excess arsenic" assuming that arsenic in the first step was only used to precipitate cobalt. The treatment time was also 45 minutes.

The results of the two steps described previously are shown in Table 5.1. In retrospect the second addition of zinc and elimination of the residue were unwarranted. However, the analysis of the solutions from the previous runs were not available when this procedure was devised. Nevertheless, the results indicate that the elimination of copper is particularly good (<0.01 ppm.). The result for cobalt shows that by not eliminating the residue a final concentration of 0.2 ppm. is achieved. Cadmium concentration, as before, is high (25 - 30 ppm.) and is, no doubt, due to the long contact time during the second step.

5.3 ARSENATE PRECIPITATION - SET NO. 3

These procedures proved to be the least satisfactory of the schemes investigated. This was in part due to the low temperature (60°C) used for a final step, where it was perceived that excess arsenic (and other impurities remaining) would be eliminated by contact

reduction with zinc. Two types of procedure were tested:

i) precipitation of impurity elements as arsenates and

ii) precipitation of residual cobalt (from solutions prepurified with zinc powder) by forming cobalt arsenate.

5.3.1 Arsenate Formation in the Presence of All Impurity

Elements. Five runs were carried out. Two steps were employed in the over-all procedure for each run. In two tests the precipitate was not eliminated prior to the second step where residual arsenic was eliminated by contact reduction with zinc. In the remaining three the precipitate was discarded prior to this second step.

A. Precipitate not Eliminated. The results are shown in Figure 5.7. Displayed also is the $E_{h_{25^{\circ}C}}$ of the solutions. In these tests arsenic was first added to the solution at three times the stoichiometric amount based on precipitation of cobalt. It should be noted that the cobalt concentration was increased by 10 ppm. prior to the run. Potassium permanganate was then introduced, once the solution was at

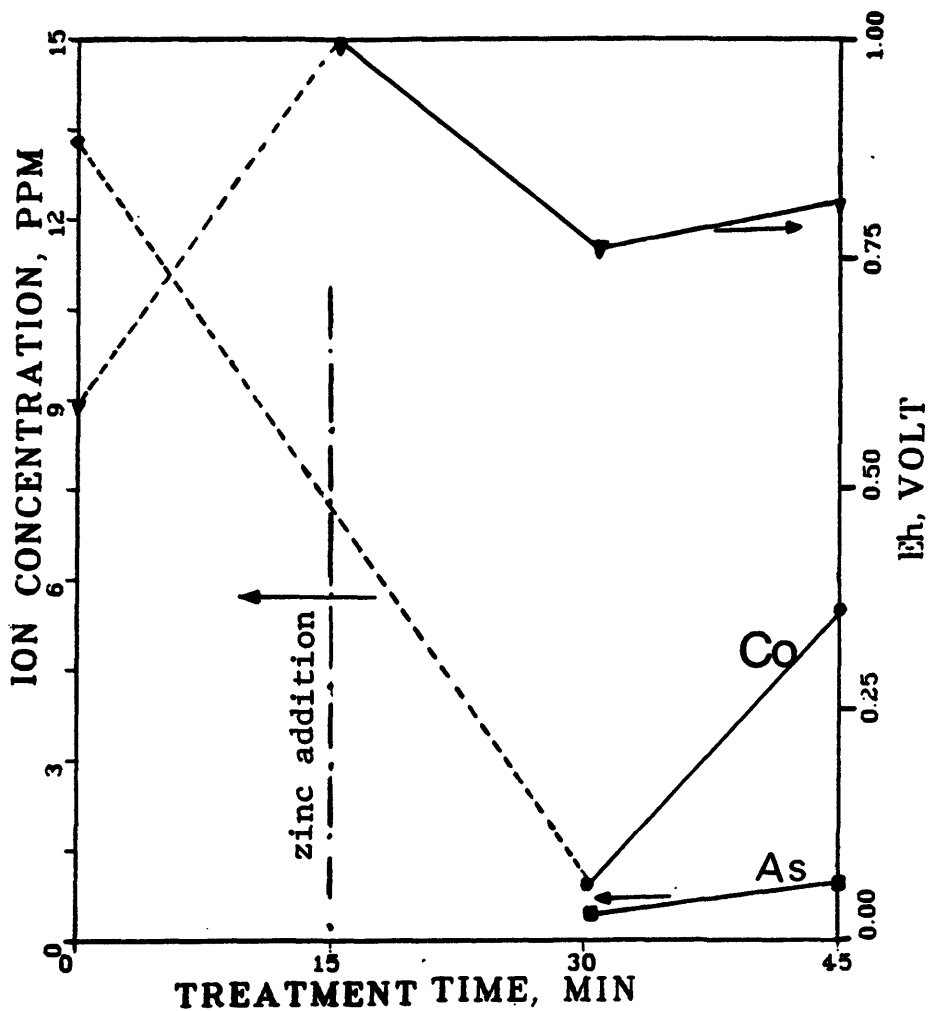


Figure 5.7 -- Variation of cobalt concentration as a function of treatment time in the two-step process of Set No. 3 when zinc dust is added without removal of precipitate from arsenic - KMnO_4 treatment. Run Nos. 32,38. See Table 4.2.

temperature (60°C), to obtain an $E_{h_{60^{\circ}\text{C}}}$ of approximately 1.0 volt. About 80 μl of 0.5 M KMnO_4 solution was added. The approximate amount needed was determined by a previous exploratory run.

The system was allowed to react for 15 minutes after which zinc dust was added and allowed to react for a further 15 minutes in Run 38 and 30 minutes in Run 32. The cobalt impurity level was approximately 1 ppm. in Run 38 but re-resolution takes place in Run 32 at the end of 45 minutes. The arsenic level at the end of 30 minutes was <0.5 ppm. and some re-resolution occurs over the next 15 minutes. The $E_{h_{25^{\circ}\text{C}}}$ in the system is seen to decrease at first and increased as the re-resolution occurred. The exact reason for this is not apparent, since it is not clear which redox reaction in the system is responsible for the potential on the platinum electrode once zinc is added.

