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*KINETICS OF GOLD CEMENTATION ON ZINC*

D. J. MACKINNON AND T. R. INGRAHAM

EXTRACTION METALLURGY DIVISION

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KINETICS OF GOLD CEMENTATION ON ZINC

by

D.J. MacKinnon<sup>1</sup> and T.R. Ingraham<sup>2</sup>

ABSTRACT

The rate of gold cementation on zinc was measured by atomic absorption spectrophotometric analysis while roasting zinc cylinders in deoxygenated alkaline cyanide solutions at controlled peripheral velocities and temperatures. The dependence of the rate constant on peripheral velocity and temperature indicates that the rate is diffusion-controlled.

Optimum rates of gold cementation on zinc were obtained from solutions containing  $1 \times 10^{-4}$  M NaOH and  $5 \times 10^{-3}$  M excess NaCN. The high initial rate decreased rapidly after the first 30 minutes of reaction time. The addition of more NaCN at this point caused the reaction to resume its initial rapid rate.

The addition of impurities such as  $\text{Na}_2\text{S}$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ , NaCNS and Cu caused a decrease in the rate constant for gold cementation on zinc. The addition of Cd, Pb and Ag increased the rate constant, but Se had no appreciable effect on it.

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Direction des mines

Rapport de recherches R 242

## CINÉTIQUE DE LA CÉMENTATION DE L'OR PAR LE ZINC

par

D.J. MacKinnon<sup>1</sup> et T.R. Ingraham<sup>2</sup>

### RÉSUMÉ

Les auteurs ont mesuré la vitesse de cémentation de l'or sur le zinc au moyen de l'analyse spectrophotométrique des spectres d'absorption atomique, en faisant tourner des cylindres de zinc dans des solutions de cyanure alcalines désoxygénées, dans des conditions bien déterminées de vitesse périphérique et de température. La nature de la dépendance du taux de cémentation sur la vitesse périphérique et sur la température montre que le taux est réglé par un phénomène de diffusion.

Les vitesses optimales de cémentation de l'or sur le zinc ont été obtenues à partir de solutions contenant  $1 \times 10^{-4}$  M NaOH et  $5 \times 10^{-3}$  M NaCN en excès. La vitesse de cémentation, que est élevée au début, décroît rapidement après les 30 premières minutes de réaction. A ce stade, l'addition d'une quantité supplémentaire de NaCN permet à la réaction de reprendre sa vitesse initiale.

L'addition d'impuretés telles que  $\text{Na}_2\text{S}$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ , NaCNS et de Cu provoque la diminution de la vitesse de cémentation de l'or sur le zinc. L'addition de Cd, Pb et de Ag augmente cette vitesse, alors que l'effet du Se n'est pas appréciable.

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CONTENTS

	<u>Page</u>
Abstract. . . . .	i
Résumé. . . . .	ii
Introduction. . . . .	1
Experimental. . . . .	1
Results and Discussion. . . . .	3
1. Cementation Kinetics. . . . .	3
2. Medium Effect . . . . .	4
3. Temperature and Peripheral Velocity Effect. . . . .	8
4. Stoichiometry . . . . .	8
5. Impurity Effect . . . . .	12
6. Nature of Deposit . . . . .	20
References. . . . .	22

TABLES

<u>No.</u>		<u>Page</u>
1.	Chemical Composition of Zinc Materials, Wt%. . . . .	2
2.	Arrhenius Parameters for Gold Cementation on Zinc. . . . .	10
3.	Effect of Impurities on the Cementation Rate Constant. . . . .	15
4.	Effect of Impurities on the Cementation Rate Constant. . . . .	18
5.	Effect of $Pb(OAc)_2$ on the Rate Constant for Gold Cementation on Disk #1 at $70^\circ C$ . . . . .	19
6.	Effect of Ag and Cu on the Rate Constant for Gold Cementation on Zinc at $60^\circ C$ . . . . .	21

FIGURES

1.	Plot of $V_t \log \left( \frac{[Au^+]_0}{[Au^+]_t} \right)$ vs time, showing the effect of additional NaCN on the cementation rate constant . . . . .	6
2.	Plot showing the rate of production of $OH^-$ during the cementation reaction . . . . .	7
3.	Plot of k vs initial gold concentration, $Au_0^+$ . . . . .	9
4.	Plot of k vs peripheral velocity . . . . .	11
5.	Plot of Au cemented and Zn dissolved vs time . . . . .	13
6.	Plots of $V_t \log \left( \frac{[Au^+]_0}{[Au^+]_t} \right)$ vs time, showing the effect of $Na_2S$ , $Na_2S_2O_3$ and NaCNS on the cementation rate. . . . .	17

## INTRODUCTION

The cyanide process for the recovery of gold consists of the dissolution of gold in dilute cyanide, followed by the cementation of the gold with zinc dust. Although the cementation of gold by zinc has been used industrially for many years as a means for recovering gold from cyanide solutions, detailed information on the kinetics of this process is lacking. In addition to gold, the alkaline cyanide leach liquors may contain such impurities as cyanide complexes of silver, copper, nickel and selenium, and alkaline sulphides, thiosulphates and thiocyanates. Some of these impurities adversely affect the dissolution and cementation of gold. This paper presents the results obtained from kinetic studies of gold cementation on zinc from pure and impure aurous cyanide solutions.

