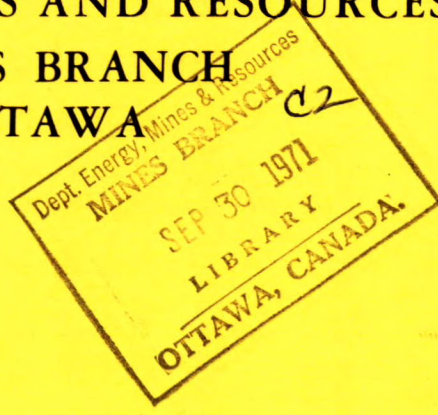CANADA

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KINETICS OF SILVER CEMENTATION
ON ALUMINUM CANNING SHEET

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KINETICS OF SILVER CEMENTATION ON
ALUMINUM CANNING SHEET

by

D.J. MacKinnon* and T.R. Ingraham**

ABSTRACT

The rate of silver cementation on rotating strips of aluminum canning sheet in alkaline argento-cyanide solution was measured as a function of temperature, peripheral velocity of the rotating strip, and the initial silver ion concentration. The results are compared with those obtained previously for silver cementation on copper and on zinc. The dependence of the rate constant on temperature and peripheral velocity suggests that the cementation of silver on aluminum is a diffusion-controlled process. The effect of impurities such as Au, Cu, Se and alkaline sulphides, thiosulphates and thiocyanates on the rate constant for silver cementation on aluminum was also studied. The results indicate that, in general, these impurities cause a decrease in the rate constant.

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CINÉTIQUE DE LA CÉMENTATION PAR L'ARGENT
DE LA TÔLE D'ALUMINIUM POUR BOÎTES DE CONSERVES

par

D.J. MacKinnon* et T.R. Ingraham**

RÉSUMÉ

Les auteurs ont mesuré le taux de cémentation par l'argent de feuillards en rotation de tôle d'aluminium pour boîtes de conserves dans une solution d'argentocyanure alcalin en fonction de la température, de la vitesse périphérique du feuillard en rotation et de la concentration initiale en ions d'argent. Les résultats sont comparés à ceux obtenus antérieurement pour la cémentation par l'argent du cuivre et du zinc. L'influence de la température et de la vélocité périphérique sur la constante du taux de cémentation laisse supposer que la cémentation de l'aluminium par l'argent est un processus de diffusion. Les auteurs ont aussi étudié les effets d'impuretés comme l'or, le cuivre, le sélénium, les sulfures alcalins, les thiosulfates et les thiocyanates sur la constante du taux de cémentation de l'aluminium par l'argent. Les résultats obtenus indiquent que ces impuretés entraînent généralement une diminution de la constante du taux de cémentation.

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INTRODUCTION

Gold and silver are usually recovered from cyanide leach solutions by cementation on zinc. Aluminum has been used as a substitute for zinc for the cementation of silver from argento-cyanide solutions.

The cementation of silver on aluminum may be expressed by the equation:

$$2NaAg(CN)_2 + 4NaOH + 2 Al \rightleftharpoons 4NaCN + Na_2Al_2O_4 + 1/2H_2 \qquad [1]$$
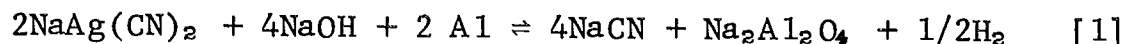
The principal difference between the two systems is that aluminum cyanide is not formed, but, in the presence of sufficient free alkali, sodium aluminate is formed and the cyanide regenerated. In view of the much higher cyanide consumption in dissolving silver, this is a decided advantage. With zinc, however, the essential reaction is a replacement of silver with the zinc going into solution as a double cyanide:

$$Zn + 2NaAg(CN)_2 \rightleftharpoons Na_2Zn(CN)_4 + 2Ag \qquad [2]$$

In 1910, aluminum dust was introduced as a precipitant for silver at a number of mines. It was replaced by sodium sulphide in 1916 when the price of aluminum became excessive. Now that there is an increase in the availability of scrap aluminum in the form of beer and soft-drink cans,

several companies are purchasing these throw-away cans as part of an anti-litter campaign. The cans may be recycled or perhaps they may be used as an effective reagent for cementation.