- B. Precipitate Eliminated. In Runs 33, 34 and 37 arsenic was added at two times the stoichiometric amount based on all impurities. The potassium permanganate addition was now about

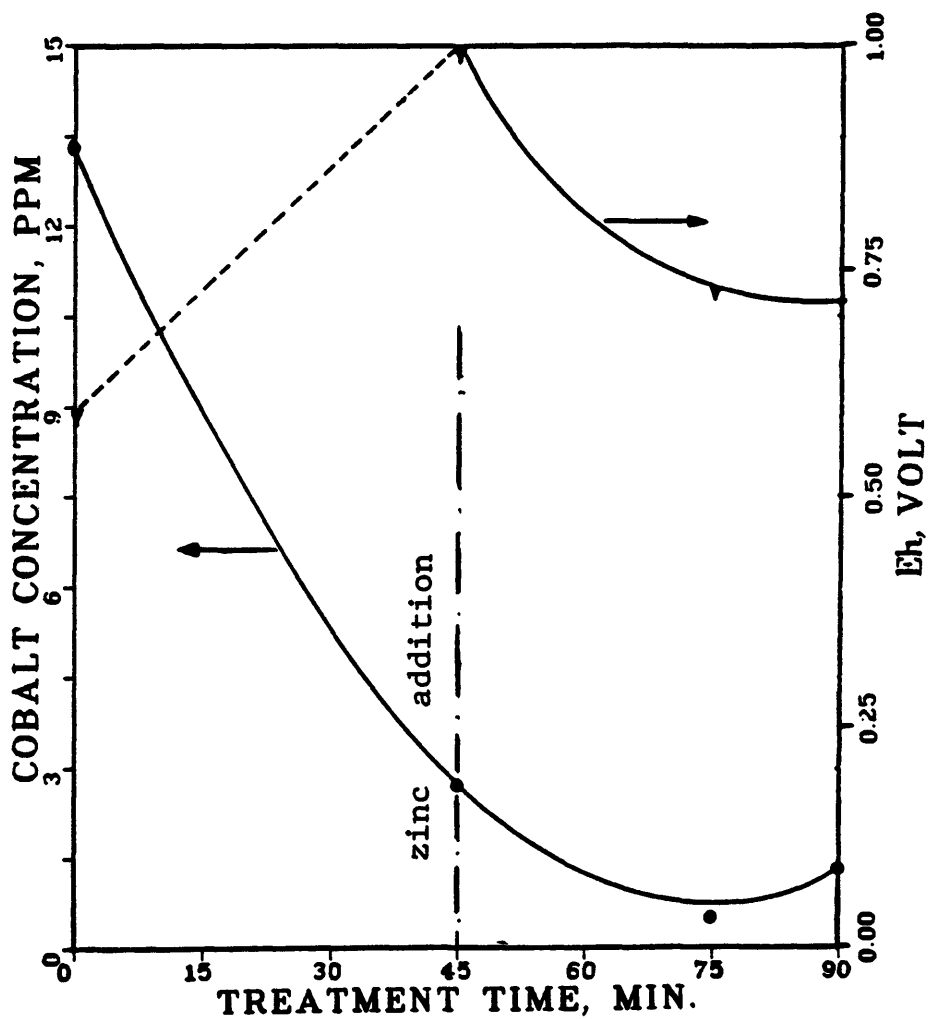


Figure 5.8 -- Variation of cobalt concentration as a function of treatment time when the first step precipitate is eliminated prior to zinc dust addition. Set. No. 3. Test Nos. 33,34,37. See Table 4.2.

2.8 ml., in order to attain an $E_{h_{60^{\circ}C}}$ of 1.0 volt. After a first step reaction time of 45 minutes, the solution was filtered and the filtrate re-processed with zinc dust as noted under Table 4.2. The cobalt concentrations at the end of 45, 75, and 90 minutes are shown in Figure 5.8. The cobalt concentration at 45 minutes was decreased to less than 0.5 ppm. and at 90 minutes re-increased to about 1 ppm.. The arsenic concentration (now shown but listed in Table A-6.1) in this period decreased from about 250 ppm. at 45 minutes to less than 0.5 ppm. at 75 minutes and thereafter. It should be noted that the arsenic concentration before zinc dust addition represents the amount of excess arsenic which was added to the system. This fact, however, appears to be solely fortuitous since, surprisingly, both the cadmium and copper concentrations were still high (126 ppm. and 99 ppm., respectively--see Table A-6.1.)

As an additional point, it should be recalled that the precipitation of zinc arsenate is thermodynamically probable, although it would appear that its rate of precipitation is

rather low as evidenced by the relatively large arsenic concentration at the end of 45 minutes prior to the zinc dust addition (Run No. 33).

The $E_{h_{25^{\circ}C}}$ is seen to decrease continuously.

5.3.2 Cobalt Arsenate Precipitation. The final runs in this set relating to arsenate formation were conducted with prepurified solutions similar to those obtained in Run No. 9 by contact reduction with zinc. Arsenic was added based on the cobalt in solution which for the purposes of these runs were increased by doping with 10 ppm.. As before $KMnO_4$ solution was added to increase the $E_{h_{60^{\circ}C}}$ to 1 volt.

After an initial reaction period of 15 minutes, zinc dust was added in an amount corresponding to three times the stoichiometric amount based on excess arsenic. The results obtained for the concentrations of cobalt and arsenic for this third treatment are shown in Figure 5.9. The cobalt concentration is still about 8 ppm. and increases at the end of 30 minutes to 9 ppm. Similarly arsenic which is present at less than 0.5 ppm. at 15 minutes increases to 1.7 ppm. at 30 minutes.

It is interesting that the $E_{h_{25^{\circ}C}}$ also shows an increase between 15 and 38 minutes. It may well

