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RECOVERY OF BISMUTH FROM HCl LEACH

SOLUTIONS BY CEMENTATION ON IRON

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RECOVERY OF BISMUTH FROM HCl LEACH SOLUTIONS

BY CEMENTATION ON IRON

by

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ABSTRACT

The feasibility of recovering metallic bismuth from strong hydrochloric acid leach liquors by cementation on iron has been investigated. Several types of iron were used to cement bismuth from solutions containing up to 4.0 g Bi/l. Zinc and lead powders were ineffective as cementing agents for bismuth from actual leach liquors. The reaction on iron, however, which produced a loose deposit of bismuth, was extremely rapid at room temperature. The effect of Cu^{++}, Zn^{++}, Fe^{++} and Fe^{+++}, which were present in the leach liquor, on the reaction rate, stoichiometry and purity of product was also determined. Of these, only Fe^{+++} had an appreciable effect, causing a decrease in the reaction rate and an increase in the consumption of iron. Other variables that had a significant effect on the reaction were temperature, surface area of iron and the type of iron used.

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LA RÉCUPÉRATION DU BISMUTH DES SOLUTIONS DE
LESSIVE D'ACIDE CHLORHYDRIQUE PAR LA CÉMENTATION SUR FER

par

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RÉSUMÉ

L'auteur a étudié la possibilité de récupérer du bismuth métallique des liqueurs fortes de lessive d'acide chlorhydrique par la cémentation sur fer. Il a utilisé plusieurs types de fer pour cimenter le bismuth des solutions contenant jusqu'à 4. 0 g Bi/ ℓ . Les poudres de zinc et de plomb étaient inefficaces comme agents de cémentation pour le bismuth des liqueurs réelles de lessive. Cependant, la réaction sur fer qui a produit un dépôt meuble de bismuth, était extrêmement rapide à la température ambiante. Il a aussi déterminé l'effet du Cu^{++}, de Zn^{++}, du Fe^{++} et du Fe^{+++}, qui étaient présents dans la liqueur de lessive, sur la vitesse de réaction, la stoichiométrie et la pureté du produit. De ceux-ci, seulement le Fe^{+++} avait un effet appréciable ayant comme résultat une diminution de la vitesse de réaction et une augmentation de la consommation du fer. D'autres variables ayant un effet significatif sur la réaction étaient la température, la surface du fer et le type de fer utilisé.

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INTRODUCTION

The purpose of this investigation was to study the feasibility of using cementation for the recovery of bismuth from a solution obtained by the hydrochloric acid leaching of a bulk sulphide concentrate of a New Brunswick ore.

Cementation provides an alternative method to the oxychloride route[1] for recovering bismuth. Precipitating bismuth as the oxychloride (BiOCl) has the disadvantage that acid is consumed by dilution and also that the bismuth oxychloride, thus obtained, must be subjected to additional treatment in order to obtain metallic bismuth. Cementation has the advantage of producing the metal directly, and the low acid consumption allows for the recycling of the acid for further leaching.

The literature contains relatively few examples of bismuth cementation, and details are sketchy. However, Ripan and Liteaner[2] used iron bars on which to cement bismuth over a 24-hr period to achieve a "yield" of 88%. Kovalenko[3] studied the rate of reduction of bismuth with lead from a nitrate solution. He states that the bismuth may be completely cemented from an acidified nitrate solution with lead. He also studied the cementation of bismuth and copper on cadmium from a zinc electrolyte. He found that the simultaneous presence of bismuth and copper in the solution

accelerated their reduction with cadmium.

Gulevitskaya and Epshtein[4] report the production of copper-free cement bismuth from the hydrochloric acid leaching of a copper concentrate. The leach liquor was first contacted with a large excess of iron filings to prevent the formation of Fe^{+++} which had been found to decrease the precipitation of both bismuth and copper. The cement product was then treated with ammonium carbonate solution to dissolve the copper.

In a later paper, Gulevitskaya[5] discussed the separation of bismuth and molybdenum from a solution, obtained from the hydrochloric acid leaching of a bismuth-molybdenum concentrate, by cementation with iron shavings. Approximately 97% Bi and 10% Mo were recovered by this method.

In the present work, both synthetic and actual leach liquors were used. The cementation of bismuth by iron was investigated with respect to both the kinetics of the reaction and the feasibility of using this method for the recovery of bismuth metal.