In previous publications[1,2], the authors have described the kinetics of copper cementation on pure aluminum and on beer-can-variety aluminum. This work was done to show that waste aluminum might be used under certain conditions as a substitute for scrap iron in the copper recovery industry. A similar possibility exists in the case of silver cementation. In this report, the results obtained from studies of silver cementation on canning sheet aluminum will be described.

EXPERIMENTAL

The apparatus and experimental technique have been adequately described in earlier publications[1,2]. The surface of the aluminum canning sheet was chemically polished to ensure reproductibility of rates. The polishing procedure consisted of spinning the aluminum strip for two minutes in a bath containing 85% H_3PO_4 and 15% HNO_3 at $100°C$. This was followed by a five-minute spin in 0.1M NaOH solution. The aluminum strip was then washed in a stream of tap water and given a final rinse with redistilled water.

The chemical composition of the aluminum beer-can strip is given in Table 1. The area of the aluminum strip was 23.48 cm^2.

The silver cyanide solutions were prepared by dilution of suitable aliquots of stock solutions. The stock solution was prepared according to a procedure described in an earlier publication[3]. To follow the course of the cementation reaction, solution samples were taken periodically and analysed for silver with a Techtron Model AA-5 atomic absorption spectrophotometer. Initial solution volumes were 1 litre and samples were 5 ml.

The change in pH that occurred during the reaction was measured with a Beckman 101900 Research pH Meter.

RESULTS AND DISCUSSION

1. Cementation Kinetics

It has been shown[4] that the rate of silver (I) cementation on zinc can be described by the equation,

$$-d[Ag^+]/dt = kS[Ag^+]/V, \qquad [3]$$

in which k is a pseudo-first rate constant, S the geometric area of the zinc, and V the solution volume. This equation

TABLE 1

Chemical Composition of Aluminum* Canning Sheet, Wt%

Impurity	Mg	Fe	Cu	Si	Mn	Zn	Ti
	4-5	0.35	0.15	0.02	0.2-0.5	0.25	0.10

*The canning sheet was obtained from the Aluminum Company of
Canada, Ltd., Kingston, Ontario.

also applies to silver cementation on aluminum, and indeed it appears to be a valid rate law for cementation reactions in general[1-5]. The integrated form of Equation 3 is:

$$V_t \log \left([Ag^+]_0 / [Ag^+]_t\right) = kSt/2.303 \qquad [4]$$

The subscript t refers to sampling time, and V_t is the solution volume corrected for the removal of samples. When S is expressed in cm^2, V in cm^3 and t in seconds, k has the dimension cm/sec.

Equation 4 is used to obtain values of k for each cementation experiment. This is done by plotting $V_t \log \left([Ag^+]_0 / [Ag^+]_t\right)$ against t, measuring the slopes b of the resulting graphs, and calculating k with the relationship:

$$k = b \times 2.303/S \qquad [5]$$

A typical graph of $V_t \log \left([Ag^+]_0 / [Ag^+]_t\right)$ vs t is shown in Figure 1.

