ELECTROCHEMICAL STUDIES
ON THE CEMENTATION OF
COPPER AND COBALT WITH ZINC

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by
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The work described in this thesis was carried out by the author during the period from July, 1984 to December, 1987 in the School of Mathematical and Physical Sciences, Murdoch University, under the supervision of Professor I.M. Ritchie.

I declare that this thesis is my own account of my research and contains work which has not previously been submitted for a degree at any University.

JIANG XIONG

December, 1987
ELECTROCHEMICAL STUDIES ON THE CEMENTATION OF COPPER AND COBALT WITH ZINC

ABSTRACT

The work described in this thesis deals mainly with a fundamental study of two cementation reactions, i.e., Cu(II)/Zn and Co(II)/Zn, using the electrochemical techniques of linear potential sweep voltammetry, cyclic voltammetry, chronopotentiometry (stripping), capacitance measurements, ring current measurements and impedance spectroscopy. In addition, solution analysis, x-ray diffraction and scanning electron microscopy were employed to achieve a better understanding of the kinetics and mechanisms of the two cementations. The half reactions of the two systems were also investigated as an essential part of the whole study. Of the two systems investigated, the Cu(II)/Zn system, was mainly used as a reference system on which some of the new techniques could be proved.

The Cu(II)/Zn reaction has been shown to be diffusion controlled. Five methods, including solution analysis, have been used to determine the rate of reaction. The values of the rate constants thus determined were in good agreement provided allowance was made for the nonstoichiometry of this reaction due to proton displacement by zinc.

The Co(II)/Zn cementation reaction, though thermodynamically highly favourable, is kinetically very sluggish. Of the factors affecting this reaction, the solution pH was found to play a substantial role. For example, while the reaction is largely under chemical control, at pH 5 the reaction rate becomes limited by the speed at which cobalt(II) ions diffuse to the reacting metal surface. The favourable influence of a higher pH on the reduction of cobalt(II) carried out either electrochemically or chemically
using zinc powder was ascribed to the increasing formation of the electro-
chemically active species, CoOH⁺. Increasing the temperature also favours
the shift from chemical control to diffusion control.

Values for the rate constants of the Co(II)/Zn reaction in the
absence of added Zn²⁺ ions were determined from Evans' diagram, chrono-
potentiometry and impedance spectroscopy. The reasons for the differences
in the values of rate thus obtained were discussed.

The presence of zinc ions in the reaction solution greatly suppressed
the rate of Co(II)/Zn cementation reaction. Several factors have been
identified as contributing to the reduced reaction rate. These are the
double layer effect, zinc ion and hydrogen atom adsorption, and precipitation
of basic zinc salts which blanket the reacting metal surface.

The action of compounds such as Sb(III) and As(III), which are
commonly used to activate the Co(II)/Zn reaction in the presence of large
amounts of Zn²⁺, was investigated mainly by impedance spectroscopy. From
the similarity of the impedance spectra for the reaction in the presence of
benzoquinone, it was inferred that one role of the activators was to
suppress the formation of adsorbed hydrogen on the reacting surface and
to allow a higher concentration of the active species, CoOH⁺.
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1. JIANG XIONG and I.M. RITCHIE, "A comparative study of different techniques for measuring the rate of the copper(II)/zinc cementation reaction" *Hydrometallurgy*, 16, 301 (1986).

**ABSTRACT**

The rate of the copper(II)/zinc cementation reaction was measured by five techniques: analysis of the reactant solution for copper(II) and zinc(II) content; intersection of the polarization curves for the reduction of copper(II) and the oxidation of zinc metal; the time taken to react for a thin electrodeposited film of zinc of known thickness; the Stern-Geary method for determining the polarization resistance; and the impedance spectroscopy method of determining the polarization resistance. It was shown that the rate of loss of copper(II) from solution did not match the rate of appearance of zinc(II) in solution because some zinc was dissolving as a result of copper-catalysed proton reduction. Depending on the measurement technique used, rate constants could be obtained for either the copper(II) loss from, or the zinc(II) appearance in the reaction solution. The various rate constants agreed within the limits of experimental error except for that determined from impedance spectroscopy.


**ABSTRACT**

A value for the diffusion coefficient of cobalt(II) in 0.5 M sodium sulphate solutions (pH 2-6) equal to (6.4±0.3) x 10^{-10} m^2 s^{-1} has been
determined by the rotating disc method. The precision of the diffusion
coefficient measurements was found to decrease significantly with decreasing
pH. This effect has been attributed to increases in both the background
current and hydrogen evolution, which causes noise in the limiting currents.
The background current is due to the discharge of protons and bisulphate ions. Since proton and bisulphate diffusion in a sulphate solution are
thought to be coupled by a rapid equilibrium, it is only possible to
determine a joint diffusion coefficient for the two species. From a series
of such measurements, a value of \((18\pm2) \times 10^{-10}\) m\(^2\) s\(^{-1}\) was determined by
extrapolation for the (hypothetical) isolated \(\text{HSO}_4^-\) species.

3. JIANG XIONG and I.M. RITCHIE, "An electrochemical study of the Co(II)/
Zn metal displacement (cementation) reaction", to be presented at the

ABSTRACT

In this paper, a mechanistic study of the cobalt(II)/zinc displacement
reaction using the techniques of linear potential sweep voltammetry, cyclic
voltammetry, chronopotentiometry, capacitance measurements and impedance
spectroscopy is described.

The cobalt(II)/zinc reaction is largely under chemical control at pH 4,
but at pH 5, the reaction rate becomes limited by the speed at which cobalt(II)
ions diffuse to the reacting surface. This effect of pH is related to the
increasing concentration of the species \(\text{CoOH}^+\) which, may be readily reduced
via \(\text{CoOH}\) to cobalt metal. Increasing the temperature also favours the shift
from chemical control to diffusion control.

The rate constant of this reaction in the absence of added \(\text{Zn}^{2+}\) was
determined by several techniques. Some results relating to the inhibition
and activation of the cobalt(II)/zinc reaction are also presented.
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1.

CHAPTER 1.
INTRODUCTION

1.1 DEFINITION OF CEMENTATION REACTIONS

A cementation or metal displacement reaction is an important hydrometallurgical unit process in which the ions of a more noble metal in a solution or melt are displaced by a less noble metal in contact with it, to give the more noble metal and the ions of the less noble metal in solution. In defining cementation in this way, reactions involving homogeneous reductants, which have also been called cementation reactions by Ford and Rizzo [1] are excluded.

The generalized equation for a metal $M_1$ displacing the cation $M_2^{2+}$ to give the metal $M_2$ and the cation $M_1^{2+}$ is

$$z_2M_1^{z_1} + z_2M_2^{z_2} \rightarrow z_2M_2^{z_1} + z_1M_2$$  \hspace{1cm} (1-1)

e.g., \hspace{1cm} Fe(s) + Cu^{2+} \rightarrow Cu(s) + Fe^{2+} \hspace{1cm} (1-2)

where $z_1$ and $z_2$ are the charges of the ions of $M_1$ and $M_2$.

In addition, cementation reactions can involve anionic species, e.g.

$$Zn(s) + 2Au(CN) \rightarrow 2Au(s) + Zn(CN)_{4}^{2-}$$  \hspace{1cm} (1-3)

Cementation reactions are clearly composed of two redox half reactions involving, on the one hand, the reduction of the more noble metal ion in solution,

$$z_1M_2^{z_2} + z_1z_2e \rightarrow z_1M_2$$  \hspace{1cm} (1-4)

and on the other hand, the oxidation of the less noble metal

$$z_2M_1^{z_1} - z_1z_2e \rightarrow z_2M_1^{z_1}$$  \hspace{1cm} (1-5)
Thus a cementation reaction is a complex process in which one metal is being plated onto the surface of the second which is simultaneously dissolving.

The cementation reaction, like any other chemical reaction, can be studied by chemical methods. Thus, the stoichiometry and reaction rate can be determined chemically, and the composition of the product layer ascertained by chemical analysis. However, because the reaction is electrochemical in nature, and is essentially a special type of corrosion reaction, electrochemical techniques can be used with great advantages to measure the rate and investigate the reaction mechanism. In the work described in this thesis, both chemical and electrochemical techniques have been used, but the emphasis is very much on the electrochemistry of the cementation reactions investigated.

1.2 HISTORICAL PERSPECTIVE

The precipitation of a metal from an aqueous solution of its salt by another metal is a very old process. The earliest known example of a cementation reaction can be dated back to more than two thousand years ago. The ancient Chinese of the Han Dynasty (206 B.C. - 220 A.D.) observed that when a solution of a copper salt, which probably occurred naturally, was treated with iron metal, copper was formed [2,3].

In Europe, as early as the first century, the Roman writer Pliny the Elder (A.D. 23 - 79) knew of the deposition of copper by iron [4], and the leaching and extraction of copper as a process can be traced back to the time of Agricola, a German who lived in the 16th century [5]. On the other side of the world, in South America, the skilful Moche metal-smiths (100 B.C. - 800 A.D.) had discovered how to coat copper with gold and silver by a cementation reaction [6]. The gold or silver is thought
to have been first dissolved in a corrosive solution made up from the minerals common to the deserts of the Peruvian coast: common salt, saltpeter and alum. When copper is put into this solution, it displaces gold from its chloro-complex:

$$2\text{AuCl}_4^- + 3\text{Cu} \rightarrow 2\text{Au} + 3\text{Cu}^{2+} + 8\text{Cl}^-$$ (1-6)

Cementation reactions contributed much to the early development of chemistry. The Greek word "chemeia" first made its appearance in about the fourth century A.D. and was then used to describe the investigations into the transmutation of gold and silver - precious metals - from base metals [7]. This was an important activity of the ancient alchemists in which a great deal of knowledge about chemicals and chemical techniques was accumulated. In modern scientific terms, many of the so-called examples of transmutation were cementations.

From the sixteenth century onward, chemists became more and more interested in this class of reactions. This was the reaction of copper-containing mine waters with iron [8]. The culmination of this research was the tables of affinity developed by Boyle in the seventeenth century. He showed that the metals could be ordered in terms of their affinity for a given acid. Thus, iron will displace copper from a copper sulphate solution because it has a greater affinity for sulphate. Boyle's affinity tables can be regarded as the forerunner of the modern electrochemical series [9].

Old as it is, the cementation reaction remains of interest to research workers because of its importance in industrial processes, mainly in the field of hydrometallurgy and solution purification. The cementation of copper with iron, the oldest of these reactions, is still extensively used in industry. In the United States, about 20% of the copper produced is by
cementation [10]. Besides copper, metals such as Au, Ag, Bi, Ge, Cd, Te and Re in aqueous solutions, and Zr, Ti and Be from the melt, may also be produced by cementation [11]. Cementation has also served as an efficient means of purifying electrolytes. For example, copper, which is an impurity in nickel sulphate solutions, can be removed by using activated nickel powder [12].

The cementation reaction is now also often used in the treatment of effluents to protect the environment from being polluted by heavy metals. For example, traces of inorganic mercury can be removed from waste streams by using a zinc filter [13].

1.3 THE ELECTROLYTIC ZINC PROCESS [14]

Zinc is one of the major nonferrous metals required by an industrial economy and cementation reactions are important in its production by the electrolytic route. In this process, zinc calcine, mainly in the form of zinc oxide produced by the roasting of zinc sulphide concentrates, is dissolved in dilute sulphuric acid. The resulting acid zinc sulphate electrolyte is then electrolyzed to produce zinc metal.

The electrolysis would be very inefficient unless some of the impurities, which include Cu, Cd, Ni and Co, were previously removed from the electrolyte. The reason is that they lower the hydrogen overpotential considerably [14] and a large fraction of the current used is then wasted on hydrogen evolution rather than zinc deposition. Therefore, purification is vital for achieving efficient electrolysis as well as deposits of good quality.

In principle, most of the metallic impurities can be removed by displacement using zinc powder. Although copper and cadmium are easily precipitated by zinc, cobalt and nickel are not. The Co(II)/Zn cement-
ation reaction is so sluggish that special measures such as the use of additives and high temperatures must be taken for the reaction to proceed at a reasonable rate.

1.4 THE SCOPE OF THE THESIS

As noted above, the copper(II)/zinc reaction proceeds quite rapidly on an industrial scale, and has been shown in laboratory studies to be controlled by the rate of transport of the copper(II) ions to the zinc metal surface [15,16]. However, much less is known about the cobalt(II)/zinc reaction which has been reported to be controlled either by some slow chemical step [17] or by slow transport of cobalt(II) ions to the zinc surface [18].

This thesis deals mainly with a fundamental electrochemical study of copper(II)/zinc and cobalt(II)/zinc cementation reactions using a variety of electrochemical methods with a view to obtaining a better understanding of their kinetics and mechanism and the inhibition and activation of Co(II)/Zn reaction. In this thesis, the copper(II)/zinc system will also act as a reference system for unproven techniques.

Five main methods have been used in this study, including impedance spectroscopy which has so far not been used for studying cementation reactions. The results from the five techniques have been critically compared and their suitability for following the kinetics of a cementation reaction under a variety of circumstances assessed.

Chapter 1, an introduction to the work, gives a general background to cementation reactions, their history and their importance in hydrometallurgy. Chapter 2 gives a brief review of the techniques for studying cementation reactions with particular emphasis being placed on how electrochemical techniques can be used to study their kinetics and
mechanisms. Chapter 3 gives the experimental details. Chapters 4 and 5 are the core of this thesis. Chapter 4 deals with the kinetic and mechanistic aspects of the copper(II)/zinc reaction and also shows how different methods of measuring the reaction rate do not necessarily yield the same rate constant when there is an interfering side reaction. Also included in this chapter is a discussion of the electrochemistry of the anodic dissolution of zinc, which is common to both the copper(II)/zinc and cobalt(II)/zinc reactions. In Chapter 5, the results of a study of the cobalt(II)/zinc cementation reaction are presented with stress being put on its inhibition and activation. Impedance spectroscopy is shown to be a valuable technique in elucidating the way in which the reaction is inhibited, and can be activated. The final part, Chapter 6, is a summary in which these two cementation reactions are compared and contrasted, and suggestions are made for future work.
REFERENCES (Chapter 1)


CHAPTER 2.
TECHNIQUES FOR STUDYING CEMENTATION REACTIONS

2.1 GENERAL REMARKS \([1,2,3]\)

As stated in Chapter 1, cementation is a reaction where ions of \(M_2\) are reduced by a metal \(M_1\) to zero valence. The generalized equation is

\[
z_2M_1 + z_1M_2^{Z_2^+} = z_2M_1^{Z_1^+} + z_1M_2
\]

(2-1)

where \(z_1\) and \(z_2\) are the charges of the ions of \(M_1\) and \(M_2\), respectively.

Obviously, cementation reactions are heterogeneous and, according to equation (2-1), involve at least three phases. For such a reaction, the following steps must be involved in the mechanism:

(a) Diffusion of \(M_2^{Z_2^+}\) ions from the bulk solution to the surface of \(M_1\);

(b) Adsorption of \(M_2^{Z_2^+}\);

(c) Electron transfer from \(M_1\) to \(M_2^{Z_2^+}\);

(d) Desorption of \(M_1^{Z_1^+}\);

(e) Diffusion of \(M_1^{Z_1^+}\) away from the surface of \(M_2\).

From the above, two properties of cementation reactions are clear. The first is that cementation reactions are electrochemical in nature, and the metal precipitation from leaching solutions by a less noble metal can be studied as an electrochemical reaction. The general equation (2-1) can be separated into two constituent half reactions with electron transfer involved in each one:

(i) cathodic half reaction

\[
z_1M_2^{Z_2^+} + z_1ze \rightarrow z_1M_2
\]

(2-2)
(ii) anodic half reaction

\[ z_2M_1 - z_1Ze^+ \rightarrow z_2M_1^{z_1+} \]  \hspace{1cm} (2-3)

Secondly, if either step (a) or (e) is rate determining, the overall reaction is said to be diffusion controlled. On the other hand, if any step other than (a) or (e) is slow, the reaction is said to be under chemical control or electrochemical control. Sometimes mixed control occurs when the rates of the diffusion and the electron charge transfer steps including adsorption are comparable. When the reaction is diffusion controlled, it is important to use an electrode geometry having well-controlled hydrodynamics and therefore, a rotating disc is used in most fundamental studies of cementation reactions.

However, only those cementation reactions which proceed at a reasonable rate have practical significance. From this point of view, kinetic studies of cementation reactions are generally much more relevant than thermodynamic ones.

2.2 SOME COMPLICATING FACTORS INVOLVED IN THE CEMENTATION REACTION

Before going into the details of the techniques for studying cementation reactions, it is desirable to have a basic understanding of some complicating factors involved in cementation reactions.

2.2.1 Deposit Effect

Deposit effects refer mainly to rate enhancements or rate retardations which are observed in cementation systems under certain circumstances. As the name implies, such phenomena can be attributed to a change in the structure of the surface deposit during reaction [3]. The variables that affect the structure of a surface deposit, such as temperature, concentration
of the more noble metal ion and presence of ligands, etc. can cause a change in the reaction rate [4].

Rate enhancements can be seen in cementation systems such as Cu$^{2+}$/Zn [5,6], Cd$^{2+}$/Zn [7,8], Ag$^+$/Zn [7], Cu$^{2+}$/Al [9] etc. For these systems, the rate enhancement can be conveniently described by means of two-stage first order kinetics. In the first stage, the reaction rate follows the Levich equation and the calculated rate constant is consistent, within the experimental error, with values determined from diffusion measurements [10]. However, when the deposit reaches a certain critical mass, the reaction rate increases as shown in Fig. 2-1. This may be explained in terms of surface roughening, in particular, the effect of dendritic protrusions of the deposited metal which cause turbulence and so increase the mass transfer flux to the disc surface [7]. In addition, a decrease in the diffusion path length or an increase in the effective area may also contribute to the rate enhancement.

From the above explanation, it is logical to infer that a smooth and dense deposit may instead lead to a rate retardation, as has been seen in the cementation of copper with iron [11]. In this case, the copper deposit formed under conditions investigated is so dense that the anodic half reaction becomes rate-determining.

Apart from the surface effect stated above, the surface deposit can also alter the apparent activation energy as noted in section 2.3.2.

The deposit effect in cementation reactions often makes the interpretation of kinetic data complicated. Sometimes, in order to eliminate the deposit effect from a kinetic study, the deposit has been continuously stripped by scraping or by means of ultrasonic vibration [12]. However, in the electrochemical measurements, the kinetic complications due to deposit effect are expected to be avoided because of a relatively short length of measuring time.
FIGURE 2-1. Schematic diagram of the two-stage first order kinetics of cementation reactions.
2.2.2 Cathodic/Anodic Area

During the course of a cementation reaction, the areas of both anodic and cathodic sites tend to change continuously. For example, consider the case in which the cathodic process is diffusion controlled, both cathodic and anodic half reactions are independent and the cathodic area is larger than the anodic one. During the reaction, the anodic area is diminishing. The reduction in the anodic area will inevitably cause an increase in the anodic current density because the total cathodic current must equalize the total anodic current. As a consequence, the mixed potential is shifted towards the positive direction, ultimately causing the reaction to be chemically controlled rather than diffusion controlled.

The change of the mixed potential with the ratio of the cathodic/anodic area is the basis for the stripping method for measuring the cementation reaction rate.

2.2.3 Codeposition

Codeposition in a cementation reaction is quite a common phenomenon. For example, as a result of codeposition, brass, palladium-copper and nickel-germanium alloys are produced in the Cu$^{2+}$/Zn [13,14], Pd$^{2+}$/Cu [15], and Ge(IV), Ni$^{2+}$/Zn [16] cementation reactions, respectively.

Codeposition may occur under various conditions. The fascinating thing is that the precipitant metal itself, after being dissolved, is redeposited from solution with the more noble metal in a cementation reaction. Power and Ritchie [1,17] have theoretically discussed this often overlooked phenomenon using Evans' diagrams and have suggested a mechanism for codeposition based on the activity difference of the less noble metal in its pure and alloyed states.
Alloy formation in cementation reactions not only causes contamination of the deposits but may also result in a change in the kinetics initially assumed by the reaction. For example, according to Lee et al., [18], when copper is codeposited with cadmium onto zinc, the initially mass-transfer controlled reaction becomes mixed controlled.

2.2.4 Side Reactions

Side reactions are highly undesirable but very common in cementation reactions carried out in aqueous solutions.

Side reactions usually involve the reduction of the dissolved oxygen (Eq. 2-4 and 2-5) or hydrogen ions (Eq. 2-6) when the solution is acidic.

\[
\begin{align*}
O_2 + 4H^+ + 4e \text{ (from precipitant metal)} & \rightarrow 2H_2O & (2-4) \\
O_2 + 2H_2O + 4e \text{ (from precipitant metal)} & \rightarrow 4OH^- & (2-5) \\
2H^+ + 2e \text{ (from precipitant metal)} & \rightarrow H_2 & (2-6)
\end{align*}
\]

In acidic solution, hydrogen evolution would be the most frequently occurring side reaction, especially when the mixed potential is sufficiently negative and the hydrogen overpotential on the deposited metal is rather small.

It is clear from equations (2-4) to (2-6) that, as a direct consequence, side reactions will cause excessive consumption of the precipitated metal. Moreover, hydroxides or basic salts may be formed as a result of the alkalization in the vicinity of the surface of the precipitant metal. These basic salts are likely to be incorporated into the deposit as an impurity and can even modify the morphology of the deposit significantly [19].

Side reactions may cause trouble in kinetic studies. For example, although the reduction of dissolved oxygen is usually insignificant due
to its small concentration in solution and subsequent slow rate of transport and electrochemical reduction, oxygen reduction can be important if the ion concentration of the more noble metal is only at the ppm level. Under these circumstances, the rate of consumption of the precipitant metal would be much greater than expected. It must be noted that the proton discharge in the cementation reaction is an important factor to be considered in the explanation of certain experimental results as will be shown in Chapters 4 and 5.

2.3 CEMENTATION KINETICS

The content under this title comprises two parts: methods of determining reaction rates and methods of elucidating reaction mechanisms.

2.3.1 Methods of Determining Reaction Rates

A cementation reaction can be considered either as a heterogeneous chemical reaction or an electrochemical one. Therefore, its kinetics can be followed either chemically or electrochemically.

2.3.1.1 Chemical Method (solution analysis)

The simplest and most commonly used technique for following the kinetics of a cementation reaction is to sample the reaction solution at suitable time intervals and then to determine the reactant and product ion concentration by analysis. Ideally, both species should be analysed unless the stoichiometry of the reaction has been unequivocally established, and the absence of competing side reactions demonstrated.

Solution analysis may be carried out by either chemical, electrochemical or physical methods. Among them, the most commonly used is atomic
absorption spectrophotometry (AA) [5], which has the advantages of being rapid, convenient and accurate down to about $10^{-5}$ M for most metal ions. Other methods such as colorimetry [20], radiotracer [21], ion-selective electrodes [22,23], and polarography [24] have also been used.

