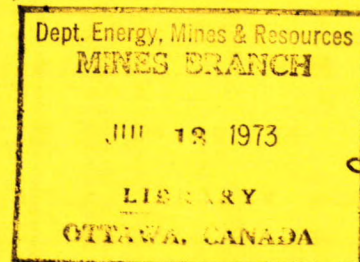


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DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA



*KINETICS OF COBALT CEMENTATION
ON ZINC*

D. J. MACKINNON

EXTRACTION METALLURGY DIVISION

APRIL 1973

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KINETICS OF COBALT CEMENTATION ON ZINC

by

D.J. MacKinnon*

ABSTRACT

Kinetics of cobalt cementation on zinc sheet from solutions of cobalt sulphate have been investigated with respect to temperature, stirring velocity, and acidity. The effect of buffered solutions on the reaction rate has also been determined. The rate of the cementation reaction was found to be strongly influenced by the presence of metallic ions other than cobalt in the solution. This effect is interpreted in terms of "alloy" formation, whereas the difficulties encountered in cementing cobalt in the absence of metallic ions is explained in terms of cobalt deposition overvoltage, hydrogen overvoltage, and inhibition by co-deposition of zinc.

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Direction des mines
Rapport de recherches R 259

LA CINÉTIQUE DE LA CÉMENTATION DE
COBALT SUR ZINC

par

D. J. Mac Kinnon*

RÉSUMÉ

L'auteur a étudié la cinétique de la cémentation de cobalt sur une feuille de zinc provenant des solutions de sulfate de cobalt du point de vue de la température, de la vitesse d'agitation et de l'acidité. Il a aussi déterminé l'effet des solutions tamponnées sur la vitesse de réaction. Il a trouvé que la vitesse de la réaction de cémentation était très influencée par la présence des ions métalliques autres que le cobalt dans la solution. L'auteur a interprété cet effet en fonction de la formation "d'alliage", tandis que les difficultés rencontrées dans la cémentation de cobalt, à l'absence des ions métalliques, ont été expliquées en fonction du survoltage du dépôt de cobalt, du survoltage associé à la libération d'hydrogène et de l'inhibition par dépôt simultané du zinc.

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INTRODUCTION

Cementation with zinc dust is a common industrial practice used for purifying zinc sulphate electrolyte prior to zinc electrolysis. Cobalt is one of the most detrimental impurities in the electrolyte and also one of the most difficult to remove by the cementation method. It has been reported^(1,2) that cobalt, if it is present in quantities as low as one part per million, causes corrosion holes in the electrodeposited zinc. A study of the kinetics of cobalt cementation on zinc was initiated in order to determine the factors which influence the cementation rate.

Previous investigations of the cobalt/zinc cementation couple in sulphate solutions^(3,4,5) indicated that both temperature and acidity had a pronounced effect on the cementation rate; (the rate increased with increasing temperature but decreased with increasing acidity). A similar behavior was found for cobalt cementation by zinc from chloride solutions⁽⁶⁾.

Nestler⁽⁵⁾ studied the effect of additions of Fe^{++} , Ni^{++} , Cd^{++} , and Ag^+ on the rate at which cobalt cements on zinc. He found that small additions of Cd^{++} increased the rate slightly and that the other ions decreased the rate. Chizhikov⁽⁴⁾ found that cobalt cementation on zinc was

inhibited by Ni^{++} . Sato⁽⁷⁾ has shown that the rate of cementation of cobalt on zinc dust added to zinc sulphate solution in the presence of either As_2O_3 or Hg_2SO_4 can be much improved by the addition of CuSO_4 .

Fischer-Bartelk and co-workers⁽⁸⁾ studied the effect of CuSO_4 , As_2O_3 , and Sb_2O_3 additions on the removal of cobalt from zinc sulphate solutions as a cement on zinc dust. They suggested that the observed increase in the rate of cobalt cementation in the presence of these additives was a result of the formation of inter-metallic phases which imparted a more positive potential to the cementation reaction.

Fontana and Winand⁽⁹⁾ have shown that the addition of Sb is necessary to cement cobalt from zinc-rich solutions and have identified CoSb and CoSb_2 compounds in their cementation product by means of X-ray diffraction. Fontana et al.⁽¹⁰⁾ have shown that a combination of CuSO_4 - PbO - Sb_2O_3 gave the best cobalt cementation under their experimental conditions. The combination of CuSO_4 - CdSO_4 - As_2O_3 also gave satisfactory results.

In this work, the effects of temperature, peripheral velocity, acidity, the addition of metallic ions other than cobalt, and the use of buffered solutions on the rate of cobalt cementing on zinc from cobalt sulphate solutions have been investigated. The results of these studies are

reported below, whereas the factors that influence cobalt cementation on zinc from zinc sulphate electrolyte, will be discussed in a later paper.

