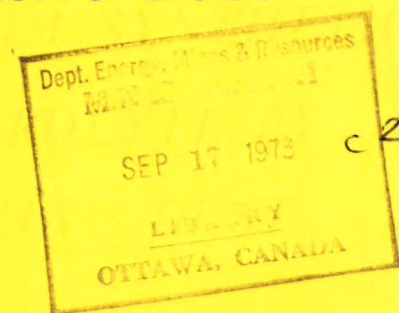CANADA

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REMOVAL OF COBALT FROM SYNTHETIC ZINC SULPHATE ELECTROLYTE BY CEMENTATION WITH ZINC DUST

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REMOVAL OF COBALT FROM SYNTHETIC ZINC SULPHATE

ELECTROLYTE BY CEMENTATION WITH ZINC DUST

by

D.J. MacKinnon*

ABSTRACT

The removal of cobalt from synthetic zinc sulphate electrolyte by zinc dust cementation has been investigated with respect to the effect of metallic ions and electrolyte impurities. At 90°C, a satisfactory rate of cobalt cementation resulted when the ratio Co:Te:Cu was 1.0:0.4:10. The cobalt cementation rate decreased with increasing zinc sulphate concentration and when the Cd^{++} concentration in the electrolyte was greater than 200 ppm. The effects of pH, type of zinc dust, stirring velocity, and initial cobalt concentration have also been determined.

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Direction des mines

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L'ENLÈVEMENT DU COBALT DE L'ÉLECTROLYTE SYNTHÉTIQUE DE SULFATE DE ZINC PAR LA CÉMENTATION DES POUDRES DE ZINC

par

D. J. MacKinnon*

RÉSUMÉ

L'auteur a étudié l'enlèvement du cobalt de l'électrolyte synthé-tique de sulfate de zinc par la cémentation des poudres de zinc du point de vue de l'effet des ions métalliques et des impuretés d'électrolyte. A 90°C, il a pu obtenir une vitesse satisfaisante de cémentation de cobalt quand le rapport de Co:Te:Cu était de 1.0:0.4:10. La cémentation de cobalt a diminué avec la croissance de la concentration de sulfate de zinc et quand la concentration de Cd^{++} dans l'électrolyte était plus que 200 ppm. Il a aussi déterminé les effets de pH, un type de poudres de zinc, la vitesse d'agitation et la concentration initiale de cobalt.

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INTRODUCTION

The removal of cobalt from zinc sulphate electrolyte by cementation using zinc dust prior to zinc electrodeposition is a common industrial practice. The presence of cobalt in zinc electrolyte at concentrations greater than 1 ppm will produce corrosion holes in the electrodeposited zinc[1,2]. If cobalt is co-deposited with zinc the current efficiency is decreased because the relatively low hydrogen-overvoltage of cobalt[3] results in hydrogen evolution. Thus cobalt removal from zinc sulphate electrolyte prior to electrolysis is essential to obtaining high-purity zinc at high current efficiencies.

Cobalt does not readily cement on zinc dust when it is present in low concentrations presumably because of its high deposition-overvoltage[4,5]. However, it has been found empirically that the addition of certain metallic compounds ($CuSO_4$, As_2O_3, Sb_2O_3) to the zinc sulphate electrolyte promotes the cementation of cobalt on zinc dust[6,7]. It has been suggested[5] that zinc deposited with some copper presents a low overvoltage-surface for the deposition of cobalt and that antimony and arsenic somehow activate the deposition process. Straumanis and Fang[8] have shown that immersion deposits of copper on zinc contained redeposited

zinc. They suggest that the zinc acts as an anode and the copper forms small cathodes on the zinc surface. The redeposition of zinc on these cathodes is possible because it is deposited in the form of a solid solution which has a deposition potential less anodic than that of zinc.

Fischer-Bartelk and co-workers[9] have suggested that these additives promote cobalt cementation on zinc because they form strong intermetallic phases with cobalt and zinc which impart a more positive potential to the cementation reaction, thus compensating for the deposition overvoltage of cobalt. These authors have identified both α brass and γ cobalt-zinc phases in their cementation products by radiographic analysis.

Fontana and Winand[10] have shown that the addition of antimony is necessary to cement cobalt from zinc-rich solutions and have identified $CoSb$ and $CoSb_2$ compounds in the cementation product by means of X-ray diffraction. Fontana et al.[11] have shown that a combination of $CuSO_4$-PbO-Sb_2O_3 gave the best cobalt cementation for their experimental conditions. The combination $CuSO_4$-$CdSO_4$-As_2O_3 also gave satisfactory results.

Sato[12] reported that the cementation of cobalt by addition of zinc dust to $ZnSO_4$ solution in the presence of As_2O_3 or Hg_2SO_4 can be much improved by the addition of

$CuSO_4$. Shome[5] has found that the addition of small amounts of As_2O_3 and Tl_2SO_4 to $ZnSO_4$ solutions containing a significant amount of $CuSO_4$ promotes the cementation of cobalt on zinc dust.