2. Temperature and Peripheral Velocity Effects

The effect of temperature change on k was investigated over the range 30 to $80°C$. The results are shown in Figure 2 as a plot of log k vs $10^3/T(°K^{-1})$. The experimental
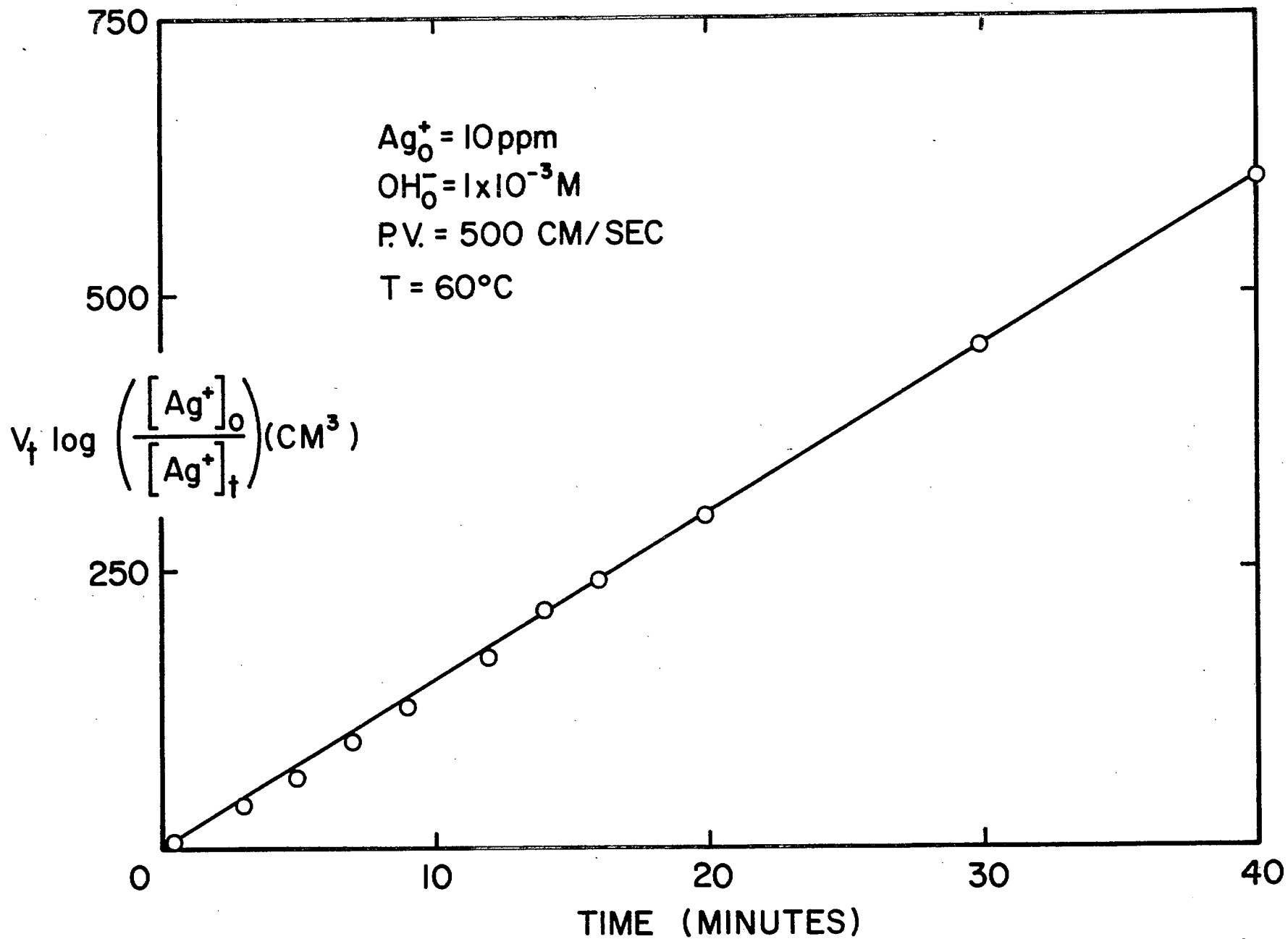
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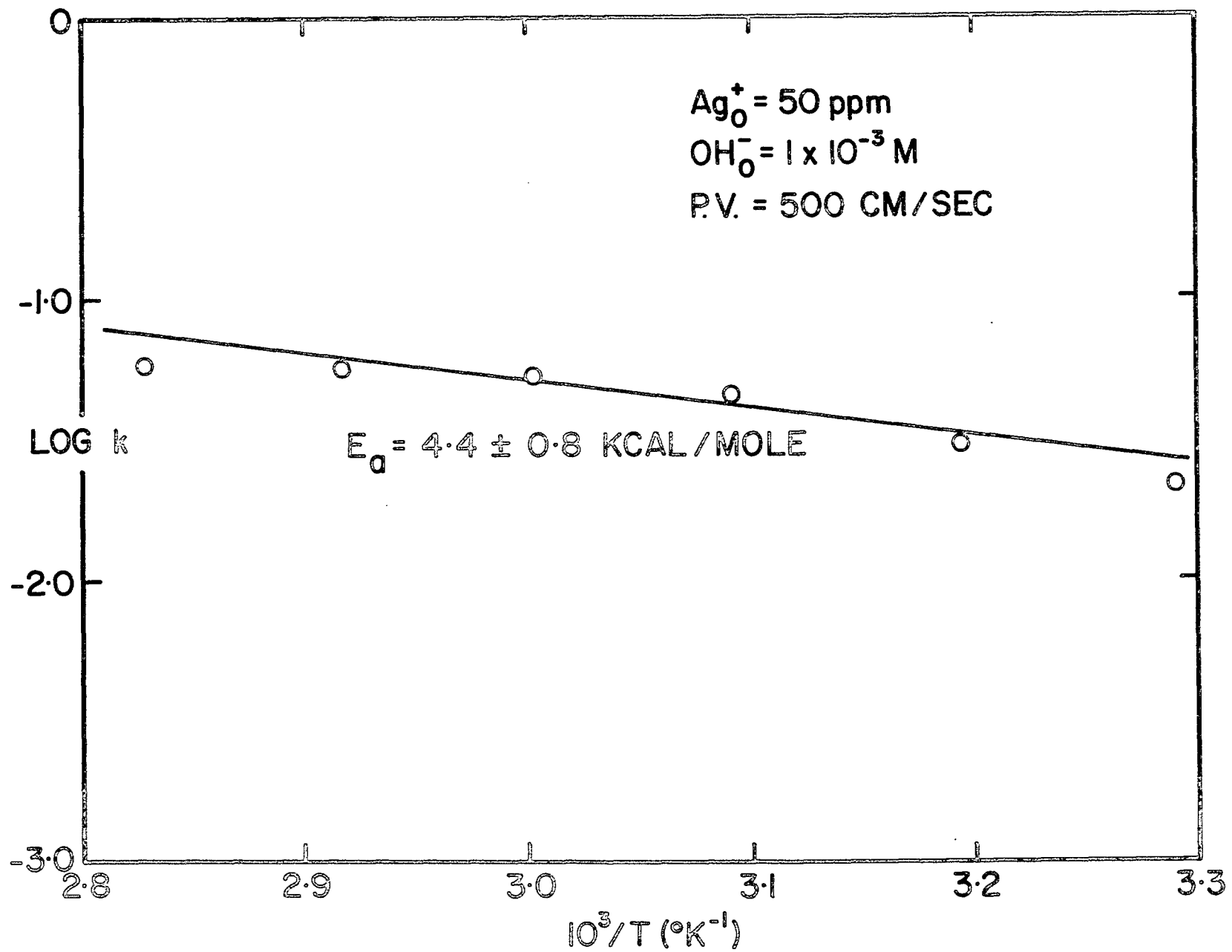Figure 1. Plot of $V_t \log ([Ag^+]_o / [Ag^+]_t)$ vs time for silver cementation on aluminum.