EXPERIMENTAL

The experimental apparatus and procedures were the same as described previously⁽¹¹⁾. Strips of zinc sheet were attached to the periphery of a lucite cylinder and rotated at controlled speeds in the cobalt sulphate solutions. Purified nitrogen was passed through the solutions via a dispersion tube. The temperature in the reaction vessel was controlled to within $\pm 0.005^{\circ}\text{C}$. To follow the course of the cementation reaction, solution samples were taken periodically and analysed for cobalt ions with a Techtron Model AA-5 atomic absorption spectrophotometer. Initial solutions were 1 litre and sample volumes were 5 ml.

Reagent-grade chemicals and redistilled de-oxygenated water were used in the preparation of the stock solutions. The cobalt sulphate stock solution was prepared from $> 99.0\%$ cobalt pellets (BDH). The buffer solution ($\text{pH} = 6.0$) was prepared by mixing the appropriate amounts of ammonium acetate and acetic acid solutions.

The zinc strips ($1 \times 23.3 \text{ cm}^2$) were cut accurately from 0.012-inch lithographic sheet*. To insure the reproducibility of rates, the exposed surfaces of the zinc strips were chemically polished for 15 minutes in a solution containing 200 g CrO_3 , 15 g Na_2SO_4 , 50 ml HNO_3 , and 950 ml H_2O ⁽¹¹⁾. Immediately after polishing, the strips were washed thoroughly under a stream of tap water and spun for 2 minutes in a 0.01 M HClO_4 solution. This was followed by rinsing with redistilled water. The back surfaces of the zinc strips were coated with a silicone rubber cement prior to attachment to the lucite cylinder.

RESULTS AND DISCUSSION

1. Reaction Conditions

The initial experiments were done to determine the best conditions for cementing cobalt on zinc from cobalt sulphate solutions. In the first series of tests, in which the pH of the solution containing 30 ppm Co^{++} was varied between 2 and 8 at 30°C , no reaction was observed. An increase in the temperature to 70°C under the same conditions gave a similar result. A reaction was observed, however, when 10 ppm of Te^{+4} was added to a solution containing

*The sheet was 99.2% zinc, as estimated by semiquantitative spectrographic analysis, and had the following impurities, given in per cent: Pb 0.32, Cd 0.29, Fe 0.06, Al 0.05, Cu 0.05, Co 0.02, Ag 0.005, Mn 0.004, Mg 0.0007.

30 ppm Co^{++} at 70°C . Tainton⁽¹²⁾ has shown that tellurium facilitates the cementation of cobalt on zinc. In addition, in previous publications^(13,14), it was reported that Te^{+4} ions activated the cementation of cadmium on zinc and of copper on nickel. In contrast to Nestler's results⁽⁵⁾, the addition of cadmium sulphate, alone or in combination with tellurium, gave poor results. However, small additions of copper sulphate caused a significant reaction to occur. A combination of copper sulphate and arsenic trioxide are used industrially in the purification of zinc sulphate electrolyte to promote the cementation of cobalt on zinc dust^(15,16). Arsenic, in addition to being detrimental to zinc electrodeposition, has the disadvantage that arsine is formed during the cementation reaction. Therefore, the substitution of a harmless, process-promoting additive for arsenic trioxide would be of technological interest. Tellurium dioxide seems to be a suitable substitute because it was found that the addition of a combination of copper sulphate and tellurium dioxide to a solution buffered at $\text{pH} = 6$ gave the fastest reaction rate. A more detailed discussion on the effect of these additives is presented in Section 6.

2. Reaction Kinetics

The cementation of cobalt on lithographic zinc strips was found to obey a first-order rate law over the

first 10 minutes of the experiment. The integrated form of the rate equation, which has been adequately described in previous publications^(11,13,14) may be conveniently expressed as follows:

$$V_t \log ([Co^{++}]_0/[Co^{++}]_t) = kSt/2.303 \quad [1]$$

Here, k is a pseudo-first-order rate constant, S the geometric area of the zinc strip, and V is the solution volume. The subscript t refers to the sampling time in minutes, and V_t is the solution volume corrected for removal of samples. If S is expressed in cm^2 , V in cm^3 and t in seconds, k is in cm/sec .

Figure 1 shows a plot of $V_t \log ([Co^{++}]_0/[Co^{++}]_t)$ against time obtained for a solution containing 30 ppm Co^{++} , 6.4 ppm Cu^{++} , 10 ppm Te^{+4} , and 100 ml of the buffer solution. The peripheral velocity (p.v.) of the zinc strip was 500 cm/sec , and the solution temperature was $68^\circ C$. The deviation from linearity after the first 10 minutes indicates at least two steps in the reaction mechanism. The first step is described by Equation [1]. In the second step, the rates are slower, and the controlling mechanism is probably one of diffusion of zinc ions through the cemented deposit into the solution. The deposit was black and adhered strongly to the surface of the zinc. X-Ray diffraction analysis showed that, in general,