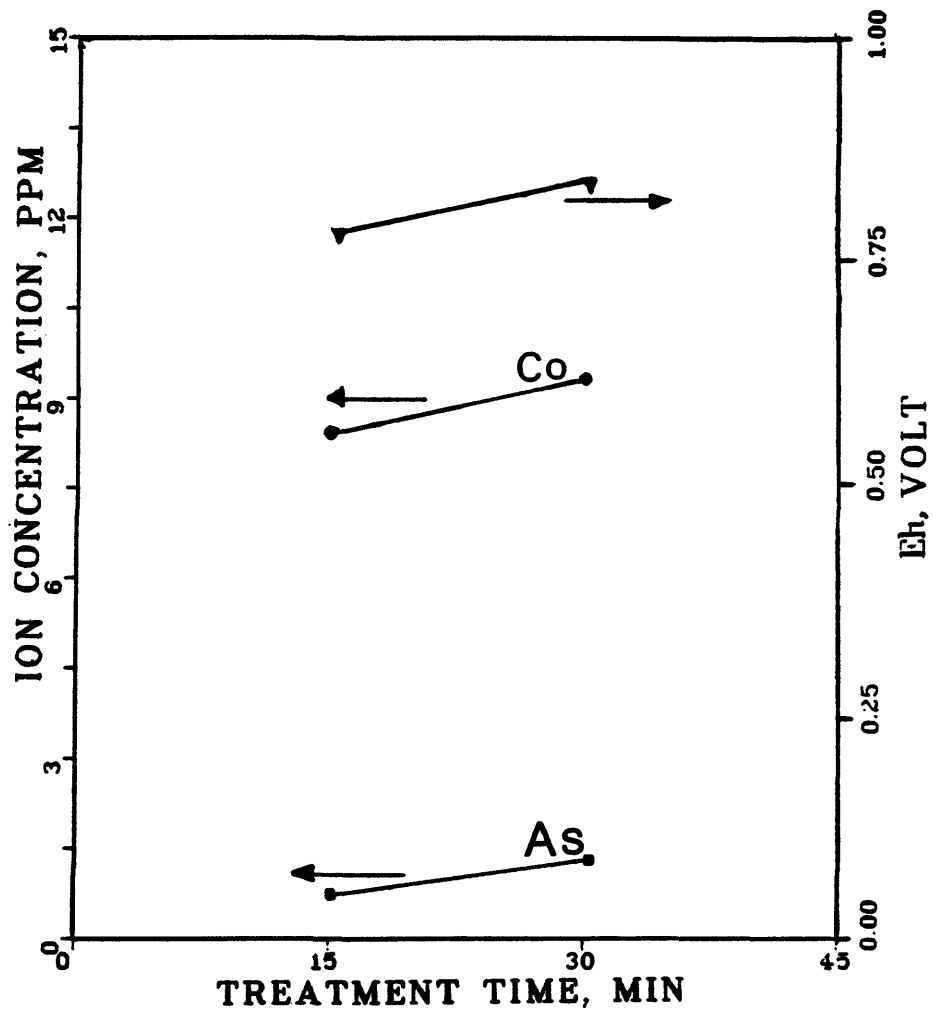


Figure 5.9 -- Variation of cobalt concentration as a function of treatment time in the third step in the three-step process of Set. No. 3 Test. Run Nos. 35-36. See Table 4.2.

be, that the manganese dioxide (probably non-stoichiometric $(\text{MnO}_{1.8})$) precipitated during the oxidation treatment (see Equation 3.45) and still present in the solution may be responsible for this behavior. It is also likely that the same is true of similar behavior seen in Figure 5.7.

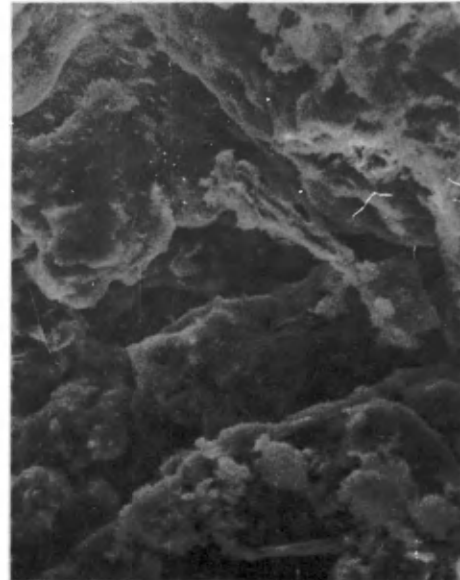
5.4 CONFIRMATION TEST

It was apparent from the preceding results that the purification schemes using zinc dust offered more promise. Consequently a number of confirmation tests was carried out in order to demonstrate the reliability of these procedures. Eight runs were, therefore, carried out and the results are shown in Table 5.2. The runs were classified into two types--four runs using zinc dust alone and four where zinc dust and arsenic were used. Also in two of each of the four runs the impure stock solution was doped with an additional 10 ppm Co.

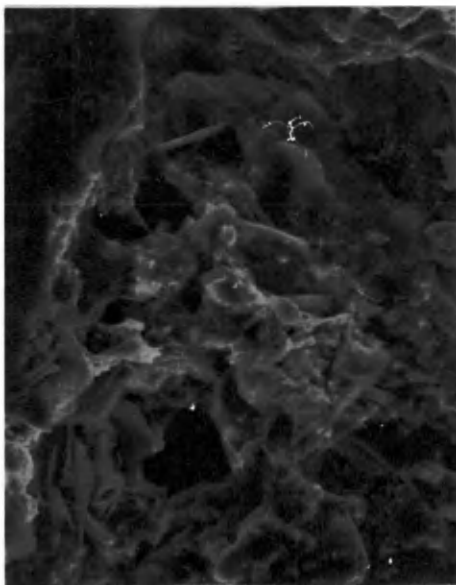
The filtered residues from these runs were subsequently examined by Scanning Electron Microscopy and photomicrographs obtained. The S.E.M. photographs do not appear to show marked differences between the different procedures. These photomicrographs are shown in Figure 5.10. However, the "filter cake" of the runs



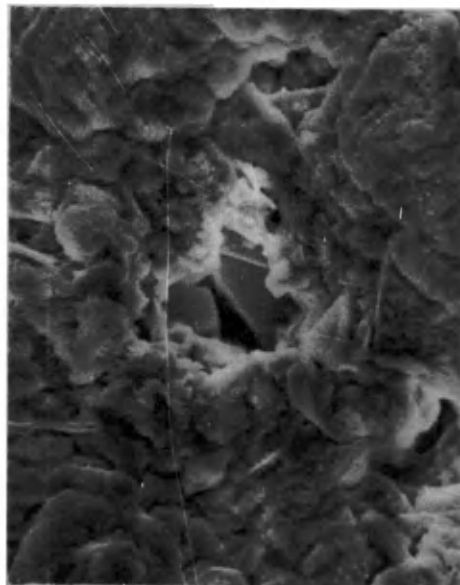
1a. Zinc Alone -- 4ppm Co .



2a. Zinc + Arsenic -- 4 ppm Co



1b. Zinc Alone -- 10 ppm Co .



2b. Zinc + arsenic -- 10 ppm Co

Figure 5.10. S.E.M. Photomicrographs of Confirmation Runs. 1 inch \equiv 34 μ m.

with arsenic, when observed with the unaided eye immediately after filtering, were black in color, whereas they were silvery when arsenic was not used. Also, it was noted that once arsenic was added to the system the zinc particles began to cluster and change to the black color mentioned previously. Photographs of the "filter cakes" are shown in Figure 5.11. Again no dramatic differences can be discerned.

5.4.1 Zinc Dust Alone. Runs 40 and 42 were carried out using the impure stock solution. The analyses for arsenic yielded values for concentration which were higher than were present in the original stock solution and could not be explained. Re-analysis of Run No. 40 did not resolve the situation. Runs 40 and 42 were replicates of the same run; however, the results obtained were drastically different. The results for Run 42 are closer to the values of concentrations of Cd, Cu and Co obtained previously and which were presented in Figure 5.2. The very low cobalt concentration for Run 42 was particularly remarkable.

