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KINETICS OF GOLD CEMENTATION ON ZINC

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by

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ABSTRACT

The rate of gold cementation on zinc was measured by atomic absorption spectrophotometric analysis while roating 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 1×10^{-4} M NaOH and 5×10^{-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 Na_2S, $Na_2S_2O_3$, 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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CINÉTIQUE DE LA CÉMENTATION DE L'OR PAR LE ZINC

par

D.J. MacKinnon[1] et T.R. Ingraham[2]

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 1×10^{-4} M NaOH et 5×10^{-3} M NaCN en excès. La vitesse de cémentation, que est élevée au début, décroit 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 Na_2S, $Na_2S_2O_3$, 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 appreciable.

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CONTENTS

TABLES

FIGURES

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[1,2]. 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_3, 15 g Na_2SO_4, 50 ml HNO_3 and 950 ml H_2O[3]. Immediately after polishing, the zinc was washed thoroughly under a stream of tap water and spun for two minutes in a 0.01M $HClO_4$ 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^2	0.0001	0.0003	0.0018	<0.004	0.001	--	--	--	--
DISK #2 Area = 23.50 cm^2	0.0001	0.0004	0.90	0.0009	<0.003	--	--	--	--
LITHOGRAPHIC SHEET Area = 23.48 cm^2	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 (ΔE) 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:

$$-d\,[Au^+]/dt = kS\,[Au^+]/V \qquad [1]$$

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:

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

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:

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

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 1×10^{-4} and 5×10^{-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

*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:

$$Zn + 4NaCN + 2H_2O \rightleftharpoons Na_2Zn(CN)_4 + 2NaOH + H_2 \qquad [4]$$
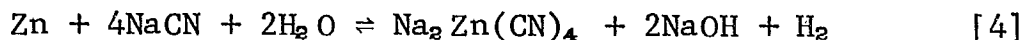
probably plays an important role in this cementation process.