Almost without exception, cementation reactions have been found to be first order with respect to $M^{Z2+}_2$ [4] and so can be described by the first order rate equation:

$$\frac{dc}{dt} = -kAC/V$$  \hspace{1cm} (2-7)

An integration of equation (2-7) gives

$$\log(C/Co) = -kAt/2.303 \ V$$  \hspace{1cm} (2-8)

It follows from (2-8) that a $\log(C/Co)$ versus $t$ plot would yield a straight line with a slope equal to $-kA/2.303 \ V$, from which the rate constant, $k$, can be calculated.

$$k = -2.303 \ V \times \text{slope}/A$$  \hspace{1cm} (2-9)

In the above equations (2-7, 2-8, 2-9),

- $Co$ - initial concentration of the ion $M^{Z2+}_2$
- $C$ - concentration of the ion $M^{Z2+}_2$ at fixed time
- $A$ - surface area of $M_1$
- $V$ - initial total volume
- $t$ - reaction time
- $k$ - rate constant

One thing that must be remembered is that a volume correction is necessary if sampling is used and the sample is not negligibly small compared with $V$. Corrected first order equations have been suggested by
Strickland and Lawson [5] and by Power and Ritchie [25] in which allowance has been made for the change in volume due to solution sampling. Ideally, it's desirable to do in situ analysis in solution by constantly monitoring the concentration of ions. The volume correction is then avoided. This can be done by, for instance, using ion-selective electrodes [23].

It is also possible to determine the rate of a cementation reaction by measuring the dissolution rate of the reactant metal or the deposition rate of the more noble metal. However, this approach is seldom used in practice because it is usually more complex than solution analysis and each experiment can only give one point on the rate curve as a result of the destruction of the metal surface during the analysis.

Despite these intrinsic difficulties, the stripping method of Barth et al. [26] (discussed below) for measuring the rate of loss of reactant metal is a valuable method for studying the early stages of reaction.

2.3.1.2 Electrochemical Methods

(a) Evans' diagram

Evans' diagrams have been extensively used by Evans [27] as well as by Antropov and Donchenko [28] in the discussion of corrosion reactions. In the field of metal displacement reactions, Sedzimir [29] seemed the first to use an Evans' diagram to discuss the reaction kinetics. The use of Evans' diagrams has recently been extended and illustrated by Power and Ritchie [1,17] for the investigation of cementation reactions.

Evans' diagrams will be discussed in more detail in section 2.3.2.3 when their uses in mechanistic studies are considered. For the present purpose, it is sufficient to know that they are constructed by plotting the two polarization curves for the two half reactions on the same
potential-lg (current density) diagram. The reaction current density (rate), \( i \), is then determined from the intersection, which gives the mixed potential, \( E_m \), of the reaction system, of the two curves [30] as shown in Fig. 2-2. The rate constant, \( k \), is then given by

\[ k = \frac{i}{nFC} \]  \hspace{1cm} (2-10)

If the reaction is diffusion controlled, the reaction current density is the limiting current density, \( i_L \). In this case, equation (2-10) becomes

\[ k = \frac{i_L}{nFC} \]  \hspace{1cm} (2-11)

where \( n \) is the number of electrons transferred in the reaction, \( F \) is the Faraday constant and \( c \) is the concentration of a given electroactive species.

Limitations to this technique for rate measurements will be given in section 2.3.2.3.

(b) Chronopotentiometry (stripping)

In this technique due to Barth et al. [26], a known amount of the precipitant metal is first electroplated as a thin layer onto an inert electrode. The thin precipitant film is then placed in the reactant solution and the mixed potential continuously monitored as a function of time. When all the metal has reacted, the potential rises rapidly to the equilibrium value of the noble metal. From the chronopotentiogram thus obtained, the reaction rate can be calculated.

This technique has been applied to a few systems such as \( \text{Ag}^+/\text{Cu} \) [26] and \( \text{Cu}^{2+}/\text{Fe} \) [31]. Its application to the \( \text{Cu}^{2+}/\text{Zn} \) and \( \text{Co}^{2+}/\text{Zn} \) systems will be described later in this thesis (Chapters 4 and 5). The stripping method has the merits of being simple, precise and able to measure the rate of
FIGURE 2-2. Schematic Evans' diagram

1. cathodic reduction of $M_2^{2+}$ to $M_2$
2. anodic dissolution of $M_1$ to $M_1^{z1+}$
cementation at very little deposit mass, in other words, in the absence of any deposit effects (see section 2.2) which might complicate the kinetic study.

On the other hand, very little use has been made of deposit analysis for measuring the reaction rate, largely because it is difficult to remove a deposit quantitatively from the substrate. Recently, Kenna et al. [32] have shown that it is possible to determine by coulometry the amount of metal deposited during an Au(I)/Fe cementation reaction, provided a solvent can be found in which the deposited metal will dissolve preferentially during anodic oxidation.

(c) Stern-Geary Method [33,34]

While chemical methods can yield accurate and reliable kinetic data, they are usually time consuming. In this respect, electrochemical methods, although indirect, have an advantage over chemical methods.

Besides the "Tafel slope extrapolation" [35] to get the reaction current density, and hence reaction rate, electrochemical methods for rate determination usually depend on the measurement of the polarization resistance, Rp, which is defined as the ratio of the potential applied to the resulting current density in the vicinity of the mixed potential (Em) or corrosion potential.

\[ Rp = (dE/di)_{E=Em} \]  \hspace{1cm} (2-12)

The polarization resistance, originally defined by Bonhoeffer and Jena [36], was further discussed by Stern and Geary [33] who found in 1957 that a linear relationship exists between potential and applied current at potentials slightly away from the corrosion potential. They derived an equation which relates Tafel slopes and polarization resistance to the
corrosion (reaction) current density, \( i \),

\[
i = \frac{1}{2.303 \ R_p \left( b_a^{-1} + b_c^{-1} \right)^{-1}}
\] (2-13)

where \( b_a \) and \( b_c \) are the Tafel slopes of the anodic and cathodic half reactions in the vicinity of the mixed (corrosion) potential. If the reaction is controlled by the diffusion of the reactant species to the surface, \( b_c \) becomes infinity and equation (2-13) is then reduced to (2-14).

\[
i = \frac{b_a}{2.303 \ R_p}
\] (2-14)

From the value of \( i \), the rate constant can be calculated using equation (2-10).

Since then, the Stern-Geary theory has been extensively used in corrosion studies to measure in situ corrosion rates of metals such as steel [37], copper [38], aluminium [39], and tin sheet [40] as well as inhibitor efficiency [41]. In a comprehensive review, Mansfeld gave a detailed description of the theory, applications, limitations and problems of the polarization resistance technique [34].

The Stern-Geary method is simple and fast. It only demands a slight polarization of the electrode by about a few millivolts from its mixed potential and the simultaneous measurement of the resulting current. It must be noted, however, that a significant error due to the uncompensated solution resistance may be introduced into \( R_p \) if the conductivity of the electrolyte is low. Accordingly, it is best if a supporting electrolyte is used in the measurement of polarization resistance.

Stern-Geary measurements have also been made with success in the study of the Ag(I)/Cu cementation reaction [42]. In the work described in this thesis, we will use the same technique to determine the reaction rate of the Cu\(^{2+}\)/Zn reaction.
(d) Impedance Spectroscopy

Another method for measuring Rp is impedance spectroscopy. The interest in the use of the impedance technique for the determination of Rp was stimulated by the investigations of Epelboin and his coworkers into the corrosion of iron in sulphuric acid [43]. Although this technique is finding increasing applications in the field of corrosion [35], so far as we are aware, no one has yet used impedance spectroscopy for the study of cementation reactions. In the work described in this thesis, attempts have been made to determine the reaction rates of the Cu(II)/Zn and Co(II)/Zn cementation reactions through impedance measurements.

When a sinusoidal potential perturbation of small amplitude is applied to a mixed potential system and the real and imaginary components of impedance measured as a function of frequency, usually from 10 KHz to 1 mHz, an impedance diagram can be produced (Fig. 2-3). According to the theory of impedance spectra [43], for a kinetically sluggish chemical system, the impedance diagram will be a single semicircle over the high frequency region and in the capacitive half plane. The polarization resistance is taken as the limiting value of the impedance at frequencies tending to zero [35] after due allowance has been made for the solution resistance.

\[
Rp = \lim_{\omega \to 0} \text{Re} \left\{ Z_f \right\}_{\text{Em}}
\]  

(2-15)

where \( \text{Re} \{ Z_f \} \) is the real part of the impedance \( Z_f \) and \( \omega \) the angular frequency of AC signal \( (\omega = 2\pi f, f \) - sinusoidal frequency). From the \( R_p \) determined by the impedance method, and using the Stern-Geary equation, the reaction current and consequently the reaction rate can be obtained.

However, in most cases, the system is more complex than a semicircle. A typical plot of impedance often has flattened capacitive semicircles with
FIGURE 2-3. Schematic experimental impedance diagrams at different polarization points of iron dissolution in sulphuric acid media based on [45]. The dashed lines indicate the decomposition of the overall impedance into a high frequency and a low frequency semi-circle.

A. impedance is capacitive
B. impedance is both capacitive and inductive

$Z'$ - real part of the impedance
$Z''$ - imaginary part of the impedance
$R_p$ - polarization resistance
$R_{ct}$ - charge transfer resistance.
more than one time constant (Fig. 2-3A), and inductive loop(s) are often observed (Fig. 2-3B). Such a circumstance makes the interpretation of impedance diagrams difficult and the treatment of impedance data more or less empirical. Therefore, despite some good results, it is still open to question as to how the impedance diagrams should be interpreted. For instance, according to Lorenz and Mansfeld [35], the corrosion rate of certain systems is unequivocally correlated with the extrapolated value of the inductive loop to zero frequency. However, it is the intercept of the capacitive arc with the real axis of the AC impedance diagrams, which Epelboin et al. [43] consider as that which can most accurately be correlated with the corrosion rate (see Fig. 2-3B). The key thing is, as Lorenz and Mansfeld put it, "experimental as well as theoretical results, established in one corroding system, cannot be generalized and applied to other corroding systems without great care" [35].

2.3.2 Methods for Elucidating Reaction Mechanisms

As noted in the introductory remarks of this chapter, cementation reactions, being heterogeneous, may be diffusion controlled, chemically controlled or under mixed control. The important step in any mechanistic study lies in the unequivocal elucidation of the nature of the rate-controlling step.

For a mechanistic study of a heterogeneous process, it is of vital importance that the sample geometry be made in such a way that the conditions governing the solution diffusion be accurately known. The rotating disc meets this requirement. It was shown in 1942 by Levich [46] that a disc-shaped electrode rotating in a liquid under conditions of laminar flow is uniformly accessible to diffusion. This important property makes the rotating disc a unique tool for mechanistic and kinetic studies of
electrode reactions at solid electrodes as well as for determinations of diffusion coefficients of dissolved species. Since then, the rotating disc technique has found wide applications in the study of various electrochemical and chemical problems (see monographs: [47], Reviews: [48,49], Papers: [5,50]).

Therefore, it has become a common practice in mechanistic studies of cementation reactions in the last fifteen years or so to use rotating disc samples of the reacting metal. The use of a rotating disc not only ensures that the hydrodynamics of the system are reproducible, but also enables the rate of the reaction, if diffusion controlled, to be accurately calculated [1]. The importance of this is obvious since most cementation reactions are diffusion controlled [3,4]. It is for this reason that a rotating disc geometry has been employed throughout this study.

2.3.2.1 Method based on the rotation speed dependence of the reaction rate - $k/\omega^{3/2}$ relation

An accurate solution of the hydrodynamic equation for the disc geometry leads to the following expression known as the Levich equation[46].

$$J = 0.62 AD^{2/3} \nu^{-1/6} \omega^{1/2} C$$  \hspace{1cm} (2-16)

or

$$k = 0.62 D^{2/3} \nu^{-1/6} \omega^{1/2}$$  \hspace{1cm} (2-17)

where $J$ is the reaction rate and $k$ is the rate constant of a reaction under diffusion control, $A$ the area of the disc, $D$ the diffusion coefficient of the electroactive species, $\nu$ the kinematic viscosity of solution, $\omega$ the angular velocity, and $C$ the bulk concentration of the diffusing species.

Although deviations from equation (2-16) may occur, as a result of, for example, additional stirring by bubbles of a gas evolving at higher current
densities, or turbulence \cite{49}, it has been shown to be very accurate in most cases, and plots of $i_L$ against $\omega^{1/2}$ are generally straight lines.

Equations (2-16) and (2-17) provide us with an accurate criterion for discriminating the controlling step. If a reaction is under diffusion control, the plot of the rate or rate constant against the square root of the angular velocity should be a straight line passing through the origin; otherwise chemical control can be involved to a greater or lesser extent. Equation (2-17) also explains the first order nature of a diffusion controlled reaction.

\subsection{2.3.2.2 Method based on the temperature-dependence of the rate constants}

This method is essentially the evaluation and interpretation of the apparent activation energy for a heterogeneous reaction. In this connection, Miller and Beckstead's work contributed a lot to the understanding of activation energies of cementation reactions \cite{3,4,12}.

As is well known, the activation energy can be obtained from the determination of the temperature dependence of the rate constants by the Arrhenius equation,

$$
\frac{d\ln k}{dT} = \frac{E_a}{RT^2}
$$

where $k$ is the rate constant, $T$ the absolute temperature, $E_a$ the apparent activation energy and $R$ the gas constant. By rewriting equation (2-18) we get

$$
E_a = -R \frac{d\ln k}{d\left(\frac{1}{T}\right)}
= -2.303 R \frac{d\log k}{d\left(\frac{1}{T}\right)}
$$

(2-19)

Thus, a plot of $\log k$ versus $T^{-1}$ would produce a straight line from the slope
of which \( E_a \) can be calculated.

As a rough rule, \( E_a \) is generally less than 25 kJ mol\(^{-1}\) for diffusion controlled reactions and greater than 40 kJ mol\(^{-1}\) for processes under chemical control [4]. It must be noted, however, that such a criterion should be used with caution. \( E_a \) has been found to be affected not only by the hydrodynamic flow regime, as evidenced by the slightly high \( E_a \) values on rotating cylinders compared with those obtained on rotating discs, but also by the surface deposit [3].

The Arrhenius plot for cementation systems has another advantage, namely, showing how the rate-controlling step can change from chemical control to diffusion control as the temperature varies (Fig. 2-4).

The useful message from Fig. 2-4 is that a reaction can be made to go faster by altering the rate-determining step from chemical control at a lower temperature to diffusion control at a higher temperature. The existence of a curved region on the Arrhenius plot is evidence of mixed control.

2.3.2.3 Evans' diagram

The Evans' diagram is simply the superposition of two \( \log \) (current density)-potential or current-potential curves, and hence has the alternative name of polarization diagram. By applying this graphical superposition method to corrosion systems, of which cementation reactions are a special example, both \( E_m \) (mixed potential) or \( E_{corr} \) (corrosion potential) and \( i \) (reaction current density) can be obtained as shown schematically in Fig. 2-5.

Furthermore, it has also been proved to be a useful tool in elucidating the rate-determining step of a reaction. This is also illustrated
FIGURE 2-4. Schematic Arrhenius plot showing the change in the reaction mechanism of a cementation reaction over different temperature range.
FIGURE 2-5. Schematic Evans' diagrams showing diffusion control (A) and chemical control (B) for a cementation reaction.

1. cathodic reduction of $M_2^{Z_2^+}$ to $M_2$
2. anodic dissolution of $M_1$ to $M_1^{Z_1^+}$
in Fig. 2-5.

It can be seen from Fig. 2-5A that the metal dissolution curve cuts the extension of the reduction curve in the limiting current region and therefore, it is the rate of diffusion of $M^{2+}_{2}$ ions from the bulk solution to the reactant surface that controls the rate of the cementation reaction. On the other hand, in Fig. 2-5B, the interception of the two polarization curves lies in the Tafel region and hence the reaction is under chemical control. Under the circumstances of Fig. 2-5A, it is possible to calculate $k$, the rate constant for the removal of $M^{2+}_{2}$ from the solution, by using equation (2-11).

The Evans' method is simple and accurate. It produces information not only about reaction rates but also about reaction mechanisms. However, it is still necessary to keep in mind that some assumptions have been made in constructing Evans' diagrams; they are

(a) Each half reaction is independent;
(b) The cathodic and anodic areas are equal;
(c) The ohmic resistance between anode and cathode is negligible.

Any failure to meet these requirements e.g. due to the effect of the deposit, the presence of an oxide film, the formation of an alloy by codeposition and the interference of one half reaction with another, would render the Evans' diagram invalid, being an oversimplification of a complex system.

2.3.2.4 Em versus $\log w$ relation

Power and Ritchie [51] and Power et al. [50] have successfully used the concept of mixed potential, which was developed by Wagner and
Traud [52], to work out the theory of a technique based on the observation of the mixed potential as a function of reactant concentrations and stirring from which certain mechanistic information can be obtained.

Consider the case common to most cementation reactions, where the cathodic half reaction is under diffusion control and the anodic one chemically controlled. In this case, the mixed potential would be proportional to the logarithm of the rotation speed. In general, four diagnostic criteria were proposed to distinguish the different situations of the kinetic control [51].

2.3.2.5 Impedance spectroscopy

Impedance measurements have been used to elucidate the mechanism of various electrochemical processes such as the anodic dissolution and corrosion of iron in sulphuric acid medium [45,53], the electrocrysallization of zinc [54], nickel [55] and cobalt [56]. The advantage of impedance spectroscopy is that it may allow the total electrode process to be decomposed into its elementary steps on the basis of different relaxation time constants, each corresponding to an important feature of the reaction mechanism.

As Epelboin et al. [45] and others [47] have shown, it is possible to simulate impedance spectra by means of a complex mathematical analysis of the reaction mechanism. However, such analyses often contain assumptions about the mechanism and several disposable constants, and their validity is yet to be established. On the other hand, a phenomenological analysis [45], though qualitative, is often straightforward and clearcut. For example, Fig. 2-3 shows the existence of two loops, one at high frequency corresponding to a charge transfer process and another at low frequency stemming
from the relaxation in the coverage of the electrode by an adsorbed species [45]. In this way, mechanistic information can be obtained from the shape of the impedance diagram [35, 58].

Among those factors which are responsible for loops of capacitive or inductive nature are charge transfer, adsorption-desorption of reaction intermediates, change of the roughness factor, change in the number of active sites and change of volume concentration in the vicinity of the electrode [57b].

It must be stressed, however, that impedance can only provide strong support to the existence of adsorbed intermediates. Impedance measurements are neither able to prove the existence of adsorbed intermediate species nor to identify them [45].

2.3.2.6 Capacitance measurements

Capacitance measurements constitute an entirely different approach to those described above, since capacitance measurements can give information about the area of a reacting surface during the course of the reaction. The use of capacitance measurements for a mechanistic study of cementation reactions has been triggered by the fact that a diffusion-controlled cementation reaction generally produces spongy, dendritic deposits having a large surface area; on the other hand, a cementation reaction under chemical control usually yields a dense and coherent deposit with a relatively smaller area.

In addition, capacitance measurements can give confirmation about the recrystallization of the deposit if it results in a change of the surface area [10].
2.3.2.7 Cyclic voltammetry

Cyclic voltammetry is an extension of voltage-sweep voltammetry in which the potential of a small, stationary working electrode is changed linearly with time in a triangular wave form, i.e., after traversing the potential region where the electrode reaction takes place, the direction of the potential sweep is reversed [44b]. Such a mode of potential change can produce a current-potential diagram, cyclic voltammogram (Fig. 2-6), and from the peak potential \((E_p)\), peak current \((i_p)\), defined below, and their dependence upon the potential sweep rate, useful information about electrode kinetics and reaction intermediates can be derived.

Cyclic voltammetry is simple and direct to use and so has become very popular in electrochemical research. It has been proved to be a useful technique especially for investigating the existence of reaction intermediates [59,60]. Although a cementation reaction cannot be usefully studied directly by cyclic voltammetry, it is a valuable technique for obtaining information about the two half reactions.
FIGURE 2-6. Schematic cyclic voltammogram.
REFERENCES (Chapter 2)


CHAPTER 3.

EXPERIMENTAL

3.1 CHEMICALS AND SOLUTIONS

All solutions were prepared from chemicals of Analar grade and high quality water from a Millipore Milli-Q reagent water system and were adjusted to the desired pH by the addition of sulphuric acid or sodium hydroxide. The pH was measured using a Metrohm E510 pH meter.

3.2 EQUIPMENT, ELECTRODES AND ELECTROCHEMICAL CELL

3.2.1 Equipment

In all electrochemical experiments, the rotating disc apparatus described by Power et al. [1] was used so as to carry out measurements under precisely controlled hydrodynamic conditions. In the kinetic studies in which the cementation rate of Cu(II)/Zn reaction was determined by solution analysis, a zinc disc with an area of about 5.2 cm² was mounted on the end of a stainless steel shaft which could be rotated and the whole coated with an inert epoxy which had been machined to give a shape like a flared cone similar to that used by Pang et al. [2]. The shaft was rotated by a laboratory stirrer motor and its angular velocity monitored by means of an optical tachometer.

The potentiodynamic polarization measurements, Stern-Geary measurements and cyclic voltammetry were carried out using a Princeton Applied Research (PAR) Model 173 potentiostat and a PAR 175 Universal Programmer in conjunction with a Bryans 26000 A3 X-Y chart recorder. A bipotentiostat (RDE 3, Pine Instrument Company) was used in the rotating ring-disc experiment.
The equipment used for the impedance spectroscopy experiments consisted of a Solartron 1186 Electrochemical Interface, 1170 Frequency Response Analyser (FRA) and a 1180 Plotter Interface with a Houston 2000 X-Y recorder. Fig. 3-1 shows the schematic block diagram of the A.C. impedance apparatus. The FRA imposes a small amplitude wave signal of known frequency to the potentiostat, which controls the potential of the working electrode. The current and voltage response of the cell is then fed back to the analyser and the impedance is thereby resolved into the in-phase (real) and out-of-phase (imaginary) components.

In the kinetic studies, a Varian AA-175 Atomic Absorption Spectrophotometer was used to analyse the amounts of copper and zinc in the solution sample.

3.3.2 Electrodes

(1) Working electrode

A variety of working electrodes in disc form including Cu, Zn, Au, Pt, Pd and glassy carbon, etc. has been employed in this study for different purposes. They were all made of high quality materials. For example, the copper disc, supplied by Koch-Light, was stated to be not less than 99.999% pure and the zinc disc had a purity greater than 99.99%.

(2) Counter electrode

A platinum wire, which was made into a spiral and placed in a thin glass tube with a frit at one end dipping into the solution, was used as a counter electrode. With this construction, possible interferences caused by reaction products from the counter electrode may be minimized. The ratio by area of the counter to the working electrode was 35-40.
Fig. 3-1 Schematic block diagram of A.C. impedance apparatus
(3) Reference electrode

Mercury/mercurous sulphate saturated with potassium sulphate was chosen as the reference electrode since the supporting electrolyte used in this study was 0.50 mol dm\(^{-3}\) sodium sulphate. Its standard potential at 22 °C has been reported to be 0.658 V [3]. All the potentials were measured with respect to this reference electrode.

The electrolytic connection between the working and reference electrodes was made with a Luggin capillary filled with the supporting electrolyte, and positioned about 2 mm away from the disc to minimize the IR drop.