EXPERIMENTAL

The experimental apparatus and procedure were essentially the same as described in previous papers[6,7]. Strips of cold-rolled iron sheet* were attached to the peripheral surface of a lucite clamping cylinder and rotated at controlled

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*cold-rolled 1010 to 1015 mild-steel sheet, 0.092 inch thick, obtained from Alexander Metals Products, Ltd., Ottawa.

speeds in either the synthetic or leach liquors. To follow
the course of the cementation reaction, solution samples were
taken periodically and analysed for Bi^{+++} with a Techtron
Model AA-5 atomic absorption spectrophotometer. Initial
solution volumes were 1 litre and the sample volumes were 2 ml.

For the experiments in which iron powder or filings*
were substituted for the iron sheet, the lucite clamping
cylinder was replaced by an all-glass stirring assembly.

The synthetic solutions were prepared from reagent-
grade chemicals and redistilled water. The use of synthetic
solutions made it possible to study the effect on the cement-
ation reaction of the individual or combined impurities that
were contained in the actual leach liquor. A typical leach
liquor analysed as follows, in g/1; Bi 3.9, Zn 1.0, Cu 0.1,
Fe 3.2, In 0.03, Mo 0.004, W <0.05, Sn 0.009, Ag 0.12, and
free HCl 100.

RESULTS AND DISCUSSION

1. Reaction Kinetics and Mechanism

Experiments in which bismuth was cemented on
rotating strips of cold-rolled iron sheet from synthetic
solutions containing approximately 4.0 g Bi/1 and 100 g free
HCl/1 showed that, for the first 15 minutes, the reaction obeys

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*The iron powder was reagent-grade hydrogen-reduced variety
and the filings were reagent-grade of about 40 mesh.

a first-order rate law which may be represented by the equation[6,7]:

$$V_t \log ([Bi^{+++}]_0/[Bi^{+++}]_t) = kst/2.303 \qquad [1]$$

where k is a psuedo-first-order rate constant, s the geometric area of the iron strip, and V the solution volume. The subscript t refers to the sampling time, 0 to zero 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 dimensions of cm/sec. This situation is shown in Figure 1 where $V_t \log ([Bi^{+++}]_0/[Bi^{+++}]_t)$ is plotted against the time in minutes. The point where the reaction deviates from first-order kinetics represents 64% bismuth cemented. This departure from linearity indicates the existence of two steps in the cementation reaction. The first step is described by equation [1]. In the second step, the rate is slower and the rate controlling mechanism is probably one involving the diffusion of ferrous ions through the cemented deposit into the solution. Because the departure from linearity occurred at approximately the same time (15 min) and at the same percentage reaction (between 64 and 70% Bi cemented) for several different solutions containing various additives (e.g., Cu^{++}, Zn^{++}, Fe^{++}, and Fe^{+++}), it appears that the change to the second step takes place at the same deposit thickness.
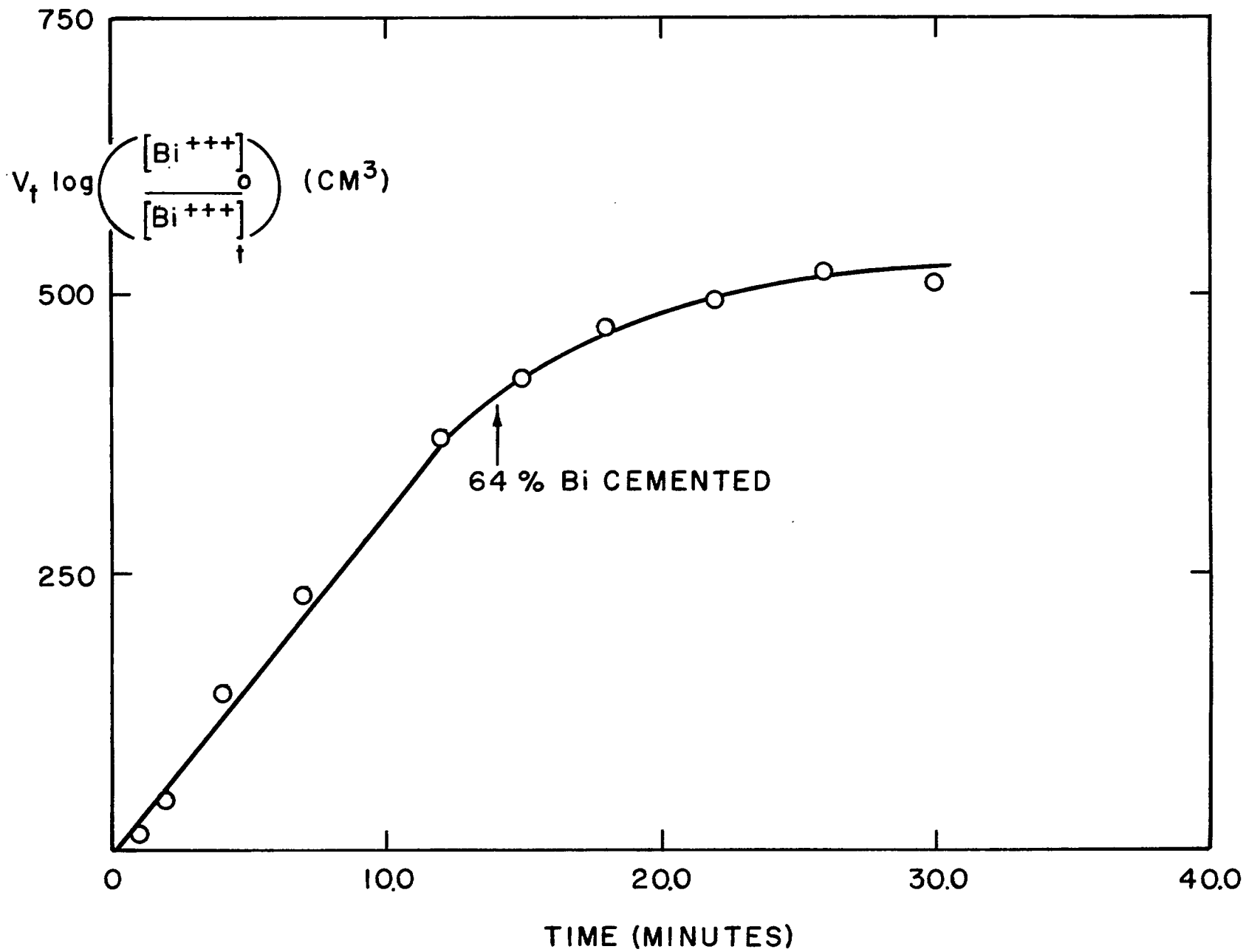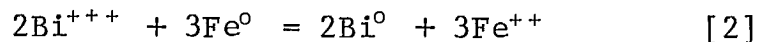
Figure 1. Plot of $V_t \log([Bi^{+++}]_0/[Bi^{+++}]_t)$ against Time for Bismuth Cementation on Iron