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
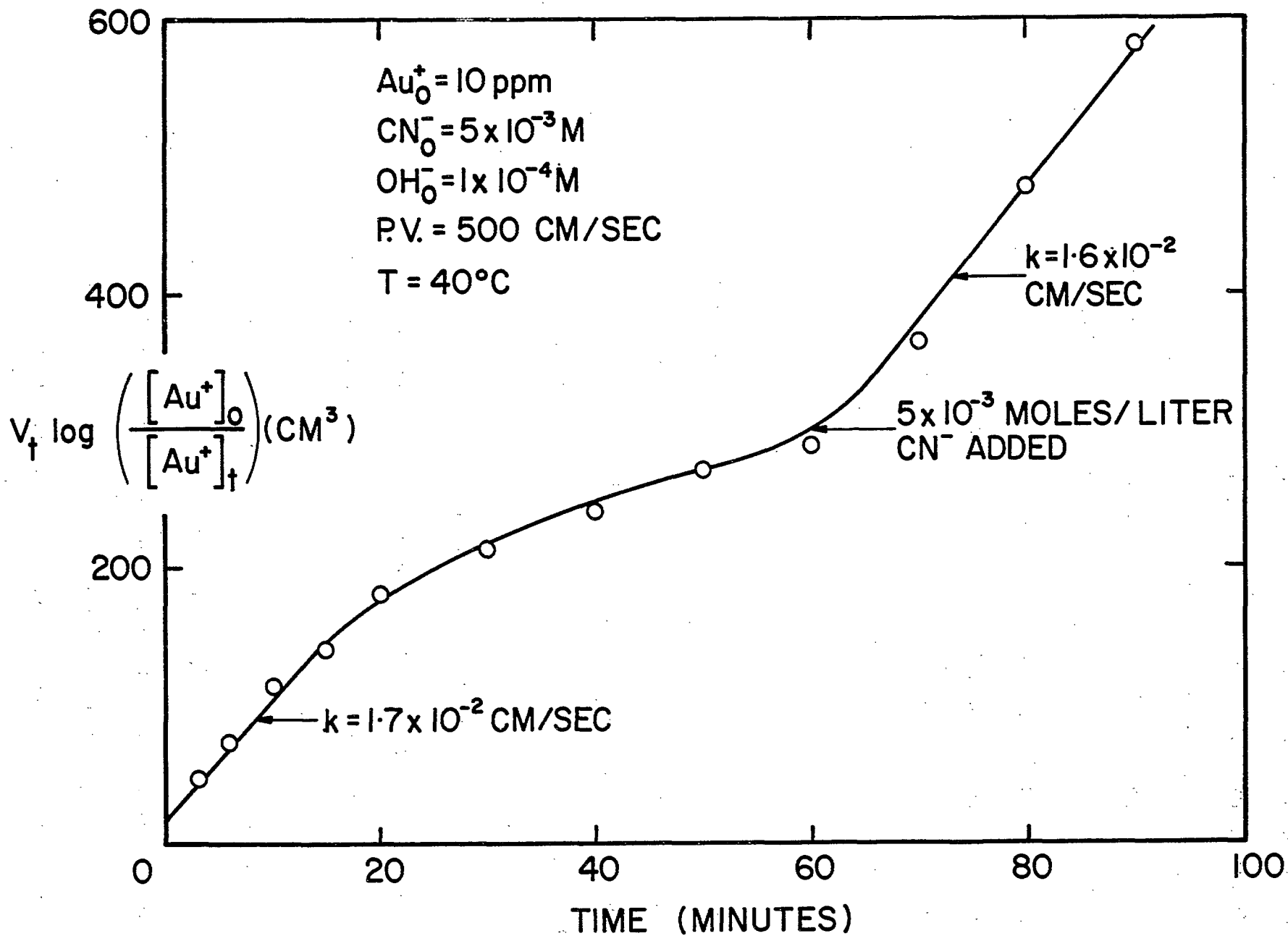
Figure I. Plot of $V_t \log ([Au^+]_0 / [Au^+]_t)$ vs time, showing the effect of additional NaCN on the cementation rate constant
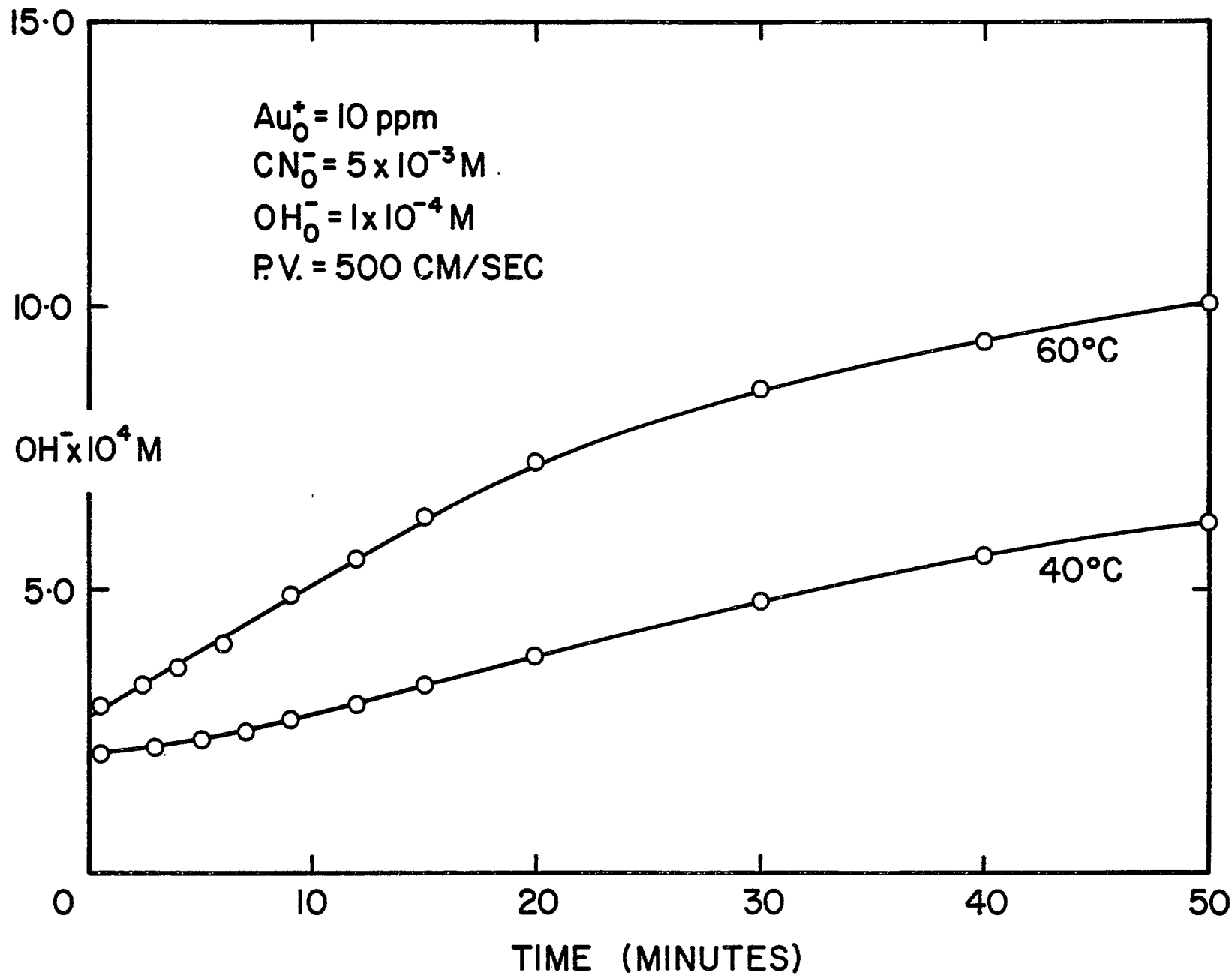
Figure 2. Plot showing the rate of production of OH⁻ during the cementation reaction