3.2.3 Electrochemical Cell

The rotating disc apparatus [1] uses a modified 100 cm\(^3\) jacketed Metrohm polarography cell which has a protruding port at the bottom to accommodate a Luggin capillary. The cap contains holes which accommodate the rotating disc, the counter electrode and facilities for degassing the solution. Approximately 50 cm\(^3\) test solution was actually needed for the electrochemical experiment.

3.3 ELECTRODE PREPARATION, TEMPERATURE CONTROL AND DEGASSING

Before each experiment, the working electrode was abraded using 1200-grade wet and dry paper and then thoroughly rinsed with distilled water. The solution was degassed beforehand with a stream of high-purity nitrogen (for Cu(II)/Zn reaction) or argon (for Co(II)/Zn reaction) (Commonwealth Industrial Gases) for an hour and maintained under an inert atmosphere by continuous bubbling of nitrogen or argon for the duration of the experiment. The use of argon is aimed at avoiding as far as possible passivation of the cobalt deposit.
The solution temperature was maintained at 25±0.1 °C (unless otherwise stated) by circulating thermostated water through the water jacket of the cell.

3.4 EXPERIMENTAL PROCEDURES

3.4.1 Kinetic Studies

In the kinetic studies, the cementation reaction was carried out in a one-litre vessel containing an initial volume of 600 ml and the vessel was fitted with a glass electrode (Orion Combination) for continuously monitoring the solution pH during the course of the reaction. Samples of 1 ml were removed at suitable time intervals and analyzed for copper and zinc content using atomic absorption spectrophotometry.

3.4.2 Electrochemical Studies

The polarization measurements and cyclic voltammetry were carried out in a conventional way and the scan rates of both methods were 2.0 mV s⁻¹ and 100 mV s⁻¹, respectively.

In the Stern-Geary measurements, a scan rate of 0.2 mV s⁻¹ was used and a potential range of 2 mV was chosen in order to guarantee that the polarization curve is linear [4]. A bucking potential was applied between the potentiostat and recorder to obtain a sufficiently sensitive potential scale, e.g., 0.25-0.50 mV cm⁻¹.

When measuring the reaction rate using the stripping method of Barth et al. [5], a copper electrode was first zinc plated from an acid bath [6] at a current density of 0.14 A dm⁻². It was established by weighing and confirmed by coulometry that the current efficiency for zinc deposition
under these circumstances is 99±1%. The reaction time was determined by monitoring the mixed potential of the plated copper electrode using a chart recorder (see Fig. 4-11 and 4-19).

In the impedance measurements, for reasons described in Chapter 5, the mixed potential of zinc was allowed to stabilize for 5 minutes in the copper-containing solution and 1 minute in the cobalt-containing solution, before being held constant by means of the potentiostat. A sinusoidal potential of small amplitude (<±10 mV) was then superimposed upon the mixed potential and frequency swept from 10 KHz to 0.01 Hz. The impedance spectra were automatically recorded on the recorder.

The capacitance measurements were made using the technique of Power and Caldwell [7].

The results are reported with an error expressed as the 95% confidence interval.
REFERENCES (Chapter 3)


CHAPTER 4.

COPPER(II)/ZINC SYSTEM

4.1 INTRODUCTION

The copper(II)/zinc cementation reaction is a thermodynamically highly favourable reaction. This can be seen from the potential-pH diagrams (Pourbaix diagram) of zinc and copper [1].

Fig. 4-1 is a superposition of the respective potential-pH diagrams of zinc and copper. It is clear from Fig. 4-1 that the equilibrium line of the Zn\(^{2+}/\text{Zn}\) couple is well below that of the Cu\(^{2+}/\text{Cu}\) couple with the two lines being separated by a margin of 1.1 volts, the electromotive force of the standard copper-zinc galvanic cell. This indicates the large driving force of the reaction by which the copper(II) ions are reduced and zinc oxidized.

The potential-pH diagram can also be used to predict the upper limit of pH for the copper(II)-containing solution, which is determined by the solubility product of Cu(OH)\(_2\). This would be approximately 6.5 for a solution containing 10 ppm or 1.57 x 10\(^{-4}\) mol dm\(^{-3}\) Cu(II), as shown in Fig. 4-1. Fig. 4-1 also indicates the possibility of cuprous oxide formation at a pH value of 5.7.

The copper(II)/zinc reaction proceeds very rapidly. It has found many practical applications and stimulated much research interest.

The aim of this work is to study the kinetics and mechanisms of the Cu(II)/Zn reaction, with the particular objective of testing the suitability of various electrochemical methods in the study of this kind of reaction. To this end, the anodic dissolution of zinc and cathodic reduction of
FIGURE 4-1. Superposition of potential-pH diagrams of zinc and copper showing the possibility of Cu(II)/Zn cementation reaction.

a. $2H^+ + 2e = H_2$

$E^0 = 0 - 0.0591 \text{ pH}$

b. $O_2 + 4H^+ + 4e = 2H_2O$

$E^0 = 1.228 - 0.0591 \text{ pH}$
copper(II), half reactions of the Cu(II)/Zn system will be first investigated.

4.2 REVIEW OF COPPER(II)/ZINC CEMENTATION REACTION AND ITS TWO
     HALF REACTIONS

4.2.1 Review of the Cu(II)/Zn Cementation Reaction

The study of Cu(II)/Zn reaction has a long history. In their investigation of 1873, Gladstone and Tribe [2] observed a black copper deposit on the surface of zinc and found zinc in the precipitated copper. Later on, the kinetics of this reaction were investigated by King and Burger [3] who, using a rotating cylinder, came to the conclusion that "there is no indication that the chemical reaction is slow enough to be a controlling factor at any stirring speed studied", implying that this reaction is diffusion controlled. The same conclusion was reached by Shestakova [4] from a consideration of the polarization curves for this reaction. Van Straten and Ehret [5] also indicated the diffusion controlled nature of this reaction based on the increase in the amount of copper deposit with increasing stirring of solution.

The most conclusive results about the kinetics of the Cu(II)/Zn reaction were obtained by Strickland and Lawson [6] using a rotating zinc disc. They found that there exists a linear relationship between the rate of copper cementation with zinc and the square root of the disc rotation speed, thus unequivocally demonstrating the diffusion controlled nature of this reaction. Furthermore, they observed that the copper deposit has a significant influence on the reaction rate and when the copper deposit exceeds a certain critical mass, the first order rate increases sharply. These authors believe that the sharp increase in rate is due to turbulence
at the disc surface caused by the increased surface roughness. This kind of deposit effect has turned out to be quite common in cementation reactions (see Chapter 2).

However, in electrochemical studies, the time necessary to determine the reaction rate is usually much shorter than it would be in a conventional chemical kinetic study. It can be expected, therefore, that results derived from electrochemical measurements in the initial stages of the reaction may well be free of the deposit effect; in other words, the results obtained in this way should be consistent with the first-stage kinetic data obtained from chemical kinetic measurements using the same sample geometry and under laminar flow conditions. This inference has been confirmed in this study.

Apart from deposit effects, another feature of the Cu(II)/Zn reaction is the codeposition of zinc with copper forming brass in the reaction. An early study of the composition and structure of the deposits obtained in the Cu(II)/Zn reaction was made by van Straten and Ehret [5] by both chemical and x-ray diffraction methods. Their results showed that a large amount of cuprous oxide and brass, mainly the \( \alpha \)-phase, were formed during the reaction. Later on, Straumanis and Fang [7] also succeeded in identifying \( \alpha \)-brass formation.

4.2.2 Review of the Anodic Dissolution of Zinc

To date, the anodic dissolution of zinc has been studied by a number of researchers, mostly using polarization curves [8,9,10,11] and impedance spectroscopy [12]. A brief review of this work was given by Brodd and Leger [32]. It is generally agreed that the dissolution as well as the deposition of zinc [13] occur through two one-electron charge transfer steps.

\[
\begin{align*}
\text{Zn} & \rightarrow \text{Zn(I)} + e \\
\text{Zn(I)} & \rightarrow \text{Zn(II)} + e
\end{align*}
\] (4-1) (4-2)
with Zn(I) being an intermediate adsorbed on the surface of the electrode. If step (2) of the above mechanism is slow, the Tafel slope would be 40 mV and if step (1) is rate-determining, a slope of 120 mV would be obtained.

In spite of this, however, controversies still exist. A mechanism of a one step two-electron charge transfer was postulated by certain authors [14,15]. In addition, a recent impedance study of the anodic dissolution of zinc in an acidic chloride electrolyte showed that there are three relaxation processes at low frequencies indicating that the zinc dissolution probably involves a more complicated mechanism than that mentioned above.

Although the step-wise electron transfer mechanism of zinc dissolution has been supported by much evidence and so nowadays has become generally accepted, it may be somewhat different under appropriate conditions. This can be clearly seen from the divergence of Tafel slopes. According to the literature, Tafel slopes for the anodic dissolution of zinc are 120 mV per decade current density in the region of higher overpotentials, both in perchlorate [8,9] and chloride [10] media, but 40 mV in the low overpotential region [8,9] in perchlorate as well as in 1 mol dm\(^{-3}\) sodium sulphate solution [11].

4.2.3 Review of the Cathodic Reduction of Copper

The kinetics and mechanism of the cathodic reduction of copper(II) in copper sulphate and sulphuric acid media have been studied in great detail [16,17,18], and a general consensus has been reached that the rate-determining step of the copper reduction in acidic media is a one-electron transfer process of the cupric ion forming a monovalent copper, Cu\(^+\), the existence of which has been experimentally confirmed by using a rotating ring-disc technique [19,20].
4.3 ANODIC DISSOLUTION OF ZINC

4.3.1 Current-Potential Curves

Fig. 4-2 shows the current-potential curves for the anodic dissolution of zinc in a sulphate medium with a total ionic strength $\mu = 1.5$, which was achieved by sodium perchlorate additions. It is clear from Fig. 4-2 that the sulphate concentration has a greater influence on the rest potential of zinc as well as the shape of the polarization curves than one might expect intuitively. With an increase in sulphate concentration, the anodic current increased considerably and the rest potential was found to shift towards the negative direction as shown in Fig. 4-3. This result indicates that the sulphate ion has a certain activating action, relative to the perchlorate ion, on the anodic dissolution of zinc.

The activating action of the sulphate ion on the anodic dissolution of zinc observed in this study agrees with that reported earlier by Baugh [11] who found that the effect of ions on the anodic current of zinc increased in the order $\text{ClO}_4^- << \text{Cl}^- < \text{SO}_4^{2-}$ who attributed this phenomenon to ion pair formation between the $\text{SO}_4^{2-}$ (or $\text{Cl}^-$) ions with $\text{Zn}^{2+}$ ions. Ion pair formation would be expected to decrease the activation energy for dissolution, possibly as a result of the favourable electrostatic attraction of $\text{Zn}^{2+}$ ions away from the zinc surface and so increase the anodic current of zinc.

4.3.2 Tafel Plot

Fig. 4-4 is a typical Tafel plot for zinc dissolution in 0.50 mol dm$^{-3}$ $\text{Na}_2\text{SO}_4$ solution. From the Tafel plots, the Tafel slopes, listed in Table 4-1, for various solutions with different sulphate concentrations but consistent total ionic strength, were estimated.
FIGURE 4-2. Current-potential curves for the anodic dissolution of zinc at various sulphate concentrations and a total ionic strength $\mu = 1.5$, pH = 5.7, 700 rpm, Cu electrode.

(1) $0.50 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$
(2) $0.40 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4 + 0.30 \text{ mol dm}^{-3} \text{ NaClO}_4$
(3) $0.30 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4 + 0.60 \text{ mol dm}^{-3} \text{ NaClO}_4$
(4) $0.10 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4 + 1.2 \text{ mol dm}^{-3} \text{ NaClO}_4$
(5) $1.5 \text{ mol dm}^{-3} \text{ NaClO}_4$
FIGURE 4-3. Rest potential of zinc as a function of sulphate concentration.

The ionic strength is kept at 1.5.
FIGURE 4-4. Tafel plot for the anodic dissolution of zinc in 0.50 mol dm\(^{-3}\) \(\text{Na}_2\text{SO}_4\), pH 5.7, 700 rpm.
Table 4-1  Tafel slopes ($b_a$) for zinc dissolution at 700 rpm and an ionic strength ($\mu$) of 1.5

<table>
<thead>
<tr>
<th>Solutions, concentrations in mol dm$^{-3}$</th>
<th>Tafel slopes mV/decade</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50 Na$_2$SO$_4$</td>
<td>60 $\pm$ 4*</td>
</tr>
<tr>
<td>0.30 NaClO$_4$</td>
<td></td>
</tr>
<tr>
<td>0.40 Na$_2$SO$_4$</td>
<td>75</td>
</tr>
<tr>
<td>0.60 NaClO$_4$</td>
<td></td>
</tr>
<tr>
<td>0.30 Na$_2$SO$_4$</td>
<td>85</td>
</tr>
<tr>
<td>0.90 NaClO$_4$</td>
<td></td>
</tr>
<tr>
<td>0.20 Na$_2$SO$_4$</td>
<td>88</td>
</tr>
<tr>
<td>1.20 NaClO$_4$</td>
<td></td>
</tr>
<tr>
<td>0.10 Na$_2$SO$_4$</td>
<td>97</td>
</tr>
<tr>
<td>1.50 NaClO$_4$</td>
<td>113 $\pm$ 3</td>
</tr>
</tbody>
</table>

*in both quiescent and stirred solution.

The data for $b_a$ listed in Table 4-1 strongly suggest that the mechanism of zinc dissolution in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$ is likely to be different from that in 1.5 mol dm$^{-3}$ NaClO$_4$.

The reliability of the $b_a$ value of 60 mV for zinc in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$ solution will be further demonstrated later when consistent values of rate constants are calculated from Stern-Geary measurements and the above $b_a$ value (see section 4.5.2.2).

4.3.3 Reaction Order with Respect to SO$_4^{2-}$

From the data in Fig. 4-4, it is possible to determine the reaction order, $\rho$, an important kinetic parameter which is defined by equation 4-3 [21].

$$\rho = \frac{\frac{3}{2} \log \frac{1}{C_{SO_4^{2-}}}}{\frac{3}{2} \log E}$$ (4-3)
FIGURE 4-5. Plot of $\log i$ versus $\log C_{SO_4^{2-}}$ at -1.50 V. Total ionic strength 1.5, pH 5.7, 700 rpm.
i.e., the reaction order is the slope of a plot of log i versus log $C_{SO_4^{2-}}$ at constant potential.

As can be seen from Fig. 4-5, the plot of log i at -1.50 V against log $C_{SO_4^{2-}}$ is a straight line whose slope is equal to 1.3±0.2. It was rather difficult to determine the reaction order with respect to $SO_4^{2-}$ over a wide range of potentials because the rest potential of zinc shifts considerably with sulphate concentrations, and useful results could only be obtained near -1.50 V.

4.3.4 Mechanism of Zinc Dissolution

Assuming that the mechanism of zinc dissolution is not affected when the sulphate concentration exceeds 0.50 mol dm$^{-3}$, then a possible reaction mechanism of zinc dissolution, which accounts for the Tafel slope and reaction order, may be proposed as follows.

$$\begin{align*}
\text{Zn} & \xrightarrow{k_1} \text{Zn}^+ + e \quad \text{fast} \\
\text{Zn}^+ + \text{SO}_4^{2-} & \xrightarrow{k_2} \text{ZnSO}_4^{-} \quad \text{slow} \\
\text{ZnSO}_4^{-} \quad & \rightarrow \text{Zn}^{2+} + \text{SO}_4^{2-} + e \quad \text{fast}
\end{align*}$$

From (4-5),

$$i = Fk_2[\text{Zn}^+][\text{SO}_4^{2-}]$$

According to steady state-theory, equilibrium (4-4) would then be governed by the Nernst equation. Assuming that the activity of zinc metal is unity, then,

$$[\text{Zn}^+] = \exp(\Delta E/RT)$$

where $\Delta E$ is the difference between the applied and rest potentials, and the other symbols have their usual meanings. By substituting (4-8) into (4-7), we get

$$i = Fk_2[\text{SO}_4^{2-}]\exp(\Delta E/RT)$$
Equation (4-9) predicts that in high sulphate concentrations, the Tafel slope for zinc dissolution at 25 °C will be 59 mV per decade of current density which is in good agreement with the present experimental findings. In addition, the reaction order with respect to the sulphate ion is expected to be unity. The experimental result of 1.3±0.2 is not far from this value.

Apart from route I (equations (4-4) to (4-9)), the zinc dissolution can take place via another route, II, which is represented by equations (4-1) and (4-2) with step (1) being rate-determining and which would be parallel to route I. This picture explains the gradual transition of $b_n$ value from 60 mV in high sulphate media to 113 mV in pure perchlorate solutions as shown in Table 4-1. Because route I is faster than route II, as a result of the involvement of the ZnSO$_4$ ion pair, sulphate ions increase the rate of zinc dissolution, and conversely, perchlorate ions can slow the rate down.

4.4 CATHODIC REDUCTION OF COPPER(II)

As noted earlier in 4.2.3, copper deposition from sulphate solution has been studied in some detail, and so the present study is only to determine polarization curves under the conditions of our cementation reactions.

4.4.1 Current-Potential Curve

Fig. 4-6 shows the cathodic current-potential curve for the reduction of cupric ions on a copper electrode, which has three features: a small potential step $a$ at less negative potentials, a limiting current region $b$ at moderate potentials and a tail part $c$ which is due to the reduction of hydrogen ions.
FIGURE 4-6. Current-potential curve for the reduction of copper(II) on a copper electrode. 10 ppm Cu$^{2+}$ in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH 5.7, 700 rpm.
The small overpotential step $\alpha$, which is independent of disc rotation speed, is only observed on a copper electrode. As others have found [19], the small step is not present when the reduction is carried out on a platinum electrode. We have confirmed this result and also found it to be true for palladium or glassy carbon electrodes. We believe that the step $\alpha$ is associated in some way with the formation of copper(I) at the copper electrode.

4.4.2 Levich Plot

A plot of the limiting current for the cathodic reduction of Cu(II) as a function of the square root of the angular velocity is shown in Fig. 4-7. From the slope of the resulting straight line, a diffusion coefficient for the cupric ion, $D_{\text{Cu}^{2+}}$, of $(7.2 \pm 0.2) \times 10^{-10}$ m$^2$ s$^{-1}$ is obtained.

The kinematic viscosity of 0.50 mol dm$^{-3}$ sodium sulphate used in the calculation of $D_{\text{Cu}^{2+}}$ was obtained by interpolation of the data obtained from a handbook [22] and was found to be $1.16 \times 10^{-6}$ m$^2$s$^{-1}$ (Fig. 4-8).

4.5 COPPER(II)/ZINC CEMENTATION REACTION

4.5.1 Kinetic Studies

4.5.1.1 Solution Analysis

The reaction rate was first measured by analysis of the solution, both reactant and product species, using atomic absorption spectrophotometry.

(a) Stoichiometry

If the cementation reaction

$$\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$$  \hspace{1cm} (4-10)
FIGURE 4-7. Levich plot for the cathodic reduction of Cu(II), in 10 ppm Cu^{2+} and 0.50 mol dm^{-3} Na_{2}SO_{4} at pH 5.7. The area of copper electrode is 7.07 \times 10^{-6} \text{ m}^2.
FIGURE 4-8. Kinematic viscosity ($\nu = \frac{\eta}{\rho}$) of sodium sulphate solution.
is stoichiometric, the decrease in the copper concentration (\(\Delta [\text{Cu}^{2+}]\)) in solution at any time should be exactly balanced by the increase in the zinc concentration (\(\Delta [\text{Zn}^{2+}]\)). However, as shown in Fig. 4-9, Zn\(^{2+}\) formation is faster than Cu\(^{2+}\) loss.

The most likely cause of this imbalance is the reaction of zinc metal with protons

\[
\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2
\]  

(4-11)

which is catalysed by the copper deposited on the zinc surface, the over-potential for the reduction of protons on copper being very much less than that of zinc [23]. Under these circumstances, one would anticipate that the increase in the zinc ion concentration should exactly balance the decrease in the copper ion concentration plus half the decrease in the proton concentration (\(\Delta [\text{H}^+]\)). It should be noted in passing that this relationship should also hold even if the zinc is being oxidized by any dissolved oxygen present in solution. Fig. 4-9 also shows the change of proton concentrations during a typical cementation reaction.

However, a careful inspection of the results in Fig. 4-9 shows that the rate of change of proton concentration is less than the difference between those of the zinc and copper.

The reason why there is a relatively small change in pH during the cementation reaction is believed to be due to the buffering action of the bisulphate ions present in the background electrolyte. As protons are removed from solution by reaction with zinc metal, they are replaced by protons from the decomposition of bisulphate ions.

\[
\text{HSO}_4^- \rightarrow \text{H}^+ + \text{SO}_4^{2-}
\]  

(4-12)

With this as a hypothesis, it is possible to make a rough estimate of pKa for the bisulphate ion in 0.50 mol dm\(^{-3}\) sodium sulphate from the results
FIGURE 4-9. Change of copper, zinc and proton concentrations during a typical cementation reaction.
initial \([\text{Zn}^{2+}] = 0\); initial \([\text{Cu}^{2+}] = 10\) ppm; initial pH 5.6; disc rotation speed 700 rpm.
shown in Fig. 4-9, using the technique described in Appendix 1.

The value of pKa so obtained was 1.3±0.2. pKa values for the bisulphate ion at infinite dilution are generally close to 2 [24] and a pKa of 0.54 was obtained for a saturated solution of sodium sulphate at 32 °C [25]. Considering the above situations, the pKa value of 1.3 and the interpretation of the results above would seem to be reasonable. Similar calculations on possible equilibria involving, for example, cation hydrolysis, showed that the effect on the pH change would be very slight.

(b) Rate law

Almost without exception, cementation reactions follow first order kinetics with respect to the cementation of the more noble metal ion [26].

Fig. 4-10(1) shows the first order plot with respect to copper(II) ions and from the slope of the straight line, the rate constant k(Cu) can be calculated. The rate of increase in the zinc ions was also found to be approximately first order (Fig. 4-10(2)). The values of k(Cu) and k(Zn) thus determined from such plots are (4.5±0.4) x 10^{-5} m s^{-1} and (5.1±0.4) x 10^{-5} m s^{-1} respectively, with errors corresponding to the 95% confidence interval. As expected, k(Zn) is greater than k(Cu).

Fig. 4-10(1) also shows the second stage first order kinetics of this reaction which was observed when it proceeded for more than two hours, the calculated rate constant being 1.2 x 10^{-4} m s^{-1}.

In this study, the correction for the change in solution volume in the determination of rate was considered unnecessary since each sample was only 0.2% of the total volume of solution.
FIGURE 4-10. First order plot for Cu(II)/Zn cementation reaction.

10 ppm Cu$^{2+}$ in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH 5.7, 700 rpm.