## EXPERIMENTAL

The apparatus and procedure have been adequately described in previous publications<sup>(1,2)</sup>. The chemical composition and exposed surface area of the zinc materials used in this work are given in Table 1. To obtain reproducibility of rates, the exposed surface of the zinc was chemically polished for five minutes in a solution containing 220 g CrO<sub>3</sub>, 15 g Na<sub>2</sub>SO<sub>4</sub>, 50 ml HNO<sub>3</sub> and 950 ml H<sub>2</sub>O<sup>(3)</sup>. Immediately after polishing, the zinc was washed thoroughly under a stream of tap water and spun for two minutes in a 0.01M HClO<sub>4</sub> solution. This was followed by

TABLE 1

Chemical Composition of Zinc Materials, Wt%

Zn Materials	Cu	Cd	Pb	Fe	Al	Co	Ag	Mn	Mg
DISK #1 Area = 23.50 cm <sup>2</sup>	0.0001	0.0003	0.0018	<0.004	0.001	--	--	--	--
DISK #2 Area = 23.50 cm <sup>2</sup>	0.0001	0.0004	0.90	0.0009	<0.003	--	--	--	--
LITHOGRAPHIC SHEET Area = 23.48 cm <sup>2</sup>	0.05	0.29	0.32	0.06	0.05	0.05	0.005	0.004	0.007



rinsing with redistilled water.

The solutions were prepared by dilution of suitable aliquots of gold cyanide stock solutions. The stock solution was prepared by dissolving a weighed amount of gold powder with a slight excess of sodium cyanide solution, and made up to volume. To follow the course of the cementation reaction, solution samples were taken periodically and analysed for gold(I) ions with a Techtron Model AA-5 atomic absorption spectrophotometer. The initial solution volumes were 1 litre and the samples were 5 ml. The change in pH during the cementation reaction was measured with a Beckmann 101900 Research pH Meter. In some experiments, the change in potential difference ( $\Delta E$ ) between the zinc disk and a saturated calomel reference electrode during the cementation reaction was also measured as a function of time by means of the same Beckmann pH Meter.

## RESULTS AND DISCUSSION

### 1. Cementation Kinetics

The rate of gold(I) cementation on zinc can be described by the equation:

$$-d [\text{Au}^+] / dt = kS [\text{Au}^+] / V \quad [1]$$

where  $k$  is a pseudo-first-order rate constant,  $S$  the geometric area of the zinc, and  $V$  the solution volume. Equation 1 appears to be a generally valid rate law for cementation

reactions (1)(2)(4). The integrated form of Equation 1 is:

$$V_t \log \left( [Au^+]_0 / [Au^+]_t \right) = k S t / 2.303 \quad [2]$$

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

Equation 2 was used to obtain values of k for each cementation experiment. This was done by plotting  $V_t \log \left( [Au^+]_0 / [Au^+]_t \right)$  against t, measuring the slope b, of the resulting graphs, and calculating k with the relationship:

$$k = b \times 2.303/S \quad [3]$$

## 2. Medium Effect

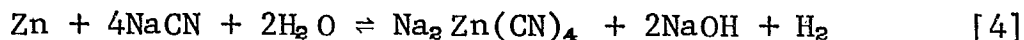
Zinc does not readily precipitate gold from alkaline aurocyanide solution in the absence of an excess of free cyanide. Therefore, the first series of experiments was done to obtain the concentrations of NaOH and free NaCN that would yield the most rapid cementation rate. The optimum concentrations of NaOH\* and NaCN were found to be  $1 \times 10^{-4}$  and  $5 \times 10^{-3} M$  respectively. Under these conditions, the initial rate of gold cementation on zinc is high. This rate is maintained for 20 to 30 minutes, after which it undergoes a sharp decrease. The original rate may be re-established if additional cyanide is

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\*The significant ion involved in the alkalinity study is  $OH^-$ . Preliminary studies showed no apparent differences in the rate when the  $OH^-$  was supplied from NaOH or  $Ca(OH)_2$ .

added to the solution. This type of behaviour is shown in Figure 1 in the form of a  $V_t \log \left( [Au^+]_0 / [Au^+]_t \right)$  vs time plot.

This result indicates that the reaction:



probably plays an important role in this cementation process. This contention is further substantiated by the fact that the pH increases during the cementation reaction, i.e., NaOH is produced. The amount of  $OH^-$  produced during a cementation experiment was calculated from the measured pH. A typical result is shown in Figure 2 in which the concentration of  $OH^-$  in moles per litre is plotted as a function of time. Initially, there is a linear increase in the  $OH^-$  concentration over the first 30 minutes of reaction time, after which the rate of  $OH^-$  production falls off rapidly. If, at this point, additional NaCN is added to the solution, the production of  $OH^-$  resumes at its former rate. This behaviour is similar to that exhibited by the  $V_t \log \left( [Au^+]_0 / [Au^+]_t \right)$  vs time plot as shown in Figure 1. Thus the change in pH gives a good indication of the progress of the cementation reaction. When the rate of increase in pH decreases, the rate of cementation of gold on zinc also decreases.