2. Stoichiometry

The stoichiometry of the reaction was determined from the same tests described in Section 1. The calculations were based on the assumption that the following reaction was taking place:

$$2Bi^{+++} + 3Fe^{o} = 2Bi^{o} + 3Fe^{++} \qquad [2]$$

The initial tests were done with solutions containing approximately 4.0 g Bi/1 and 100 g free HC1/1. The results of several tests indicated that, on the average, the excess iron consumed was 1.7 times the stoichiometric amount of iron required by reaction [2]. This excess iron consumption may be attributed to several side reactions, the most probable being the discharge of hydrogen ions according to the reaction:

$$2H^{+} + Fe^{o} = Fe^{++} + H_2 \qquad [3]$$
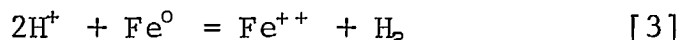
The role of this reaction in the cementation of copper by iron was studied in some detail by Rickard and Fuerstenau[8]. They showed that reaction [3] is very slow in this case but that its rate increases as the rate of copper cementation decreases.

It is also possible that, because the leach liquor contains dissolved arsenic, iron is consumed by the evolution of arsine gas (AsH_3). Because this creates a potential health hazard, the cementation of bismuth by iron should be done in

well-ventilated space.

Another reaction that may cause excess iron comsumption is:

$$6H^+ + 2Bi^0 = 2Bi^{+++} + 3H_2 \qquad [4]$$
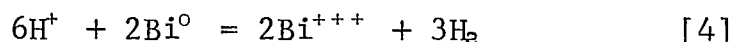
However, this reaction is probably of minor importance in this case because bismuth does not dissolve in HCl, except very slowly while oxygen is present[9]. The results of the above tests are listed in Table 1 which also shows the effect of Cu^{++}, Zn^{++}, Fe^{++} and Fe^{+++} on excess iron consumption. The results indicate that only ferric ion causes an additional increase in iron consumption. This result may be attributed to the reaction:
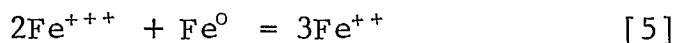
$$2Fe^{+++} + Fe^0 = 3Fe^{++} \qquad [5]$$

The importance of this reaction in copper cementation on iron has also been determined by Rickard and Fuerstenau[8]. They showed that both Cu^{++} and Fe^{+++} reduction by Fe^0 are first-order reactions but that the rate of Fe^{+++} reduction is about half of that of Cu^{++} reduction. It is likely that the same situation applies for bismuth cementation on iron.