In a previous publication[13], the author described a kinetic study of the cementation of cobalt on lithographic zinc sheet from cobalt sulphate solutions. The results indicated that Te^{+4} (TeO_2 dissolved in HCl) could be used as an effective replacement for As_2O_3 and Sb_2O_3 for the cementation of cobalt on zinc. Although As_2O_3 and Sb_2O_3 promote cobalt cementation, they also form highly toxic arsine and stibine during the cementation reaction, whereas TeH_2, if formed, is less volatile and more soluble than AsH_3 and SbH_3. In this study, zinc dust was used in place of the lithographic sheet. Also, a new set of reaction conditions had to be established because much zinc sulphate was present.

EXPERIMENTAL

The experimental apparatus and procedures were essentially the same as described in the previous paper[13]. However, because zinc dust was substituted for the lithographic sheet, the lucite clamping cylinder used in the previous work was replaced by a plexiglass circulating disc. The disc, 3.0 inches in diameter and 3/8 inch thick, was connected to

a 3/8-inch-diameter plexiglass shaft. Four equally spaced 3/8-inch holes were drilled at 60° angles to the central shaft around the flat surface of the disc at 3/8 inch from the edge of the disc. This design allowed for thorough mixing of the zinc dust with the solution.

The synthetic $ZnSO_4$ electrolyte contained the following cations in g/l: Zn^{++} 80, Cd^{++} 0.68, Cu^{++} 0.30, Te^{+4} 0.010, Ni^{++} 0.012 and Co^{++} 0.30. The electrolyte was prepared from reagent-grade chemicals and distilled water. The required amount of $ZnSO_4$ was placed in the reaction vessel and dissolved in about 200 cc of distilled water. The appropriate amounts of the other metallic sulphates were then added as aliquots from previously prepared stock solutions. The volume of solution was adjusted to 1 litre with distilled water and the reaction vessel was placed in a constant-temperature bath. When the experimental temperature was achieved, NaOH pellets were added to adjust the pH to approximately 4.0. The addition of the zinc dust marked the beginning of the experiment. To follow the course of the reaction, 5-ml samples were taken at intervals and analysed for Co, Cu, Te, Ni, and Cd with a Techtron Model AA-5 atomic absorption spectrophotometer. The samples were drawn through a glass frit to ensure that no zinc particles were entrained in the samples.

Two sizes of zinc dust*, averaging 100 to 150-mesh (149 to 105-μ) and 25 to 65-mesh (710 to 210-μ), prepared by the air-atomization process were used in the experiments. Several tests were also done on 1600-μ (10-mesh) zinc pellets, obtained from the Fisher Scientific Co. The screen analyses of the zinc dust obtained from C.E.Z. is given in Table 1.

TABLE 1

Screen Analyses of C.E.Z. Zinc Dust

Size (μ)	+840	+710	+210	+149	+105	+74	+44	-44
Coarse	1.0	17.2	47.8	20.2	5.8	5.4	1.2	1.4
Fine	--	--	4.0	22.6	33.0	22.8	11.0	6.6

RESULTS AND DISCUSSION

1. Cobalt Cementation in the Presence of Zinc Sulphate

The cementation of cobalt on zinc dust proved to be more difficult from solutions containing large amounts of $ZnSO_4$ than from $ZnSO_4$-free solutions[13]. Much larger additions of copper sulphate were required in order to achieve complete removal of the cobalt at a reasonable rate from the $ZnSO_4$ solution. The addition of approximately 0.30 g/l Cu^{++} and 0.010 g/l Te^{+4} to a zinc sulphate electrolyte, containing

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*The zinc dust was obtained from Canadian Electrolytic Zinc, Valleyfield, P.Q.

0.030 g/1 Co^{++} and heated to 90°C, resulted in a satisfactory rate of cobalt cementation. In other experiments, to be discussed, the effects of varying the concentrations of the various constituents, of the synthetic electrolyte, on the cementation rate were determined.