The effect of increasing the initial  $Au^+$  concentration on the rate constant was studied using zinc disk #2 (see Table 1). The result, shown in Figure 3, indicates that the rate constant decreases with increasing  $Au^+$  concentration. This effect is

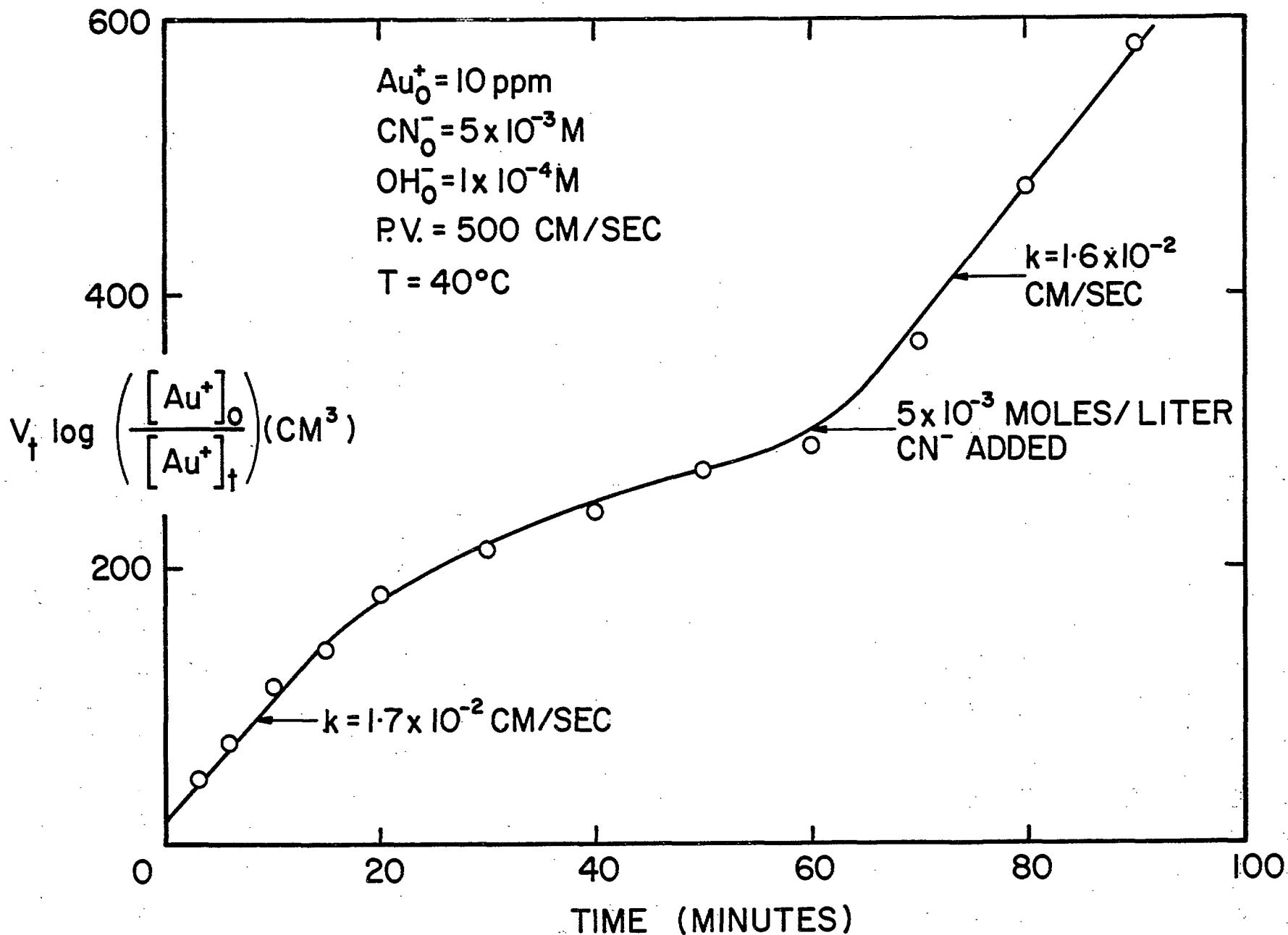


Figure 1. Plot of  $V_t \log ([Au^+]_0/[Au^+]_t)$  vs time, showing the effect of additional NaCN on the cementation rate constant