Figure 2. Arrhenius plot of k for silver cementation on aluminum.

conditions are given in the caption. The activation energy, E_a, and frequency factor, A, were calculated by regression analysis. The results were:

E_a = 4.4 ± 0.8 kcal/mole and A = 1.54 ± 0.06 cm/sec

Figure 3 illustrates the effect of changing the peripheral velocity (p.v.) of the aluminum strip on k. The curve shows a marked dependence of k on p.v. These results are similar to those found for the cementation of silver on copper[3] and zinc[4] in alkaline cyanide solutions. The fact that E_a = 4.4 kcal/mole, and the nature of the dependence of k on p.v., both suggest that the reaction is diffusion-controlled.

3. Medium Effects

The effect of increasing the initial silver ion concentration on the rate constant is shown in Figure 4. The rate constant increases with increasing initial silver ion con-centration up to Ag_o^+ = 50 ppm. There is no significant variation of k at Ag_o^+ > 50 ppm. This result is in contrast to that obtained for silver cementation on zinc[4]. In that case there was no variation of k with changes in Ag_o^+. Silver cementation on zinc was characterized by deposits that were
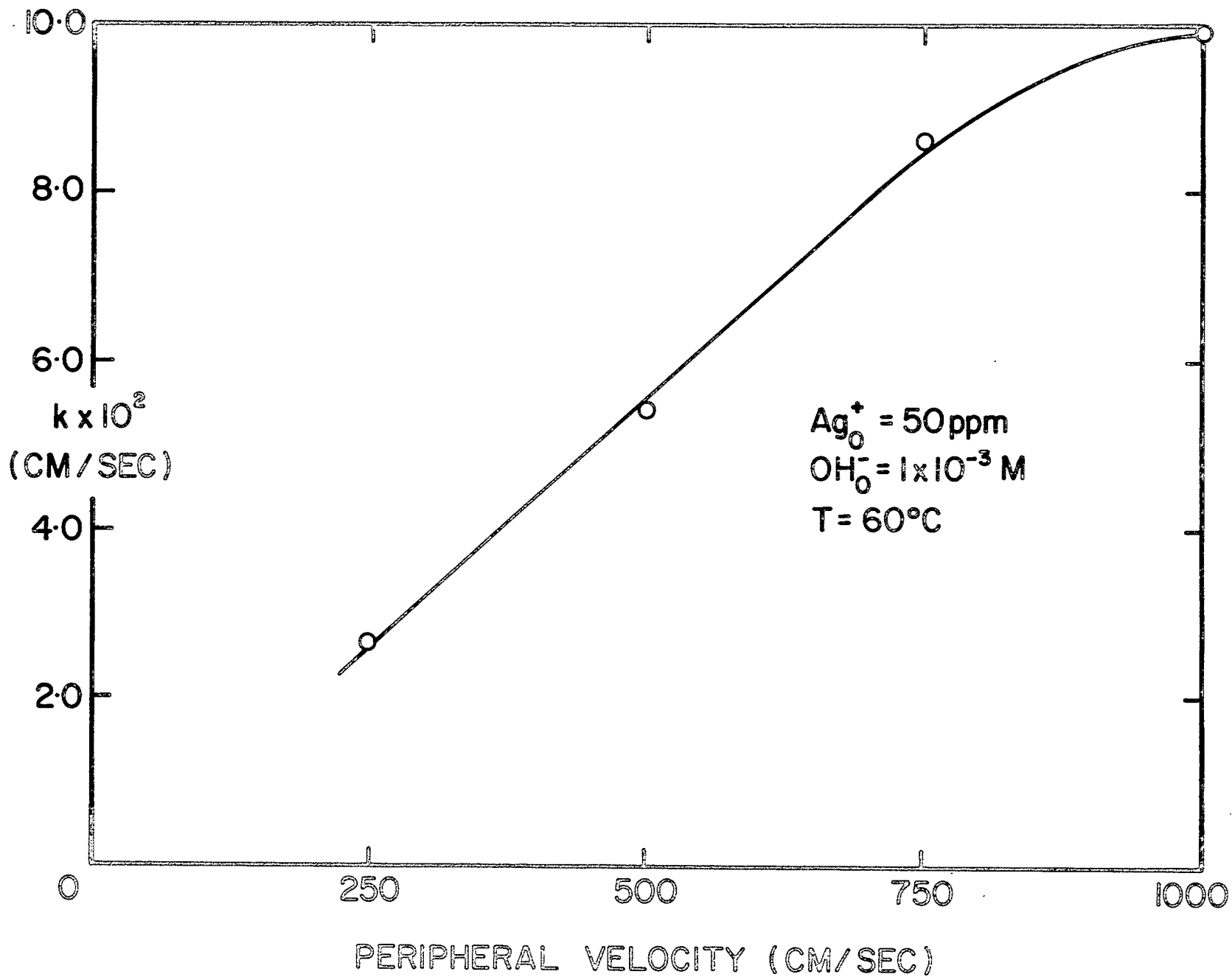
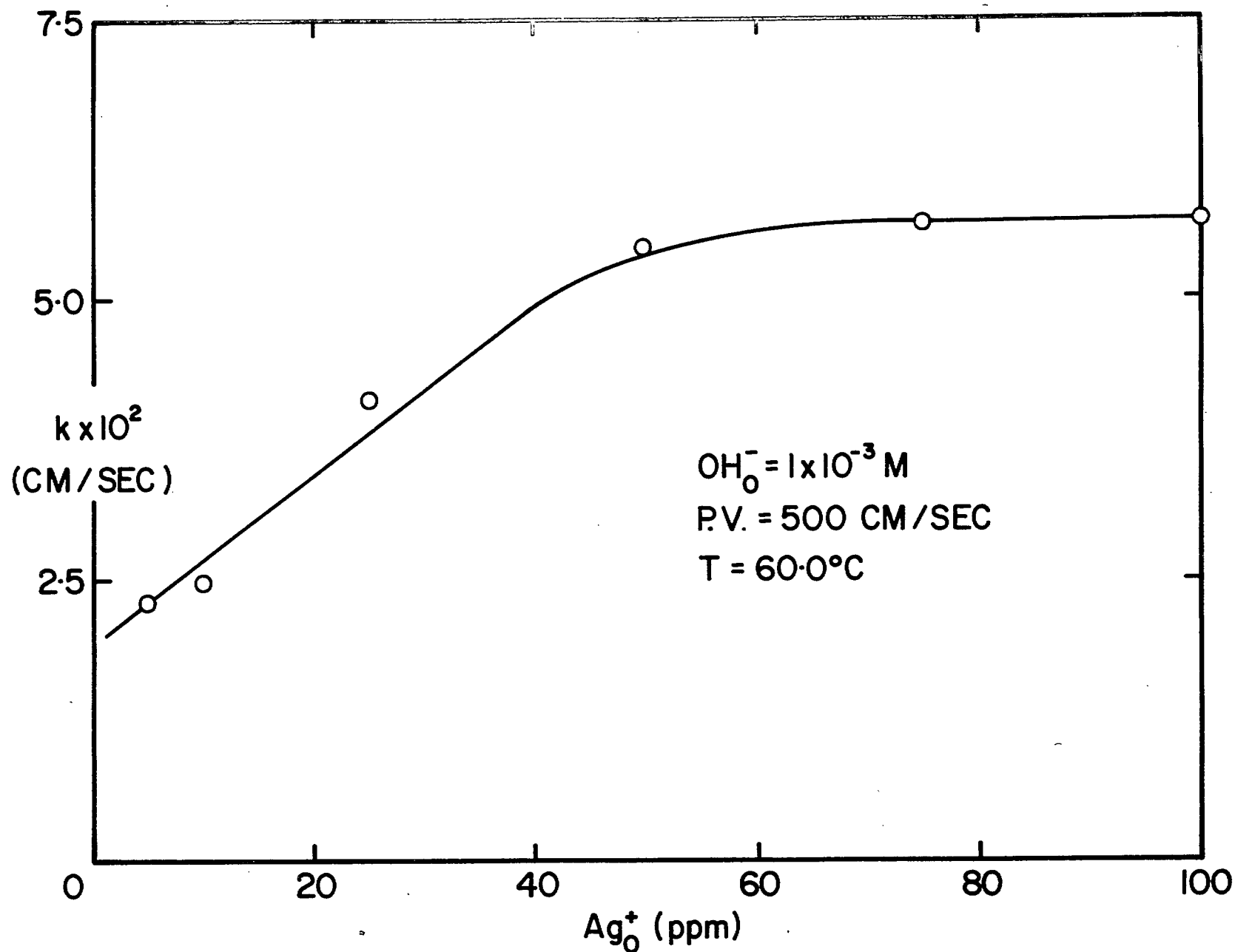Figure 3. Plot of k vs peripheral velocity for silver cementation on aluminum.