In the doped runs (41 and 45) the agreement between the concentrations of Cd, Cu and Co was reasonable, but the cobalt concentrations (2 and 4 ppm.) appear to be rather high.

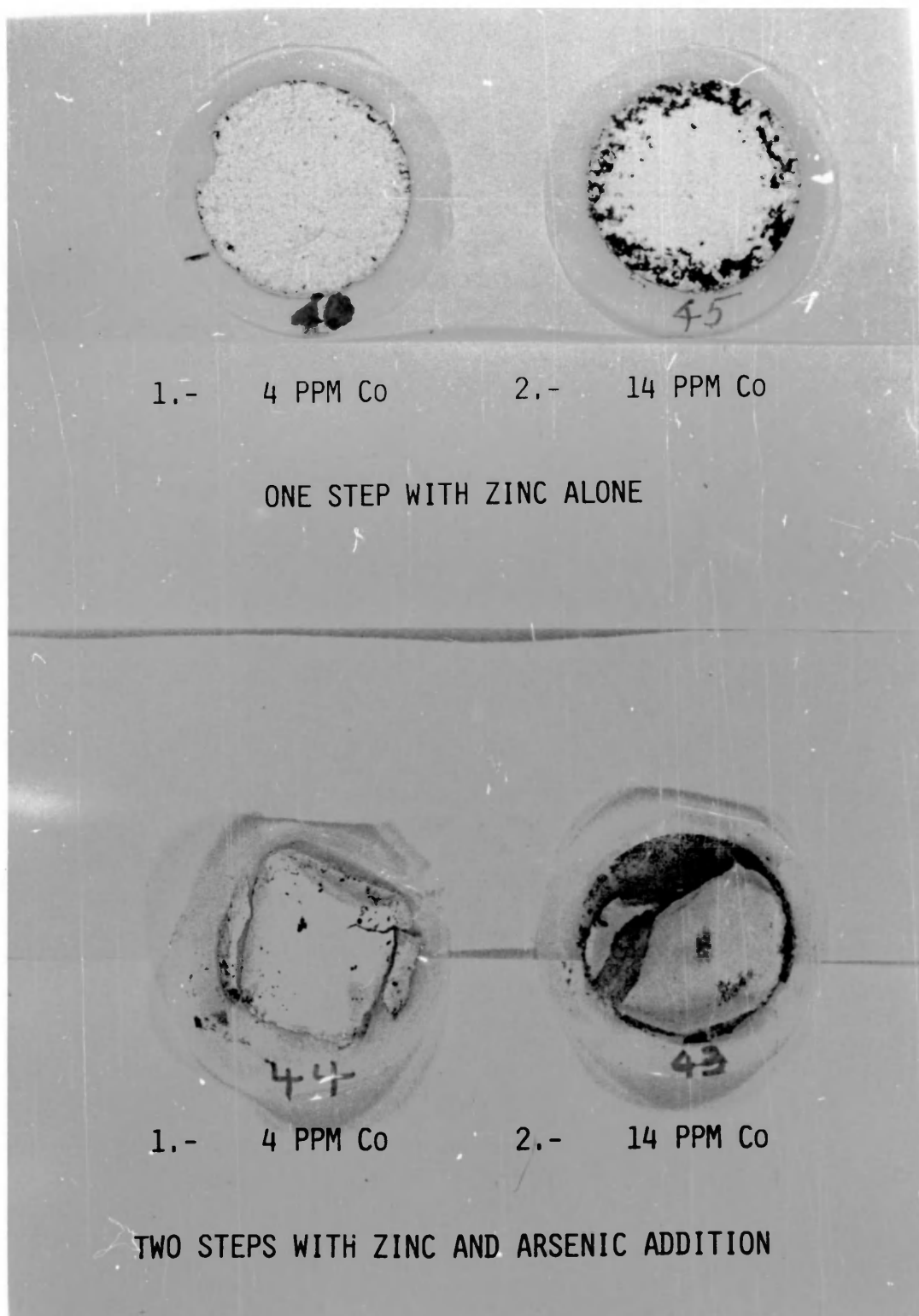


Figure 5.11. Photographs of "filter cakes" on cellulose filters. 47 mm filter and 35 mm diameter "cakes".

5.4.2 Two Steps - Zinc Dust Followed by Zinc Dust and Arsenic. These runs were satisfactory both in terms of reproducibility and the final levels of As, Cd, Co and Cu. As already discussed, the high cadmium could perhaps be avoided by using a short treatment time in the second step. The agreement with results previously presented in Figure 5.6 was also satisfactory. Except for cadmium the impurity levels of As, Cu and Co are acceptable for zinc electrowinning.

5.5 FINAL CONCENTRATIONS OF LOW LEVEL IMPURITIES

The final concentration levels for the low level impurities -- antimony, germanium, tellurium, selenium, nickel and iron (in some runs arsenic as well) -- could not be determined so as to assess the degree to which they were removed. This limitation was imposed by the analytical method available for these determinations -- flame and graphite furnace Atomic Absorption Spectrophotometer. For Ge this was < 1 ppm, for As and Sb < 0.5 ppm and for Fe, Ni, Se and Te it was < 0.1 ppm.

Chapter 6

CONCLUSION

This final chapter summarizes the results of the investigation carried out and presents conclusions based on these findings. Suggestions for further work make up the last section.

6.1 DISCUSSION AND CONCLUSIONS

This investigation has examined the problem of impurity elimination from zinc sulphate solutions in regard to the specifications required for zinc electro-winning. Of the several techniques available the most promising appears to be contact reduction (cementation) with zinc dust in the presence of added arsenic, so as to form intermetallic compounds. Although cementation processes have been widely studied during the last twenty years, very little fundamental work on co-reduction of ions has been attempted. In addition, the mass transfer phenomena associated with very small diameter particulate precipitant are not entirely

understood. The role of turbulent eddies which are of the same size as the particles as well as agglomeration due to bridging brought about by the deposited impurity metal, is still another area which has received little attention.

The laboratory tests carried out to evaluate the various procedures have provided only limited insight into the behavior of these complex systems. It was conceived as an attempt to demonstrate some of the existing schemes in use industrially, under ideal conditions. Although the approach does not address the problems of mixing in the reactor and filtration of the contact reduced metal impurities (or precipitates), it can nevertheless allow these problems to be identified and subsequently assessed in cases where poor industrial performance is contradictory to the present findings.