2. The Effect of Zinc Dust

The effect of zinc dust on the cementation of cobalt from the synthetic zinc sulphate electrolyte was studied with respect to both the amount and type of zinc dust used. The effect of varying the amount of 149 to 105-μ zinc dust on the rate of cobalt cementation is shown in Figure 1. These results were obtained using the synthetic electrolyte described in the Experimental Section. The initial solution pH was 4.0, the temperature was 90°C and the electrolyte was stirred at a rate of 1250 rpm. The corresponding surface area of the zinc dust equivalent to its weight (in grams) is also shown on the graph. The areas of the 149 to 105-μ zinc dust was 440.2 ± 4.4 cm^2/g as determined by the BET (krypton gas) absorption method. Figure 1 shows that the rate of cementation increases linearly with increasing amounts of zinc dust. Therefore, the reaction rate is directly proportional to the surface area of the zinc dust. The slope of the line in Figure 1 gives a rate constant of 5.7 X 10^{-3} mg/cm^2/min.
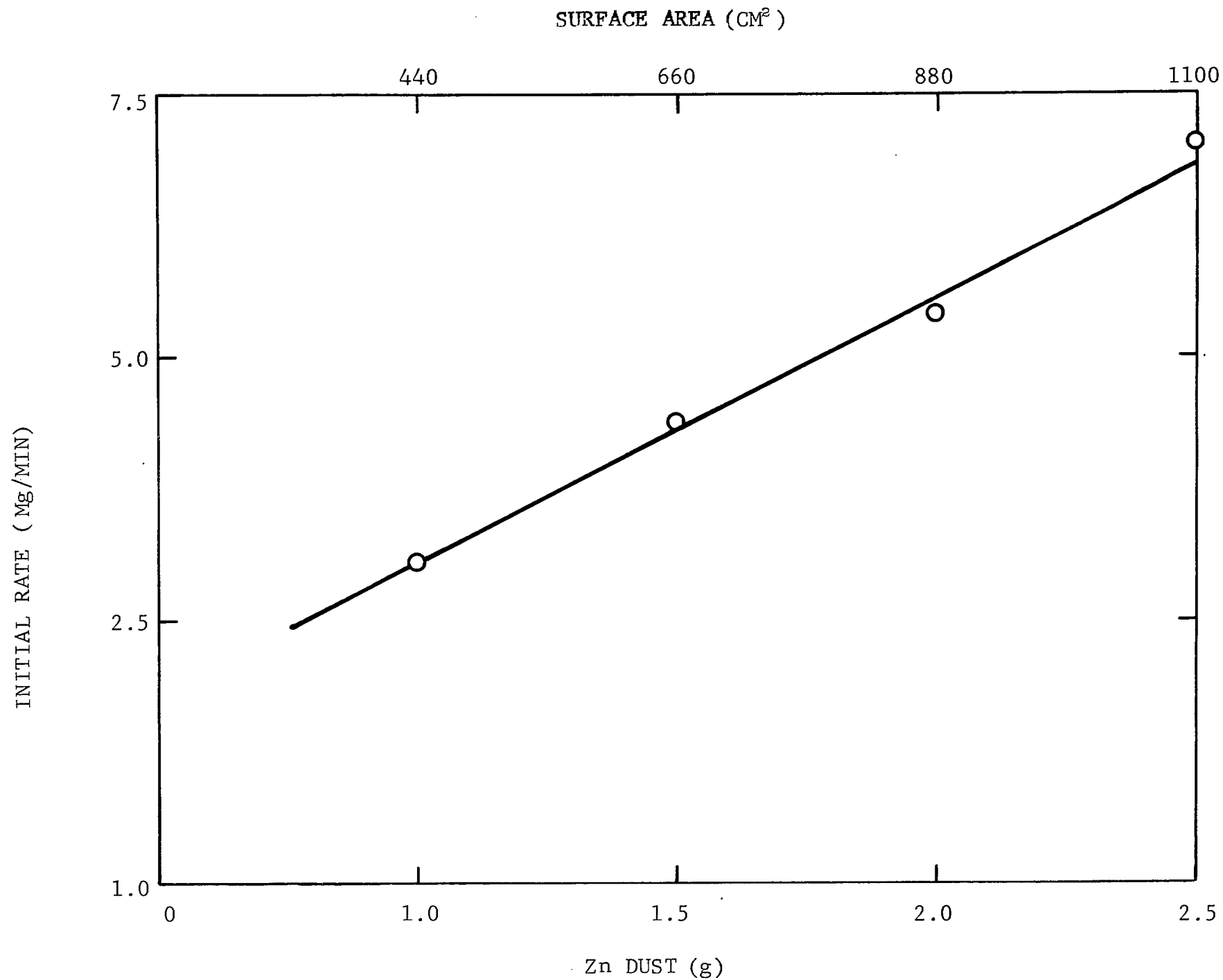
Figure 1: Plot Showing the Effect of Zinc Surface Area on the Rate of Removal of Cobalt from Synthetic Zinc Sulphate Electrolyte.

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The effect of zinc dust on the amount of cobalt
cemented from the synthetic electrolyte is shown in Figure 2.
These tests were done at 90°C using 2.0 g/l of zinc dust.
The initial pH was 4.0 and the stirring velocity was 1250 rpm.
The results indicate that the amount of cobalt cemented from
solution increased with decreasing particle size of the zinc
dust. Only 7% of the cobalt was cemented after 10 minutes
with 1600-μ zinc pellets as compared to 97 and 87% respect-
ively for the 149 to 105-μ and 710 to 210-μ dust for the same
reaction time. This behavior may be attributed to the specific
surface area of the various types of zinc. The amount of
cobalt cemented per unit time decreases as the specific
surface area of the zinc decreases in the order 149 to 105-μ
$>$ 710 to 210-μ $>$ 1600-μ. The results also indicate that the
cobalt layer formed on the zinc surface hinders the reaction.