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:

$$2NaAu(CN)_2 + Zn \rightleftharpoons Na_2Zn(CN)_4 + 2Au \qquad [5]$$
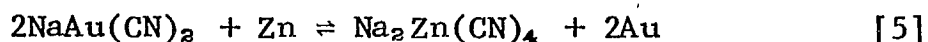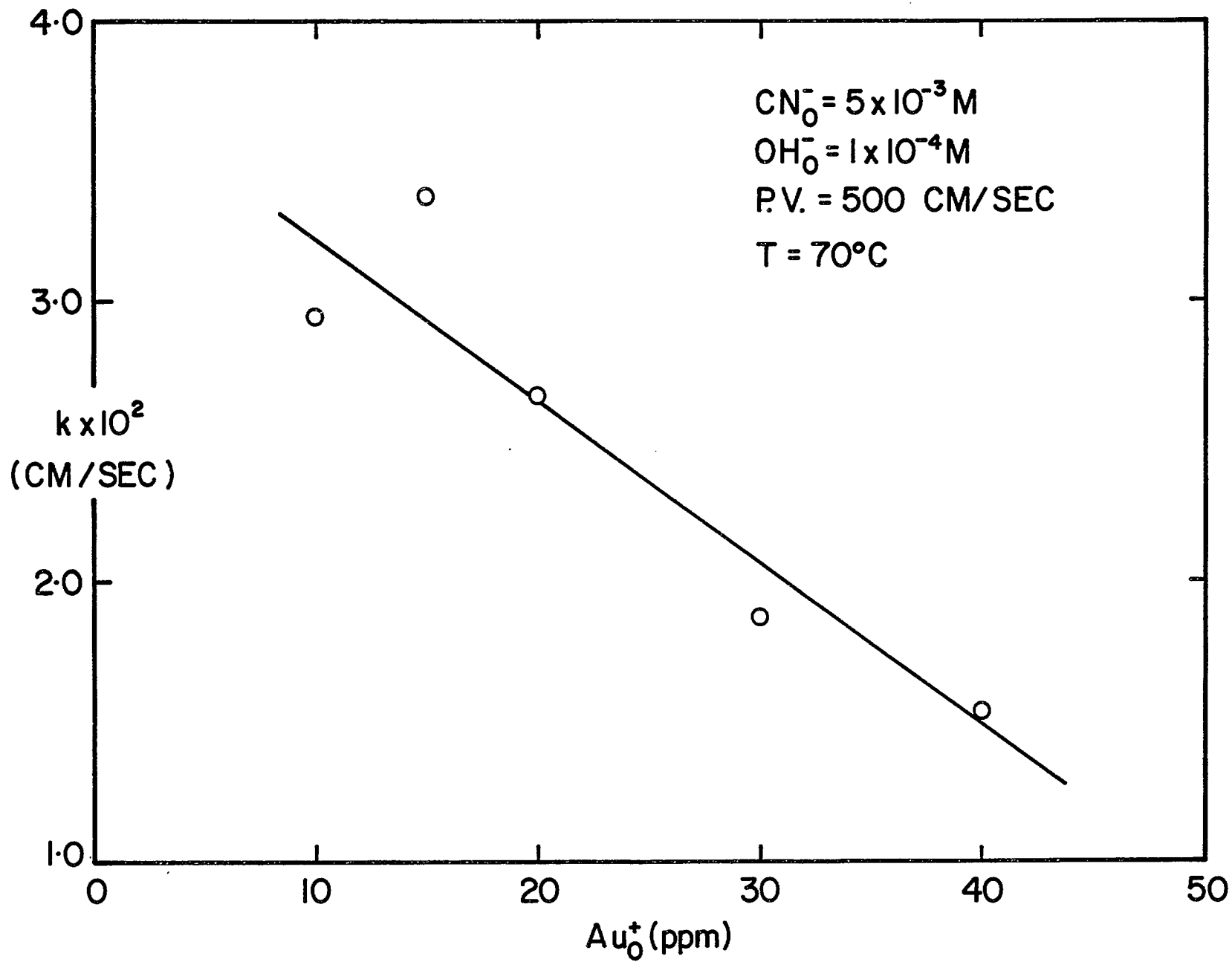
Figure 3. Plot of k vs initial gold concentration, Au_o^+