The results of the laboratory tests using the three techniques selected are summarized below:

- i) Contact Reduction with Fine Dust Alone. The results of these tests indicate that using zinc dust alone at a temperature of 80°C will allow Co, Cd, Cu and As to be removed to low levels of concentration (<0.1 ppm) which would be acceptable for zinc electro-winning. However, re-solution of these

contact reduced impurities presents a serious problem of process control. Reasons for the resolution behavior were presented in Chapter 5.

- ii) Contact Reduction with Zinc Dust on Arsenic Addition. This technique was the most successful of the three tested. Arsenic was added to the system as a second step in the procedure. The formation of intermetallic compounds of Co, and Cu with arsenic, apparently, is responsible for stabilizing these impurities once they are contact reduced. However, re-resolution of cadmium still occurs. This behavior may be attributed to contact reduction of excess arsenic by dislodged particles of cadmium and also dissolution of these particles in the reactor. There appears to be no advantage in removing the first residue of contact reduced impurities before addition of arsenic. In fact the morphology of this "first residue" appears to offer distinct advantages with regard to Co and Cu removal. The cadmium resolution problem, it is felt, can be solved

either by proper control of the treatment time and/or a suitable addition of zinc dust in the final step of the treatment.

iii) Oxidation with KMnO_4 to Form Arsenates.

These procedures proved to be the least satisfactory. This was in part due to the low reaction temperature of the treatment (60°C). The results of the tests were therefore inconclusive. However it should be pointed out that zinc arsenate precipitation is likely to make this approach untenable.

The removal of low level impurities in the system could not be assessed because of insufficient sensitivity of the Atomic Absorption Spectrophotometric methods available. Thus, questions relating to Fe, Ni, Sb, Ge, Se and Te cannot be resolved.

6.2 RECOMMENDATIONS FOR FURTHER WORK

The following items are recommended for further work.

- i) Optimize the purification scheme where zinc dust and arsenic are used. This, in terms of reagent addition and reaction time. It

should be recalled that the "first residue" should not be eliminated.

- ii) The behavior of the low level impurities mentioned previously needs to be ascertained. In this connection the removal of nickel as intermetallic compound with arsenic would be of particular interest.
- iii) With regard to (i) the mechanism of cadmium reappearance in the solution might warrant separate study.

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APPENDIX 1

TABLES OF THERMODYNAMIC PROPERTIES
AND STANDARD HALF-CELL POTENTIALS

TABLE A1.1

Standard Free Energy of Formation ΔG_f° the Standard Entropies, S° and Heat Capacity at 298°K for interpolation of Standard Free Energies to high temperatures in the range $298^\circ\text{K} - 448^\circ\text{K}$

(Data taken from references 50, 51, 56, 57)

Formula	ΔG_{298}° Kcal/mole	S_{298}° cal/mole $^\circ\text{K}$	C_{p298}° cal/mole $^\circ\text{K}$
As	0	8.40	$5.23 + 0.00222T$
HAsO ₂	- 96.25		
Sb	0	10.50	$5.51 + 0.00174T$
HSbO ₂	- 97.50		
Cd	0	12.30	$5.31 + 0.00294T$
Cd ⁺⁺	- 18.50	-14.60	
Co	0	6.80	$4.72 + 0.0043T$
Co ⁺⁺	12.80	-27	
Co ⁺⁺⁺	28.90	-15	
Cu	0	7.96	$5.41 + 0.0015T$
Cu ⁺⁺	15.53	-23.6	
Ge	0	10.14	$5.98 + 0.00082T$
H ₂ GeO ₃	-186.80		
Fe	0	6.49	$3.37 + 0.00710T$
Fe ⁺⁺	- 20.30	-27.10	
Fe ⁺⁺⁺	- 2.52	-70.1	
Ni	0	7.20	$4.06 + 0.00704T$

Formula	ΔG_{298}° Kcal/mole	S_{298}° cal/mole $^{\circ}$ K	C_{P298} cal/mole $^{\circ}$ K
Ni ⁺⁺	- 11.53	-12.65	
Se	0	10.00	4.53 + 0.00550T
HSeO ₃ ⁻	- 98.30	39.90	
Te	0	11.80	4.58 + 0.00525T
HTeO ₃ ⁻	-104.34	41.50	
Pb	0	15.51	5.82 + 0.00190T
Pb ⁺⁺	- 5.81	5.10	
Sn	0	12.30	4.42 + 0.00630T
Tl	0	15.40	5.26 + 0.00346T
Tl ⁺⁺	- 7.76	-12.50	
Zn	0	9.95	5.35 + 0.00240T
Zn ⁺⁺	- 35.18	-25.45	
Sn ⁺⁺	- 6.28	5.90	
Cu ₂ O	- 34.98	10.40	14.90 + 0.00570T
H ₂ O	- 56.69	16.72	18.03
H ⁺	0	0	23

TABLE A1.2

Summary of Entropy Constants for Eq. 3.20 (in cal. mole⁻¹ deg.⁻¹)
(taken from reference 47)

T, °C	Cations, X ⁺		Anions & OH ⁻		X ⁻		Oxy anions, XO _n ^{-m}		Acid oxy anions, XO _n (OH) _l ^{-m}		Std. state entropy of H ⁺ (aq)		
	a _(T)	b _(T)	a _(T)	b _(T)	a _(T)	b _(T)	a _(T)	b _(T)	a _(T)	b _(T)	a _(T)	b _(T)	
25	0	1.000	0	1.000	0	1.000	0	1.000	0	1.000	0	1.000	-5.0
60	3.9	0.955	-5.1	0.969	-14.0	1.217	-13.5	1.380	-13.5	1.380	-13.5	1.380	-2.5
100	10.3	0.876	-13.0	1.000	-31.0	1.476	-30.3	1.894	-30.3	1.894	-30.3	1.894	2.0
150	16.2	0.792	-21.3	0.989	-46.4	1.687	-50.0*	2.381*	-50.0*	2.381*	-50.0*	2.381*	6.5
200	23.9*	0.711*	30.2*	0.981*	-67.0*	2.020*	-70.0*	2.960*	-70.0*	2.960*	-70.0*	2.960*	11.1*

* These constants were estimated by extrapolation of corresponding values of a_(T) and b_(T) from lower temperatures and are subject to greater error.