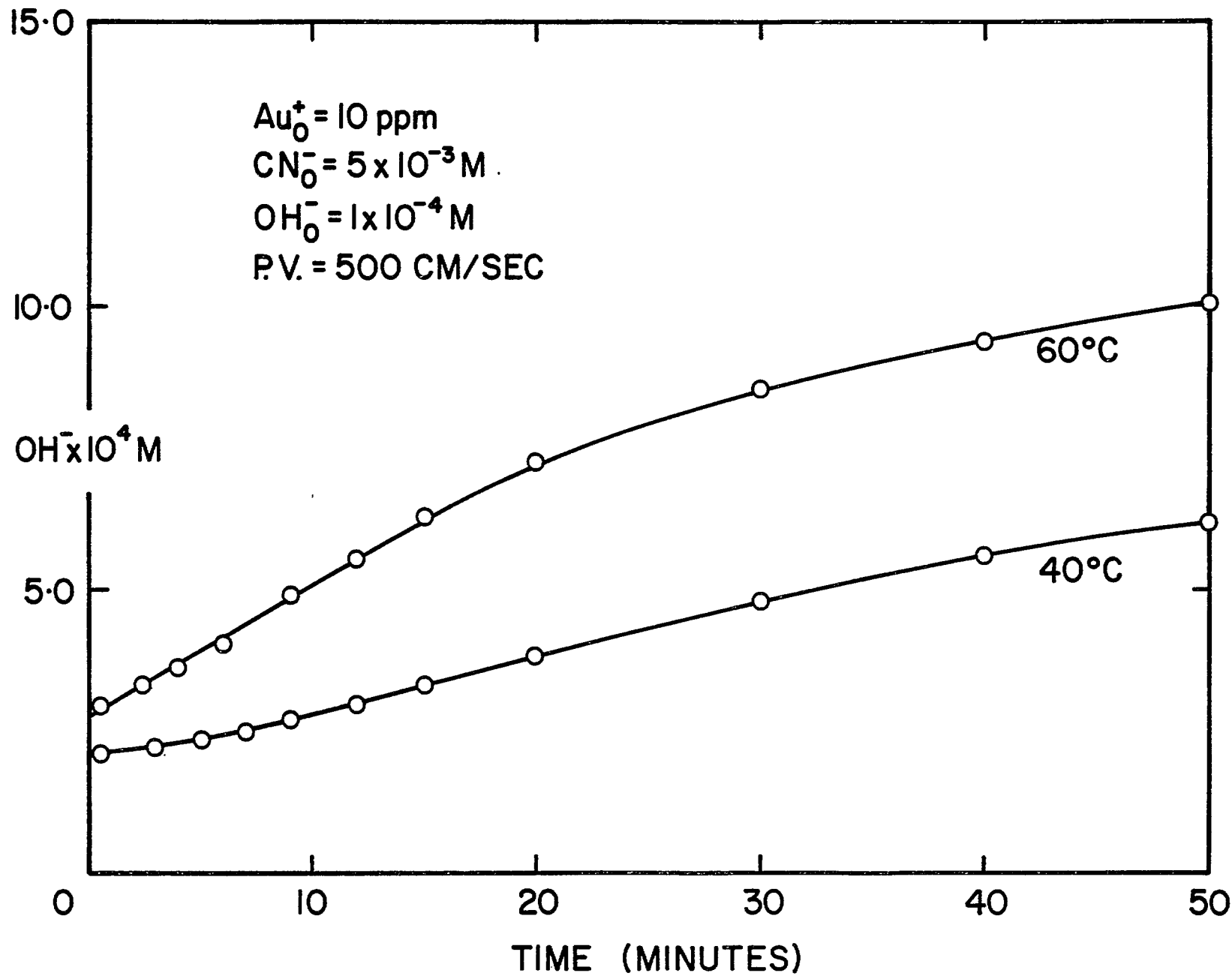


Figure 2. Plot showing the rate of production of  $OH^-$  during the cementation reaction

probably caused by an increase in the thickness of the diffusion layer. This conclusion is supported by the low values of the activation energy shown in Table 2.

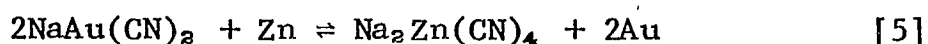
### 3. Temperature and Peripheral Velocity Effect

The effect of temperature changes on the rate constant for gold cementation on all three types of zinc (see Table 1) was studied. The results are summarized in Table 2. The effect of increasing the peripheral velocity on the rate constant is shown in Figure 4. The materials used and the conditions under which this effect was determined are included in Figure 4. The low values for the activation energy listed in Table 2, and the fact that the rate constant was always found to increase with increasing peripheral velocity (see Figure 4), indicate that the reaction rate is probably diffusion-controlled.

At a given temperature, the largest rate constants were obtained when a lithographic sheet was used as a cementing agent. Disk #2 (see Table 1) produced the lowest k values, while Disk #1 yielded k values that were intermediate between the sheet and Disk #2.

### 4. Stoichiometry

The experimental results indicate that the cementation of gold by zinc is not effected by the simple displacement reaction:



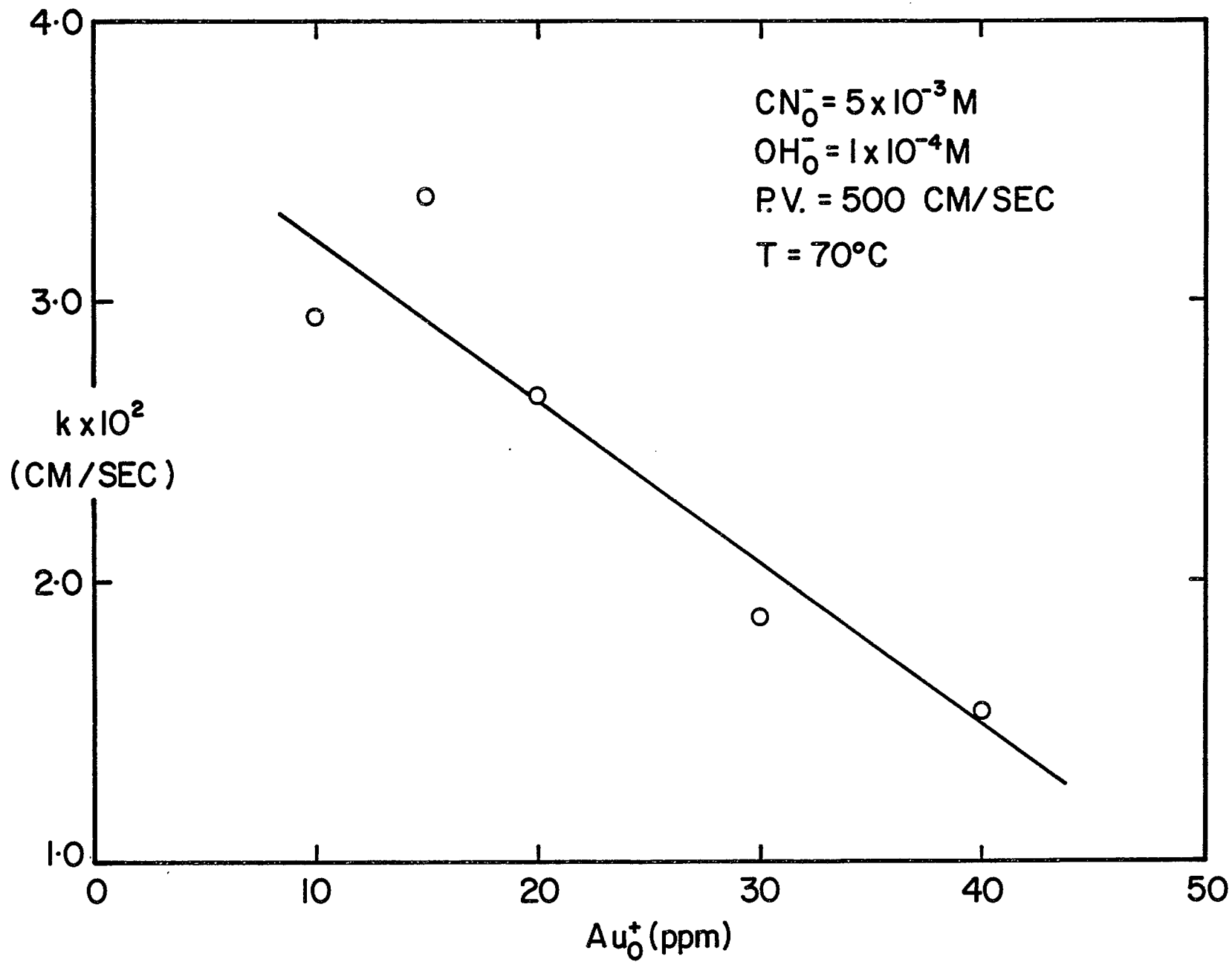


Figure 3. Plot of  $k$  vs initial gold concentration,  $\text{Au}_0^+$

TABLE 2

Arrhenius Parameters for Gold Cementation on Zinc

Zinc Material	Regression Equations	$E_a$ (kcal/mole)
DISK #1	$\log k = 0.947 - 0.85 \times 10^3 / T$ (T = 305 to 352°K)	3.9 ± 1.6