3. Effect of Stirring Velocity

The effect of varying the stirring speed on the
rate of cobalt cementation from the synthetic electrolyte
was determined at 90°C with initial pH = 4.0. Figure 3
shows a plot of the cementation rate against rpm$^{1/2}$. The
straight-line relationship indicates that, for these conditions,
the cementation of cobalt from the electrolyte is likely
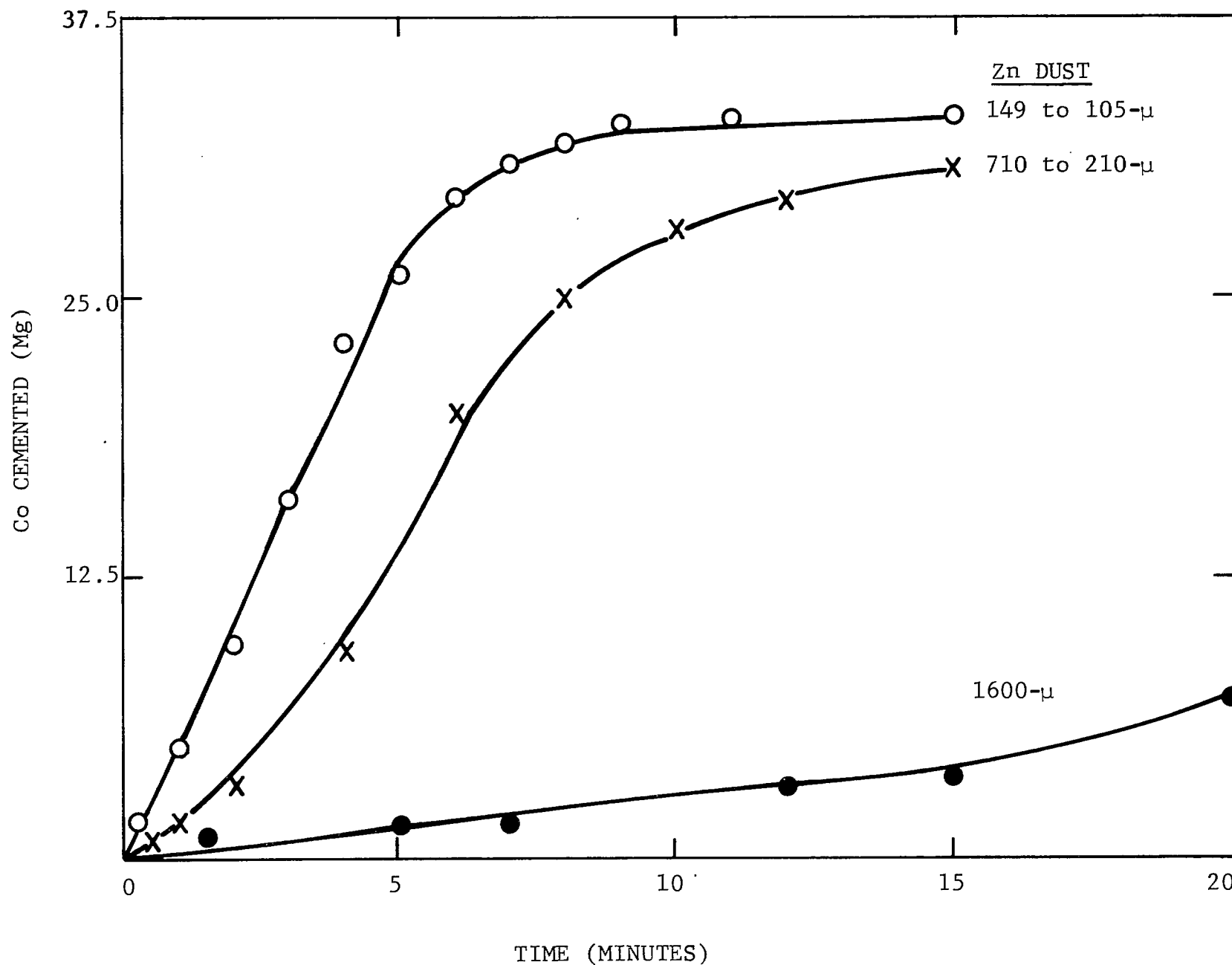diffusion controlled.