TABLE A1.3

Summary of Heat Capacity Constants for Equation 3.23

(taken from reference 47)

T, °C	Cations, X ⁺		Anions & OH ⁻		Oxy anions, XO _n ^{-m}		Acid oxy anions, XO _n (OH) ^m _l		H ⁺ C _p ^T J ²⁵
	α(T)	β(T)	α(T)	β(T)	α(T)	β(T)	α(T)	β(T)	
60	35	-0.41	-46	-0.28	-127	1.96	-122	3.44	23
100	46	-0.55	-58	0.00	-138	2.24	-135	3.97	31
150	46	-0.59	-61	-0.03	-133	2.27	-143*	3.95*	33
200	50*	-0.63*	-65*	-0.04*	-145*	2.53	-152*	4.24*	35*

* These values are derived from extrapolated values of the corresponding entropy terms from lower temperatures and are thus subject to greater error.

TABLE A1.4
Standard Half-cell Potentials in Aqueous
Reduction at Different Temperatures

Half-cell Reaction	E_T° (volts)			
	25°C	60°C	100°C	150°C
As ³⁺ /As	1.391	1.370	1.342	1.302
Sb ³⁺ /Sb	1.401	1.388	1.360	1.390
Cd ²⁺ /Cd	-0.403	-0.378	-0.357	-0.337
Co ²⁺ /Co	-0.277	-0.253	-0.231	-0.212
Co ³⁺ /Co	0.408	0.377	0.324	0.249
Cu ²⁺ /Cu	0.337	0.362	0.383	0.402
Fe ²⁺ /Fe	-0.440	-0.415	-0.394	-0.375
Fe ³⁺ /Fe	0.036	0.077	0.130	0.205
Ge ⁴⁺ /Ge	2.052	2.017	2.006	2.001
Ni ²⁺ /Ni	-0.250	-0.225	-0.204	-0.184
Pb ²⁺ /Pb	-0.126	-0.110	-0.080	-0.060
Se ⁴⁺ /Se	1.066	1.058	1.047	1.042
Sn ²⁺ /Sn	-0.136	-0.111	-0.090	-0.071
Te ⁴⁺ /Te	1.131	1.123	1.112	1.107
Tl ²⁺ /Tl	-0.340	-0.280	-0.199	-0.087
Zn ²⁺ /Zn	-0.763	-0.739	-0.717	-0.697

TABLE A1.5

SELECTED VALUES OF SOLUBILITY PRODUCTS
AT 25°C FOR ARSENATES

Formula	Solubility Product
$\text{Ni}_3(\text{AsO}_4)_2$	3.09×10^{-29}
$\text{Cu}_3(\text{AsO}_4)_2$	7.59×10^{-36}
$\text{Zn}_3(\text{AsO}_4)_2$	1.07×10^{-27}
$\text{Mn}_3(\text{AsO}_4)_2$	1.09×10^{-29}
FeAsO_4	5.75×10^{-29}
$\text{Co}_3(\text{AsO}_4)_2$	7.59×10^{-29}
$\text{Cd}_3(\text{AsO}_4)_2$	2.19×10^{-33}
$\text{Pb}_3(\text{AsO}_4)_2$	4.07×10^{-36}

APPENDIX 2
 FORMATION OF INTERMETALLIC COMPOUNDS
 WITH ARSENIC BY CONTACT REDUCTION

Simultaneous reduction of certain metal ions (Co, Ni) together with arsenic can lead to intermetallic compounds. The consequences of their formation is now examined from a thermodynamic point of view. It should be realized that in addition to any thermodynamic benefits, the electrode kinetics of these compounds may also be important in preventing re-resolution of impurities.

CoAs Intermetallic Compound



Using Tables A1.1 and A2.5, we get:

$$\Delta G_{298}^{\circ} = 111.27 \text{ Kcal/mole}$$

The equilibrium constant at 298°K is obtained from:

$$\Delta G^{\circ} = -RT \ln K \quad \text{A2.2}$$

Therefore, $\log K_{298} = 81.57$

and $K_{298} = 3.733 \times 10^{81}$

To determine the cobalt concentration at equilibrium the

the activity coefficients are assumed equal to 1. the activity will then be equal to the concentration of the ions, thus:

$$K = \frac{[Zn^{++}]^{2.5}}{[HAsO_3] [H^+]^3 [Co^{++}]} \quad A2.3$$

The following concentration values are considered in order to estimate the cobalt concentration in this system.

$$\begin{array}{ll} Zn^{++} = 140 \text{ g/l} & [Zn^{++}] = 2.15 \\ pH = 5.45 & [H^+] = 3.54 \times 10^{-6} \\ As = 38 \text{ ppm} & [HAsO_2] = 5.06 \times 10^{-4} \end{array}$$

where we get:

$$[Co^{++}] = 8.03 \times 10^{-62} \text{ mol/l}$$

NiAs Intermetallic Compound

To determine the equilibrium concentration for nickel in the Ni, $HAsO_2/Zn$ system, the previous method may be used:



Using Tables A1.1 and A2.5 we get:

$$\Delta G_{298}^{\circ} = -109.79 \text{ Kcal/mole}$$

and the equilibrium constant at $298^{\circ}K$ is obtained from:

$$\Delta G = -RT \ln K \quad A2.5$$

Hence, $\ln K_{298} = 185.41$

and $K_{298} = 3.325 \times 10^{80}$

For determining the nickel equilibrium concentration at equilibrium the activity coefficients are assumed equal to 1. Therefore, the activity will be equal to the concentration of the ions, thus:

$$K = \frac{[\text{Zn}^{++}]^{2.5}}{[\text{HAsO}_2] [\text{H}^{+3}] [\text{Ni}^{++}]} \quad \text{A2.5}$$

The following concentrations values are considered to determine the nickel concentration in the system.

$\text{Zn}^{++} = 140 \text{ g/l}$	$[\text{Zn}^{++}] = 2.15$
$\text{pH} = 5.45$	$[\text{H}^{+}] = 3.54 \times 10^{-6}$
$\text{As} = 38 \text{ ppm}$	$[\text{HAsO}_2] = 5.06 \times 10^{-4}$

Applying these values the equilibrium concentration for nickel is:

$$[\text{Ni}^{++}] = 1.01^{-60} \text{ mol/l}$$

TABLE A2.1

Thermodynamics Values for Co-As and Ni-As
 Precipitation as Intermetallic Compounds
 at 25°C of Temperature

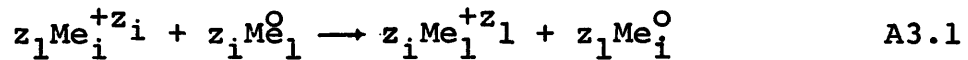
(Taken from references 55 and 56)

Intermetallic Compounds	ΔG_{298}° kcal/mole	H_{298}° kcal/mole	S_{298}° cal/mole
NiAs	-16.23	-17.20 \pm 0.90	12.40 \pm 2.70
CoAs	-18.98	-13.60 \pm 1.50	15.40 \pm 1.00

APPENDIX 3

STOICHIOMETRIC ZINC DUST REQUIREMENTS

The overall contact-reduction is given by the following equation:



where $\text{Me}_i^{+z_i}$ may be Cd, Cu, Co, Ni, Fe, Ge, Te, Se, Sb, or As and M_1 is zinc dust.