DISK #2	$\log k = 2.23 - 1.33 \times 10^3 / T$ (T = 304 to 353°K)	6.1 ± 2.2
LITHOGRAPHIC SHEET	$\log k = 1.96 - 0.67 \times 10^3 / T$ (T = 304 to 351°K)	3.1 ± 0.5



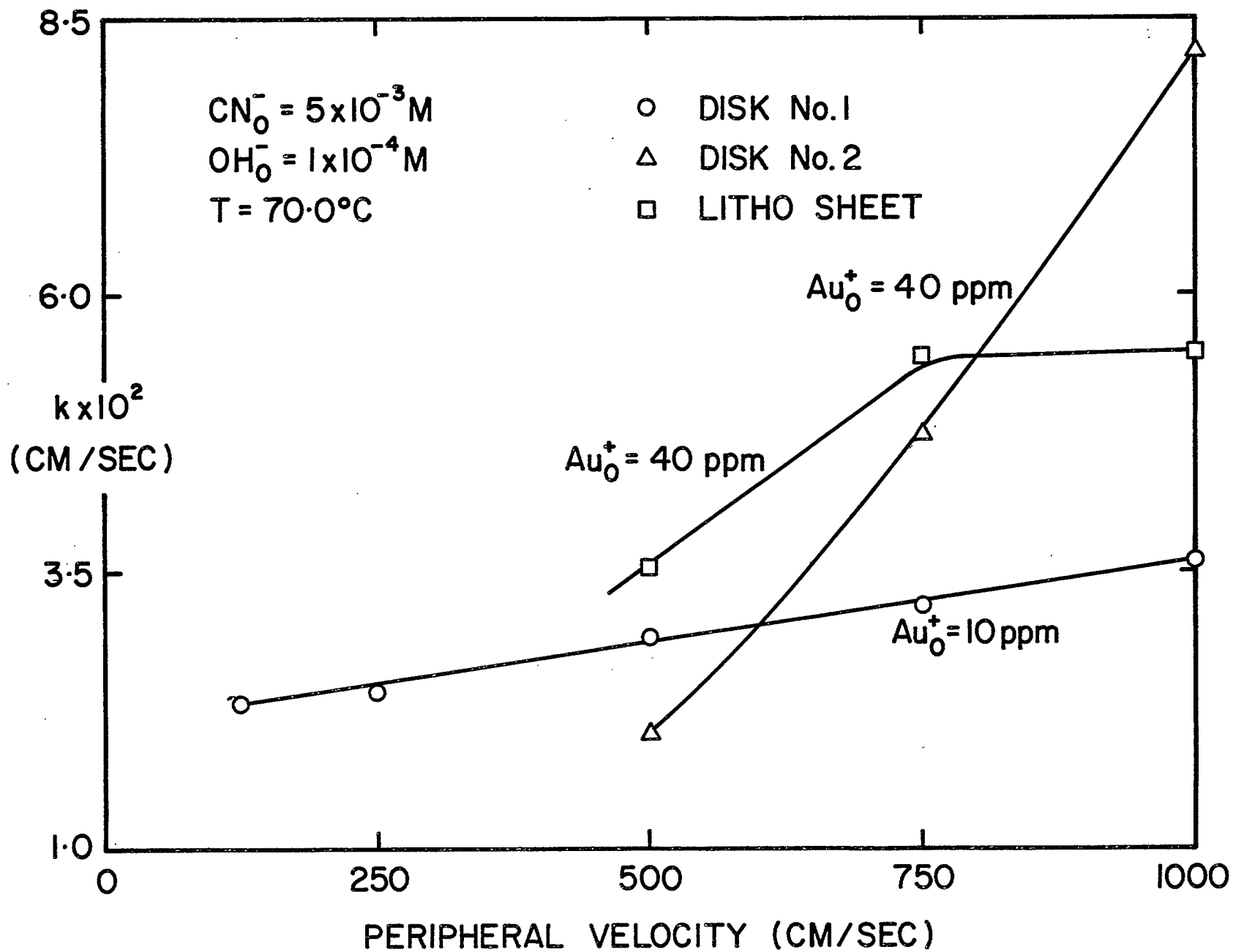
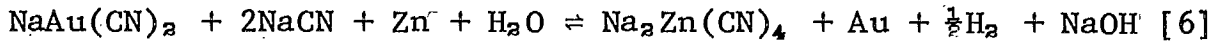