Co = [Cu$^{2+}$]$_0$, C$_t$ = [Cu$^{2+}$]$_t$(1) and [Cu$^{2+}$]$_0$-[Zn$^{2+}$]$_t$(2)
4.5.1.2 Chronopotentiometry (stripping)

The value of $k(Zn)$ can also be determined by chronopotentiometry or the stripping method (see Chapter 2). A thin zinc film is electroplated onto an inert copper electrode and placed in a solution containing copper(II) with which it reacts. When the zinc is completely consumed, the potential of the reacting zinc-plated electrode rises to the equilibrium value of a copper electrode in the given solution.

A typical chronopotentiogram for the reaction of a zinc film with copper(II) and protons is given in Fig. 4-11(1) from which it can be seen that the potential, after a slow start, increases rapidly (a) until a plateau $b$ is attained. This is followed by a second small potential rise to a second plateau $c$ corresponding to the final potential of the reaction. By analysing the electrode surface using the energy dispersive x-ray analysis facility on the scanning electron microscope, it was established that zinc was present all along the curve $a$ but was absent on the plateau $b$.

The reason why the potential increases rapidly in the region $a$ is the increase in the ratio of cathodic to anodic area. As zinc is stripped from the inert copper electrode surface during the cementation reaction, the anodic area is decreased and the cathodic area is correspondingly increased due to the deposition of fresh copper.

Since plateau $c$ is clearly the equilibrium potential of a copper electrode in a solution containing 10 ppm, i.e. $1.57 \times 10^{-4}$ mol dm$^{-3}$ copper(II) (the measured potential is -0.45 V which may be compared with the potential of -0.43 V calculated from the Nernst equation, assuming an $E^0$ of 0.34 V vs SHE [22]), the question arises as to what is the origin of plateau $b$. By observing the electrode surface during plateau $b$, it was
FIGURE 4-11. 1. Chronopotentiogram for the reaction of a zinc film with copper(II) solution.

initial [Cu$^{2+}$] = 10 ppm in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH 5.7, 700 rpm.

2. Capacitance (c)-time (t) relation corresponding to (1).
noted that the electrode gradually changes its colour from black to dull brass, although no zinc could be detected in the product layer. During plateau $b$, it would therefore appear that the finely divided black copper deposit has recrystallised to a more massive form which reflects light. The brassy colouration might also be due to the formation of a thin layer of cuprous oxide on the copper surface.

Confirmation of surface recrystallization was obtained from capacitance measurements on the reacting surface as a function of time. These capacitance measurements, a typical one being shown in Fig. 4-11(2), give information about the area of the reacting surface during the course of the reaction. It can be seen that in the initial stage of the reaction, the area rises rapidly as copper is deposited on the zinc surface. The area is essentially constant when plateau $b$ is reached but drops sharply towards the end of plateau $b$. And finally, the curve levels off indicating a stable value of the area due to the completion of the surface recrystallization, which corresponds to the second plateau $c$. This is the sort of behaviour that would be expected of a finely divided surface which is recrystallizing, and has already been reported for fresh, finely divided silver surfaces [27].

From the chronopotentiogram, the dissolution time, $t_d$, can be estimated by extrapolating the rapidly increasing section $a$ and the first plateau $b$. The change of copper concentration during the course of reaction is negligible. This is because the copper solution typically contains $7.8 \times 10^{-6}$ mol copper(II), whereas there is only $5 \times 10^{-8}$ mol zinc in the film. As a result, the reactant concentration and hence the reaction rate is essentially constant. Thus, the reaction rate, expressed as a corrosion current density, $i_c$, can be given by

$$i_c = \eta \ I_p \ t_p / A \ t_d$$  \hspace{1cm} (4-13)
Having obtained $i_C$ in this manner, $k$ can be calculated from the equation

$$k = \frac{i_C}{2F[Cu^{2+}]} \quad (4-14)$$

The $k$ calculated in this way is $k$(Zn) because the zinc film is reacting with both copper(II) ions and protons. Under the conditions of 10 ppm Cu$^{2+}$, 700 rpm and 25 °C, the value of $k$(Zn) determined from this stripping method is $(5.0\pm0.2) \times 10^{-5}$ m s$^{-1}$.

4.5.2 Electrochemical Studies

In addition to the kinetic studies described above, the Cu(II)/Zn reaction was also investigated using polarization measurements and Evans' diagrams, and polarization resistance measurements.

4.5.2.1 Evans' diagram

This approach to the determination of the reaction rate is to plot the two polarization curves for the dissolution of Zn and the reduction of copper(II) ions on the same potential-log (current density) diagram and then determine the reaction current density, $i$, from the intersection of the two curves [28].

Fig. 4-12 shows the Evans' diagram for the copper(II)/zinc cementation reaction. The zinc dissolution curve 1 is essentially linear with a Tafel slope of approximately 60 mV per decade of current density and is independent of rotation speed. The polarization curve 2 for the reduction of copper(II) ions, already discussed in 4.4, is characterized by three features: a small potential step $a$ at less negative potentials, a limiting current part $b$ at moderate potentials and a tail part $c$ which is due to hydrogen evolution.
FIGURE 4-12. Evans' diagram for the Cu(II)/Zn cementation reaction.

1. for the reaction of Zn → Zn$^{2+}$ + 2e on a zinc electrode in 10 ppm Zn$^{2+}$ and 0.50 mol dm$^{-3}$ Na$_2$SO$_4$ at pH 5.7 and 700 rpm.

2. for the reaction of Cu$^{2+}$ + 2e → Cu on a copper electrode in 10 ppm Cu$^{2+}$ and 0.50 mol dm$^{-3}$ Na$_2$SO$_4$ at pH 5.7 and 700 rpm.
From Fig. 4-12, it can be seen that the rate at which copper(II) is removed from solution in the cementation reaction will be determined by the speed at which copper(II) diffuses to the zinc surface, provided the anodic and cathodic reactions of the copper proceed independently on that surface. This is because the zinc dissolution curve cuts the extension of the copper deposition curve in the limiting current \( b \). Under these circumstances, it is possible to calculate \( k(\text{Cu}) \) using equation (4-14) and the value of the limiting current. The values of \( k(\text{Cu}) \) so obtained are proportional to the square root of the rotation speed of the zinc disc (Fig. 4-16c). At 700 rpm and 25 °C, \( k(\text{Cu}) \) is \((4.1 \pm 0.3) \times 10^{-5} \text{ m s}^{-1}\).

The diffusional control nature of the copper(II)/zinc cementation reaction can also be demonstrated by the dependence of the mixed potential of zinc on rotation speed (see Chapter 2) as shown in Fig. 4-13.

It can be seen from Fig. 4-13 that the plot of mixed potential against the log (angular velocity) is a straight line with a positive slope, as predicted by the theory [29], implying that in the case of Cu(II)/Zn reaction, the cathodic half reaction is diffusion controlled and the anodic half reaction is electrochemically controlled. But the slope is about 20 mV, rather than 30 mV as predicted by the theory. It is almost certain that this difference is due to the fact that the hydrogen evolution reaction is involved and is chemically controlled.

4.5.2.2 Stern-Geary method

The reaction current density of an electrochemical system can also be calculated by means of the Stern-Geary equation

\[
i = \frac{1}{2.303 R_p (b_a^{-1} + b_c^{-1})^{-1}} \quad (2-13)
\]

provided the polarization resistance, \( R_p \), as well as \( b_a \) and \( b_c \) are known.
FIGURE 4-13. Mixed potential of zinc as a function of the logarithm of the angular velocity for the Cu(II)/Zn cementation reaction in 10 ppm Cu$^{2+}$ and 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH 5.7.
In this section, polarization resistances for the Cu(II)/Zn reaction, measured by both Stern-Geary technique and impedance spectroscopy, are reported.

In the case of the cementation of copper from solution by zinc, however, the system is complicated by the simultaneous displacement of protons from solution. Generally speaking, it is not possible to calculate either \( k(\text{Cu}) \) or \( k(\text{Zn}) \) unless we are sure of the contribution of the Cu(II)/Zn and \( H^+/\text{Zn} \) reactions to the polarization resistance.

If it is assumed that the Cu(II)/Zn and \( H^+/\text{Zn} \) reactions proceed independently and in parallel on the zinc surface, then the total polarization resistance, \( R_p \), may be estimated from the equation

\[
\frac{1}{R_p} = \left( \frac{1}{R_p(\text{Cu})} \right) + \left( \frac{1}{R_p(\text{H})} \right)
\]  

(4-15)

where \( R_p(\text{Cu}) \) and \( R_p(\text{H}) \) are the polarization resistances of the Cu(II)/Zn and \( H^+/\text{Zn} \) reactions, respectively.

\( R_p(\text{Cu}) \) and \( R_p(\text{H}) \) can be calculated from equation (2-13). For the Cu(II)/Zn reaction, from Fig. 4-12, \( i = 1.24 \text{ A m}^{-2}, b_a = 0.06 \text{ V}, b_c = \infty \). The calculated value of \( R_p(\text{Cu}) \) is therefore \( 2.10 \times 10^{-2} \Omega \text{m}^2 \). For the \( H^+/\text{Zn} \) reaction, from Fig. 4-12 again, \( i = 0.24 \text{ A m}^{-2}, b_a = 0.06 \text{ V}, \) and \( b_c = 0.115 \text{ V} \) for the discharge of protons on copper [23]. A combination of these figures gives a value of \( R_p(\text{H}) \) of \( 7.15 \times 10^{-2} \Omega \text{m}^2 \). Then, from equation (4-15), a total \( R_p \) (calculated) of \( 1.62 \times 10^{-2} \Omega \text{m}^2 \) is obtained. The experimental value from the Stern-Geary technique averaged over five measurements is \( (1.63 \pm 0.07) \times 10^{-2} \Omega \text{m}^2 \), in good agreement with the calculated value. Thus the application of the Stern-Geary method to the measurement of the rate of metal cementation reactions seems justified. In other words, in the case of Cu(II)/Zn reaction, the measured \( R_p \) can be used to calculate the apparent rate constant, \( k(\text{Zn}) \).
4.5.2.3 Impedance spectroscopy

The impedance spectrum for the cementation of copper(II) from solution by a rotating disc is shown in Fig. 4-14.

It can be seen from Fig. 4-14A that the impedance spectrum probably consists of three flattened overlapped semicircles. Besides the capacitive loop at high frequency, there are two low-frequency capacitive loops on the impedance diagram. According to the phenomenological analysis of experimental impedance diagrams [30], this may be explained by assuming two relaxation processes which may be related to the existence of two adsorbed intermediates.

In order to get further information about the nature of the adsorbed species, impedance measurements were made of the two half reactions of the Cu(II)/Zn cementation reaction. It can be seen from Fig. 4-15 that, under the same conditions as that for the Cu(II)/Zn reaction, the impedance spectrum of zinc dissolution, A, shows a low frequency capacitive loop fairly similar to that for Cu(II)/Zn reaction (Fig. 4-14A), but the impedance spectrum of copper deposition, B, is remarkably different. In addition, in the presence of a trace amount of benzoquinone, an oxidant, the spectrum for the Cu(II)/Zn reaction loses one low frequency capacitive loop as shown in Fig. 4-14B. One likely explanation of the above fact is that the adsorption of hydrogen, a by-product of the Cu(II)/Zn cementation reaction, may be involved in the Cu(II)/Zn cementation reaction.

On the grounds of the results of the impedance measurements as well as of zinc dissolution results discussed in Section 4.3, it seems reasonable to suppose that the adsorbed species involved in the Cu(II)/Zn reaction are likely to be $\text{ZnSO}_4^{2-}\text{ads}$ and $\text{H}_\text{ads}$.

From Fig. 4-14A, it is possible to determine the polarization resistance of the Cu(II)/Zn reaction. This can be done by simply extrapolating
FIGURE 4-14. Impedance spectra for the Cu(II)/Zn cementation reaction.

A. 10 ppm Cu$^{2+}$ in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$ at -1.528 V,
pH 5.7, 700 rpm, 18 °C.

B. A + 10$^{-6}$ mol dm$^{-3}$ benzoquinone

$Z'$ - real part of the impedance
$Z''$ - imaginary part of the impedance.
FIGURE 4-15. Impedance spectra of the half reactions of the Cu(II)/Zn cementation reaction.

A. zinc dissolution at -1.528 V
B. copper reduction at -1.528 V at which the limiting current is reached.

Other conditions are the same as described in Fig. 4-14.
to zero frequency to get \((R_p + R_\infty)\) with \(R_\infty\), the resistance of solution and electrode surface, being 3-5 ohms as determined from the high frequency intercept with the real axis. From \(R_p\) a rate constant of \((4.5\pm0.3) \times 10^{-5}\) m s\(^{-1}\) was calculated using equations (2-10) and (2-14). Since the impedance spectrum is basically that of zinc, it would seem reasonable to suppose that the rate constant is \(k(Zn)\). The rate obtained, while quite reproducible, is appreciably less (10%) than values of \(k(Zn)\) obtained by other methods (see Table 4-2). This is not surprising since Lorenz and Mansfield [31] have stated that an accurate determination of \(R_p\) from an impedance spectrum is only possible if the spectrum is a simple one with only one time constant. Although the rate constants calculated from impedance spectra are not so accurate, they do show the expected variation with \(\omega^{1/2}\) for a diffusion controlled reaction.

4.5.3 Comparison of \(k(Cu)\) and \(k(Zn)\) determined from the various methods

The rate constants measured by a variety of methods are summarized in Table 4-2.

Table 4-2 Rate constants for the \(Cu(II)/Zn\) cementation reaction.

<table>
<thead>
<tr>
<th>Method</th>
<th>(10^5 k(Cu)/m\ s^{-1})</th>
<th>(10^5 k(Zn)/m\ s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution analysis</td>
<td>4.5±0.4</td>
<td>5.1±0.4</td>
</tr>
<tr>
<td>Evans' diagram</td>
<td>4.1±0.3</td>
<td>4.9±0.3</td>
</tr>
<tr>
<td>Chronopotentiometry (stripping)</td>
<td></td>
<td>5.0±0.2</td>
</tr>
<tr>
<td>Stern-Geary</td>
<td></td>
<td>5.3±0.3</td>
</tr>
<tr>
<td>Impedance spectroscopy</td>
<td></td>
<td>4.5±0.3</td>
</tr>
</tbody>
</table>
The results obtained from solution analysis, while time consuming, are those which must be regarded as the most reliable, although the particular case of the copper(II)/zinc reaction clearly illustrates the need to check on the stoichiometry of the reaction. The stripping method can give accurate results and is convenient in practice; it provides an elegant way for the determination of the reaction rate of cementation reactions by following the dissolution rate of a solid reactant. However, the interpretation of chronopotentiograms is not always straightforward, as shown in the copper(II)/zinc system. The method based on the construction of an Evans' diagram gives accurate results for the start of the reaction, and shows up problems like hydrogen evolution. However, it is not a good technique if the two half reactions interfere with each other, as they may well do if the reaction is chemically controlled, or if the deposit blocks the reacting surface or the product ion interferes in the deposition of a noble ion.

It should be noted that it is not possible to obtain the rate directly from the Stern-Geary measurements because the information of Tafel slopes is needed for the eventual calculation of k. It is certainly a rapid and convenient method for making an instantaneous measurement of the cementation rate. Even though Cu(II)/Zn cementation is associated with the $\text{H}^+/\text{Zn}$ reaction, the Stern-Geary measurements can still lead to a right value of $k(\text{Zn})$. It therefore seems likely that the Stern-Geary measurements would have given a reliable value for $k(\text{Cu})$ had the $\text{H}^+/\text{Zn}$ reaction been absent.

Although the impedance technique gives a k value of the right order of magnitude, it should be used with care because of the complications involved in the interpretation of impedance spectra. It is also not very clear how the side reaction e.g. $\text{H}^+/\text{Zn}$ reaction is contributing to the spectrum.
4.5.4 Other Factors Affecting the Reaction Rate

4.5.4.1 Rotation speed

Fig. 4-16 shows the dependence of rate constants (k) obtained by various methods on the square root of the angular velocity. The linear relationship of the k vs. $\omega^{1/2}$ plot in the case of Evans' diagram (c) is self evident. The fairly good linear plots when k values are obtained by stripping (a) and impedance spectroscopy (b) further confirm the conclusion that the Cu(II)/Zn cementation reaction proceeds under diffusion control.

4.5.4.2 Copper(II) concentration

Most experimental studies of cementation reactions have shown that the reaction rate follows first order kinetics with respect to the concentration of the noble metal ion [26]. In principle, the first order rate constant k is independent of the initial concentration, but in practice, some slight dependence is observed because k depends on the diffusion coefficient and kinematic viscosity which are themselves slightly concentration dependent. This is also true for the copper(II)/zinc reaction. Fig. 4-17 shows the effect of the initial copper concentration on the rate constants, k(Zn), obtained by the stripping method.

It can be seen from Fig. 4-17 that, within the copper(II) concentration range from 10 to 100 ppm, the rate constants vary within 10% as the noble metal ion concentration increases. This is similar to the results obtained by Strickland and Lawson [6] that the initial copper(II) concentration over the range 5 to 10 ppm does not affect the reaction rate at the first stage. Considering how much less copper is deposited in the stripping method, say about 0.04 mg/cm$^2$ copper, then the critical mass needed for the second stage kinetics [6] is not reached, and so the values of k(Zn) obtained in this way are believed to be free of deposit effect.
FIGURE 4-16. Rate constants as a function of the rotation speed.

a. $k_{Zn}$ by stripping
b. $k_{Zn}$ by impedance spectroscopy
c. $k_{Cu}$ by Evans' diagram.
FIGURE 4-17  Initial copper(II) concentration dependence of $k(\text{Zn})$.

0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH 5.7, 700 rpm.
A significant drop in the rate constant is observed when the initial concentration is high. For example, the rate constant for 1270 ppm copper is, from the Evans' diagram, $3.3 \times 10^{-5} \text{ m s}^{-1}$, 20% less compared with $4.1 \times 10^{-5} \text{ m s}^{-1}$ at an initial concentration of 10 ppm copper. Presumably, this may be ascribed to the activity coefficient effect [26].

4.5.4.3 Zinc ions

An understanding of the effect of zinc ions on the reaction rate of the Cu(II)/Zn cementation reaction is of practical significance because in the industrial situation, the removal of copper from zinc sulphate is carried out in the presence of high concentrations of zinc.

In the case of the Cu(II)/Zn cementation reaction, the influence of zinc ions can be simply ascertained by measuring the limiting currents for copper(II) reduction in solutions containing various concentrations of zinc(II). From these measurements, rate constants can be estimated by using equation (4-14). Table 4-3 lists the values of $k(\text{Cu})$ under various conditions.

Table 4-3  Effect of zinc ions on the rate constant, $k(\text{Cu})$.

<table>
<thead>
<tr>
<th>Concentration of Cu(II), in ppm</th>
<th>$k(\text{Cu})/10^{-5} \text{ m s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$</td>
</tr>
<tr>
<td>10</td>
<td>4.1</td>
</tr>
<tr>
<td>1270</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Values of $k(\text{Cu})$ in Table 4-3 indicate that the cementation reaction rate decreases by more than 50% under the influence of high concentrations of zinc. A detailed discussion about the possible reasons for this will be given in section 5.3 of Chapter 5.
4.5.4.4  Solution pH

Fig. 4-18 shows the effect of solution pH on the rate constants measured by the Evans' diagram and stripping methods.

Theoretically, in acidic solution, the rate for the Cu(II)/Zn cementation reaction would not be affected by the solution pH. This is the case shown in Fig. 4-18(1) where k(Cu) is independent of hydrogen ion concentration within a pH range from 2 to 6. However, the rate constant diminishes as the solution pH further increases. This is most probably due to the formation of the hydroxyl-copper(II) complex whose diffusion coefficient would be expected to be smaller than the uncomplexed Cu(II).

On the other hand, k(Zn) decreases steadily with increasing pH even within the pH range from 5 to 6. Eventually k(Zn) and k(Cu) become coincident at about pH 6. This is caused by the diminishing effect of the side reaction of zinc with protons.

4.5.4.5  Oxygen

Apart from protons, oxygen, when dissolved, will be the main source of side reactions and increase the consumption of the precipitant zinc. Consequently, if the cementation reaction rate is determined as the rate of zinc dissolution, the value of k(Zn) will be larger than it would be in the absence of the dissolved oxygen. This effect is clearly illustrated by Fig. 4-19 in which two chronopotentiograms in the presence and absence of the dissolved oxygen are contrasted. In the presence of oxygen (air), the chronopotentiogram shows a plateau, which is due to the reduction of oxygen in solution, before reaching the end point of the reaction \( t_d \) which is less than \( t_d \), the time needed for the complete dissolution of zinc in the absence of oxygen. As a result, the measured rate constant in the presence of oxygen is greater than that in its absence.
FIGURE 4-18. Effect of solution pH on rate constants measured in 10 ppm 
Cu$^{2+}$ and 0.50 mol dm$^{-3}$ Na$_2$SO$_4$ at 700 rpm.
1. $k$(Cu) by Evans' diagram
2. $k$(Zn) by stripping method.
FIGURE 4-19. Effect of the dissolved oxygen on the chronopotentiogram obtained by the stripping method.
1. solution degassed by Ar-bubbling
2. solution in equilibrium with air
Conditions are the same as in Fig. 4-11.
Despite the fact that oxygen reduction is usually not significant because its concentration in solution is small, and because the transport of oxygen and the subsequent reduction at the rotating surface are slow, great care should be exercised to avoid oxygen interference in the experiment when the concentration of the noble metal ion is at the ppm level.

4.5.5 Codeposition

Codeposition is a rather common phenomenon in cementation reactions (see Chapter 2). In this work, x-ray diffraction was used to identify brass, formed in the copper(II)/zinc reaction, which gives a strong characteristic line with a d-spacing around 2.13±0.02 Å.

There is a strong tendency for zinc, dissolved during the course of the reaction, to be codeposited with copper. This can be seen from the results in Table 4-4 from EDAX. The results also show that when the solution is slightly agitated, the deposit obtained from the cementation contains hardly any pure copper.

Table 4-4 Composition of the deposits obtained from the Cu(II)/Zn cementation reaction*.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alloy composition</th>
<th>Agitation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu %</td>
<td>Zn %</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>90</td>
<td>10</td>
<td>800 rpm</td>
</tr>
<tr>
<td>2</td>
<td>75</td>
<td>25</td>
<td>slightly by N₂ bubbling</td>
</tr>
</tbody>
</table>

*in 500 ppm Cu²⁺ solution at room temperature
On the other hand, the copper content of the deposit increases with increasingly strong agitation, indicating that the codeposition of zinc with copper follows the same rule as for alloy plating. According to the theory of alloy electroplating [33], the enhanced agitation would favour the deposition of the more noble metal. In addition, agitation will have the effect of reducing the surface concentration of Zn\(^{2+}\). This will also tend to reduce codeposition.

The redeposition of zinc has often been found in cementation reactions using zinc as a precipitant [7]. This kind of side reaction, while not affecting the stoichiometry of the cementation, is a prime source of the product impurity.