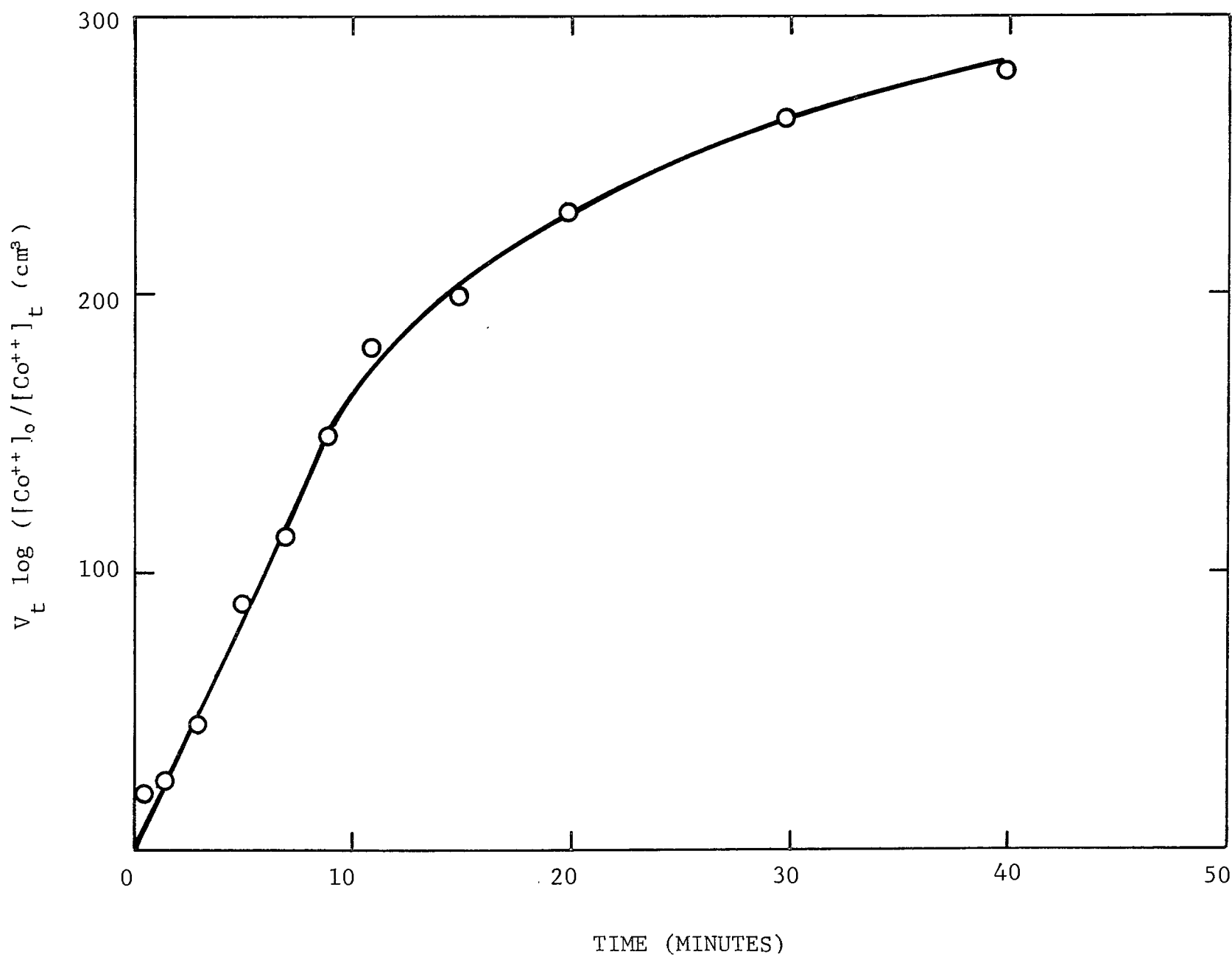


Figure 1. Plot of $V_t \log ([Co^{++}]_0 / [Co^{++}]_t)$ against Time for Cobalt Cementation on Zinc

the deposits were not well crystallized so it was impossible to identify the components.

3. Temperature and Peripheral Velocity Effects

A series of experiments was done to examine the effect of temperature variation on the initial cementation rate. The results, shown in Figure 2 in the form of an Arrhenius plot, are for the temperature range between 30 and 80°C. These results were obtained for the conditions: 30 ppm Co^{++} , 6.4 ppm Cu^{++} , 10 ppm Te^{+4} , and 100 ml of the buffer solution at a p.v. = 500 cm/sec. The activation energy, as determined from the slope of the plot, has the value of 7.1 ± 1.3 kcal/mole. This is in reasonable agreement with the value of 7.5 kcal/mole obtained by Chizhikov et al.⁽⁴⁾.