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:

$$NaAu(CN)_2 + 2NaCN + Zn + H_2O \rightleftharpoons Na_2Zn(CN)_4 + Au + \tfrac{1}{2}H_2 + NaOH \quad [6]$$

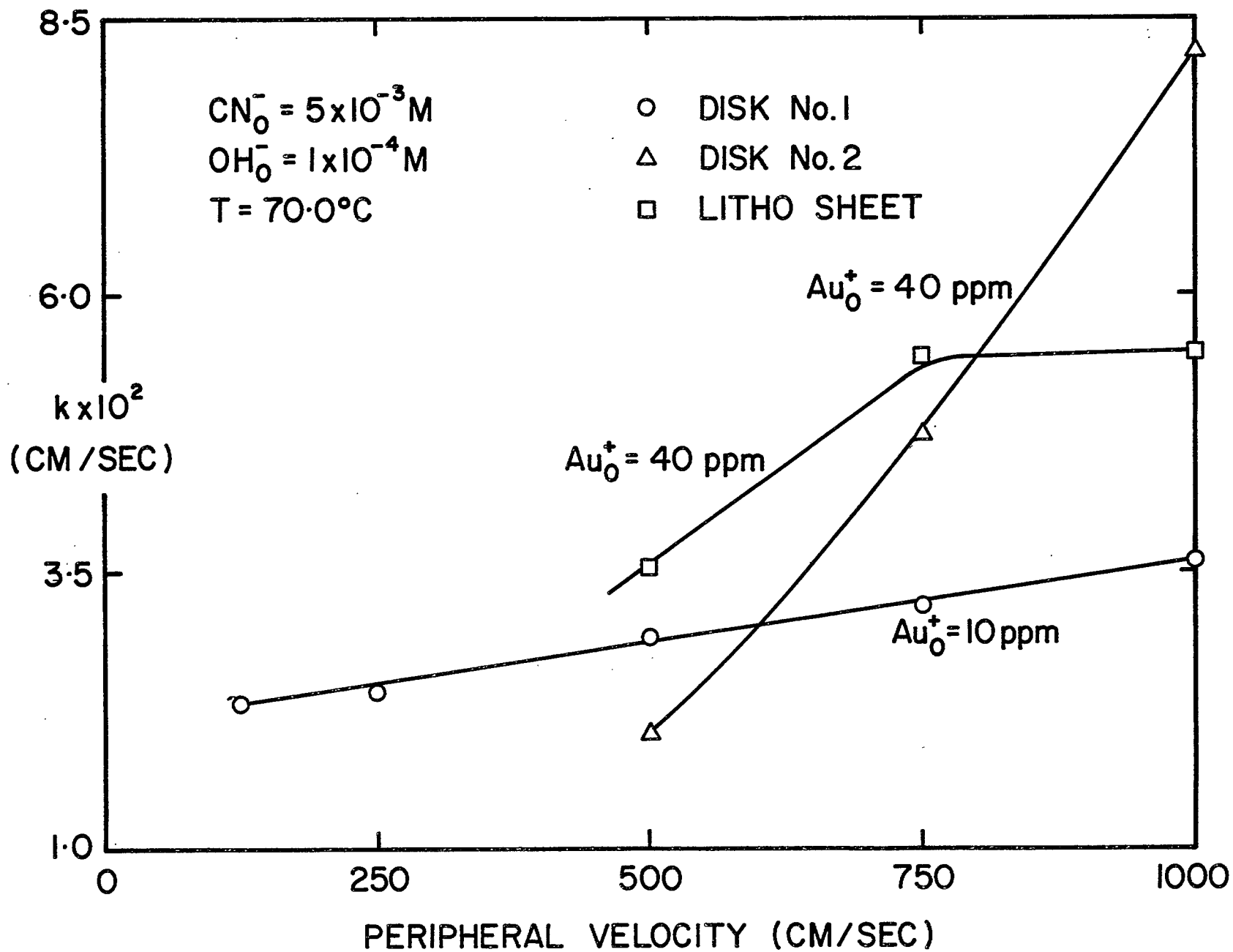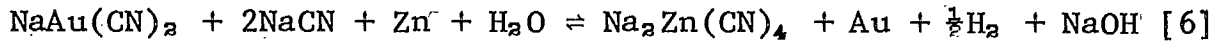which also accounts for the production of NaOH as discussed earlier. Equation 6 indicates that 0.33 ppm