The mass stoichiometric ratio for a particular impurity is:

$$\text{M.S.R.} = \frac{z_i \text{M}_1}{z_1 \text{M}_i} \quad \text{A3.2}$$

where M_1 is the molecular weight of zinc

M_i is the molecular weight of the ion

$[\text{Me}_i^{+z_i}]$ is the mass concentration (mg/l) of any impurity.

Then, the mass stoichiometric amount of zinc dust for any impurity will be:

$$m_{\text{Zn}} = [\text{Me}_i^{+z_i}] \frac{z_i \text{M}_1}{z_1 \text{M}_i} ; \text{ mg zinc dust of soln.} \quad \text{A3.3}$$

For example, in the case of cadmium cementation onto zinc the required amount of zinc dust to precipitate cadmium

would be obtained as follows:

$$[\text{Cd}^{++}] = 200 \text{ mg/l}$$

$$M_i = \text{molecular weight of cadmium} = 112.4$$

$$M_1 = \text{molecular weight of zinc} = 65.4$$

$$z_1 = z_i = 2$$

Then, the stoichiometric amount of zinc to precipitate cadmium would be:

$$m_{\text{Zn}} = (200 \text{ mg/l}) \frac{2 \times 65.37}{2 \times 112.40}$$

$$m_{\text{Zn}} = 116.30 \text{ mg zinc dust/liter of sol.}$$

Thus, 116.30 mg of Zn is required to precipitate 200 mg/l of cadmium from one liter of the impure zinc sulphate solution.

Similar calculations for the other impurities lead to the quantities appearing in Table A3.1 for the amounts of zinc dust required to precipitate the 10 impurities contained in one liter of impure zinc sulphate solution.

TABLE A3.1

Stoichiometric Zinc Dust Required to Precipitate Impurities
Contained in One Liter of the Zinc Sulphate Solution

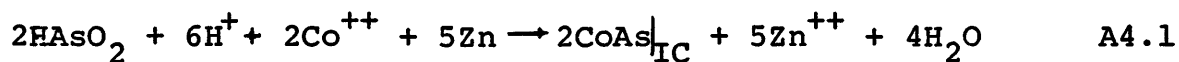
Element	Concentration mg/l	Stoichiometric Ratio (M.S.R.-Eq. A3.2)	Zinc dust mg
As	0.5	1.309	0.655
Cd	200.0	0.582	116.400
Co	4.0	1.113	4.452
Cu	150.0	1.029	154.350
Fe	3.0	1.170	3.510
Ge	0.1	0.180	0.018
Ni	0.5	1.113	0.557
Sb	1.5	0.805	1.208
Se	0.1	1.655	0.166
Te	0.1	1.024	0.102
Total zinc dust (mg)			281.418

The quantities appearing in the above table must be multiplied by the actual volume (in liters) of solution to be treated. Excess amounts of zinc dust were calculated based of multiples of the stoichiometric amount.

APPENDIX 4

STOICHIOMETRIC ARSENIC AND ZINC DUST TO PRECIPITATE
COBALT AS INTERMETALLIC COMPOUNDS

The overall reaction to precipitate cobalt as inter-metallic compound may be represented by the following equation :



i) Arsenic Requirement The mass stoichiometric amount of arsenic to react with cobalt is:

$$m_{\text{As}} = [\text{Co}^{++}] \frac{M_{\text{As}}}{M_{\text{Co}}} \quad ; \text{ mg arsenic/l of solution} \quad \text{A4.2}$$

where M_{As} and M_{Co} are the molecular weights of As and Co respectively, and $[\text{Co}^{++}]$ is the mass concentration (mg/l) of cobalt.

Hence, the stoichiometric mass amount of arsenic to precipitate a solution containing 10 mg/l of cobalt is given by:

$$m_{\text{As}} = (10 \text{ mg/l}) \frac{75}{59}$$

$$m_{\text{As}} = 12.71 \text{ mg As/l of sol.}$$

Thus, 12.71 mg of As is required to precipitate 10 mg/l of cobalt from one liter of the impure zinc sulfate solution.

ii) Zn Dust Requirement The mass stoichiometric amount of zinc according to equation A4.1 is:

$$m_{Zn1} = [Co^{++}] \frac{5 M_{Zn}}{2 M_{Co}} ; \text{ mg/l of sol.}$$

Substituting for the mass concentration of cobalt, $[Co^{++}]$ and the molecular weights of zinc and cobalt, the mass stoichiometric amount of zinc is obtained:

$$m_{Zn1} = 27.70 \text{ mg Zn/l of solution}$$

Hence, 27.70 mg of zinc is required to precipitate 10 mg/l of cobalt from one liter of the impure zinc sulphate solution.

If, for example, 3 times the stoichiometric amount of arsenic is added to precipitate cobalt, there will be excess arsenic equivalent to twice this stoichiometric amount. To precipitate this, zinc dust will be required.

Thus, the additional amount of zinc dust required, is calculated according to equation A3.3, from the following relationship:

$$m_{Zn2} = [2m_{As}] \frac{3M_{Zn}}{2M_{As}} ; \text{ mg Zn/l of solution}$$

Where M_{Zn} and M_{As} are the molecular weights of Zn and As respectively and $[2m_{As}]$ is the excess mass concentration (mg/l) of arsenic.

Then, the stoichiometric mass amount of zinc for excess arsenic will be:

$$m_{Zn2} = 42.25 \text{ mg Zn/l of soln.}$$

Therefore, 42.25 mg of zinc is required to precipitate 25.42 mg/l of excess arsenic from one liter of the impure zinc sulphate solution. If this is added to the requirement for 10 mg/l of Co as the intermetallic compound, then

$$(m_{Zn1} + m_{Zn2}) = 69.95 \text{ mg Zn/l of soln.}$$

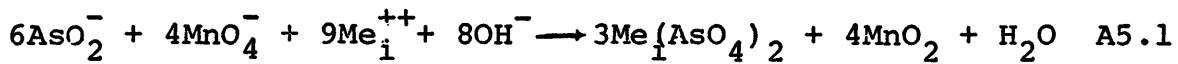
These quantities must be multiplied by the actual volume (in liters) of solution to be treated. Excess amounts of zinc and arsenic were calculated based on multiples of the stoichiometric amount.