Figure 3 shows a plot of the rate constant as a function of peripheral velocity (p.v.). The k values were obtained for the conditions: 30 ppm Co^{++} , 6.4 ppm Cu^{++} , 10 ppm Te^{+4} , and 100 ml of the buffer solution at a temperature of 68°C. Initially, the rate constant increases with increasing values of p.v. but then begins to level off at a p.v. of 750 cm/sec. This behavior and the low value of the activation energy indicate that a diffusion process is the most likely rate controlling step.

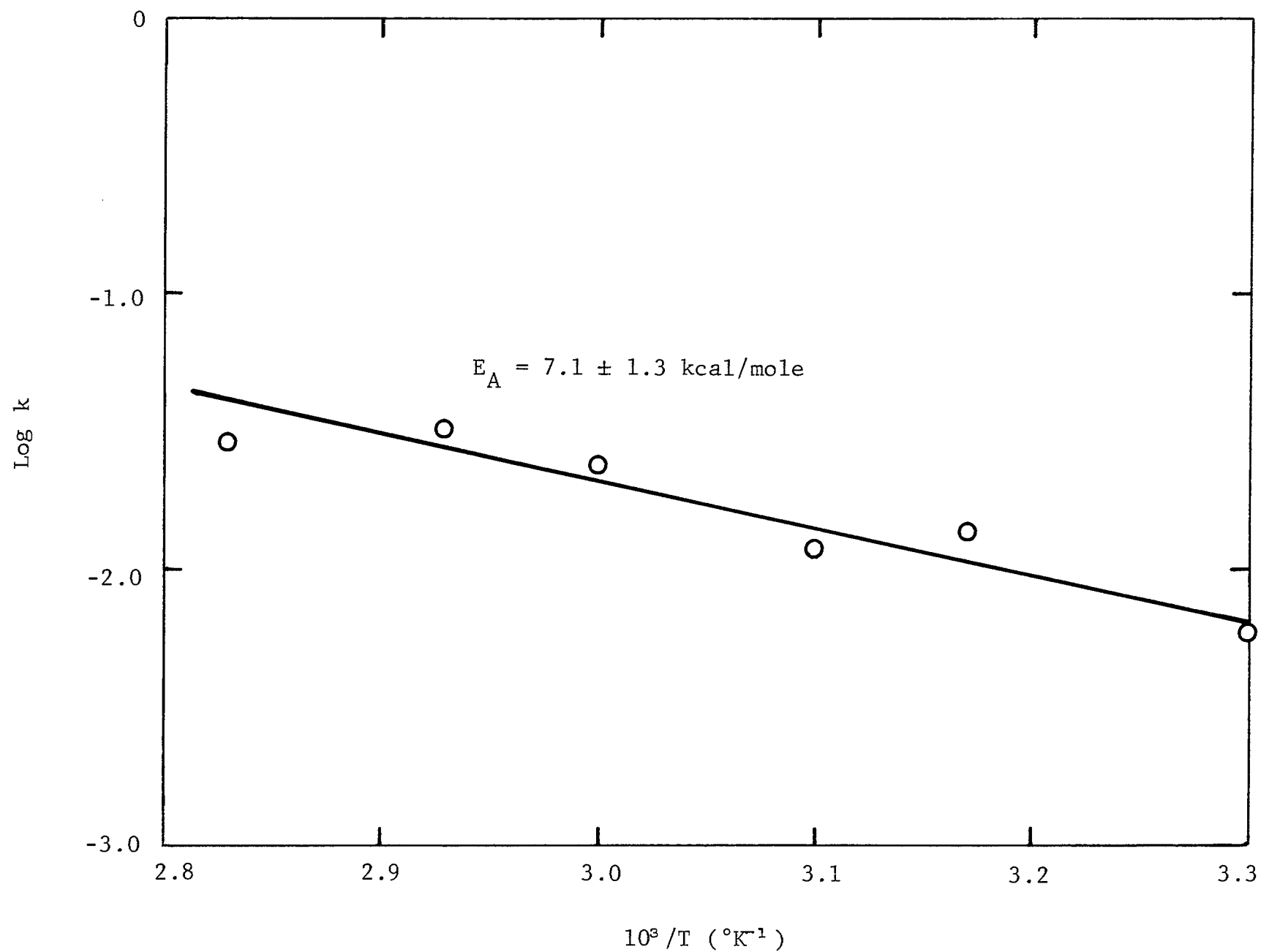


Figure 2. Arrhenius Plot of k for Cobalt Cementation on Zinc

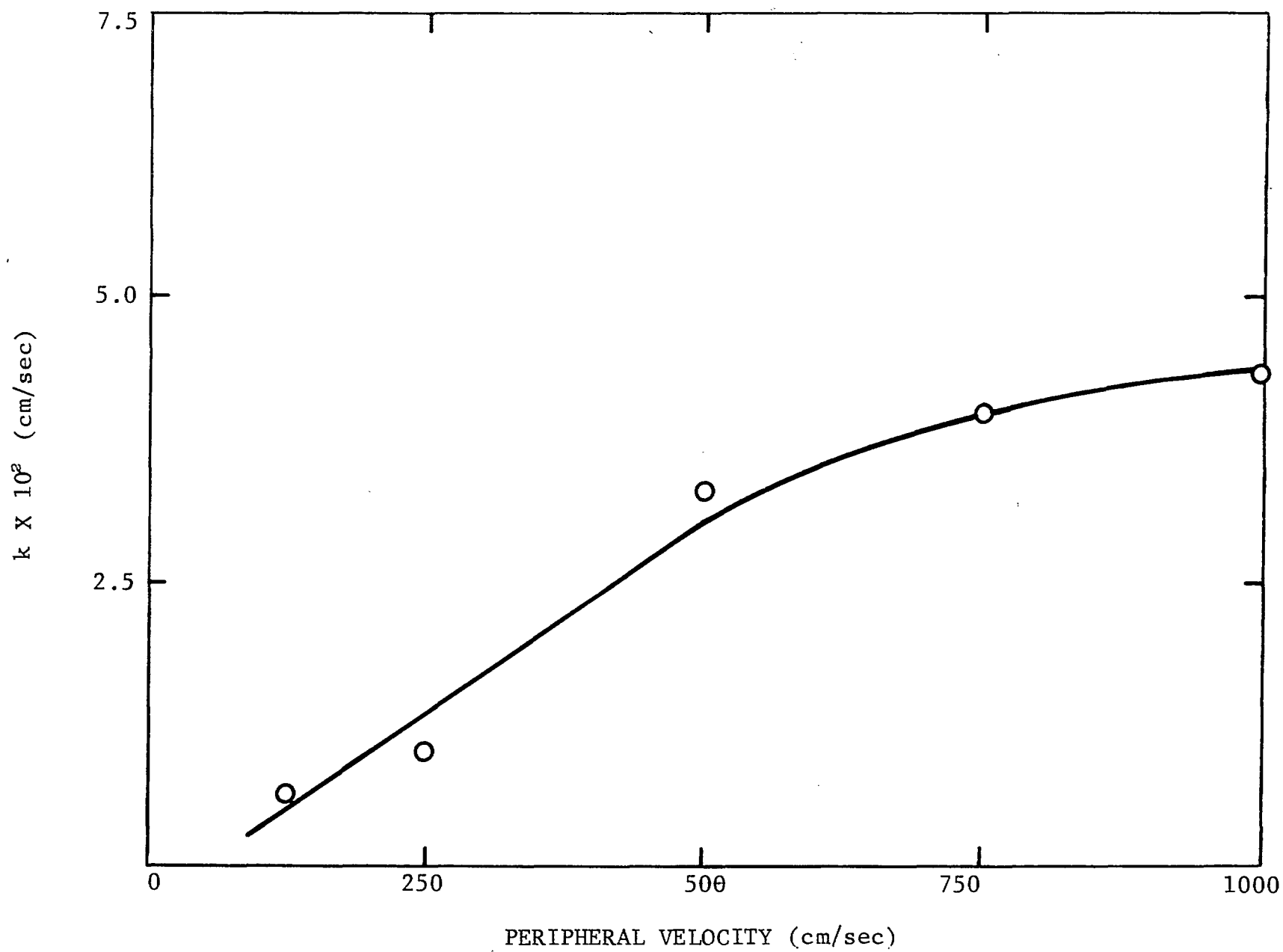


Figure 3. Plot of k against Peripheral Velocity for Cobalt Cementation on Zinc

4. Effect of Initial pH

The effect of variations in the initial pH of the cobalt sulphate solutions on the rate constant is shown in Figure 4. These results were obtained for the conditions: 30 ppm Co^{++} , 6.4 ppm Cu^{++} , and 10 ppm Te^{+4} at 68°C and p.v. = 500 cm/sec. The desired initial pH was obtained by adding either H_2SO_4 or NH_4OH to the solution, which was then buffered by 100 ml of the appropriate ammonium acetate-acetic acid solution. According to Figure 4, the rate constant increases linearly with increasing initial pH until a pH of 5.0 is reached. This behavior could be related to a decrease in the competing hydrogen evolution reaction, which becomes less probable as the initial pH is increased.

5. Effect of Ammonium Acetate-Acetic Acid Buffer Solution

The effect of ammonium acetate-acetic acid buffer solution on the cementation rate is shown in Figure 5, which compares two plots of $V_t \log ([\text{Co}^{++}]_0 / [\text{Co}^{++}]_t)$ against time. These rate curves were obtained for identical experimental conditions (30 ppm Co^{++} , 6.4 ppm Cu^{++} , 10 ppm Te^{+4} , 68°C , initial pH = 6.0, and p.v. = 500 cm/sec) except that only one solution contained 100 ml of the ammonium acetate-acetic acid buffer solution. The curves shown in Figure 5 indicate that both the cementation rate and the amount of cobalt cemented are increased in the presence of