of Zn is required to cement 1 ppm of Au. Experimentally, the amount of Zn required to precipitate 1 ppm of Au was found to be much greater than this value. A typical result is shown in Figure 5 for 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
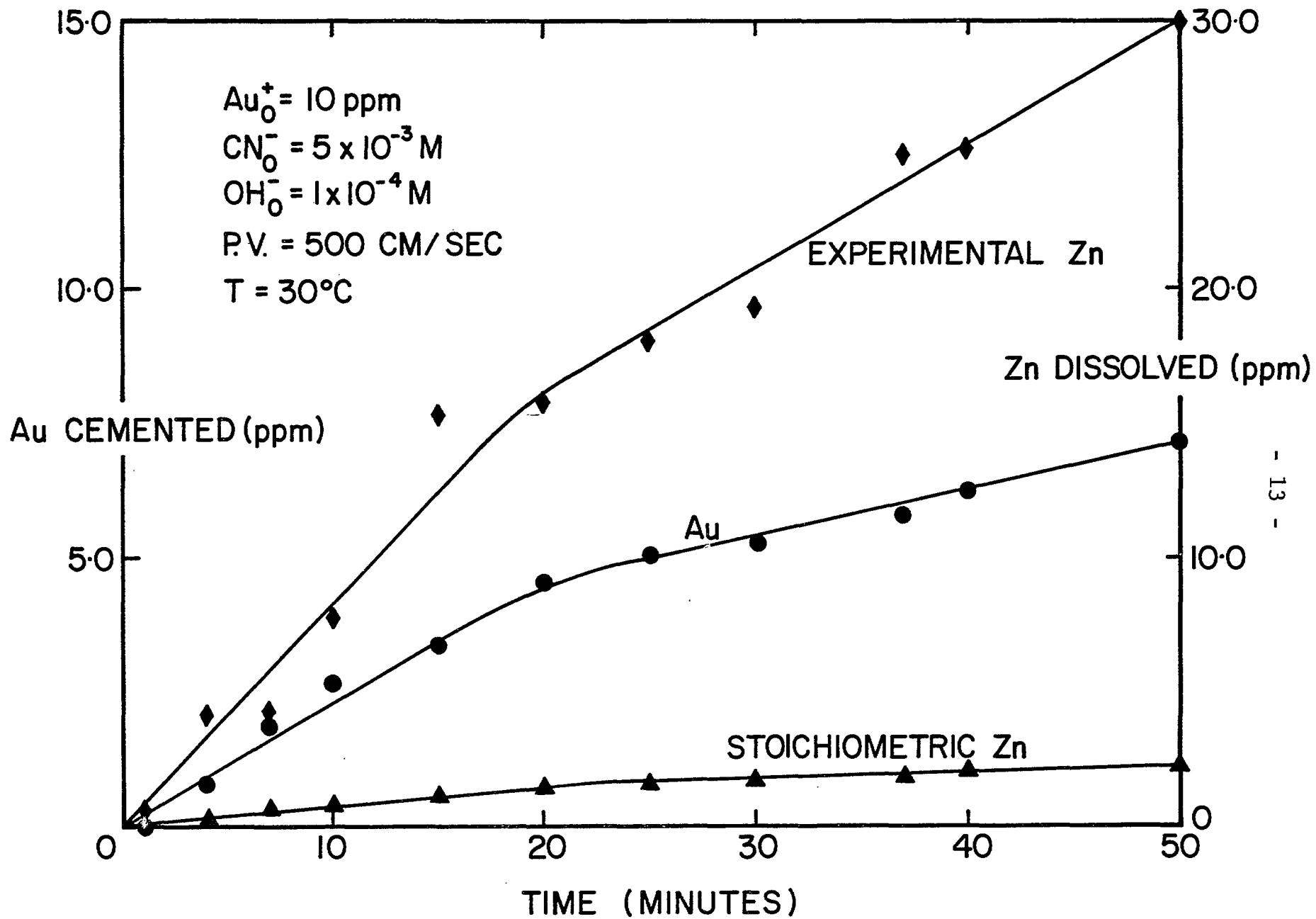
Figure 5. Plot of Au cemented and Zn dissolved vs time