Similar calculations were made for impure zinc sulfate solution with 4 mg/l of cobalt.

APPENDIX 5

STOICHIOMETRIC OF ARSENIC REQUIREMENTS
TO PRECIPITATE IMPURITIES AS ARSENATES

The overall reaction to precipitate impurities as arsenate compounds may be represented by the following equation:



where Me_i^{++} may be Cd, Co, Cu, Fe, Ge, Ni, Se, or Te. The mass stoichiometric ratio for a particular impurity is:

$$\text{M.S.R.} = \frac{6 M^\circ}{9 M_i} \quad \text{A5.2}$$

where M° is the molecular weight of arsenic ion

M_i is the molecular weight of the ion

$[\text{Me}_i^{++}]$ is the mass concentration (mg/l) of a particular impurity.

Hence, the mass stoichiometric amount of arsenic for any impurity is:

$$m_{\text{Me}_i} = [\text{Me}_i^{++}] \frac{6 M^\circ}{9 M_i} ; \text{ mg arsenic/l of soln.} \quad \text{A5.3}$$

For example, in the case of cobalt precipitation the required amount of arsenic to precipitate cobalt as an arsenate com-

pound would be obtained as follows:

$$[\text{Co}^{2+}] = 10 \text{ mg/l}$$

$$M_i = \text{molecular weight of cobalt} = 59$$

$$M^o = \text{molecular weight of arsenic} = 75$$

Then, the stoichiometric amount of arsenic to precipitate cobalt is given by:

$$m_{\text{As}} = (10 \text{ mg/l}) \frac{6 \times 75}{9 \times 59}$$

$$m_{\text{As}} = 8.475 \text{ mg arsenic/liter of solution}$$

Thus, 8.48 mg of As is required to precipitate 10 mg/l of cobalt from one liter of the impure zinc sulphate solution.

Similar calculations for the other impurities lead to the quantities appearing in Table A5.1 for the amount of arsenic required to precipitate the 8 impurities contained in one liter of impure zinc sulphate solution.

TABLE A5.1

Stoichiometric Arsenic Required to Precipitate Impurities
Contained in One Liter of the Zinc Sulphate Solution

Element	Concentration mg/l	Stoichiometric Ratio	Arsenic mg
Cd	200.0	0.410	82.048
Co	10.0	0.848	8.478
Cu	150.0	0.786	119.910
Fe	3.0	0.894	2.683
Ge	0.1	0.688	0.069
Ni	0.5	0.851	0.425
Se	0.1	0.410	0.041
Te	0.1	0.391	0.039
Total arsenic (mg)			213.693

The quantities appearing in the above table must be multiplied by the actual volume (in liters) of solution to be treated. Excess amounts of arsenic were calculated based on multiples of the stoichiometric amount.

APPENDIX 6

RESULTS OF EXPERIMENTS CARRIED OUT
IN THIS INVESTIGATION

TABLE A6.1
RESULTS OF RUNS CARRIED OUT IN THIS INVESTIGATION (ppm)

Element	Impure Soln.	Run N ^a										
		1	2	3	4	5	6	7	7A	8		
As	0.5	< 0.5	< 0.5	ND	ND	< 0.5	ND	ND	ND	ND	ND	ND
Sb	2.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cd	137	89.0	25.5	183	3.9	0.17	0.08	0.08	1.90	20.3		
Co	3.3	2.9	1.3	2.4	2.0	0.10	0.60	0.10	0.20	1.1		
Cu	107	2.7	0.14	10.3	1.6	0.12	0.06	0.05	0.08	0.1		
Ge	1.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fe	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Mn	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ni	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Se	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Te	0.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Zn*	107	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Final pH	4.85 ¹	5.29	5.43	5.47	5.48	5.47	5.42	5.43	5.53	5.54		
Final Eh	0.57 ²	0.55	0.50	0.39	0.42	0.29	0.45	0.42	0.42	0.42		

TABLE A6.1 continued

Element	Run N ^a																
	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35
As	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sb	ND	ND	<0.5	<0.5	ND	ND	ND	<0.5	<0.5	ND	ND	ND	<0.5	ND	ND	ND	ND
Cd	48.6	41.6	37.0	50.0	1.90	ND	10.0	34.8	62.4	34.6							
Co	0.10	0.10	0.08	0.08	3.80	2.0	0.6	0.1	0.1	0.9							
Cu	0.10	0.08	0.05	0.05	ND	ND	0.05	0.05	0.05	0.05							
Ge	ND	ND	<1.0	<1.0	ND	ND	ND	<1.0	ND	ND							
Fe	<0.1	<0.1	ND	ND	ND	ND	ND	ND	ND	ND							
Mn	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND							
Ni	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1							
Se	ND	ND	<0.5	<0.5	ND	ND	ND	<0.5	ND	ND							
Te	ND	ND	<0.5	<0.5	ND	ND	ND	ND	ND	ND							
Zn*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND							
Final pH	5.55	5.60	5.62	5.57	5.56	5.80	5.58	5.55	5.41	5.53							
Final Eh	0.43	0.41	0.42	0.41	0.39	0.38	0.41	0.41	0.41	0.42							

TABLE A6.1 continued

Element	Run N ^a													
	29	31	32	33	34	35	36	37	38	39	40	41	42	43
As	<0.5	5.10	0.77	250	<0.5	<0.5	1.70	<0.5	<0.5	<0.5	1.70	<0.5	<0.5	<0.5
Sb	<0.5	<0.5	<0.5	1.10	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Cd	24.6	ND	ND	126	5.0	ND	ND	20.0	4.80					
Co	0.20	5.10	5.50	2.70	1.30	8.40	9.20	<0.50	0.90					
Cu	0.05	ND	ND	99.0	0.13	ND	ND	0.5	0.5					
Ge	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0					
Fe	<0.1	<0.1	<0.1	ND	<0.1	ND	<0.1	<0.1	<0.1					
Mn	ND	ND	ND	49.0	<0.1	ND	ND	ND	30.0					
Ni	<0.1	<0.1	<0.1	0.20	<0.1	<0.1	<0.1	<0.1	<0.1					
Se	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5					
Te	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5					
Zn*	ND	ND	ND	99.0	ND	ND	ND	ND	106					
Final pH	5.53	5.16	5.20	2.58	5.12	5.53	5.63	5.74	5.56					
Final Eh	0.43	0.65	0.83	1.00	0.72	0.78	0.85	0.74	0.78					

* gpl ¹Initial pH ²Initial Eh ND = Not determined