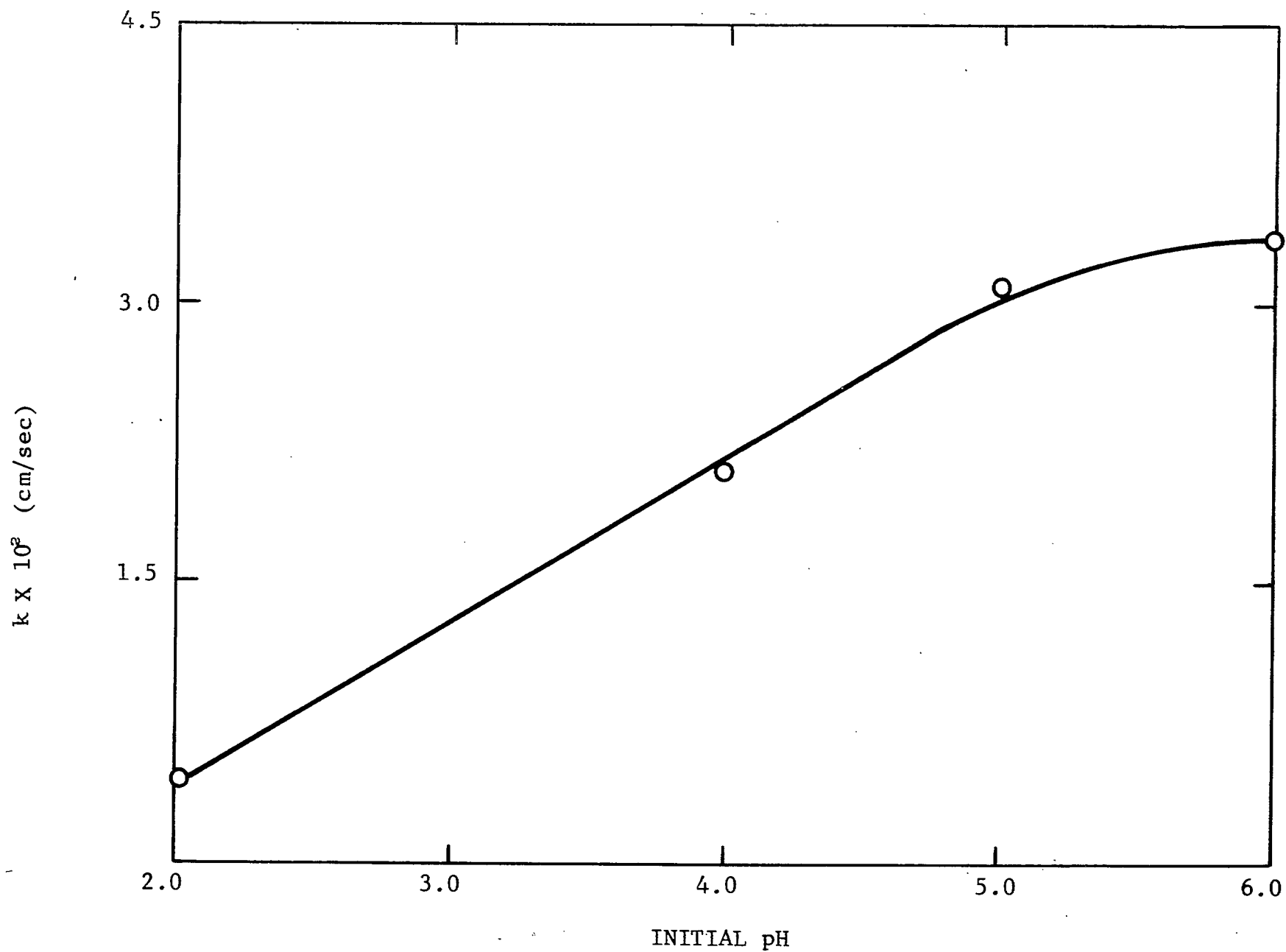


Figure 4. Plot of k against Initial pH for Cobalt Cementation on Zinc

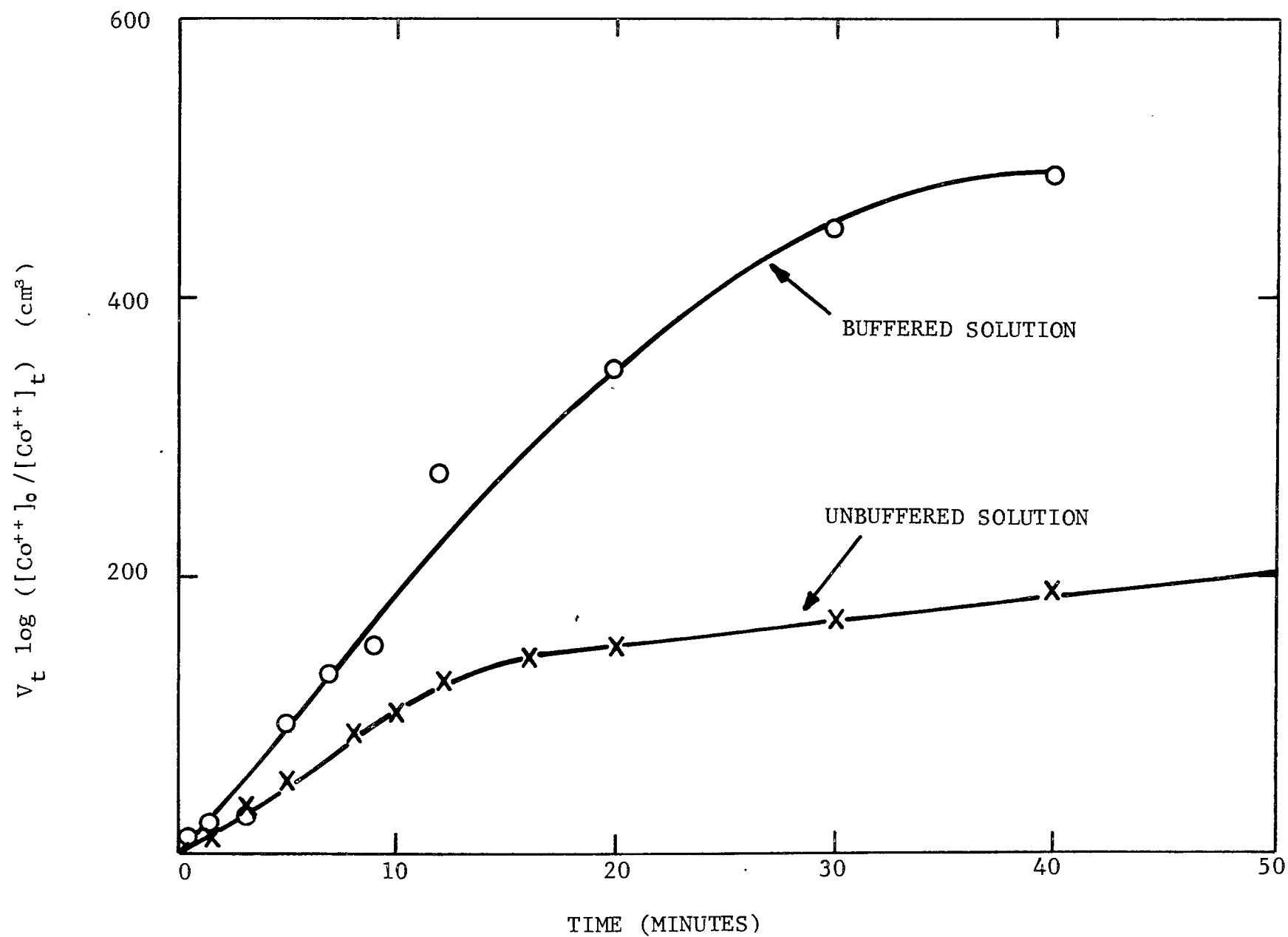


Figure 5. Plots of $V_t \log ([Cu^{++}]_0 / [Cu^{++}]_t)$ Against Time Showing the Effect of Buffer on the Cementation of Cobalt on Zinc

buffer. The corresponding initial rate constants for the buffered and unbuffered solutions are 3.31×10^{-2} and 1.74×10^{-2} cm/sec respectively. This effect may be related to the fact that, for the unbuffered solution, the pH gradually increased as the reaction proceeded with the probable formation of a film of zinc hydroxide on the metal surface⁽¹⁷⁾. Such a film could inhibit the discharge of Co^{++} by preventing its access to the surface. In the presence of the buffer, the initial pH remains constant to prevent the possible formation of hydroxide but to permit the discharge of Co^{++} ions.

6. Effect of Metallic Ions

Varying amounts of copper, tellurium, cadmium, nickel, and mercury were added to the cobalt sulphate solution as aqueous solutions of copper, cadmium, and nickel sulphates, mercury chloride (HgCl_2), and tellurium dioxide dissolved in hydrochloric acid. These tests were done for the conditions: 30 ppm Co^{++} buffer at pH = 6.0, temperature = 68°C , and p.v. = 500 cm/sec. The effect of these ions on the cementation rate was markedly influenced not only by the type of metal ion added but by its concentration.