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_2S 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 $Au(CN)_2^-$ 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_2S.

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 compari-son, the rate curve obtained in the absence of impurities is included with those obtained for solutions containing 5 ppm of Na_2S, $Na_2S_2O_3$ and NaCNS respectively. The results indicate that Na_2S has the most detrimental effect - the rate constant becomes zero after approximately 20 minutes. For $Na_2S_2O_3$ and NaCNS, although the cementation rate decreases after 20 minutes, cementation does not stop altogether as in the case of Na_2S.

TABLE 3

Effect of Impurities on the Cementation Rate Constant

Impurity	Na_2S	$Na_2S_2O_3$	NaCNS
(ppm)	$k \times 10^2$ (cm/sec)	$k \times 10^2$ (cm/sec)	$k \times 10^2$ (cm/sec)
0	3.19	3.19	3.19
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 $Na_2S > Na_2S_2O_3 > NaCNS$.

Values of the rate constant obtained at 60°C in the

presence of $CdSO_4$, $Pb(NO_3)_2$, $Pb(OAc)_2$ and sodium selenocyanate

are listed in Table 4. The rate constant increases in the

presence of $CdSO_4$ but decreases in the presence of $Pb(OAc)_2$

and $Pb(NO_3)_2$. However, at much higher concentrations of

$Pb(OAc)_2$, 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 Cd^{++} and Pb^{++} is probably the result of the for-