Figure 2: Plot Showing the Effect of Zinc Particle Size on the Rate of Removal of Cobalt from Synthetic Zinc Sulphate Electrolyte.
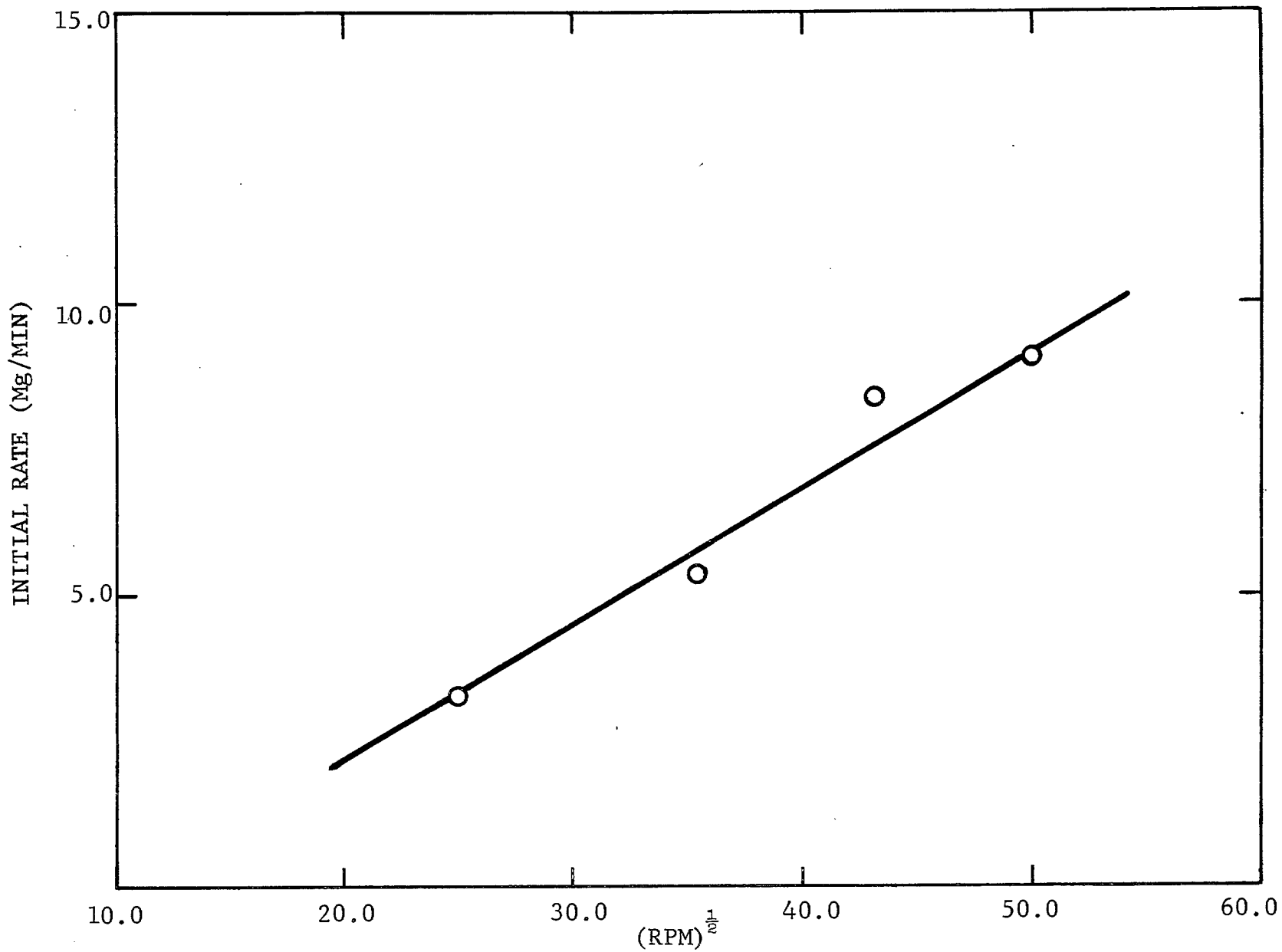
Figure 3: Plot Showing the Effect of Stirring Velocity on the Rate of Cobalt Removal from Synthetic Zinc Sulphate Electrolyte.

4. Medium Effects

The effect of varying the initial Co^{++} concentration in the synthetic electrolyte on the cementation rate is shown in Figure 4. The temperature was 90°C, initial pH = 4.0 and the stirring velocity was 1250 rpm. The rate of Co cementation on zinc dust 149 to 105-μ increased linearly with increasing Co^{++} concentrations up to 30 mg/l.