Figure 4. Plot of k vs peripheral velocity

The fact that excess free cyanide is required has already been mentioned in section 2. In the presence of free cyanide, the cementation of gold may be represented by the equation:



which also accounts for the production of NaOH as discussed earlier. Equation 6 indicates that 0.33 ppm of Zn is required to cement 1 ppm of Au. Experimentally, the amount of Zn required to precipitate 1 ppm of Au was found to be much greater than this value. A typical result is shown in Figure 5 for gold cementation on lithographic sheet. The amount of gold cemented and the corresponding experimental amount of zinc dissolved were determined by atomic absorption analysis. The corresponding stoichiometric amount of zinc dissolved was calculated from Equation 6. The excess Zn dissolution can, however, be accounted for by the increase in NaOH production. Thus, Equation 6 appears to satisfy the stoichiometric requirements for the cementation of gold on zinc from cyanide solutions.

##### 5. Impurity Effect

When sulphide minerals are dissolved in cyanide solutions, some of the products of the reaction, in addition to cyanide complexes, are alkaline sulphides, thiosulphates, and thiocyanates. Accordingly, a series of experiments were done with cyanide solutions containing these impurities in order to assess their effect on the cementation of gold on

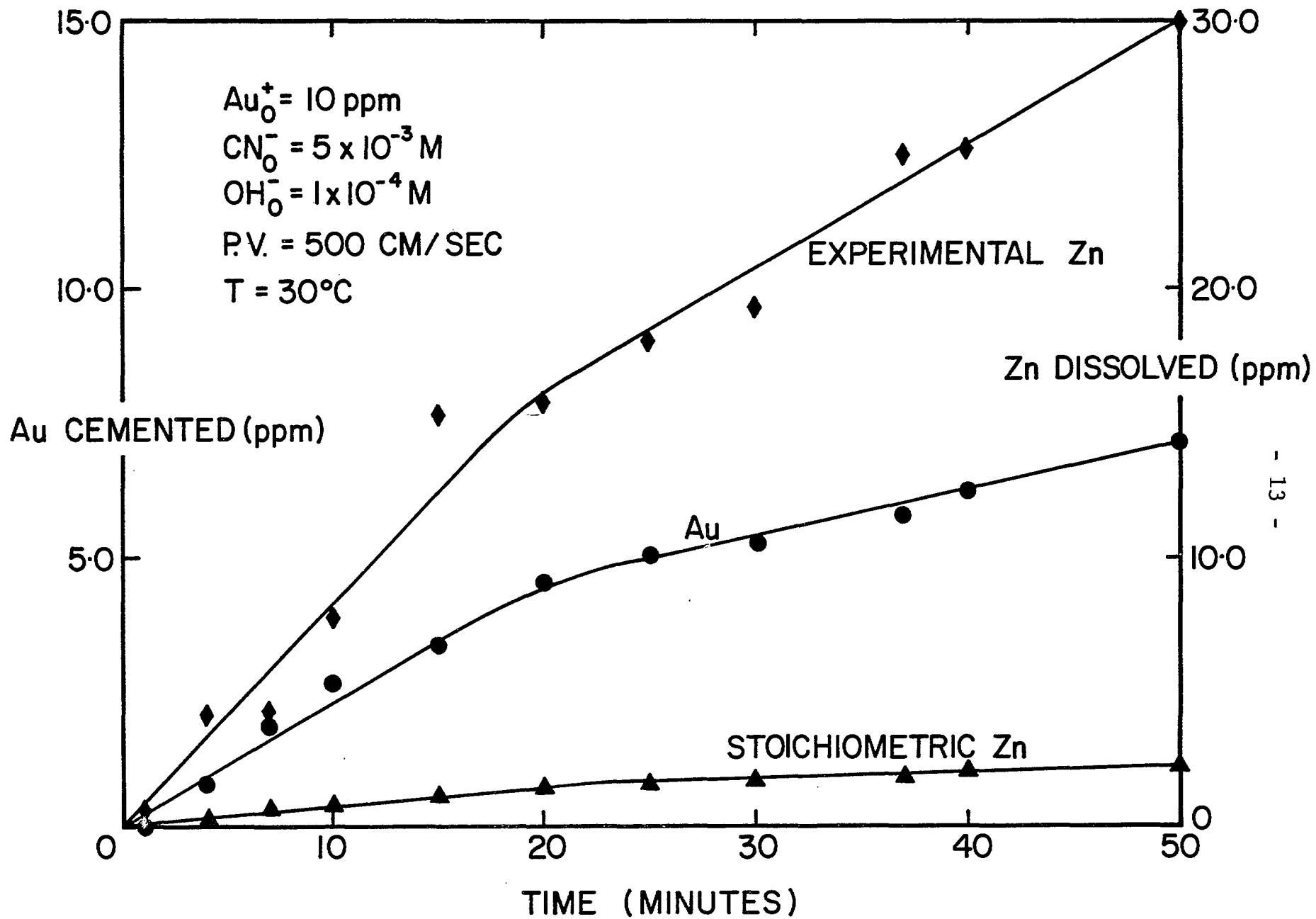


Figure 5. Plot of Au cemented and Zn dissolved vs time

lithographic sheet. The effect of alkaline sulphides, thio-sulphates, and thiocyanates on the rate constant for gold cementation on zinc at 60°C is shown in Table 3. These results indicate that all three substances have an adverse effect on the rate constant. In fact, when Na<sub>2</sub>S is present in concentrations > 5 ppm, the cementation reaction does not occur. This effect on k in the presence of these anions is associated with a decrease in the potential difference (ΔE) for gold cementation on zinc. In each case, the measured ΔE was always less for solutions containing these anions than for solutions containing Au(CN)<sub>2</sub><sup>-</sup> only. The lowest ΔE value was obtained for solutions containing sulphide ions. For example, gold cementation on zinc from a pure aurous cyanide solution occurred at a measured ΔE value of -41mV, whereas the measured ΔE value was only -14mV for a solution containing 5 ppm of Na<sub>2</sub>S.

The effect of these impurities on the overall rate of gold cementation on zinc is shown in Figure 6 in the form of a  $V_t \log \left( [Au^+]_0 / [Au^+]_t \right)$  vs time plot. For the purpose of comparison, the rate curve obtained in the absence of impurities is included with those obtained for solutions containing 5 ppm of Na<sub>2</sub>S, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and NaCNS respectively. The results indicate that Na<sub>2</sub>S has the most detrimental effect - the rate constant becomes zero after approximately 20 minutes. For Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and NaCNS, although the cementation rate decreases after 20 minutes, cementation does not stop altogether as in the case of Na<sub>2</sub>S.



TABLE 3

Effect of Impurities on the Cementation Rate Constant

Impurity	Na <sub>2</sub> S	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	NaCNS
(ppm)	$k \times 10^3$ (cm/sec)	$k \times 10^3$ (cm/sec)	$k \times 10^3$ (cm/sec)
0	3.19	3.19	3.19
5	1.00	0.93	2.46
10	0	2.18	1.39
20	0	1.29	1.20

In the presence of 5 ppm of these impurities, the rate constant decreases in the order  $\text{Na}_2\text{S} > \text{Na}_2\text{S}_2\text{O}_3 > \text{NaCNS}$ .

Values of the rate constant obtained at 60°C in the presence of  $\text{CdSO}_4$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{OAc})_2$  and sodium selenocyanate are listed in Table 4. The rate constant increases in the presence of  $\text{CdSO}_4$  but decreases in the presence of  $\text{Pb}(\text{OAc})_2$  and  $\text{Pb}(\text{NO}_3)_2$ . However, at much higher concentrations of  $\text{Pb}(\text{OAc})_2$ , in the order of 200 ppm and higher, the rate constant for gold cementation on Disk #1 increased. These results are given in Table 5. The increase in the rate constant in the presence of  $\text{Cd}^{++}$  and  $\text{Pb}^{++}$  is probably the result of the formation of a lead-zinc and cadmium-zinc couple in which the second metal is the cathode. The gold cements on this cathode without slowing down the dissolution of zinc. In addition, oxidized zinc films are not formed on these cathodic sections. The increase in the rate of cementation of gold on zinc when Cd or Pb is present can be explained by the larger specific surfaces of the cathodic sections with respect to the geometric area occupied by them. This complicates proper evaluation of the reaction surface and hence leads to higher values for the rate constant. In addition, Cd and Pb, like Zn, have a high hydrogen overvoltage that favours gold cementation on these metals.

Values of the rate constant for gold cementation at 60°C on zinc immersed in solutions containing varying amounts