4.5.6 Rotating Ring-disc Measurements

It is well-known that the cathodic reduction of copper(II) proceeds via a two-step electron transfer with the formation of an intermediate monovalent copper, Cu\(^+\), which has been experimentally detected by the rotating ring-disc technique [19,20]. In order to detect intermediates during the cementation reaction of copper(II) with zinc, a gold ring-disc electrode was used with the disc being zinc plated in advance using the acid bath described in a book by Kuhn [34]. This zinc plated ring-disc electrode was then placed in a 0.01 mol dm\(^{-3}\) CuSO\(_4\) solution rotating at 1600 rpm and the ring current measured as a function of increasing anodic potential. Fig. 4-20 shows the ring current (I\(_r\))-ring potential (E\(_r\)) curve for the Cu(II)/Zn reaction.

A comparison of the ring current curve 2 with curve 1 indicates that during the displacement reaction, the reaction intermediate Cu\(^+\) is formed which must be responsible for the increase in ring currents. It
FIGURE 4-20. Ring current - ring potential curves for the Cu(II)/Zn cementation reaction at its mixed potential, 0.01 mol dm$^{-3}$ CuSO$_4$, 1600 rpm, scan rate 5 mV/s for ring potential.
1. ring current at 1600 rpm and at a Au ring - Au disc electrode.
2. ring current at 1600 rpm and at a Au ring - zinc plated Au disc electrode.
is thus confirmed that, as expected, the formation of a monovalent copper is also involved in the Cu(II)/Zn cementation reaction.

4.5.7 Summary

On the basis of the electrochemical studies carried out on the Cu(II)/Zn cementation reaction, the following conclusions about its kinetics and mechanism and the suitability of the various methods can be reached.

1. Kinetics and mechanism

The Cu(II)/Zn reaction is diffusion controlled. It is non-stoichiometric mainly due to the side reaction of zinc with protons. Because of this side reaction, it is necessary to define two kinds of first order rate constants, namely, k(Cu) and k(Zn) with k(Zn) being always somewhat greater than k(Cu). The electrochemical side reaction, i.e., codeposition of zinc with copper, while not affecting the stoichiometry of the reaction, is an important source of impurity in the deposit of copper.

From the results presented in this study, it is clear that the copper reduction in the Cu(II)/Zn reaction also proceeds via Cu(I) and probably an adsorbed monovalent zinc species.

2. Methodology

Because of the electrochemical nature of cementation reactions, electrochemical methods are highly advantageous in kinetic and mechanistic studies giving a wide range of information about the rate, controlling step, reaction intermediates and the change of surface area during the reaction, etc.

Electrochemical measurements are relatively quick and easy to make, and so can be used to study the initial stage of a reaction when deposit effects are not usually pronounced.
REFERENCES (Chapter 4)


CHAPTER 5.

COBALT(II)/ZINC SYSTEM

5.1 INTRODUCTION

The electrolyte solution obtained by leaching zinc sulphide calcine with sulphuric acid also contains small amounts of cobalt which is known to be one of the most detrimental impurities for zinc electrowinning [1]. Even 1 ppm cobalt in the zinc electrolyte can produce corrosion holes in the electrolytic zinc [2]. If cobalt is codeposited with zinc, the current efficiency will drop because of the relatively low hydrogen overpotential of cobalt [3,4]. Therefore, it is highly desirable to remove the cobalt impurity from the zinc sulphate electrolyte before it is subjected to electrolysis.

Theoretically, cobalt(II) ions can be removed from solution by zinc dust treatment (cementation). This can be demonstrated by superimposing the potential-pH diagrams (Pourbaix diagrams) of zinc and cobalt (Fig. 5-1) [5]. The potential-pH diagram can also tell us the upper pH limit of the cobalt(II)-containing solution, which is determined by the solubility product of Co(OH)_2. For a solution of 500 ppm Co(II), (i.e. 8.48 x 10^{-3} mol dm^{-3}) which is used in this study, the maximum pH above which Co(OH)_2 will be precipitated is about 7.2 according to Fig. 5-1. In solutions containing high concentrations of zinc ions, basic zinc sulphate will be precipitated before cobalt hydroxide.

It can also be seen from Fig. 5-1 that the equilibrium line for the Zn^{2+}/Zn couple is well below that of the Co^{2+}/Co couple. From the standard electromotive force of the cobalt-zinc galvanic cell, 0.48 volt [6], an equilibrium constant of 2 x 10^{16} can be obtained, which implies that by
FIGURE 5-1. Superposition of the potential-pH diagrams of zinc and cobalt showing the possibility of the Co(II)/Zn cementation reaction.

a. $2\text{H}^+ + 2\text{e} = \text{H}_2$
   \[ E^0 = 0 - 0.0591 \text{ pH} \]

b. $\text{O}_2 + 4\text{H}^+ + 4\text{e} = 2\text{H}_2\text{O}$
   \[ E^0 = 1.228 - 0.0591 \text{ pH} \]
applying the zinc dust treatment to the cobalt(II)-containing electrolyte solution, complete removal of the cobalt impurity should be achieved. Nevertheless, under ordinary conditions, the rate of the Co(II)/Zn reaction is very low, and the kinetic sluggishness of this reaction has been said to be caused by the high deposition overpotential of cobalt [3] and zinc inhibition of the reaction [7,8,9]. Therefore, it is kinetic rather than thermodynamic factors which control the Co(II)/Zn cementation reaction.

The problem is so great that unless special measures such as addition of activators (e.g. Sb₂O₃ or As₂O₃) have been taken, the Co(II)/Zn reaction is practically useless for the removal of cobalt and in practice, larger amounts of cobalt are removed from solution by use of the reagent 1-nitroso-2-naphthol [4].

This chapter deals mainly with a fundamental electrochemical study of the Co(II)/Zn cementation reaction aimed at obtaining a better understanding of its kinetics and mechanism, and the inhibition and activation of this reaction.

5.2 REVIEWS OF THE COBALT(II)/ZINC CEMENTATION REACTION AND THE CATHODIC REDUCTION OF COBALT(II)

5.2.1 Review of the Cobalt(II)/Zinc Cementation Reaction

Since the Co(II)/Zn reaction is kinetically slow under ordinary conditions, research work has been aimed at counteracting unfavourable factors and achieving a greater reaction rate acceptable to industry.

5.2.1.1 Effect of Stirring

For research purposes, solution stirring through the use of a rotating disc or cylinder is highly desirable because it allows a reliable diagnosis
of the nature of the controlling step of a cementation reaction. This is the reason why the rotating disc geometry has been extensively used in the study of the Co(II)/Zn reaction, as can be seen from Table 5-1.

On the other hand, because the cementation reaction is heterogeneous, agitation is an indispensable condition in industrial practice for the maximum reaction to be achieved. Stirring would be most effective in increasing the rate when the reaction is diffusion controlled.

5.2.1.2 Effect of pH

As a general rule, the pH of a solution should be so chosen that it prevents the precipitation of basic zinc sulphate. If the pH is low enough to avoid this, according to the equation for the Co(II)/Zn reaction, the solution pH should not have any marked effect on the rate of Co(II)/Zn reaction. However, this is not so.

According to MacKinnon [8], a higher solution pH is more or less favourable to cobalt removal from a synthetic zinc sulphate electrolyte by the Co(II)/Zn displacement reaction. A linear increase in rate was observed in the absence of added zinc ions when the initial pH was increased from 2.0 up to a pH of 5.0 [10]. The explanation of this phenomenon given by the author was that the competing hydrogen evolution reaction was lessened as the initial pH was increased. An additional explanation of this favourable pH effect on the Co(II)/Zn cementation reaction is presented in Section 5.3 of this chapter.

However, a higher solution pH is not always advantageous to the rapid removal of cobalt by the Co(II)/Zn reaction. When As$_2$O$_3$ is used as an activator (see below), the deposition rate of cobalt onto the zinc surface increases as the initial solution pH decreases [11]. Apparently,
TABLE 5-1. Some results on the Co(II)/Zn cementation reaction

<table>
<thead>
<tr>
<th>Composition of solutions</th>
<th>Experimental conditions</th>
<th>Activation energies ($E_\text{a}$), kJ mol$^{-1}$</th>
<th>Controlling step</th>
<th>Refs</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ppm Co$^{2+}$</td>
<td>Reaction without added Zn(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500 ppm Co$^{2+}$</td>
<td>rotating disc, stripping 25-50°C</td>
<td>25.7</td>
<td>diffusion</td>
<td></td>
<td>1987</td>
</tr>
<tr>
<td>pH 5.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 g/l Co$^{2+}$</td>
<td>rotating zinc-plated pt at 60 rpm</td>
<td>31.5</td>
<td>diffusion</td>
<td>[12]</td>
<td>1950</td>
</tr>
<tr>
<td>pH 3.5-4.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300 ppm Co$^{2+}$</td>
<td>Reaction with added Zn(II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80 g/l Zn, pH 4</td>
<td>rotating disc, chemical analysis, 90°C</td>
<td></td>
<td>diffusion</td>
<td>[8]</td>
<td>1973</td>
</tr>
<tr>
<td></td>
<td>Reaction with added Zn(II), As(III), Sb(III) and other additives</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 ppm As(III)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 ppm Co$^{2+}$, 100 g/l Zn 20 ppm As(III)</td>
<td>rotating disc, chemical analysis, 55-105°C</td>
<td>40$^a$</td>
<td>chemical</td>
<td>[11]</td>
<td>1981</td>
</tr>
<tr>
<td>30 ppm Co$^{2+}$</td>
<td>rotating cylinder, chemical analysis, 30-80°C</td>
<td>29.7±5.4</td>
<td>diffusion</td>
<td>[10]</td>
<td>1973</td>
</tr>
<tr>
<td>6.4 ppm Cu$^{2+}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 ppm Te$^{4+}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 g/l Na$_2$SO$_4$</td>
<td>50°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 m g/l Sb(III)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a.* in the initial rate region  
*b.* in the second rate region
this is due to the need for protons in the reduction of both cobalt(II) and arsenic(III) during the formation of the intermetallic compound CoAs, as is clear from equation (5-1) [11].

\[ 2\text{HAsO}_2^- + 2\text{Co}^{2+} + 6\text{H}^+ + 5\text{Zn} \rightarrow 2\text{CoAs} + 5\text{Zn}^{2+} + 4\text{H}_2\text{O} \quad (5-1) \]

5.2.1.3 Effect of Temperature

No one doubts that an elevated temperature is essential to attaining a reasonably high cementation rate in the industrial purification of zinc sulphate electrolyte. As a result, all industrial processes are usually carried out at temperatures above 60°C.

Several authors have investigated the effect of temperature on the rate of the Co(II)/Zn reaction, and obtained activation energies which are listed in Table 5-1.

It can be seen from Table 5-1 that the Co(II)/Zn cementation reaction may be either chemically controlled or diffusion controlled, depending on conditions such as temperature, pH, the presence of zinc ions or activators. The data for \( E_a \) listed in Table 5-1, though limited, show that when the reaction is under chemical control, it has a higher activation energy but, as expected, a lower \( E_a \) is obtained if it is diffusion controlled.

5.2.1.4 Effect of the Nature of Precipitant Metals

Recently, attempts were made to improve the effectiveness of the Co(II)/Zn cementation reaction by developing and adopting new types of cementation agents. Very considerable attempts have been made to produce active zinc, i.e., very finely divided zinc dust. It has also been reported that zinc powder containing trace amounts of tin is more effective in the
removal of the cobalt impurity from zinc sulphate electrolyte, and an increase in the content of tin in zinc powder enhances the efficiency of the cobalt removal [14]. This was ascribed to the formation of more activated spots on the zinc particles as well as to the prevention of proton discharge.

5.2.1.5 Inhibition

The greatest problem in using the Co(II)/Zn cementation reaction for the purification of zinc sulphate electrolytes has been the inhibition of the reaction by zinc ions present in large quantities in solution. Even very small amounts of zinc ions can exert a significant inhibiting action on the deposition of cobalt [7, 8, 9, 11].

Zinc inhibition in the reduction of cobalt was observed even in the 50's when the codeposition of zinc with cobalt was investigated. It was found that zinc, though considerably less noble than cobalt, was preferentially deposited [15]. The retardation of cobalt deposition compared with that of zinc was then tentatively ascribed to adsorption of zinc hydroxide [16] whose presence was recently confirmed by surface film resistance measurements [17]. Yunus et al. were the first to make a detailed study of zinc inhibition in the Co(II)/Zn cementation reaction. According to these authors [7], the preferential adsorption of zinc ions on the surface of the precipitant zinc reduces the rate of nucleation of cobalt. In addition, colloidal zinc hydroxide is formed in the immediate vicinity of the precipitant by the reaction of zinc ions and hydroxyls generated during the reduction of protons. This will act as a secondary inhibition, which may reduce the number of active sites on the cathode. By using techniques such as x-ray diffraction, De Blander and Winand [9] succeeded in identifying the substances incorporated in the product of the Co(II)/Zn reaction at pH 5.4 as being a mixture of the basic salts of zinc, ZnSO₄·3Zn(OH)₂·4H₂O and ZnSO₄·6Zn(OH)₂.
Although the aforementioned explanations have become widely accepted as the reasons for zinc inhibition, it is still not clear as to whether the inhibition is only due to deposits of salts or something intrinsic to the Co(II)/Zn reaction. For these reasons, the electrochemical study described in this thesis was undertaken.

5.2.1.6 Activation

As mentioned before, temperature enhancement is the usual way to speed up the Co(II)/Zn reaction. Alternatively, this reaction can be made to go faster by codepositing the cobalt with certain elements, known as activators, which can be introduced by the addition of compounds such as As$_2$O$_3$ [11] and Sb(III) including Sb$_2$O$_3$, antimonyl tartrate, antimonyl potassium tartrate etc. [23].

Among the inorganic activators, the most widely used in industry are As$_2$O$_3$ [4,18] and Sb$_2$O$_3$ [19,20].

As already shown in both industrial production and research, when As(III) or Sb(III) compounds are present, cobalt is deposited quite rapidly on zinc. This kind of activation is generally ascribed to the formation of intermetallic compounds such as CoAs and CoAs$_2$ [11], CoSb and CoSb$_2$ [21] and CoCuSb [9] during cementation. These intermetallic compounds have high integral heats of formation which partly compensate for the high overpotential of cobalt deposition and hence benefit the reduction of cobalt(II).

Besides the use of a single activator, combinations such as CuSO$_4$-PbO-Sb$_2$O$_3$ and CuSO$_4$-CdSO$_4$-As$_2$O$_3$ [22], CuSO$_4$-TeO$_2$, CuSO$_4$-TeO$_2$-NiSO$_4$ and CuSO$_4$-TeO$_2$-HgCl$_2$ [10], have also been reported to give good results.

Recently, it has been reported that the Co(II)/Zn cementation reaction can also be activated by the addition of metallic antimony [23,24] and even
intermetallic compounds such as Cu₃As and Cu₂Sb [25]. The activating action of metallic antimony is thought to be related to the presence of Sb(III) which is produced during the displacement by metallic antimony of copper(II) already present in the zinc sulphate electrolyte [23].

5.2.2 Review of the Cathodic Reduction of Cobalt(II)

As has been stressed before, a cementation reaction is electrochemical in nature, and therefore knowledge about the cathodic reduction of cobalt(II) is essential to a better understanding of the Co(II)/Zn cementation reaction.

The electroreduction of cobalt(II) has been investigated by many authors [26-34] using various electrochemical methods such as polarization curve measurements [26-31], polarography [32,33] and impedance spectroscopy [34]. These authors have studied the factors affecting cobalt(II) reduction such as pH, temperature, cations and anions present... Among these factors, the effect of pH was found to be particularly significant.

5.2.2.1 Effect of pH

The pH of solution turns out to be a critical factor in the cathodic reduction of cobalt(II). It has been found that, when the pH is increased, the polarization curves are displaced towards more positive potentials [29,35] while the Tafel slopes are significantly decreased [26,30] (Table 5-2). That means the reaction becomes more reversible as the pH rises. This phenomenon has been ascribed to the participation of hydroxy-complexes such as CoOH⁺ [35].

The effect of pH on cobalt(II) reduction has been further confirmed in this study. It would seem that it is completely responsible for the effect of pH on the Co(II)/Zn cementation reaction.
TABLE 5-2  Tafel slopes ($b_C$) for the cathodic reduction of cobalt(II).

<table>
<thead>
<tr>
<th>pH</th>
<th>Temp./°C</th>
<th>$b_C$/mV</th>
<th>Solutions</th>
<th>Methods</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>25</td>
<td>174*</td>
<td>0.05 mol dm$^{-3}$ CoCl$_2$</td>
<td>polarization curve</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.9 mol dm$^{-3}$ NaCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>25</td>
<td>111±7</td>
<td>0.5 mol dm$^{-3}$ CoSO$_4$</td>
<td>galvanostatic, steady-state</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3 mol dm$^{-3}$ H$_3$BO$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>25</td>
<td>127*</td>
<td>0.19 mol dm$^{-3}$ CoSO$_4$</td>
<td>polarization curve</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30 g/l H$_3$BO$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10 g/l NaCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>25</td>
<td>114±7</td>
<td>0.5 mol dm$^{-3}$ CoSO$_4$</td>
<td>galvanostatic steady-state</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3 mol dm$^{-3}$ H$_3$BO$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.4</td>
<td>20</td>
<td>48±7</td>
<td>0.4 mol dm$^{-3}$ Co(ClO$_4$)$_2$</td>
<td>galvanostatic, from initial potential value</td>
<td>[26]</td>
</tr>
<tr>
<td>~4.9</td>
<td>not given</td>
<td>75*</td>
<td>0.05 mol dm$^{-3}$ CoSO$_4$</td>
<td>polarization curve</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5 mol dm$^{-3}$ K$_2$SO$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>25</td>
<td>60*</td>
<td>0.05 mol dm$^{-3}$ CoCl$_2$</td>
<td>polarization curve</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.9 mol dm$^{-3}$ NaCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.4</td>
<td>20</td>
<td>26±4</td>
<td>0.11 mol dm$^{-3}$ Co(ClO$_4$)$_2$</td>
<td>galvanostatic, steady-state</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.11 mol dm$^{-3}$ BaClO$_4$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* estimated according to the Tafel plot given in the paper.
5.2.2.2 Effect of Temperature

As expected, temperature enhancement causes depolarization and facilitates the reduction of cobalt(II) ions [28].

5.2.2.3 Effect of Supporting Electrolyte (cations and anions)

Several authors have investigated the effect of supporting electrolytes on the cathodic reduction of cobalt(II) [28,30,31,36]. It was found that inert cations remarkably inhibit cathodic reduction and their inhibiting ability increases in the sequence \( \text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Mg}^{2+} \) [30]. In addition, when the cobalt ion is reduced at the dropping mercury electrode, the polarographic wave height decreases with increasing concentration of sodium sulphate; meanwhile, the half wave potential of cobalt(II) reduction shifts to the negative side [36]. This shift was ascribed to the formation of a coordination compound between \( \text{SO}_4^{2-} \) and \( \text{Co}^{2+} \) ions. As for the effect of anions such as halide ions, polarographic studies showed [31] that the \( \text{Cl}^- \), \( \text{Br}^- \) and \( \text{I}^- \) ions have a "stimulating effect" on the reduction of cobalt(II) which was explained by assuming a specific adsorption of anions that may induce adsorption of cations.

Not surprisingly, the inhibiting action of cations has been a major problem in the purification of zinc sulphate electrolyte by the addition of zinc dust and therefore has attracted much attention.

5.2.2.4 Kinetics and Mechanism

It has been long recognized through polarographic studies that strongly hydrated ions are reduced slowly and irreversibly [32,36,37]. On the other hand, if certain complexing agents are present in solution, the half-wave potential is more anodic and the waves become more reversible in appearance.
[33,38]. This is likely to occur as a result of the change of the solvation energy in different media. For example, a positive shift of half-wave potential results as the medium changes from water to acetonitrile in which the solvation energy of Co$^{2+}$ is comparatively low [32].

Although various mechanisms have been proposed to explain the experimental results, a general consensus has been reached that during the cathodic reduction of Co$^{2+}$ ions in an aqueous acidic media [26,27,29], an intermediate (CoOH)$_{ads}$ is formed and adsorbed at the electrode, which can either undergo further reduction or act as a catalyst for more Co$^{2+}$ ions to be reduced. It is still open to question as to whether the intermediate acts as a catalyst or a compound to be consumed at the electrode in the course of the second electron transfer step [34].

In the present work, a study of the cobalt(II) reduction was carried out using polarization measurements, cyclic voltammetry, and impedance spectroscopy. Emphasis was placed on obtaining an understanding of the pH dependence of Tafel slopes, the effect of cations and the detection of reaction intermediate as well in the cathodic reduction of cobalt(II) ions.

5.3 CATHODIC REDUCTION OF COBALT(II)

The reduction of cobalt(II) is a constituent half reaction of the Co(II)/Zn system. Therefore, information about the cobalt(II) reduction is important to a better understanding of the displacement reaction.

5.3.1 Current-Potential Curve

5.3.1.1 General Features

Curve 1 in Fig. 5-2 is a typical current potential-curve for the cathodic reduction of cobalt(II) ions at pH 4.0. It can be seen that this
FIGURE 5-2. Polarization curves for the cathodic reduction of cobalt(II) at pH 4.0 and various temperatures. 500 ppm Co$^{2+}$ in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, 700 rpm, Cu electrode. 1 - 25°C, 2 - 40°C, 3 - 50°C.
polarization curve has an unusual shape which is characterized by four regions.

(a) Chemical and Mixed Control Region

In region \( \alpha \), between \(-1.35\) to \(-1.48\) V, the reduction of cobalt(II) at pH 4 is under chemical control. This can be proved by the linear Tafel plot shown in Fig. 5-3 from which a slope \( (b_c) \) of \( 246 \pm 15 \) mV per decade of current density is obtained. The reason for such a large \( b_c \) value will be discussed later.

However, in the approximate potential range \(-1.40\) to \(-1.60\) V, the cobalt(II) reduction was found to be under mixed control. The evidence for this is that when \( 1/I \) is plotted against \( 1/\omega^{1/2} \) at a fixed potential straight line plots of positive slope which do not pass through the origin are obtained [39a], as shown in Fig. 5-4. From the Tafel plot using I values obtained by extrapolating \( \omega^{-1/2} \) to zero to eliminate the effect of diffusion, a slope of about 200 mV is obtained which is basically in congruence with the value obtained in a usual way.

(b) Limiting Current Region

If the maximum current of region \( \beta \) in curve 1 of Fig. 5-2 is plotted against the square root of the angular velocity, a straight line passing through the origin is obtained, as shown in Fig. 5-5. The existence of the limiting current region is thus justified although it is not a well-defined plateau at pH 4.
FIGURE 5-3. Tafel plot for the cathodic reduction of cobalt(II).

500 ppm Co$^{2+}$ in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH 4.0, 700 rpm, Cu electrode.
FIGURE 5-4. \( I^{-1} \) vs \( \omega^{-1/2} \) plots for the cathodic reduction of cobalt(II).