The effect of various solution conditions such as buffered, pH adjusted, etc. on the rate of removal of Co^{++} from the synthetic electrolyte is shown in Figure 5 for a temperature of 90°C and a stirring velocity of 1250 rpm. Although the fastest initial rate was obtained on a solution buffered at pH 4.0 with ammonium acetate-acetic acid, the best Co^{++} removal rate was achieved when the initial pH was adjusted to 4.0 but not buffered. For example, after 11 minutes reaction time, virtually all the Co^{++} was removed from a solution in which the initial pH had been adjusted to 4.0, whereas, with a solution buffered at pH 4.0, about 1 ppm Co^{++} remained. With no pH alteration, (initial pH = 2.6) about 2 ppm Co^{++} remained after 11 minutes. The fact that some Co^{++} remained in the buffered solution after this time may be attributed to the possibility that hydrogen evolution becomes significant when the Co^{++} concentration is very low
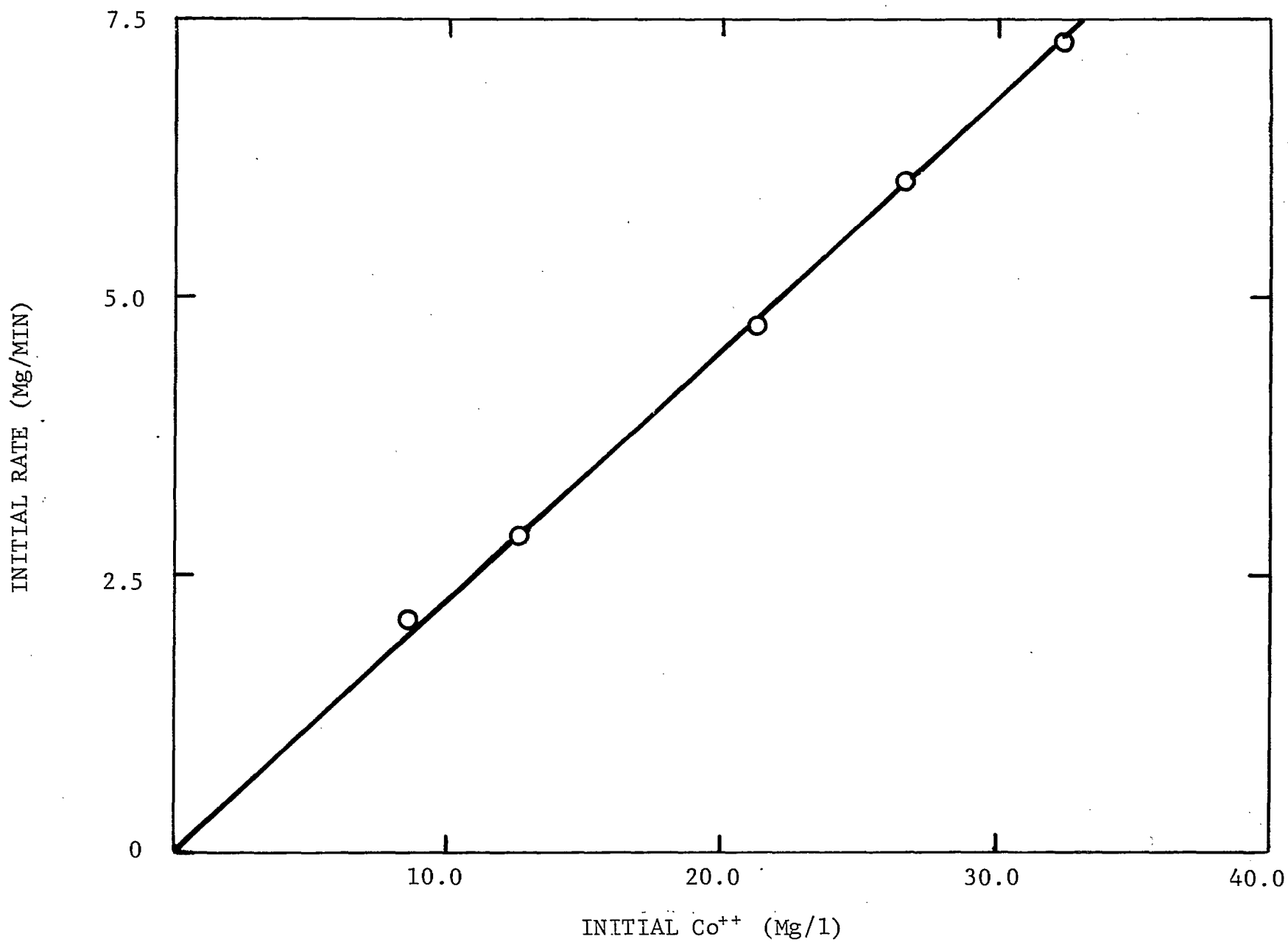
Figure 4: Plot Showing the Effect of Initial Co^{++} Concentration on the Rate of Removal of Cobalt from Synthetic Zinc Sulphate Electrolyte.
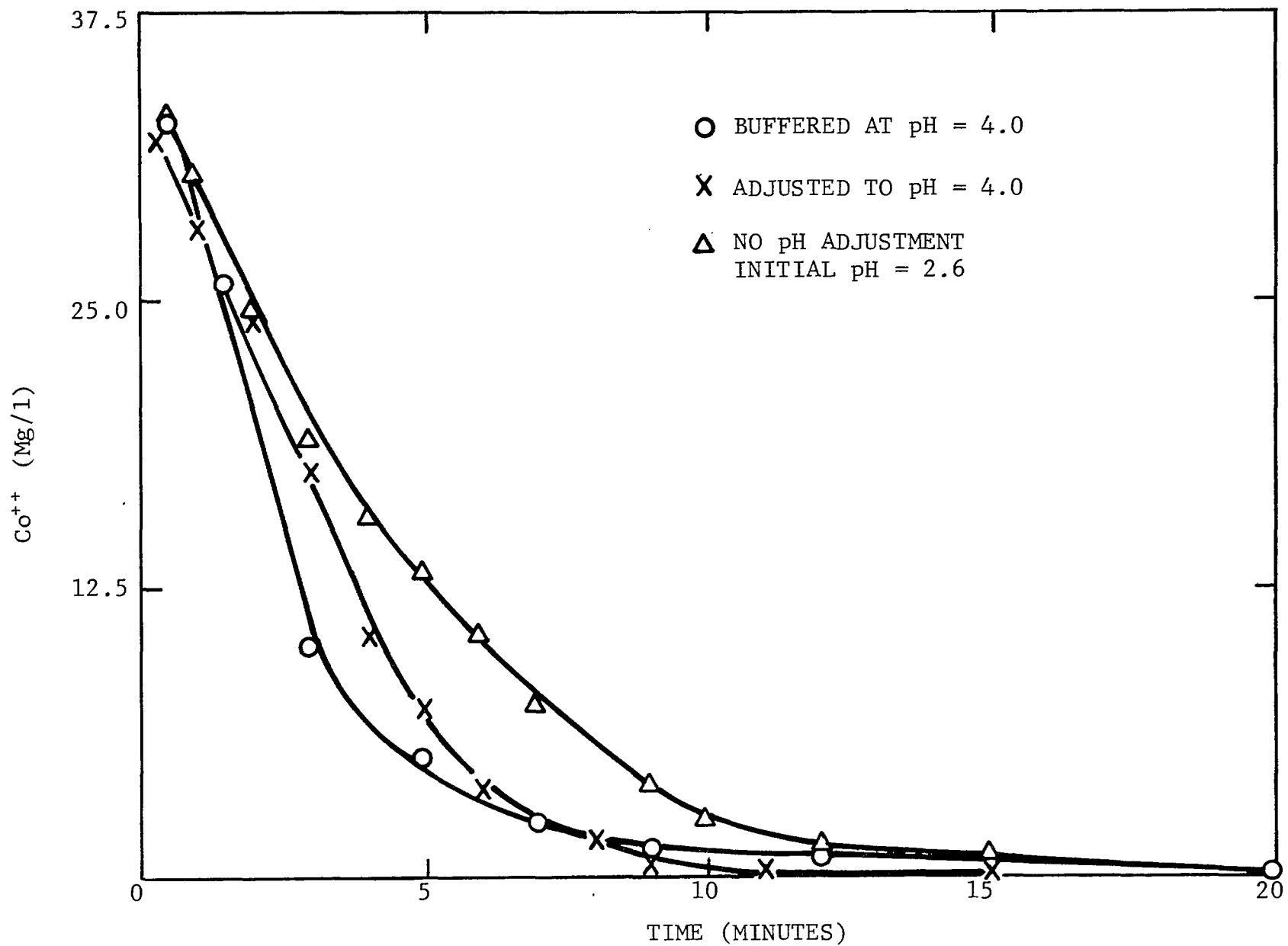
Figure 5: Plot Showing the Effect of Solution pH on the Removal of Cobalt from Synthetic Zinc Sulphate Electrolyte.