Table 1 shows that the addition of 6.4 ppm Cu^{++} and 10 ppm Te^{+4} caused the largest increase in the cobalt cementation rate constant. As mentioned in Section 1, virtually no

TABLE 1

EFFECT OF METALLIC IONS ON THE COBALT CEMENTATION

RATE CONSTANT

| CuSO ₄ (ppm) | TeO ₂ (ppm) | CdSO ₄ (ppm) | NiSO ₄ (ppm) | HgCl ₂ (ppm) | k X 10 ² (cm/sec) |
|----------------------------|---------------------------|----------------------------|----------------------------|----------------------------|---------------------------------|
| 6.4 | 10.0 | -- | -- | -- | 3.31 |
| 12.8 | 10.0 | -- | -- | -- | 2.61 |
| 6.4 | -- | -- | -- | -- | 1.18 |
| -- | 10.0 | -- | -- | -- | 0.23 |
| -- | 10.0 | 10.0 | -- | -- | 0.57 |
| 6.4 | 10.0 | 10.0 | -- | -- | 1.12 |
| -- | 10.0 | -- | 13.2 | -- | 0.52 |
| 6.4 | 10.0 | -- | 13.2 | -- | 3.00 |
| 6.4 | 10.0 | 10.0 | 13.2 | -- | 0.82 |
| 6.4 | -- | -- | -- | 10.0 | 2.87 |
| -- | 10.0 | -- | -- | 10.0 | 1.47 |
| 6.4 | 10.0 | -- | -- | 10.0 | 2.93 |

(Co⁺⁺ = 30 ppm; solution buffered at pH = 6.0; Temperature =
68°C and p.v. = 500 cm/sec)

cementation occurred unless some additive was present.

Increasing the amount of Cu^{++} to 12.8 ppm decreases the rate constant by approximately 2%, whereas eliminating the Te^{+4} causes a 60% decrease in the rate constant. Te^{+4} alone reduces the rate constant to 0.23 cm/sec, 93% less than that obtained in combination with Cu^{++} . Increasing the Te^{+4} concentration above 10 ppm, either with or without copper, causes the rate constant to decrease. The effect of other combinations of additives can be readily seen from Table 1.

The difficulties associated with the cementation of cobalt on zinc are probably caused in part by the fact that, once some cobalt is deposited, hydrogen evolution becomes the preferred reaction because cobalt has a fairly low hydrogen overvoltage⁽¹⁸⁾. This is in agreement with the observed pH effect mentioned earlier. In addition, the deposition of cobalt from its simple salt solutions at room temperature is accompanied by an overvoltage of 0.2 to 0.3 volt⁽¹⁹⁾ so that the e.m.f. for the Zn/Co couple is decreased by this amount to render Co deposition more difficult.

In the presence of Cu^{++} , for example, the increased cobalt cementation rate is likely a result of the formation of a Cu/Zn alloy. According to Straumanis and Fang⁽²⁰⁾, this alloy formation is caused by a redeposition of zinc which increases the hydrogen overvoltage, thereby favoring Co^{++}

discharge. The deposition potential of the Cu/Zn alloy is less anodic than that of the anode (Zn)⁽²⁰⁾ and, therefore, Cu/Zn can be deposited by the e.m.f. of Zn itself. Fischer-Bartelk and co-workers⁽⁸⁾ have shown, by means of radio-graphic analysis, that the zinc in the cementation products obtained in the presence of Cu^{++} does not occur as elementary zinc but in the form of the ϵ -brass phase. Once formed, this brass phase makes possible the cementation of cobalt on zinc because it imparts a more positive potential (approx. 23 mV as determined by e.m.f. measurements⁽⁸⁾) than does pure zinc. Thus, copper ions in the solution act as potential improvers because brass phases are formed on their discharge that bond elementary zinc.

As mentioned earlier, it is a common industrial practice to promote the cementation of cobalt on zinc by means of additives such as CuSO_4 , As_2O_3 , and Sb_2O_3 etc. This work has shown that the combination of CuSO_4 and TeO_2 also promotes this reaction while eliminating the chance of arsine or stibine being evolved.

Fischer-Bartelk and co-workers⁽⁸⁾ suggest that the addition of As_2O_3 , Sb_2O_3 , etc. further promotes the cementation of cobalt on zinc because they can form strong inter-metallic cobalt compounds that have high integral heats of formation which impart more positive potential to the

cobalt-containing mixed phase, thereby increasing cobalt cementation. They further suggest that other noble elements which form intermetallic compounds with cobalt should promote the cementation of cobalt by zinc in a manner similar to As or Sb. They obtained satisfactory results for cobalt removal by zinc when Cu^{++} and Sn^{++} were present in the zinc sulphate solutions. The cobalt-tin system contains several inter-metallic compounds that have considerable integral heats of formation⁽⁸⁾.

Because tellurium also forms binary alloys with both copper and cobalt⁽²¹⁾, the above interpretation of Fischer-Bartelk et al.⁽⁸⁾ may apply to explain the beneficial effect of tellurium on cobalt cementation by zinc.

CONCLUSIONS

Small amounts of Te^{+4} (10 ppm) can be used as an effective replacement for either As_2O_3 or Sb_2O_3 as a promoter for the cementation of cobalt on zinc dust. The advantage of using Te^{+4} over As_2O_3 or Sb_2O_3 is that the production of toxic arsine or stibine during the cementation reaction is not possible.

Optimum rates of cobalt cementation were obtained when the pH of the cobalt sulphate solution was controlled at 6.0 with an ammonium acetate-acetic acid buffer.

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