500 ppm Co\(^{2+}\) in 0.50 mol dm\(^{-3}\) \( \text{Na}_2\text{SO}_4 \), pH 4.0, on a copper electrode. 1 -1.60 V, 2 -1.55 V, 3 -1.50 V, 4 -1.40 V.
(c) Blocking Region

After the potential attains the value at which the limiting current is reached, a significant current drop occurs in region $a$. A visual inspection of the deposits obtained at the different stages of cobalt(II) reduction showed that a silvery cobalt deposit can be obtained in region $a$ and $b$ but it becomes bluish in region $c$. The current drop at $c$ must be caused by some resistance occurring at this stage. As will be discussed later in impedance study (see section 5.4), the simultaneous discharge of protons, though to a less extent at stage $a$, will result in the formation of adsorbed hydrogen atoms which constitute an inhibition of the cobalt(II) reduction. When the potential for diffusion-controlled cobalt(II) reduction is reached, proton reduction may become significant which would inevitably lead to an increase in pH in the vicinity of the electrode surface and the consequent formation of cobalt(II) hydroxide which is blue [40], as observed. The current drop would then probably be due to the increase in the deposition overpotential of cobalt on the hydroxide-covered electrode.

(d). Hydrogen Evolution

Finally, when the potential is made more negative than about 1.8 V, proton discharge predominates and this accounts for the drastic current rise at the final stage of the polarization curve, $d$. Gas evolution can be observed at this point.

5.3.1.2 Diffusion Coefficient of Co$^{2+}$

From the slope of the $I_L$ vs. $\omega^{1/2}$ plot (Fig. 5-5) and on the basis of the Levich equation [41], an apparent diffusion coefficient for Co(II)(D$_{Co^{2+}}$) can be calculated using the kinematic viscosity of a 0.50 mol dm$^{-3}$ sodium
FIGURE 5-5. Limiting currents of cobalt(II) reduction as a function of the square root of angular velocity. 500 ppm Co$^{2+}$ in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH 4.0.
sulphate, $1.164 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$, obtained by interpolation from the data
given in the literature (see Fig. 4-8, Chapter 4).

However, the $D_{\text{Co}^{2+}}$ thus obtained turned out to be pH-dependent and
it becomes incredibly high when the pH is decreasing. For example, the
apparent $D_{\text{Co}^{2+}}$ thus calculated is $19 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at pH 3.0. The reason
for this is the background current due to discharge of protons and
bisulphates [42].

The above difficulty in determining $D_{\text{Co}^{2+}}$ can be overcome by
subtracting the background current from the measured limiting current.
A true value of the diffusion coefficient for cobalt(II) in 0.50 mol dm$^{-3}$
sodium sulphate solutions thus obtained is $(6.4 \pm 0.3) \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ (see
Appendix 3).

The diffusion coefficient can also be estimated from the mixed
control equation [43]. From the slope of the $I/I_0$ vs. $\omega^{-1/2}$ plot in Fig. 5-4.
$D_{\text{Co}^{2+}}$ was calculated to be $(6.5 \pm 0.4) \times 10^{-10} \text{ m}^2 \text{s}^{-1}$. The good agreement
between the two values is expected because in both cases the interference
due to proton discharge is supposed to be eliminated or absent.

Table 5-3 is a list of values of $D_{\text{Co}^{2+}}$ determined by various methods.
The unusually large $D_{\text{Co}^{2+}}$ may be most likely due to the failure to eliminate
the interference by the associated proton discharge.
<table>
<thead>
<tr>
<th>Year</th>
<th>Method</th>
<th>Solution</th>
<th>D/10^{-10} m^2 s^{-1}</th>
<th>Temp./°C</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1975</td>
<td>Not known</td>
<td>Sulphate solution</td>
<td>8.6-24.8</td>
<td>Not known</td>
<td>Cited by 9</td>
</tr>
<tr>
<td>1970</td>
<td>polarography</td>
<td>0.001 mol dm^{-3} Co^{2+} in 0.1 mol dm^{-3} NaClO_4</td>
<td>13.6</td>
<td>Not given</td>
<td>18</td>
</tr>
<tr>
<td>1965</td>
<td>chronopotentiometry</td>
<td>Supporting electrolyte:</td>
<td>0.014 mol dm^{-3} Co^{2+}</td>
<td>8</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.027-0.055 mol dm^{-3} Co^{2+}</td>
<td>6</td>
<td>25</td>
<td>44</td>
</tr>
<tr>
<td>1987</td>
<td>RDE corrected for</td>
<td>8.48 x 10^{-3} mol dm^{-3} Co^{2+} in 0.50 mol dm^{-3} Na_2SO_4,</td>
<td>6.4±0.3</td>
<td>25</td>
<td>this work, 42</td>
</tr>
<tr>
<td></td>
<td>background current</td>
<td>pH 4-6.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1987</td>
<td>RDE data treated by</td>
<td>as above, pH 4.0</td>
<td>6.5±0.4</td>
<td>25</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>mixed control equation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1987</td>
<td>^{60}Co tracer diffusion</td>
<td>8.48 x 10^{-3} mol dm^{-3} CoSO_4, pH 2.5-6.</td>
<td>5.4</td>
<td>25</td>
<td>45</td>
</tr>
</tbody>
</table>
5.3.1.3 Effect of Temperature

As expected, an increase in the temperature shifts the polarization curve towards the positive side, as shown by the curves 2 and 3 in Fig. 5-2. In other words, an enhanced temperature is conducive to the lowering of the polarization of cobalt(II) reduction.

5.3.1.4 Effect of Cations

In the presence of zinc ions with a concentration comparable with that of Co(II), the cathodic polarization curve for the cobalt(II) reduction shifts significantly towards the negative side, as shown in Fig. 5-6. This means that the reduction of cobalt(II) becomes more difficult.

Fig. 5-6 also shows that at certain potentials the limiting reduction current for both Co$^{2+}$ and Zn$^{2+}$ ions is actually concurrently attained. This is proved by the approximate additivity of the respective limiting currents for Co$^{2+}$ and Zn$^{2+}$ ions. This fact indicates that, although the standard potential of zinc is about 0.5 V more negative than that of cobalt, Zn$^{2+}$ is still able to be codeposited with Co$^{2+}$ under appropriate conditions. The preferred deposition of zinc and the retardation of cobalt(II) reduction by Zn$^{2+}$ are believed to be associated with the adsorption of zinc ions or the formation of zinc hydroxide [7] (see section 5.2.1).

Curve 2 in Fig. 5-6 shows a small shoulder, which also appears during the cathodic reduction of Zn$^{2+}$, whether the zinc concentration is at the ppm level or much higher. This shoulder is probably due to the underpotential deposition of zinc on copper.

In order to study the effect of a high concentration of zinc ions on the reduction of cobalt(II), 2.3 mol dm$^{-3}$ (NH$_4$)$_2$SO$_4$ and MgSO$_4$ were
FIGURE 5-6. Effect of Zn\textsuperscript{2+} on the cathodic reduction of cobalt(II) at pH 4.0, 700 rpm and on a copper electrode.

(1) 500 ppm Co\textsuperscript{2+} in 0.50 mol dm\textsuperscript{-3} Na\textsubscript{2}SO\textsubscript{4}

(2) (1) + 500 ppm Zn\textsuperscript{2+}
used as supporting electrolytes. The concentration of 2.3 mol dm\(^{-3}\) was chosen because it is the concentration of zinc(II) ions in the zinc electrolyte stream. It was found that the limiting reduction current \(I_L\) of cobalt(II) in the presence of 2.3 mol dm\(^{-3}\) \((\text{NH}_4)_2\text{SO}_4\) and MgSO\(_4\) was significantly lowered relative to 0.5 mol dm\(^{-3}\) Na\(_2\)SO\(_4\) and the lowering became even more pronounced as the valence of the cation was increased. This is clearly seen from Table 5-4.

**TABLE 5-4.** Cation effect on the limiting current of cobalt(II) reduction. 500 ppm Co\(^{2+}\), pH 4.0, 700 rpm, copper electrode.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Percentage of (I_L) with (I_L) of cobalt(II) reduction in 0.50 mol dm(^{-3}) Na(_2)SO(_4) as 100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{NH}_4)_2\text{SO}_4)</td>
<td>82</td>
</tr>
<tr>
<td>MgSO(_4)</td>
<td>41</td>
</tr>
</tbody>
</table>

The fact that an electrochemical reaction is affected by the indifferent supporting electrolyte was recognised as early as 1933 by the noted electrochemist Frumkin [46] and was explained by ionic adsorption and the variation of double layer structure. According to double layer theory, the cation of a supporting electrolyte can affect the potential (\(\phi\)) at the outer Helmholtz plane (OHP) as a result of its adsorption [39b]. Cation adsorption causes \(\phi\) to become more positive, thus leading to a reduction in the surface concentration of the electroactive cobalt(II) ion and hence in the reduction current. The higher the valence of a cation is, the stronger its effect will be. Thus, as can be seen from Table 5-4, divalent Mg\(^{2+}\), by virtue of its stronger electrostatic attraction, has a much
stronger effect than monovalent NH$_4^+$ with other conditions being identical.

The double layer effect will also be an important factor in the Co(II)/Zn cementation reaction in the presence of 2.3 mol dm$^{-3}$ ZnSO$_4$ as is the case in the industrial process.

5.3.1.5 Effect of pH

Of the factors affecting cobalt(II) reduction such as pH, temperature and cation present etc., the effect of pH is particularly significant. Rather surprisingly, it has been found that the polarization curves are displaced towards more positive potentials when the pH is increased, i.e., the reaction becomes more reversible at a higher solution pH. For example, the half-wave potential of cobalt(II) reduction shifts from $-1.47$ V to $-1.33$ V when the pH changes from 4.0 to 5.0. This is shown in Fig. 5-7.

Correspondingly, when the pH is increased, the Tafel slope is decreased drastically, for example, from $246\pm15$ mV at pH 4.0 to $40\pm3$ mV at pH 5.0. Table 5-5 lists $b_C$ values for the electrochemical reduction of cobalt(II) under different temperature and pH conditions.

5.3.1.6 Effect of Benzoquinone

In the presence of benzoquinone, the current-potential curve for the reduction of cobalt(II) is shifted by a considerable margin towards the positive side in a way similar to that which occurs as the solution pH is increased. Fig. 5-8 shows the effect of benzoquinone on the reduction of cobalt(II).

The favourable potential shift occurred during the cobalt(II) reduction in the presence of benzoquinone, as shown by curve 2 of Fig. 5-8, can be caused, firstly, by the removal of the adsorbed H atoms which other-
FIGURE 5-7. pH effect on the cathodic reduction of cobalt(II).

500 ppm Co^{2+} in 0.50 mol dm^{-3} Na_{2}SO_{4}, 700 rpm, Cu electrode.

pH : 1 - 4.0; 2 - 5.0; 3 - 6.0.
FIGURE 5-8. Effect of benzoquinone on the cathodic reduction of cobalt(II).

500 ppm Co^{2+} in 0.50 mol dm^{-3} Na_{2}SO_{4}, pH 4.0, 700 rpm, copper electrode. 1 - no benzoquinone; 2 - 1 × 10^{-3} mol dm^{-3} benzoquinone.
wise block the surface, secondly, by speeding up proton consumption giving rise to an increased surface pH which then aids the formation of CoOH⁺. The second action is actually due to the reduction of benzoquinone which is so quick that it already attains its limiting current at a potential of -0.5 V, as shown in Fig. 5-8. In addition, the limiting current peak in the presence of benzoquinone is unaltered in magnitude, and is followed by surface blocking leading to current reduction, the reason for which is almost certainly due to cobalt(II) hydroxide formation as discussed earlier.

**TABLE 5-5. Determined b_c values for the cathodic reduction of cobalt(II)**

<table>
<thead>
<tr>
<th>b_c/mV</th>
<th>temp./°C</th>
<th>pH</th>
<th>Solution</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>246±15</td>
<td>25</td>
<td>4.0</td>
<td>500 ppm Co²⁺ in</td>
<td>Potentiodynamically,</td>
</tr>
<tr>
<td>40±3</td>
<td>25</td>
<td>5.0</td>
<td>0.50 mol dm⁻³</td>
<td>rotating copper disc,</td>
</tr>
<tr>
<td>36±4</td>
<td>25</td>
<td>5.5</td>
<td>Na₂SO₄</td>
<td>700 rpm.</td>
</tr>
<tr>
<td>137±8</td>
<td>50</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>46±3</td>
<td>50</td>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>70</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The pH dependence of b_c is a consequence of the experimental observation that the Co(II) ion is easier to be reduced in a solution of pH 5.0 than 4.0.

The shapes of the polarization curves and the pH dependence of the Tafel slopes for the reduction of cobalt(II) may be associated with the formation of hydroxy-complexes such as CoOH⁺ [27,29,35]. It is likely that this species, CoOH⁺, being weakly hydrated and also rapidly adsorbed [27] on the electrode, is more prone to charge transfer than Co²⁺. A higher pH favours CoOH⁺ formation and so cobalt(II) reduction.
The wide ranging change in the Tafel slopes, as indicated in Table 5-5, strongly suggests that the cathodic reduction of cobalt(II) may follow totally different mechanisms at different pH's and temperatures. The unusually large $b_c$ value at pH 4.0 is related to a high degree of irreversibility in the reduction of the hydrated cobalt(II) ion, Co$^{2+}$(aq), as has been deduced from polarographic studies [32,36,37]. It may also be related to the inhibition of the cobalt(II) reduction by adsorbed hydrogen as discussed earlier and also in 5.3.3.
5.3.2 Cyclic Voltammetry

Cyclic voltammetry is mainly used here to detect whether any reaction intermediates exist in the reduction of cobalt(II) ions.

(a) In the absence of Zn²⁺

Fig. 5-9 is a typical cyclic voltammogram of cobalt in a still solution and in the absence of Zn²⁺. From Fig. 5-9 it can be seen that there are two cathodic peaks (1 and 2) and two anodic peaks (3 and 4) in the cyclic voltammogram. For the present purpose, we shall confine ourselves to the cathodic peaks.

Peak 1, sharp and well-defined on copper as well as on gold and cobalt electrodes, is characteristic of the cyclic voltammogram for the reduction of cobalt(II) and is not affected by agitation. When the solution pH is low, e.g. 4.0, the initial cathodic scan does not produce peak 1 but only peak 2. Peak 1 is only observed after the first cathodic scan extends to some critical potential value, e.g., -1.55 V for the copper electrode, when the surface pH has presumably become slightly alkaline as a result of proton discharge. However, at pH 5.0 or above, even the first cathodic scan generates peak 1, whose potential is not affected by agitation. In addition, the occurrence of both peaks 1 and 2 are pH dependent. For example, as far as the first scan is concerned, peak 1 is observed only when the pH is 5.0 or above; with the lowering of the pH, peak 2 appears and peak 1 becomes smaller and finally vanishes. However, the peak potentials for both peaks are basically pH independent.

From the facts described above, it can be inferred that two species may be involved in the production of the two reduction peaks. One is likely to be some cobalt(II)-hydroxy species such as CoOH⁺ and the other is Co²⁺ ions.
FIGURE 5-9  Cyclic voltammogram of cobalt on a copper electrode.

500 ppm Co$^{2+}$ in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH 4.0, still solution.
As noted previously, CoOH\textsuperscript{+} would be more electroactive than Co\textsuperscript{2+}, and it has also been recognised that the strongly hydrated Co\textsuperscript{2+} ions are reduced irreversibly [32,36,37]. It is thus possible that the cobalt(II) reduction may take place via two paths: a fast one where the species CoOH\textsuperscript{+} is involved producing reduction peak 1, and a slow one where the species Co\textsuperscript{2+} is reduced producing peak 2. Both peaks will involve the transfer of two electrons since the intermediate cobalt(I) is so unstable.

However, there is some evidence for the formation of a passivating layer associated with peak 1. It can be seen from Fig. 5-9 that the peak current of 1 drops off sharply after the scan passes the peak potential and therefore, some non-conducting passivating film must have formed during the reduction of CoOH\textsuperscript{+}. This speculation is further supported by capacitance measurements which were conducted simultaneously with the potential scan during the cyclic voltammetry. A sudden increase in the capacitance at the peak potential of peak 1 was observed, suggesting that some high dielectric substance may be formed, presumably Co(OH)\textsubscript{2}.

(b) In the presence of Zn\textsuperscript{2+}

In order to understand further the effect of zinc ions on the reduction of cobalt(II), cyclic voltammetry was carried out with a solution containing Zn\textsuperscript{2+} at a concentration equivalent to that of Co\textsuperscript{2+}. Fig. 5-10 shows a typical cyclic voltammogram under such conditions. Because the reduction peaks for Zn\textsuperscript{2+} and Co\textsuperscript{2+} overlap, anodic dissolution peaks, which are well separated, are used for comparison. The peak height can be considered as a direct measure of the amount of metal deposited.

It can be seen from Fig. 5-10 that in the presence of Zn\textsuperscript{2+} the anodic dissolution peak of cobalt or zinc is much smaller than that obtained when either ionic species, Co\textsuperscript{2+} or Zn\textsuperscript{2+}, is present by itself. This fact
FIGURE 5-10  Cyclic voltammograms of cobalt and zinc on a copper electrode.

1. 500 ppm Zn$^{2+}$ + 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH 4.0
2. 500 ppm Co$^{2+}$ + 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH 4.0
   (For simplicity only oxidation peaks are shown)
3. 500 ppm Co$^{2+}$ + 500 ppm Zn$^{2+}$ + 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH 4.0
unequivocally demonstrates that, under the given experimental conditions, the reduction of either ion is inhibited by the other ionic species present in the solution. Such an inhibition tends to become stronger as the ion concentration increases. Under these circumstances, it is not surprising that cobalt deposition will be greatly hampered by the very high concentrations of zinc ion present in the zinc sulphate used for zinc electrowinning.

5.3.3 Impedance Spectroscopy

Fig. 5-11 shows the impedance spectra for the cathodic reduction of cobalt(II) at different pH's but at the same potential.

The impedance spectrum for the cathodic reduction of cobalt(II) at pH 4.0, as shown in Fig. 5-11A, features two capacitive semicircles, the second one being pH dependent. When the solution pH is increased to 5.0, as the case of Fig. 5-11B, the second capacitive semicircle disappears and a new inductive loop emerges in the fourth quadrant which is characteristic of the electrolytic deposition of cobalt and nickel and is indicative of an intermediate : (CoOH)_{ads} or (NiOH)_{ads} [34]. The pH effect on the second capacitive loop suggests that it is likely to be associated with the relaxation of adsorbed hydrogen on the electrode surface, which may play a role in the kinetic sluggishness of the cobalt(II) reduction at pH 4.0.

The increase in pH not only changes the shape of the impedance spectrum but also its magnitude. As indicated in Fig. 5-11B, the impedance drops significantly when the pH is increased from 4.0 to 5.0. This fact is consistent with the earlier findings that the cathodic reduction of cobalt(II) is greatly favoured at a higher pH.
FIGURE 5-11 Impedance spectra for the cathodic reduction of cobalt(II).

500 ppm Co$^{2+}$ in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, 700 rpm, Au electrode.

A. pH = 4.0, at -1.28 V
B. pH = 5.0, at -1.28 V

$Z'$ - real part of the impedance
$Z''$ - imaginary part of the impedance
5.3.4 Mechanism of Cobalt(II) Reduction

The evidence of the cyclic voltammetry, the polarization measurements and the impedance spectroscopy all point to two different reduction mechanisms, one at high pH and one at low pH with a crossover somewhere between pH 4 and 5. We will first consider the reduction at high pH values, since this appears to be the simpler of the two mechanisms.

The reduction of cobalt(II) at pH's greater than about 5 has the following characteristics: it is relatively rapid (Fig. 5-7) and has a Tafel slope in the vicinity of 40 mV per decade of current density (Table 5-5); the impedance spectrum is reasonably straightforward consisting of a capacitive semicircle and an inductive loop; and finally, the hydroxyl ion is clearly implicated in the mechanism.

The fact that the Tafel slope is about 40 mV per decade of current density suggests a mechanism in which the two electrons are transferred successively, the first of these transfers being fast, i.e.,

\[ \text{Co(II)} + e \xrightarrow{\text{fast}} \text{Co(I)}_{\text{ads}} \quad (5-2) \]
\[ \text{Co(I)}_{\text{ads}} + e \xrightarrow{\text{slow}} \text{Co} \quad (5-3) \]

Since the hydroxyl species is essential for this process, it seems likely that the reaction will be

\[ \text{CoOH}^{+} + e \xrightarrow{\text{fast}} \text{CoOH}_{\text{ads}} \quad (5-4) \]
\[ \text{CoOH}_{\text{ads}} + e \xrightarrow{\text{slow}} \text{Co} + \text{OH}^{-} \quad (5-5) \]

This is consistent with the fact that CoOH$^+$ is likely to be more easily reduced than Co$^{2+}$.

However, this mechanism will not, of itself, give rise to the inductive loop in the impedance spectrum and so we have postulated a somewhat
more complex mechanism outlined in Appendix 2 involving a variable coverage \( \theta \) of the species \( \text{CoOH}_{\text{ads}} \). This latter mechanism is similar to that proposed by Heusler for the deposition of cobalt [27].

The onset of passivation immediately following cobalt deposition at pH 5 in cyclic voltammetry, but not in the corresponding rotating disc experiments, is probably due to \( \text{Co(OH)}_2 \) deposition. In an unbuffered solution, the surface pH is likely to rise when protons are discharged on a fresh cobalt surface at a stationary electrode. As a consequence, the solubility product will be ultimately exceeded and cobalt(II) hydroxide will be deposited. However, when the surface is being rotated, the hydroxide species at the surface will be spun off, and the surface pH will be maintained at a much lower value, thus preventing the deposition of cobalt hydroxide.

At pH's less than 4.5, the reaction becomes much slower, and the Tafel slope much higher (246 mV at pH 4) than is common in most metal deposition reactions. As will now be shown, there is good evidence that the reaction is inhibited, and so the high Tafel slope is probably a consequence of the resistance at the surface associated with the inhibition of the reaction.

The impedance spectrum shown in Fig. 5-11 demonstrates very clearly that a large part of the electrode impedance is associated with the second capacitive loop which is pH dependent. When benzoquinone, an oxidizing agent and consequently a depolarizer [47], is added, the second capacitive loop is suppressed, and the deposition is accelerated markedly (Fig. 5-8). Since it is known that the action of benzoquinone is to scavenge adsorbed hydrogen atoms according to the equation,

\[
\text{benzoquinone} + 2H \rightarrow \text{hydroxybenzoquinone}
\]  

(5-6)
it seems likely that the inhibition of the cobalt deposition reaction at a lower pH, e.g. 4.0, is due to hydrogen adsorption. Because the cobalt deposition is largely inhibited, it is difficult to know the details of the underlying mechanism.

It is interesting to note in passing that the CoOH⁺ species plays a crucial role in the reduction of cobalt(II) even though its equilibrium concentration is only about 0.05 ppm, i.e., \( \alpha \cdot 10^{-6} \) of the non-complexed Co(II) under the given experimental conditions (500 ppm Co(II), pH 5.0).

Another important factor in the reaction mechanism is the effect of inert cations on the deposition rate, which is influenced apparently through their effect on the double layer. Cations, particularly those of the higher valences, can have a profound effect on the reduction current.

5.4 COBALT(II)ZINC CEMENTATION REACTION

In this part of the thesis, the rate, inhibition and activation of the Co(II)/Zn cementation reaction will be investigated in some depth by polarization measurements, the construction of Evans' diagrams, impedance spectroscopy, capacitance measurements, chronopotentiometry (stripping) and x-ray diffraction, with particular attention being focussed on the effect of pH on the various facets of this reaction.