(~1 ppm) and the pH remains at 4.0. In the absence of buffer, the pH increased as the reaction proceeded so that the final pH was always about 5.0.

The rate of Co^{++} removal from the synthetic electrolyte was found to decrease with increasing concentration of Zn^{++} in the electrolyte as shown in Figure 6. These results were obtained at 90°C, initial pH = 4.0 and stirring velocity = 1250 rpm. It has been postulated[14] that trace amounts of zinc inhibit the cathodic deposition of Co^{++} from sulphate solutions. M. Yunas and co-workers[14] suggest that Zn^{++} reduces the rate of nucleation of cobalt because it is specifically absorbed on active cathodic sites, thus favoring the competitive hydrogen evolution reaction.

According to these same authors, while Zn^{++} is present in concentrations about 6% M $ZnSO_4$, it can inhibit the discharge of Co^{++} because an increase in H^+ discharge occurs which makes the solution alkaline in the immediate vicinity of the cathode. Precipitation of coloidal zinc hydroxide can occur and act as a secondary inhibitor by causing a decrease in the active surface of the cathode. Such a film can completely cover the cathode surface to prevent access of Co^{++}. The Zn^{++} concentration effect may also be related to a decrease in the rate of Zn^{++} diffusing into solution because of the lower concentration gradient.
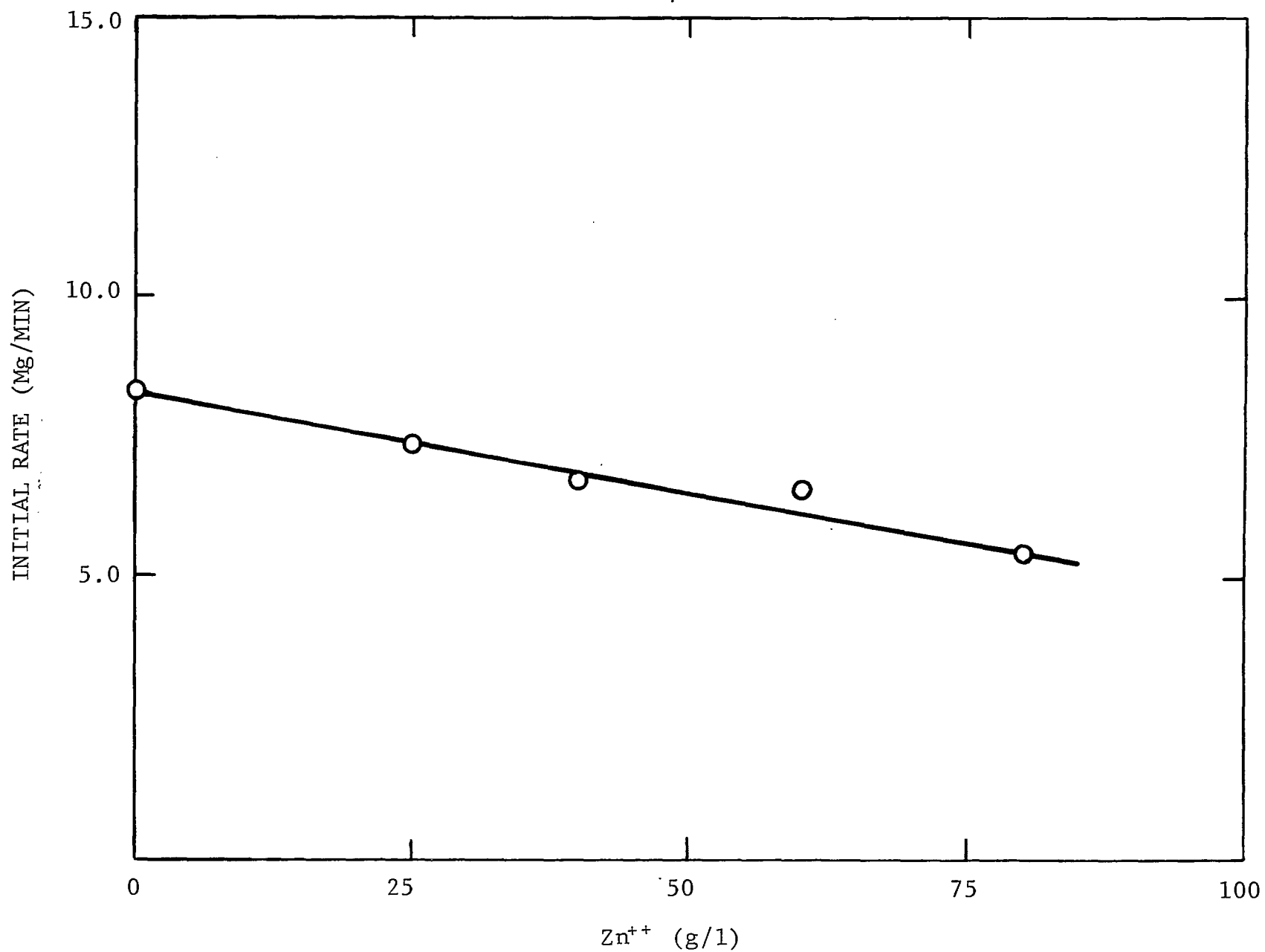
Figure 6: Plot Showing the Effect of $ZnSO_4$ on the Rate of Removal of Cobalt from Synthetic Zinc Sulphate Electrolyte.