Figure 4. Plot of k vs initial silver ion concentration, Ag_o^+, for silver cementation on aluminum.

smooth, shiny and adherent and, hence, tended to inhibit the reaction. On the other hand, silver formed a dull, powdery deposit on the aluminum which promoted the cementation rate. Enhanced cementation rates have been found to occur with the formation of powdery deposits for silver cementation on zinc in perchloric acid medium[4] and for copper cementation on aluminum[1, 2]. For example, at 30° C the rate constant for silver cementation on aluminum was 2.22 x 10^{-2} cm/sec, while that for silver cementation on zinc was only 1.62 x 10^{-2} cm/sec under identical experimental conditions. In addition, for Ag_o^+ = 50 ppm, the rate constant for silver cementation on zinc became zero after only 10 minutes, whereas that for silver cementation on aluminum was enhanced because of the formation of a powdery, loosely adherent deposit of silver. The deposit obtained in this work was identified by means of X-ray diffraction analysis as silver only--rather than a silver-aluminum alloy.

4. Stoichiometry

The atomic absorption analysis of the solution sample for both Ag and Al indicates that Equation 1 (see Introduction) adequately represents the cementation of silver on aluminum canning sheet from alkaline cyanide solution. Based on Equation 1, it requires 0.25 ppm of Al to cement 1 ppm of Ag.

Solution analysis, however, showed that the amount of aluminum dissolved was in excess of that required by Equation 1. This excess can be adequately accounted for by the decrease in NaOH concentration that occurred during the cementation reaction. The effect of NaOH on A is given by Equation 6:

$$2Al + 2NaOH + 2H_2O \rightleftharpoons 2NaAlO_2 + 3H_2 \qquad [6]$$
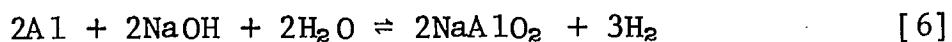
The variation in the NaOH concentration with time was calculated from the measured pH. Typical variations of OH$^-$ with time are shown in Figure 5.

5. Impurity Effects

The effect of gold, copper and seleno-cyanates on the rate constant for silver cementation on aluminum is shown in Table 2. The initial silver ion concentration was 50 ppm and the temperature was 30° C. The variation in k with concentration of impurity for the most part is insignificant as these variations are within the limit of experimental error. However, for gold and copper concentrations of 10 ppm, the rate constant for silver cementation on aluminum is substantially reduced. Copper had a similar effect on the rate constant for gold cementation on zinc, whereas the presence of silver increased the rate constant for gold cementation on
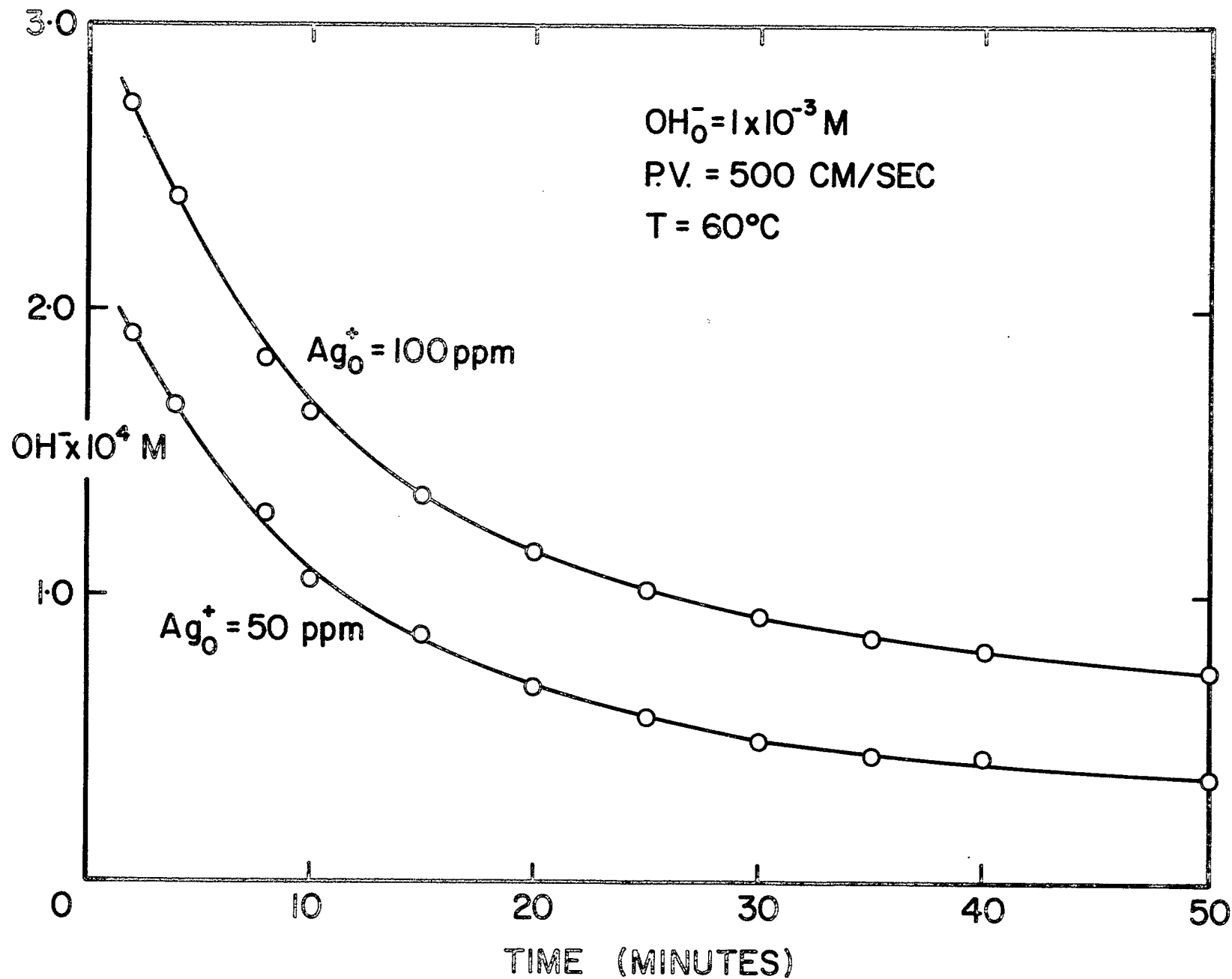
Figure 5. Plot showing the decrease in OH^- with time for silver cementation on aluminum.