5.4.1 Rate

The reaction rate of the Co(II)/Zn reaction has been studied using Evans' diagrams, chronopotentiometry and impedance spectroscopy.
5.4.1.1 Evans' Diagram

The Evans' diagram was constructed in the same way as previously. Fig. 5-12 shows the Evans' diagram obtained at 25 and 50°C where $a$ represents the anodic dissolution of zinc, and $b$, the reduction of Co(II). $i_1$ and $i_2$ are the expected reaction current densities (rates) of the Co(II)/Zn cementation reaction at 25 and 50°C, respectively.

It can be seen from Fig. 5-12 that the intersections of the anodic and cathodic polarization curves lie approximately in the Tafel region of the Co(II) reduction curve. In other words, one can expect the reaction to be under chemical control. At the mixed potential of the reaction, $\alpha = -1.47$ V, the cobalt(II) reduction is actually under mixed control, as shown earlier in section 5.3.

Since $i_2$ is greater than $i_1$, it is obvious that the reaction rate increases with increasing temperature. Furthermore, the point of intersection is approaching the diffusion controlled region, and so it can be inferred that when the temperature attains a sufficiently high value, the reaction rate will be increased to such an extent that the Co(II)/Zn reaction will no longer be under mixed control. Instead, it will be determined by the speed at which Co(II) diffuses to the zinc surface, which is the maximum reaction rate possible at any given temperature and cobalt(II) concentration. This is what is desired in plant operation and so cobalt cementation in industry is invariably carried out at high temperatures.

Another factor which has a dramatic effect on this cementation reaction is pH. This can be seen by comparing the Evans' diagrams at pH 5.0 in Fig. 5-13 with those at pH 4.0 in Fig. 5-12.

Fig. 5-13 clearly indicates that the cobalt(II)/zinc reaction will become diffusion controlled when the pH is increased from 4 to 5. This
FIGURE 5-12 Evans' diagrams for the Co(II)/Zn cementation reaction.

500 ppm Co$^{2+}$ in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH 4.0, 700 rpm,

a. for the reaction of Zn - 2e $\rightarrow$ Zn$^{2+}$

b. for the reaction of Co$^{2+}$ + 2e $\rightarrow$ Co, (copper electrode).

1 - 25°C; 2 - 50°C.
FIGURE 5-13 Evans' diagrams for the Co(II)/Zn cementation reaction.

500 ppm Co\(^{2+}\) in 0.50 mol dm\(^{-3}\) Na\(_2\)SO\(_4\), pH 5.0, 700 rpm,

a. for the reaction of Zn - 2e → Zn\(^{2+}\)

b. for the reaction of Co\(^{2+}\) + 2e → Co; (copper electrode)

1 - 25°C; 2 - 50°C.
change is not surprising when the pH effect on the cobalt(II) reduction, described in section 5.3, is remembered.

For the type of reaction shown in Fig. 5-13, the rate constants at both temperatures can be estimated by simply measuring the limiting currents for cobalt(II) reduction and using equation (2-11). The calculated rate constants, as well as the activation energies, together with the k values obtained by other methods, are listed in Table 5-6 (see below) and will be discussed in 5.4.1.5

5.4.1.2 Chronopotentiometry (stripping)

If a thin zinc film is electroplated onto an inert copper electrode and then placed in a solution containing cobalt(II) with which it reacts, then the reaction rate can be obtained by measuring the time, $t_d$, necessary for the complete dissolution of the zinc film [48]. $t_d$ is determined by following the change in mixed potential with time as shown in Fig. 5-14. The reaction rate thus obtained is $(0.64\pm0.03) \times 10^{-5}$ m s$^{-1}$ which is much smaller than that inferred from the Evans' diagram. The reason for this will be discussed in 5.4.1.5.

5.4.1.3 Capacitance Measurements

As mentioned in Chapter 2, capacitance measurements can produce information about the changing area of the reacting surface. Fig. 5-15 shows the capacitance, measured by the technique of Power and Caldwell [49], as a function of time during one Co(II)/Zn cementation experiment.

It can be seen from Fig. 5-15A that the interfacial capacitance increases rapidly within the first minute of reaction and then decreases slightly during the rest of the reaction. The sharp increase in capacitance
FIGURE 5-14  Chronopotentiogram for the rate determination of the Co(II)/Zn cementation reaction.  500 ppm Co$^{2+}$ in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH 5.0, 700 rpm.
FIGURE 5-15  Capacitance as a function of time during Co(II)/Zn cementation reaction.  500 ppm Co$^{2+}$ in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH 4.0, 700 rpm.

a. degassing by passing argon for 1 hour

b. in the presence of air
presumably corresponds to an increase in surface area associated with the deposit formation. The subsequent slight reduction in capacitance (or area) must be caused by some slight restructuring of the deposit. In any event, this behaviour is quite different to the silver(I)/copper system where the capacitance increases as the square root of time [50].

During the capacitance measurements, we found that the interfacial capacitance is very sensitive to the presence of air (oxygen) as illustrated in Fig. 5-15B in which the initial capacitance increases rapidly in the presence of air. Such an initial rapid increase in the capacitance in the presence of air is believed to be caused by the build-up of oxide or hydroxide on the surface of zinc, which, being less conducting, may eventually lead to the passivation of the reacting surface. When the passivation occurs, the capacitance increases rapidly to a large value as shown in Fig. 5-15B.

5.4.1.4 Impedance Spectroscopy

(1) Effect of pH

Fig. 5-16 shows typical impedance spectra for the Co(II)/Zn cementation reaction at pH 4.0 and 5.0. At both pH's, in addition to the capacitance semicircle(s), there is an inductive loop in the fourth quadrant, which is characteristic of cobalt(II) reduction no matter how it is carried out, either electrochemically or chemically using zinc.

From Fig. 5-16A, it can be seen that, apart from a high frequency capacitive semicircle (flattened), there is another low frequency capacitive loop which is highly pH-dependent. If the solution pH is increased, this second capacitive loop shrinks and finally disappears at above pH 4.5. In this case, Fig. 5-16A is reduced in shape to 16B which is obtained at pH
FIGURE 5-16  Impedance spectra for the Co(II)/Zn cementation reaction.  
500 ppm Co^{2+} in 0.50 mol dm^{-3} Na_{2}SO_{4}, at 700 rpm and at 
the system's mixed potential. 

pH:  A - 4.0;  B - 5.0

Z' - real part of the impedance

Z'' - imaginary part of the impedance

Frequency is expressed in Hertz by numbers on the impedance loci.
5.0 and consists of only a high frequency flattened semicircle and a low frequency inductive loop, and the size of the high frequency loop is decreased corresponding to an increase in rate.

In Fig. 5-16B, a semicircle fitted to the high frequency end of the spectrum has been drawn and this will be discussed later in this section.

The question arises as to what kind of steps these loops should be ascribed. It is generally agreed and also theoretically established that the high frequency semicircle is probably due to a charge transfer process. On the basis of the pH dependence and the effect of benzoquinone discussed in 5.4.1.4, we have reason to believe that the second capacitive loop is due to the adsorption of hydrogen which is produced simultaneously with the reduction of cobalt(II).

If the above interpretation is correct, then the adsorbed hydrogen on the surface of cobalt would block the access of more cobalt(II) ions. As a result, the reduction of cobalt(II) becomes more difficult at lower pH values. A visual inspection indicates that less cobalt is deposited at pH 4.0 than at pH 5.0, which also favours the explanation. As already discussed in 5.3, the inductive loop may be associated with the adsorbed intermediate CoOH formed by a single electron transfer to CoOH⁺.

The effect of pH on the impedance behaviour of the Co(II)/Zn reaction is actually somewhat more complex than described above. This can be seen from the plot of the real part of the impedance for the high frequency semicircle, Z', against pH, shown in Fig. 5-17.

The appearance of a maximum in the Z'/pH plot is in fact a consequence of the existence of the side reaction of hydrogen evolution. At low pH, the measured impedance is predominantly due to proton reduction. In this case the zinc surface is evenly attacked with little or no cobalt being
FIGURE 5-17  pH dependence of the real part of impedance of the high frequency semicircle for the Co(II)/Zn cementation reaction. 500 ppm Co$^{2+}$ in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, 700 rpm.
deposited on it. The reaction is rapid and the impedance is low. When the pH is increased, proton discharge becomes more difficult and so the impedance increases. On the other hand, a higher pH favours the reduction of cobalt(II) because more CoOH$^+$ is formed and as this reaction grows in importance, the impedance tends to decrease. Therefore, when the pH reaches a certain value, approximately 3.5, a further pH increase results in a drop in the measured impedance. This occurs when the Co(II)/Zn reaction outweighs the H$^+$/Zn reaction. In confirmation of this argument, cobalt deposits are observed to form in the pH range above about pH 3.5.

It follows therefore, that for a cementation system involving two or more competing reactions, the impedance of the high frequency semicircle on the complex plane may be composed of contributions from all of these reactions. Under these circumstances, it is the resultant that determines the apparent impedance value.

Finally, we have to explain why the centre of the high frequency semicircle lies below the Z' axis. Theoretically, the high frequency semicircle can be modelled as a resistor in parallel with a double layer capacitance [51]. But this is not true for many systems, including the Co(II)/Zn and Cu(II)/Zn cementation systems investigated in this study, and the experimental data often form semicircles with their centres lying below the real impedance axis. Such a centre can be obtained by rotating clockwise the measured flattened semicircle by a certain angle which was found to be between 15 and 19° for the Co(II)/Zn reaction. In this case, according to Iseki et al. [52], the reaction resistance equals the length of chord, lying on the real axis, of the rotated semicircle and so the magnitude of the impedance represented by the chord can be used to calculate the rate constant of the reaction [53]. The physical meaning of the rotation of the semicircle on the complex plane is not yet completely understood; it may be
related to the surface roughening of the electrode during the reaction [52].

(2) Effect of rotation speed

Fig. 5-18 illustrates the effect of rotation speed on the impedance spectra of the Co(II)/Zn cementation reaction at pH 5. Also given are the semicircles which fit the initial high frequency portion of the spectrum and the corresponding reaction impedances represented by A, B, C and D [53].

Since the rate is proportional to the reciprocal of the reaction impedance (Z'), a plot of 1/Z' as a function of the square root of the rotation speed (rpm) should be linear if the reaction is under diffusion control. From Fig. 5-19, it can be seen that there is indeed a linear relation between the 1/Z' and (rpm)$^{\frac{1}{2}}$. This is clear evidence that the Co(II)/Zn cementation reaction at 25°C and in a solution of pH 5, is controlled by the rate of diffusion of Co(II) from the bulk of solution towards the reacting surface.

Another meaningful conclusion that can be drawn from the linear 1/Z' vs. (rpm)$^{\frac{1}{2}}$ relationship is that the method of rotation of semicircle can lead to reliable data of the reaction impedance represented by A, B, C and D in Fig. 5-18 provided that the reaction is diffusion controlled. This statement is only justified if the rates so calculated agree well with, say, stripping or some other independent rate measurement (not Evans' diagrams).

(3) Effect of Zn$^{2+}$

The effect of Zn$^{2+}$ on the impedance spectrum of Co(II)/Zn cementation reaction is very significant. Even 10 ppm Zn$^{2+}$ in a solution (pH 5) containing 500 ppm Co$^{2+}$ can result in a three-times increase in the impedance for the Co(II)/Zn reaction. Meanwhile, the impedance spectrum characteristic of
FIGURE 5-18  Effect of the rotation speed (given in rpm) on the impedance spectra of Co(II)/Zn cementation reaction. 500 ppm Co$^{2+}$ in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH 5.0. 1 - 100; 2 - 200; 3 - 400; 4 - 700.
FIGURE 5-19  Rotation speed dependence of the reciprocal of the impedance ($Z'$) for the Co(II)/Zn cementation reaction. Data from values at points A, B, C and D in Fig. 5-18.

500 ppm Co$^{2+}$ in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH = 5.0.
Co(II)/Zn reaction is severely distorted with no inductive loop appeared in the fourth quadrant. On the other hand, when concentrated, say, 2.3 mol dm$^{-3}$, zinc sulphate is present, the impedance spectrum of Co(II)/Zn reaction completely loses its original characteristics and assumes a locus characteristic of the Zn$^{2+}$ + 2e $\rightleftharpoons$ Zn equilibrium, as shown in Fig. 5-20.

The above fact simply means that under the given conditions, the Co(II)/Zn cementation reaction is totally inhibited and the overriding process at the interface is the Zn$^{2+}$/Zn equilibrium instead of the Co(II)/Zn reaction. This is consistent with the experimental observation that little or no cobalt is deposited by the Co(II)/Zn reaction in the presence of high concentrations of zinc at room temperature.

(4) Effect of Benzoquinone

As described above, there is a second capacitive loop in the impedance spectrum when the solution pH is lower than 4.5. This second loop was assumed to be caused by hydrogen adsorption because it is pH dependent. To further prove this, benzoquinone, a readily reducible oxidant, which consumes adsorbed hydrogen atoms was added to the solution. The resulting spectrum, which is illustrated in Fig. 5-21, is very informative.

It is clear from Fig. 5-21B that in the presence of benzoquinone the second capacitive loop shown in Fig. 5-21A is eliminated, proving that it is due to adsorbed hydrogen, and the measured impedance is significantly reduced as the reaction rate increases.

(5) Some considerations concerning the study of cementation reactions using impedance spectroscopy.

(a) Parallel reactions

Parallel reactions are very common in corrosion and cementation systems.
FIGURE 5-20  Effect of Zn$^{2+}$ on the impedance spectrum of the Co(II)/Zn cementation reaction. 500 ppm Co$^{2+}$ in 2.3 mol dm$^{-3}$ ZnSO$_4$, pH 5.0, 700 rpm.
FIGURE 5-21  Effect of benzoquinone (B) on the spectrum for the Co(II)/Zn cementation reaction. 500 ppm Co$^{2+}$ in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH 4.0, 700 rpm.

A. [B] = 0

B. [B] $\sim$1 x 10$^{-3}$ mol dm$^{-3}$
Take the Co(II)/Zn reaction as an example. There are at least two competitive reactions taking place in this system in an aqueous medium: displacement of cobalt(II) ions and protons by zinc.

It has been established from d.c. polarography that the total d.c. current at a given potential is equal to the algebraic sum of the currents of each concurrent reaction. It is reasonable to assume that this kind of additivity also holds true for a.c. current when more than one reaction occurs. This simply means that the impedance of the concurrently occurring reactions would be in parallel in the equivalent circuit [54] and so the total reaction impedance would be the sum of the individual reaction impedances in parallel. It is this principle which governed the shape of the $Z'$/pH plot for the Co$^{2+}$/Zn reaction (Fig. 5-17).

It follows that, if a system involves more than one charge-transfer process, it is essential in an impedance study to consider the impedance of the high frequency capacitive semicircle as being the resultant of the impedance of the reactions that are simultaneously taking place at the reaction site. Only under special circumstances where the conditions are so carefully controlled that only one reaction occurs or predominates can we assign a single charge transfer process to the high frequency capacitive semicircle.

(b) Interfacial area

The surface roughness of a solid electrode is known to have a great influence on the values of the impedance of a given reaction [55,56].

In a cementation reaction, this roughening effect is particularly significant since the deposit produced in most cementation reactions is powdery and dendritic, a consequence of their being diffusion controlled.

The change in surface area during the course of a cementation reaction,
which is especially pronounced during the first few minutes, causes difficulties in making impedance measurements since the measured impedance is time-dependent. To overcome this, it is very important to select an appropriate time after which a fairly stable surface state has been achieved and the mixed potential of the system is reasonably constant and can be fixed by the potentiostat while the impedance spectrum is run.

(c) Surface deposit effects

The most common effect in a cementation reaction is the rate enhancement associated with surface roughening due to the formation of dendritic protrusions which cause turbulence [57].

The impedance measurements are usually not affected by the surface deposits because they are made in the first stage of the reaction only. However, it has been found in experiments that a heavy deposit may result in a drop in the measured impedance value. For example, when the Cu$^{2+}$/Zn displacement reaction was previously carried out for two hours before measuring the impedance of the reaction, the impedance thus measured is decreased by $\alpha$. 50 percent relative to the initial rate. This simply means that the reaction is accelerated under the influence of the already deposited precipitate.

The case of Co(II)/Zn reactions, however, was found to be different. When rather heavy cobalt deposited by the previous Co(II)/Zn reaction exists on the surface of zinc before starting impedance measurements, the measured impedance, instead of being decreased considerably, is basically unchanged. In this case, a white substance, possibly zinc hydroxide or its basic salt, can be observed on the zinc surface. It is likely in this case that the expected deposit effect is counteracted by the inhibition of this reaction by zinc(II).
5.4.1.5 Calculation of \( k \) from Impedance Measurements

Impedance measurements provide us with a new approach to the determination of the rate of cementation reactions. The question is what quantity, \( R_p \) or \( R_{ct} \), should be used in the calculation of \( k \).

As pointed out in Chapter 2, the choice depends on the system. Since no universal approach is available at the present stage of research, we adopted a way in which the results obtained from impedance measurements were compared with those of other methods which are generally accepted or have already been proved reliable and accurate.

We have already used \( R_p \) \([58]\), for the calculation of the rate constant for the Cu(II)/Zn reaction and obtained a fairly good result (see Chapter 4). The justification is the good agreement of \( k \) values from five methods.

For the Co(II)/Zn system, however, it is the charge transfer resistance, \( R_{ct} \), as suggested by Epelboin et al. \([53]\), together with equations (2-14) and (2-10) that has been used for the calculation of \( k \), given that the Tafel slope for zinc dissolution is 60 mV per decade current density. \( R_{ct} \) can be obtained by constructing a rotated high frequency semicircle as shown in Fig. 5-16B and Fig. 5-18. The rate constant thus calculated is \( (0.77 \pm 0.07) \times 10^{-5} \text{ m s}^{-1} \) at 25°C, which is in reasonable agreement with that obtained from chronopotentiometry (stripping), \( (0.64 \pm 0.03) \times 10^{-5} \text{ m s}^{-1} \), but much smaller than that from the Evans' diagram as shown in Table 5-6. On the other hand, if \( R_p \) is used, then the calculated \( k \) would be four times greater than that calculated when \( R_{ct} \) is used. This is unreasonable.

Despite this, it seems theoretically more justifiable to use the \( R_{ct} \) value represented by the diameter, instead of the chord (see section 5.4.1.4(1)), of the rotated semicircle (Fig. 5-16B) in the calculation of the rate constant. Certainly, if there was no rotation, the diameter would be used. If the
calculation is made in this way, \( R_{ct} \) increases by about 5%; in other words, \( k \) decreases to \( 0.73 \times 10^{-5} \text{ m s}^{-1} \), a value closer to that from stripping measurements.

5.4.1.6 Comparison of the Rate Constants Determined by Various Methods

Table 5-6 lists the rate constants determined by the various methods as well as the associated activation energies for the Co(II)/Zn cementation reaction.

<table>
<thead>
<tr>
<th>Methods</th>
<th>( k/10^{-5} \text{ m s}^{-1} )</th>
<th>25°C</th>
<th>50°C</th>
<th>( E_a/\text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evans' diagram</td>
<td>3.7±0.2</td>
<td>5.1±0.2</td>
<td>10.3</td>
<td></td>
</tr>
<tr>
<td>Impedance</td>
<td>0.77±0.07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chronopotentiometry (stripping)</td>
<td>0.64±0.03</td>
<td>1.4±0.1</td>
<td>25.7</td>
<td></td>
</tr>
</tbody>
</table>

It can be seen from Table 5-6 that the rates inferred from the Evans' diagrams are very much faster than those measured experimentally by the stripping method. There is a good reason for this. Rate constants from Evans' diagrams depend on the assumption that the two half reactions do not interfere with each other. It is known, as will be discussed below, that zinc ions strongly inhibit the Co(II)/Zn displacement reaction. In the present case, the zinc ions produced in the reaction and present in the double layer will therefore interfere with the cobalt deposition. This argument is reinforced by the values of activation energies. It can be seen from Table 5-6 that the \( E_a \) obtained from chronopotentiometry is
significantly larger than that from the Evans' diagram. The $E_a$ inferred from the Evans' diagram is for a diffusion limited value free of any chemical interferences and is therefore likely to be low. When the measurements are made directly on the reacting system, zinc inhibition will occur to a certain extent, and this is reflected in the value of the activation energy.

5.4.2 Inhibition

The inhibition of the Co(II)/Zn cementation reaction has been studied by a number of electrochemical techniques as well as x-ray diffraction. Some of the results have already been presented in the preceding sections and therefore details will be omitted here and only conclusions presented.

5.4.2.1 Polarization Measurements

The significant drop in the reduction current of cobalt(II) in the presence of 2.3 mol dm$^{-3}$ $(\text{NH}_4)_2\text{SO}_4$ and MgSO$_4$ suggests that the double layer effect may also be responsible for the inhibition of the Co(II)/Zn reaction by zinc ions.

5.4.2.2 Cyclic Voltammetry

Cyclic voltammetry shows that when the concentrations of Co$^{2+}$ and Zn$^{2+}$ are comparable, the inhibition of the two reduction reactions is mutual (see 5.3.2).

5.4.2.3 Capacitance Measurements

The capacitance measurements carried out in the presence of air during the Co(II)/Zn cementation reaction showed that the oxygen in the air also contributes to the retardation of this reaction (see 5.3.2).
5.4.2.4  *Impedance Measurements*

The inhibiting action of Zn\(^{2+}\) strongly manifests itself in the impedance measurements. Even 10 ppm Zn\(^{2+}\) in a solution containing 500 ppm Co\(^{2+}\) can produce a 3-fold increase in the impedance of the Co(II)/Zn cementation reaction.

The impedance measurements also help to identify another cause of inhibition in cobalt(II) reduction, that is, inhibition due to adsorbed hydrogen whether the reduction proceeds cathodically or chemically using zinc (see 5.3.3 and 5.4.1).

5.4.2.5  *X-Ray Diffraction (XRD) Determination*

In order to know more about the causes of inhibition of the Co(II)/Zn reaction, we have used XRD to identify substances that may cover the surface of the cobalt deposit during the Co(II)/Zn reaction. For this purpose, samples were prepared from the following solution and under the following conditions:

- 500 ppm Co\(^{2+}\) + 250 ppm Sb(III) + 2.3 mol dm\(^{-3}\) ZnSO\(_4\)
- pH = 5.0, 50°C, 320 rpm

(The action of Sb(III) will be discussed in section 5.4.3)

The XRD shows a strong peak at 10.8 Å and a small peak at 5.4 Å which are most likely due to the basic zinc salt ZnSO\(_4\)•3Zn(OH)\(_2\)•4H\(_2\)O, as identified earlier by De Blander and Winand [9] using x-ray diffraction.

5.4.2.6  *Summary of Inhibiting Actions*

On the basis of the experimental results obtained in this study, as well as the results of previous authors, inhibition occurring in the Co(II)/Zn cementation reaction can be the combined effect of the following five main types, namely:
(1) inhibition due to the double layer effect of the concentrated zinc sulphate.