5. Effect of Metallic Ions

In Section 1, it was established that the presence of Cu^{++} and Te^{+4} were required in order to achieve satisfactory removal of cobalt from $ZnSO_4$ electrolyte. The effect of varying the concentration of these and other metallic ions on the cementation rate is shown in Table 2.

The fact that cobalt cementation on zinc occurs in the presence of Cu^{++} and Te^{+4} has been attributed[13] to the formation of a Cu/Zn alloy which imparts a more positive potential than pure zinc to the Co/Zn cementation couple. This potential is further enhanced by the addition of Te^{+4} because tellurium can form strong metallic phases with cobalt[15].

In this work, it was found that at least ten times the amount of Cu^{++}, used previously[13], was necessary to achieve a reasonable rate of cobalt cementation if the solution contained large quantities of $ZnSO_4$. In fact, for a solution containing 80 g/1 Zn^{++}, optimum results were obtained when 192 ppm Cu^{++} (6.4 ppm X 30) was added to the solution (see Table 2). Larger additions of Cu^{++} slightly decreased the cementation rate. Sato[12] found that excessive Cu^{++} resulted in a redissolution of the cemented cobalt. Table 2 also indicates the optimum amount of Te^{+4} to be 12 ppm

TABLE 2

Effect of Metallic Ions on the Rate of Co Removal from

Synthetic $ZnSO_4$ Electrolyte

$(Zn^{++}$ = 80 g/1; Temp. = 90°C; Initial pH = 4.0; Stirring Velocity = 1250 rpm)

Cu^{++} (ppm)	Te^{+4} (ppm)	Cd^{++} (ppm)	Ni^{++} (ppm)	Hg^{++} (ppm)	Rate (mg/min)
64	10	680	12	--	5.8
192	10	680	12	--	6.0
320	10	680	12	--	5.4
320	0	680	12	--	2.3
320	5	680	12	--	2.3
320	12	680	12	--	6.7
320	15	680	12	--	5.6
320	10	--	12	--	8.2
320	10	340	12	--	5.1
320	10	170	12	--	8.8
320	--	680	12	5	2.6
320	--	680	12	10	2.6
320	--	680	12	15	2.9
320	--	680	12	20	2.7
320	10	680	--	--	5.8

which is similar to that found for cobalt cementation on zinc from $ZnSO_4$-free solutions[13]. Therefore, the best condition for cobalt removal was obtained when the Co:Te:Cu ratio was 1:0.4:10.

When Hg^{++} was substituted for Te^{+4}, the cementation rate was about the same as that obtained in the absence of Te^{+4} (see Table 2). Varying the amount of Hg^{++} also failed to increase the cementation rate. This is in agreement with the results obtained previously[13] for $ZnSO_4$-free solutions.

The most significant increase in the cementation rate occurred when $CdSO_4$-free solutions were used. This result also agrees with the previous work[13] where it was found that the rate of cobalt cementation on zinc decreased in the presence of cadmium. However, in this work, Cd^{++} concentrations up to 200 ppm could be tolerated before a significant decrease in the rate occurred. It should be mentioned that very little cadmium is removed from solution under the conditions used for cobalt cementation. In some plants[5,6], cadmium is removed later in a second cementation step by the addition of more Cu^{++} and zinc dust at a lower temperature.

The presence of Ni^{++} had no substantial effect on the rate of Co^{++} removal from $ZnSO_4$ electrolyte. This is in agreement with the previous work on cobalt cementation from

$ZnSO_4$-free solution[13] and is probably because Ni^{++} behaves in much the same manner as Co^{++} [9] because both are removed from the electrolyte simultaneously[5]. This behavior was confirmed by atomic absorption analysis of the solution for Ni^{++} after the cementation reaction.

CONCLUSIONS

The rate of cobalt removal from zinc sulphate electrolyte by cementation on zinc dust is directly proportional to the surface area of the zinc dust. The cementation rate decreased with increasing zinc sulphate concentration when the Cd^{++} concentration in the electrolyte was greater than 200 ppm. TeO_2 is an effective replacement for the toxic additives, As_2O_3 or Sb_2O_3, currently used to promote cobalt cementation on zinc.

ACKNOWLEDGEMENTS

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