TABLE 2

Effect of Au, Cu and Se on k at 30°C

NaAu(CN)$_2$		Na$_3$Cu(CN)$_4$		NaAu(CN)$_2$ + Na$_3$Cu(CN)$_4$		Sodium Selenocyanate	
Conc (ppm)	k x 10^2 (cm/sec)	Conc (ppm)	k x 10^2 (cm/sec)	Conc (ppm)	k x 10^2 (cm/sec)	Conc (ppm)	k x 10^2 (cm/sec)
0	2.22	0	2.22	0+0	2.22	0	2.22
5	2.22	5	2.23	5+5	1.73	5	1.81
10	1.45	10	1.61	5+10	2.51	10	2.04
				10+10	1.99	15	1.87
						20	2.04

that metal[5]. In the present work, analysis of solution
samples for gold showed that the initial rate of gold cementa-
tion is extremely high.

Thus, it seems that in the presence of gold, the
rate constant for silver cementation on aluminum is reduced
because gold is cemented in preference to silver. Thus silver
has a catalytic effect on the cementation of gold on zinc[5]
and on aluminum.

The effect of alkaline sulphides, thiosulphates and
thiocyanates on the rate constant for silver cementation on
aluminum at $30^{\circ}C$ is shown in Table 3. As in the case of gold
cementation on zinc[5], these impurities had an adverse effect
on the rate constant. However, the effect on k was not as
pronounced, particularly in the case of Na_2S, as it was for
gold cementation on zinc. The decrease in k, as was shown
previously for gold cementation on zinc[5], may be associated
with a decrease in the potential difference for the reaction
when these anions are present.

6. Conclusions

The advantages of using aluminum as a cementing
agent for silver are:

    a. NaCN is regenerated.

    b. A loose silver powder is formed.

TABLE 3

<u>Effect of Impurities on the Cementation Rate</u>

<u>Constant at 30° C. (Ag_0^+ = 50 ppm)</u>

Impurity	Na_2S	$Na_2S_2O_3$	NaCNS
conc.(ppm)	k x 10^2 (cm/sec)	k x 10^2 (cm/sec)	k x 10^2 (cm/sec)
0	2.22	2.22	2.22
5	1.23	1.52	1.22
10	1.35	1.50	1.33
20	1.14	1.47	1.47

c. The rate constant is larger than that
obtained when zinc is used.

When the leach solutions contain impurities such as
Au^+, Cu^{++}, $Se^=$, $S_2O_3^=$ and CNS^-, the rate constant tends to be
decreased.

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