(2) inhibition due to adsorbed hydrogen.

(3) inhibition due to the blanketing of the surface with products such as zinc hydroxide or basic zinc sulphate [9], which are produced as a result of hydrolysis of Zn\(^{2+}\) at high temperatures, and the local alkalization in the vicinity of zinc surface due to simultaneous proton displacement by zinc metal.

(4) inhibition due to air which may cause passivation of the surface of the precipitant zinc or deposited cobalt.

(5) inhibition due to the preferential adsorption of Zn\(^{2+}\) at the active sites of zinc which reduces the rate of nucleation of cobalt deposition [7].

5.4.3 Activation

In the work described in this thesis, potassium antimony tartrate (K\(_2\)SbOC\(_4\)H\(_4\)O\(_6\)) is used as an activator for the Co(II)/Zn cementation reaction, the aim of the work being to determine the way in which the Sb(III) acts as an activator. In addition, the reduction behaviour of antimony was investigated.

5.4.3.1 Cathodic Reduction of Sb(III)

Fig. 5-22 shows typical cathodic current-potential curves for the reduction of antimony(III) at two temperatures.

It can be seen from Fig. 5-22 that these curves look very unusual in their shape and four regions can be distinguished:
FIGURE 5-22  Current-potential curves for the cathodic reduction of antimony(III). 250 ppm Sb(III) in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$, pH 4.0, Au electrode, 700 rpm.

1 - 25°C;  2 - 50°C
(1) first limiting current region, $a$
(2) current jump region, $a \rightarrow b$
(3) second limiting current region, $b$
(4) hydrogen evolution region, $c$

The limiting current ($I_L$) regions $a$ and $b$ can be easily identified by inspection of Fig. 5-22 and the $I_L$ versus $\omega^{1/2}$ plot for both cases shows a straight line passing through the origin. Region $c$ is apparently due to hydrogen evolution. What is unusual is the appearance of two limiting current regions and the current jump, $a \rightarrow b$.

The region of the feature $a$, is almost certainly due to the reduction of SbO$^+$, the electroactive species in the potassium antimony tartrate solution [59]. This species, after going through a 3-electron transfer, is reduced to metallic antimony which can be seen on the electrode. From the Levich equation, a diffusion coefficient for SbO$^+$ can be calculated as being $2.9 \times 10^{-10} \text{ m s}^{-1}$.

The origin of the current jump and the second limiting current $b$ is not quite certain. It might be connected with the further reduction of metallic antimony to stibine, SbH$_3$. The equilibrium potential [60] shows that the formation of SbH$_3$ is possible in the highly cathodic region. According to an early investigation [61], stibine is formed during the electrolytic reduction of trivalent antimony, and the process probably takes place in two main stages: the deposition of Sb metal followed by the reduction of the metal to SbH$_3$. If this is the explanation of our results, then the important piece of information that this experiment reveals is that the mixed potential of zinc in a solution containing Co(II) and Sb(III) is negative enough to cause a further reduction of antimony to stibine, a toxic substance. Therefore, while Sb(III) is in widespread use as an activator in the removal of cobalt impurity from zinc sulphate, it must be borne in
mind that its addition may run the risk of producing a highly toxic stibine.

5.4.3.2 Effect of Sb(III) on the Reduction of Co(II)

Fig. 5-23 gives the current-potential curves which show the effect of Sb(III) on the reduction of cobalt(II).

It can be seen from Fig. 5-23 that the addition of Sb(III) seems to benefit the reduction of Co(II) by shifting, although by not much, the polarization curve towards positive potentials. This positive shift was also observed by some French authors [62] who investigated the effect of Sb(III) on the reduction of Co(II) at a micro-Hg electrode. Curve 2 in Fig. 5-23 looks rather strange, but as a matter of fact, it is a combination of the features of both the Co(II) and Sb(III) reduction curves (Figs. 5-23 and 5-22(2)). The region \( \alpha \) of curve 2 is obviously due to the reduction of Sb0\(^+\) ions, followed by a joint reduction of Co(II) and Sb(III) to CoSb, an intermetallic species or even SbH\(_3\) (region \( \beta \)). The apex \( \gamma \) and subsequent recess \( \delta \) essentially repeat the features of cobalt(II) reduction, although the dip due to inhibition is considerably reduced. And finally, \( \epsilon \), is apparently due to hydrogen evolution.

5.4.3.3 Evans' Diagram

Experiments showed that zinc can readily displace Sb(III) from an aqueous solution at a room temperature. In order to ascertain the nature of the controlling step, an Evans' diagram was constructed as shown in Fig. 5-24.

Fig. 5-24 unequivocally demonstrates that this reaction is under diffusion control. From the Evans' diagram, a rate constant of \( 2.7 \times 10^{-5} \) m s\(^{-1}\) for the Sb(III)/Zn reaction was calculated using the same method as described above.
FIGURE 5-23  Effect of Sb(III) on the cathodic reduction of cobalt(II).

500 ppm Co$^{2+}$ in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$,
pH 4.0, 700 rpm, 50°C, Cu electrode.

1 - no Sb(III);  2 - 250 ppm Sb(III).
FIGURE 5-24  Evans' diagram for the Sb(III)/Zn cementation reaction.

250 ppm Sb(III) in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$,
pH 4.0, 700 rpm, Cu electrode.

1. for the reaction of Zn $\rightarrow$ 2e $\rightarrow$ Zn$^{2+}$
2. for the reaction of Sb(III) $\rightarrow$ 3e $\rightarrow$ Sb (i.e. curve a from Fig. 5-22).
The Sb(III)/Zn reaction is facile even in the presence of concentrated, say, 2.3 mol dm\(^{-3}\) ZnSO\(_4\) as shown by the fact that a black deposit is quickly formed on the zinc surface during the reaction. To further confirm this, the cathodic reduction of Sb(III) was carried out under the following conditions: a solution of pH 5.0 containing 250 ppm Sb(III), 500 ppm Co(II) and 2.3 mol dm\(^{-3}\) ZnSO\(_4\), was electrolysed at 50°C using a Cu electrode rotating at 700 rpm, the potential being set at the same value as the mixed potential of zinc in this solution. It was found that more than half of the deposit thus obtained was antimony. A typical result for the analysis of the deposit by energy dispersive x-ray analysis was 62% Sb, 35% Zn and 3% Co.

The above results lead us to a conclusion, which is helpful to our understanding of Sb(III) as an activator, that in the Co(II)/Zn system containing Sb(III) as an activator, the Sb(III)/Zn reaction will proceed at a rate much higher than that of Co(II)/Zn reaction. As a result, the deposited antimony, being more electropositive than cobalt and high in surface area, will provide more cathodic sites for the deposition of cobalt(II), which otherwise has a high deposition overpotential.

5.4.3.4 Impedance Measurements

A remarkable feature of Sb(III) is its ability to get rid of the otherwise present second capacitive loop generated in the Co(II)/Zn cementation reaction (see Fig. 5-16), as shown in Fig. 5-25A. As(III) has the same effect as Sb(III). By analogy, it was thought that selenium dioxide (SeO\(_2\)) might have a similar effect and when tried, a similar result was obtained (Fig. 5-25B).

From these results, it is inferred that one role of these activators is to suppress the formation of adsorbed hydrogen on the reacting metal surface by consuming protons in their reduction, and so allows a higher
FIGURE 5-25  Effect of Sb(III) and Se(IV) on the impedance spectra of Co(II)/Zn cementation reaction.

500 ppm Co$^{2+}$ in 0.50 mol dm$^{-3}$ Na$_2$SO$_4$,
pH 4.0, 700 rpm.

A. - 500 ppm Sb(III);  B. - 25 ppm Se(IV).
concentration of the active species, CoOH$^+$ to be formed on the electrode surface.

5.4.3.5 Summary of Activating Action

On the basis of the experimental results obtained in this study as well as the results of previous authors, the modes of activation of Sb(III) and As(III) compounds in the Co(II)/Zn cementation reaction can be summarised as follows:

(1) Activation due to the formation of Sb and intermetallic compounds such as CoSb, CoSb$_2$, CoAs, CoAs$_2$, which partly reduce the large deposition overpotential of cobalt [62].

(2) Activation due to the elimination of the inhibition caused by adsorbed hydrogen.

(3) Activation due to more CoOH$^+$ formation as a result of favourable pH. CoOH$^+$, being weakly hydrated and adsorbed on the electrode, may be readily reduced.
REFERENCES (Chapter 5)


CHAPTER 6.

CONCLUDING REMARKS AND SUGGESTIONS FOR FUTURE WORK

In this final chapter, we compare and contrast the behaviour of the Cu(II)/Zn and Co(II)/Zn cementation reactions. Also included are some suggestions for future work in cementation reactions.

6.1 THERMODYNAMICS

It is well known that the Cu(II)/Zn and Co(II)/Zn cementation reactions investigated in this thesis are both thermodynamically very favourable as indicated by their $\Delta E^\Theta$, i.e. 1.1 V and 0.48 V respectively. The driving forces for these two reactions are thus very strong although that for the Cu(II)/Zn reaction is clearly much greater than that for the Co(II)/Zn reaction.

With such large $\Delta E^\Theta$'s one would anticipate that the reaction would go to completion, but in fact, equilibrium is not achieved, and the extent of reaction in both cases is determined by the reaction rate rather than equilibrium thermodynamics.

6.2 KINETICS

The Cu(II)/Zn reaction is much faster than the Co(II)/Zn reaction. The former has been shown to be under diffusion control, whereas the latter is most often under chemical control, although under certain circumstances can be under diffusion control. The following are seen as contributing factors to this difference.
(a) Reactions having large $\Delta E^\Theta$ values are more likely to be under diffusion control than reactions having small $\Delta E^\Theta$ values. This can be readily understood by reference to Fig. 6-1. In this diagram, reactions 1 and 2 have identical electrochemical kinetics (i.e., same exchange current density and charge transfer coefficient), but reaction 1 is under chemical control, and reaction 2 is under diffusion control simply because $\Delta E_2 > \Delta E_1$.

It is on the basis of a diagram similar to Fig. 6-1 that Power and Ritchie [1] formulated the rule that reactions for which $\Delta E^\Theta > 0.36 \text{ V}$ would probably be under diffusion control. In the present circumstances, where one reaction ($\text{Co(II) \rightarrow Co(0)}$) is very slow, it might be more useful to say that the greater $\Delta E^\Theta$ is, the more likely the cementation reaction is to be under diffusion control.

(b) A corollary of the above is that if $\Delta E^\Theta$ is of such a magnitude that the polarization curve for the reduction half-reaction cuts the polarization curve for the oxidation half-reaction in a region of electrochemical control, then even minor changes in the shape of the former can cause quite large changes in the reaction rate. On the other hand, such changes would have little effect on a reaction in which $\Delta E^\Theta$ is large: quite large changes in the electrochemically controlled region of the polarization curve for the reduction reaction would still leave the overall reaction under diffusion control.

It is thought that the above may well account for the effect of temperature on the two cementation reactions. In the Cu(II)/Zn case, the effect of temperature is relatively slight. The reaction is under diffusion control and the activation energy of such reactions is only 15-20 kJ mol$^{-1}$. On the other hand, increasing the temperature of the Co(II)/Zn reaction can cause it to shift from chemical control through to diffusion control and
FIGURE 6-1. Schematic Evans' diagram showing the effect of the driving force $\Delta E$ on the controlling step of cementation reactions.
the consequent increase in rate is very marked.

The different effects of high concentrations of inert cations on the two reaction rates may well have a similar explanation. The so-called double layer effect, will depress the electrochemically controlled portion of both the Cu(II) and Co(II) polarization curves. This will not be of any great significance to the diffusion controlled Cu(II)/Zn reaction, but it is of considerable importance to the Co(II)/Zn reaction, because in the presence of high concentrations of zinc ions, the reaction is brought to a virtual standstill.

(c) The effect of hydrogen discharge on the two reactions is quite different because the \( \text{H}^+/\text{H}_2 \) equilibrium potential lies below that for Cu(II)/Cu and above that for Co(II)/Co. Moreover, the deposition of copper is a relatively reversible process whereas hydrogen discharge on copper is quite slow [2]. As a consequence, copper(II) is discharged prior to protons, and the hydrogen deposition reaction has little or no effect on that of the metal. However, the situation is quite different for the deposition of cobalt. The reversible potential for a hydrogen electrode in a solution of pH 4 is -0.24 V whereas the reversible potential for a cobalt electrode (500 ppm Co\(^{2+}\)) is -0.34 V. Hydrogen discharge on cobalt is relatively rapid and so it can be seen that there is a good chance that the two reactions will proceed more or less simultaneously. In fact, as has been shown by the work described in this thesis, there is very good evidence that adsorbed hydrogen atoms formed during the proton discharge reaction contribute significantly to the inhibition of cobalt deposition during the cementation reaction. The Tafel slopes for Co(II) reduction at pH 4 are also very high (~ 240 mV per decade of current density) and this may again be due to interference by simultaneous proton discharge.
In contrast, at pH 5 the Co(II)/Zn cementation reaction, and also the electrolytic deposition of zinc, proceed quite smoothly. Although this is generally accepted as being due to the participation of the CoOH⁺ species, it could possibly be due to the lack of interference by the hydrogen discharge reaction. The H⁺/H₂ reversible potential will decrease by 0.06 V and the overpotential will increase and so hydrogen discharge may then take place after cobalt deposition.

6.3 THE REQUIREMENTS FOR A FAST Co(II)/Zn REACTION

The above discussion provides a framework for understanding current practice in the electrolytic zinc industry. Copper(II) can be removed from the zinc electrolyte under relative mild conditions. The zinc used for cementation is relatively coarse; high temperatures are not required, and activators are unnecessary, but good stirring is essential.

For a diffusion controlled reaction like the Cu(II)/Zn cementation system, efficient agitation is generally sufficient to achieve the maximum rate of reaction preferred in industry. This measure, however, is inadequate to speed up the Co(II)/Zn reaction because of its intrinsic kinetic sluggishness.

Several measures need to be taken to overcome the slowness of this reaction. They are:

1. Use of finely divided zinc

   In order to cement cobalt(II) efficiently from the zinc electrolyte, the zinc must be as finely divided as possible, i.e., making ΔE° as large as possible.
2. Operation at high temperatures

3. Use of activators

   This has been proved essential for the efficient removal of cobalt impurity from zinc sulphate electrolyte.

4. Control of pH

   To the above list, we would add the suggestion that the pH be made as high as possible, consistent with the other requirements and limitations of the process.

6.4 SUGGESTIONS FOR FUTURE WORK

1. This study was carried out under relatively uncomplicated conditions, i.e., at room temperature and in the absence of added zinc ions. It is desirable that future work be carried out under conditions similar to those used in industry, for example, at elevated temperatures and in the presence of zinc ions.

2. Deposits often have marked effects on the rates of cementation reactions. The work described in this thesis has largely avoided such effects, which may well be important in practice. It is therefore worthwhile to study the reactions using the electrochemical techniques described here under conditions where deposit effects are pronounced. In so doing, further information about the applicability of electrochemical techniques to the study of cementation reactions may be obtained.
3. Although some valuable results concerning cementation reactions have been obtained using impedance spectroscopy, much work remains to be done in order to explore fully the potential of the impedance technique for cementation reactions. Some aspects of cementation reactions which would merit further study using the impedance technique would be the effects of side reactions (proton discharge and oxygen reduction) and deposits and codeposition on the impedance behaviour, and the interrelation of the impedance behaviour between a cementation system and its component half reactions.
REFERENCES (Chapter 6)


APPENDIX 1.

CALCULATION OF pKa FOR BISULPHATE ION FROM KINETIC DATA

Provided the bisulphate ion concentration is small, it is given by

\[ [\text{HSO}_4^-] \approx [\text{SO}_4^{2-}]_a [H^+] / K_a \] (1)

where activities have been approximated by concentrations, denoted by square brackets, \([\text{SO}_4^{2-}]_a\) is the total amount of sulphate, as sulphate or bisulphate, in solution and \(K_a\) is the acidity constant for the bisulphate ion. Because zinc metal can react with protons and bisulphate ions as well as copper ions, we can write,

\[ \Delta[Zn^{2+}] = -\Delta[Cu^{2+}] - b_2\Delta[H^+] - b_2\Delta[\text{HSO}_4^-] \] (2)

where \(\Delta\) denotes a change in concentration.

It follows from (1) that

\[ \Delta[\text{HSO}_4^-] \approx \Delta[H^+] [\text{SO}_4^{2-}] / K_a \] (3)

Eliminating the \(\Delta[\text{HSO}_4^-]\) term from equations (2) and (3) and rearranging,

\[ K_a = -b_2[H^+] [\text{SO}_4^{2-}] / (\Delta[Zn^{2+}] + \Delta[Cu^{2+}] + b_2 \Delta[H^+]) \] (4)

from which \(pKa\) can be calculated.

As an example, at the 60th minute, \(-\Delta[H^+] = -0.79 \times 10^{-6} \text{ mol dm}^{-3}\), \(-\Delta[Cu^{2+}] = 20 \times 10^{-6} \text{ mol dm}^{-3}\), \(\Delta[Zn^{2+}] = 26 \times 10^{-6} \text{ mol dm}^{-3}\), \([\text{SO}_4^{2-}] = 0.50 \text{ mol dm}^{-3}\). The calculated \(pKa\) is 1.5. The average value from four runs is 1.3±0.2 which is reasonable compared with 2 at infinite dilution [1] and 0.54 in a saturated \(\text{Na}_2\text{SO}_4\) solution at 32°C [2].
References


APPENDIX 2.

MECHANISM OF THE CATHODIC REDUCTION OF COBALT(II)

\[
\begin{align*}
\text{Co}^{2+} + H_2O & \xrightarrow{k_1 / k_{-1}} \text{CoOH}^+ + H^+ \quad \text{fast} \\
\text{CoOH}^+ + e & \xrightarrow{k_2 / k_{-2}} \text{CoOH} \quad \text{fast} \\
\text{CoOH} + H^+ + e & \xrightarrow{k_3} \text{Co} + H_2O \quad \text{slow}
\end{align*}
\]

where \( k \) is the rate constant, its negative subscript representing the backward reaction.

According to the Butler-Volmer equation, the current flow for (3) is

\[
i = k_3 \Theta \text{CoOH}^+ \cdot C_{H^+} e^{-\beta F n / RT}
\]

where \( \Theta \) is the coverage of a given species on the electrode surface, \( C_{H^+} \) is the concentration of protons, \( \beta \) is the symmetry factor, \( n \) is the overpotential, and other quantities have their usual meanings.

Because we have a steady state system prior to the slow step, from (2)

\[
k_2 C_{\text{CoOH}^+}(1-\Theta_{\text{CoOH}}) e^{-\beta F n / RT} = k_{-2} \Theta_{\text{CoOH}} e^{(1-\beta)F n / RT}
\]

therefore,

\[
\frac{\Theta_{\text{CoOH}}}{1-\Theta_{\text{CoOH}}} = k_2 C_{\text{CoOH}^+} e^{-F n / RT}
\]

Similarly, from (1)

\[
k_1 C_{\text{Co}^{2+}} = k_{-1} C_{\text{CoOH}^+} \cdot C_{H^+}
\]

therefore,

\[
C_{\text{CoOH}^+} = k_1 \frac{C_{\text{Co}^{2+}}}{C_{H^+}} \quad K_1 = \frac{k_1}{k_{-1}}
\]
By substituting (8) into (7), we get

\[
\frac{\Theta_{\text{CoOH}}}{1 - \Theta_{\text{CoOH}}} = \frac{K_2 K_1 C_{\text{Co}^{2+}}}{C_{\text{H}^+}} \cdot e^{-\frac{F n}{R T}} \tag{9}
\]

Assuming \( \Theta_{\text{CoOH}} \ll 1 \), and so \( 1 - \Theta_{\text{CoOH}} \sim 1 \)

\[
\Theta_{\text{CoOH}} \sim \frac{K_2 K_1 C_{\text{Co}^{2+}}}{C_{\text{H}^+}} \cdot e^{-\frac{F n}{R T}} \tag{10}
\]

Substituting (10) into (4) gives

\[
i = k_3 K_2 K_1 C_{\text{Co}^{2+}} \cdot e^{-\frac{\beta F n}{R T}} \cdot e^{-\frac{F n}{R T}} \tag{11}
\]

By taking logarithms and assuming \( \beta = 0.5 \)

\[
n = \text{const.} - \frac{2.3 R T}{(1 + \beta)} \lg i \tag{12}
\]

therefore \( \frac{3 n}{3} \log i = \frac{59}{3/2} \text{ mV} = 39 \text{ mV} \)
APPENDIX 3.

DETERMINATION OF THE DIFFUSION COEFFICIENT
OF COBALT(II)

In order to determine the true diffusion coefficient of cobalt(II), limiting currents were measured as a function of pH in 0.50 mol dm\(^{-3}\) sodium sulphate without cobalt(II). By assuming that the cobalt(II) and any other electroactive species in sodium sulphate solutions are reduced independently, limiting currents for cobalt(II) alone can be calculated from

\[ i_L(\text{Co}^{II}) = i_L(\text{Co}^{II} + \text{Na}_2\text{SO}_4) - i_L(\text{Na}_2\text{SO}_4) \]

then, from the corrected values of the limiting current, the true diffusion coefficient for cobalt(II) can be calculated from the Levich equation [1].

The apparent and corrected diffusion coefficient of cobalt(II) are listed in the following table.

<table>
<thead>
<tr>
<th>pH</th>
<th>6.00</th>
<th>5.00</th>
<th>4.50</th>
<th>4.00</th>
<th>3.50</th>
<th>3.00</th>
<th>2.50</th>
<th>2.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D_{\text{ppp}}/10^{-10}) m(^2) s(^{-1})</td>
<td>6.3</td>
<td>6.8</td>
<td>6.8</td>
<td>7.4</td>
<td>10</td>
<td>19</td>
<td>59</td>
<td>233</td>
</tr>
<tr>
<td>(D_{\text{corr}}/10^{-10}) m(^2) s(^{-1})</td>
<td>6.2±0.2</td>
<td>6.6±0.3</td>
<td>6.3±0.2</td>
<td>6.3±0.2</td>
<td>5.8±0.7</td>
<td>5.5±0.8</td>
<td>5.5±0.8</td>
<td>16</td>
</tr>
</tbody>
</table>

It can be seen that, with the exception of the value for \(D_{\text{Co}^{2+}}\) at pH 2, the results now agree within the limits of experimental error over the given
pH range. The high value at pH 2 is undoubtedly caused by the turbulent mixing at the electrode surface due to rapid hydrogen evolution on the freshly plated cobalt electrode. This effect would be less pronounced when the polarization curve is measured in sodium sulphate solutions without cobalt(II), because the overpotential for hydrogen evolution is greater for copper than for cobalt [2]. An average value for the diffusion coefficient of cobalt(II) in 0.50 mol dm$^{-3}$ sodium sulphate was calculated from the data in the pH range from 4-6 where the effect of hydrogen evolution on convection to the electrode surface is least, and the uncertainty in the measurements is smallest. The value obtained was $(6.4\pm0.3) \times 10^{-10}$ m$^2$ s$^{-1}$.

References