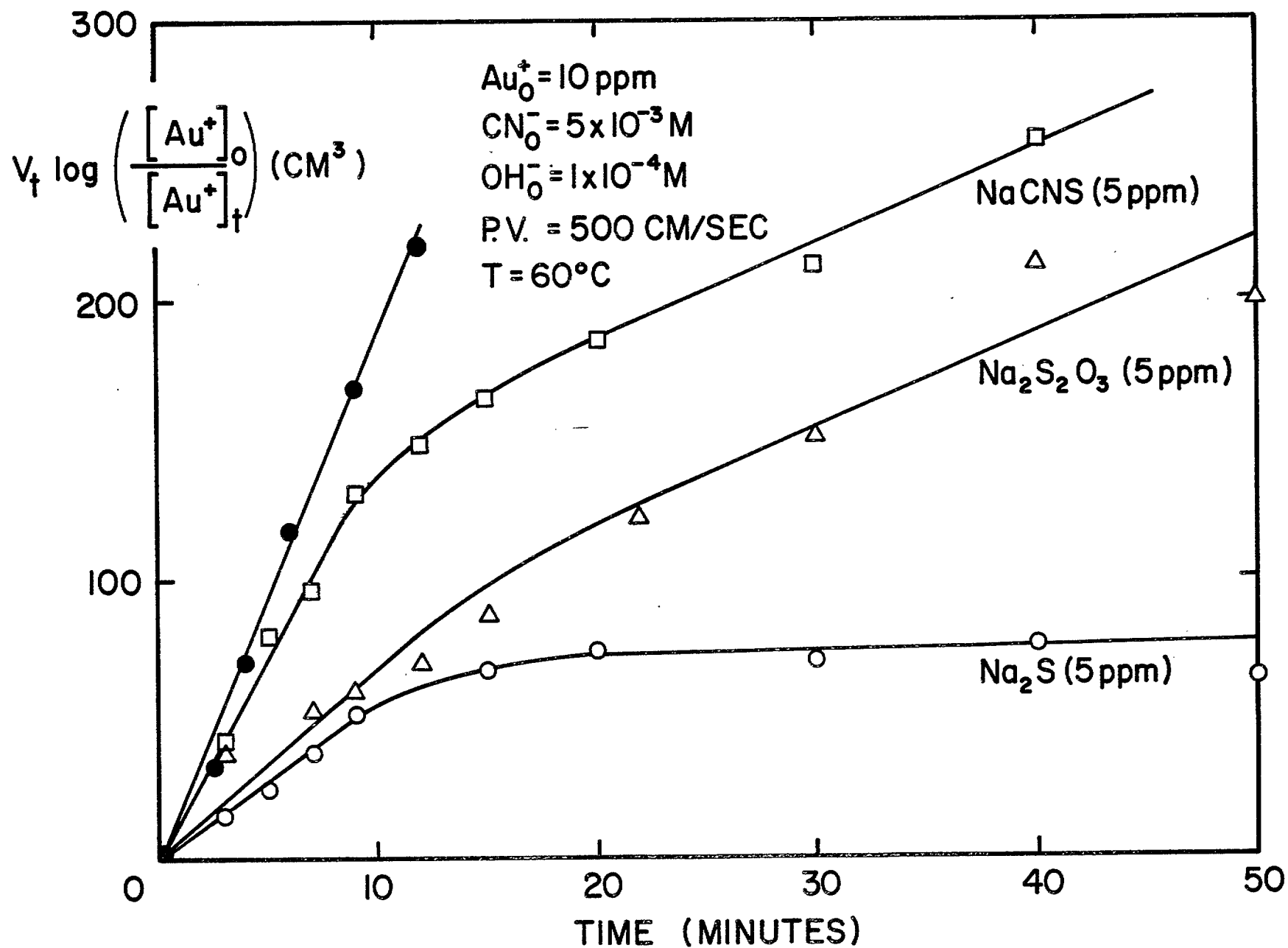


Figure 6. Plots of  $V_t \log([Au^+]_0/[Au^+]_t)$  vs time, showing the effect of  $Na_2S$ ,  $Na_2S_2O_3$  and  $NaCNS$  on the cementation rate

TABLE 4

Effect of Impurities on the Cementation Rate Constant

Impurity	CdSO <sub>4</sub>	Pb(OAc) <sub>2</sub>	Pb(NO <sub>3</sub> ) <sub>2</sub>	Sodium Selenocyanate
(ppm)	$k \times 10^2$ (cm/sec)	$k \times 10^2$ (cm/sec)	$k \times 10^2$ (cm/sec)	$k \times 10^2$ (cm/sec)
0	3.19	3.19	3.19	3.19
3	-	-	-	3.29
5	5.15	1.11	0.88	3.28
7	-	-	-	2.69
10	4.96	0.79	0.68	3.51
20	5.57	0.33	1.27	-
30	3.94	0.48	1.27	-

TABLE 5

Effect of  $\text{Pb}(\text{OAc})_2$  on the Rate Constant for Gold  
Cementation on Disk #1 at 70°C

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$\text{Pb}(\text{OAc})_2$	$k \times 10^3$
(ppm)	(cm/sec)
0	2.42
38	1.33
190	5.04
379	3.54
568	7.60
758	5.32

of  $\text{NaAg}(\text{CN})_2$  and/or  $\text{Na}_3\text{Cu}(\text{CN})_4$ , are listed in Table 6. The rate constant increases in the presence of  $\text{NaAg}(\text{CN})_2$  and decreases when  $\text{Na}_3\text{Cu}(\text{CN})_4$  is present. When both substances are present, the rate constant also increases.

Nickel adversely affects the efficiency of gold cementation on zinc. Hancock and Thomas<sup>(5)</sup> explain the deleterious effect of nickel in terms of hydrogen overvoltage. Nickel deposits on the zinc, thereby lowering the hydrogen overvoltage of zinc and thus interfering with gold cementation. This interpretation may also explain the decrease in the rate constant for gold cementation on zinc when copper is present in the solution.

The increase in the rate constant for gold cementation on zinc in the presence of silver may also be the result of the formation of a silver-zinc couple (cf. Cd and Pb).

## 6. Nature of Deposit

X-ray diffraction analysis showed that the cementation product obtained in the absence of impurities was gold only. The deposit obtained under these conditions was in the form of a porous black powder that indicated that the cemented gold was finely divided.

When impurities such as Pb, Ag and Cu were present in the solution, x-ray diffraction analysis showed that the cemented product consisted of a mixture of gold plus the impurity.

TABLE 6

Effect of Ag and Cu on the Rate Constant for Gold  
Cementation on Zinc at 60°C

NaAg(CN) <sub>2</sub> (ppm)	k x 10 <sup>2</sup> (cm/sec)	Na <sub>3</sub> Cu(CN) <sub>4</sub> (ppm)	k x 10 <sup>2</sup> (cm/sec)	NaAg(CN) <sub>2</sub> + Na <sub>3</sub> Cu(CN) <sub>4</sub> (ppm)	k x 10 <sup>2</sup> (cm/sec)
0	3.19	0	3.19	0 + 0	3.19
5	3.86	5	2.41	5 + 5	3.72
10	5.70	10	1.65	10 + 5	4.36
20	4.63	20	1.75	10 + 10	4.42

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