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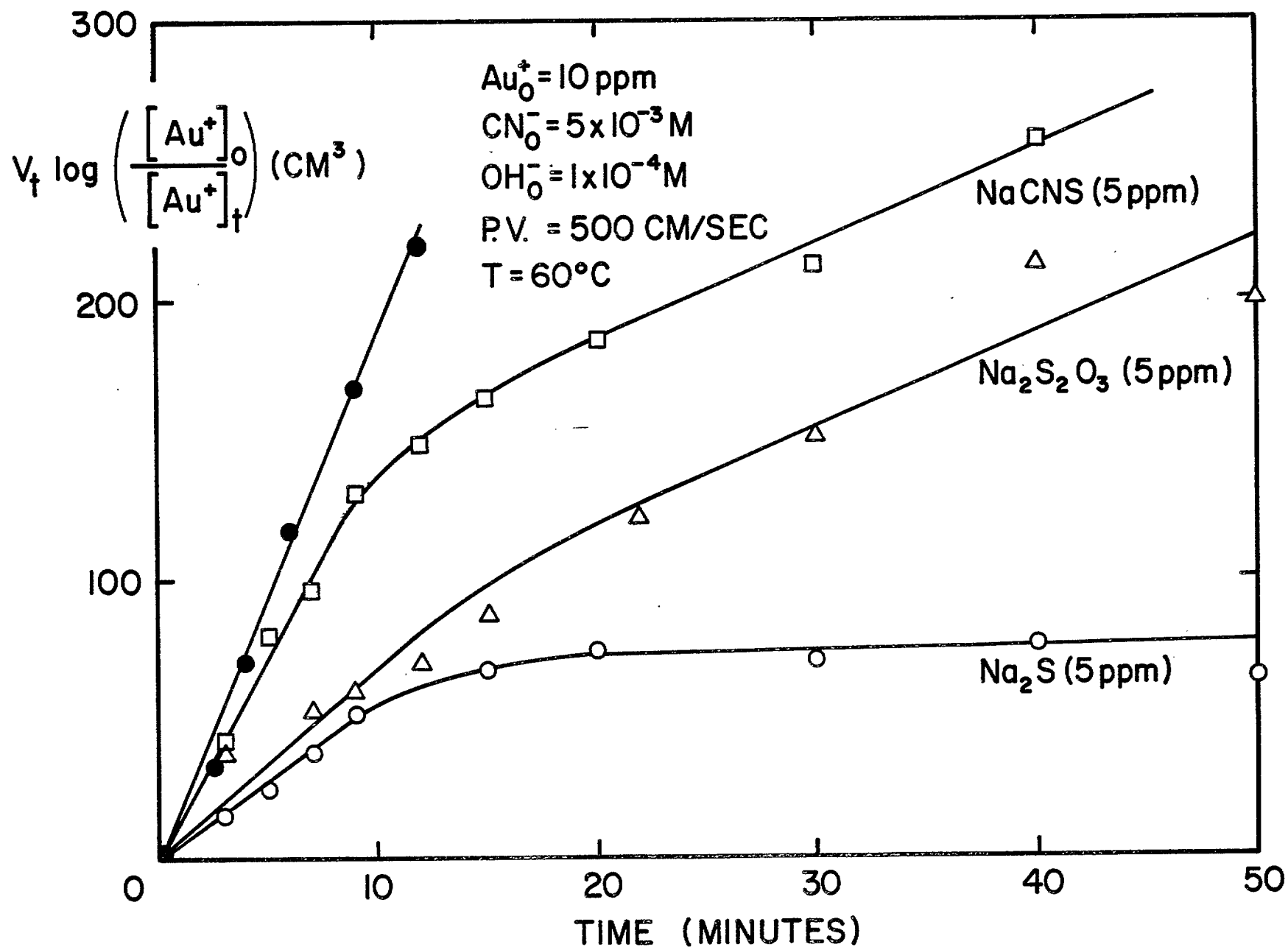
Figure 6. Plots of $V_t \log([Au^+]_o/[Au^+]_t)$ vs time, showing the effect of Na_2S, $Na_2S_2O_3$ and NaCNS on the cementation rate

The figure shows a graph with:

Y-axis: $V_t \log\left(\dfrac{[Au^+]_o}{[Au^+]_t}\right)$ (CM^3)

X-axis: TIME (MINUTES)

Conditions:
$Au_o^+ = 10\,ppm$
$CN_o^- = 5 \times 10^{-3}\,M$
$OH_o^- = 1 \times 10^{-4}\,M$
P.V. $= 500\,CM/SEC$
$T = 60°C$

Curves labeled: NaCNS (5 ppm), $Na_2S_2O_3$ (5 ppm), Na_2S (5 ppm)

TABLE 4

Effect of Impurities on the Cementation Rate Constant

Impurity	$CdSO_4$	$Pb(OAc)_2$	$Pb(NO_3)_2$	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 $Pb(OAc)_2$ on the Rate Constant for Gold
Cementation on Disk #1 at 70°C

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

of NaAg(CN)$_2$ and/or Na$_3$Cu(CN)$_4$, are listed in Table 6. The
rate constant increases in the presence of NaAg(CN)$_2$ and
decreases when Na$_3$Cu(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[5] 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

$NaAg(CN)_2$ (ppm)	$k \times 10^2$ (cm/sec)	$Na_3Cu(CN)_4$ (ppm)	$k \times 10^2$ (cm/sec)	$NaAg(CN)_2$ + $Na_3Cu(CN)_4$ (ppm)	$k \times 10^2$ (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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