3. Effect of Metallic Icns

The effect of metallic ions on the reaction rate is also shown in Table 1. Ferrous ion has no apparent effect on the reaction rate, but either a combination of ferrous and ferric ions or ferric ion, alone, causes a decrease in the rate. In

TABLE 1

EFFECT OF METALLIC IMPURITIES ON EXCESS IRON DISSOLUTION

AND ON THE CEMENTATION RATE

Bi^{+++} (gm/1)	Cu^{++} (gm/1)	Fe^{++} (gm/1)	Fe^{+++} (gm/1)	Zn^{++} (gm/1)	AMT. Fe CONSUMED / STOICHIOMETRIC AMT.	RATE (mg/cm^2/sec)
3.52	--	--	--	--	1.7	1.46
3.60	--	--	--	--	1.6	1.53
3.60	--	3.0	--	--	1.9	1.53
3.67	0.1	3.0	--	--	1.6	1.61
3.96	0.1	3.0	--	1.0	1.7	1.83
3.83	0.1	1.5	1.5	1.0	3.0	1.17
4.00	0.1	--	3.0	1.0	2.6	1.31
3.80	--	--	3.0	1.0	3.0	1.17

addition to consuming iron directly by reaction [5], ferric

ion can consume iron indirectly by the reaction:

$$Bi^o + 3Fe^{+++} = Bi^{+++} + 3Fe^{++} \qquad [6]$$

This would account for the decrease in the apparent

cementation rate in the presence of ferric ions. Nadkarni

and Wadsworth[10] showed that this type of reaction was very

important in copper cementation by iron. They found that

the rate of the reaction:

$$Cu^o + 2Fe^{+++} = Cu^{++} + 2Fe^{++} \qquad [7]$$
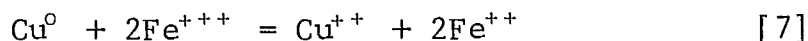
was proportional to the surface area of Cu^o. Therefore, the rate

of reaction [7] increased with time because the area of Cu^o

increased as a result of the cementation reaction.

4. Effect of Fe Type

Several tests were done with an actual leach

liquor containing 1.4 g Bi/l using three types of iron, viz.,

hydrogen-reduced iron powder, 40-mesh iron filings, and

cold-rolled iron strips, to determine the effect of the

nature of the cementing agent and of its surface area on the

cementation rate. By far the fastest rate was achieved by using

hydrogen-reduced iron powder. The amount of powder used

represented an excess of 2.6 times that required by the

stoichiometry based on Equation [2]. After only 6 minutes

at 25°C, 97% of the bismuth was cemented. All the iron was

consumed in about 20 minutes and after this time

some of the cement bismuth began to redissolve. This

behavior, which is similar to that mentioned by Gulevitskaya

and Epehtein[4], indicates the presence of some oxidizing agent

in solution, most probably ferric ions. So it seems

essential that excess iron be present to prevent the re-solution

of the cement bismuth.

A series of three tests was done using different

amounts of 40-mesh iron filings.   The rates were much slower

than those observed for reduced powder. However, the rates were

found to increase with increasing amounts of iron filings up to

a Fe/Bi ratio of about 5.4. This result is shown in Figure 2,

together with the per cent bismuth cemented as a function of

the Fe/Bi ratio. Figure 2 indicates that the per cent bismuth

cemented reaches a maximum of 87% for a Fe/Bi ratio of about

5.0. It should be noted that the rate of bismuth cementation,

with an Fe/Bi of 1.1 using hydrogen-reduced iron powder, was

twenty times faster than that observed for the same amount of

iron filings but was only three times faster than that

observed for a Fe/Bi ratio of 5.4 using iron filings. Also,

the fact that the rate increased with increasing amounts of

iron filings indicates that it is proportional to the surface

area available for cementation. In addition to having a much

larger surface area, the fact that the iron powder was

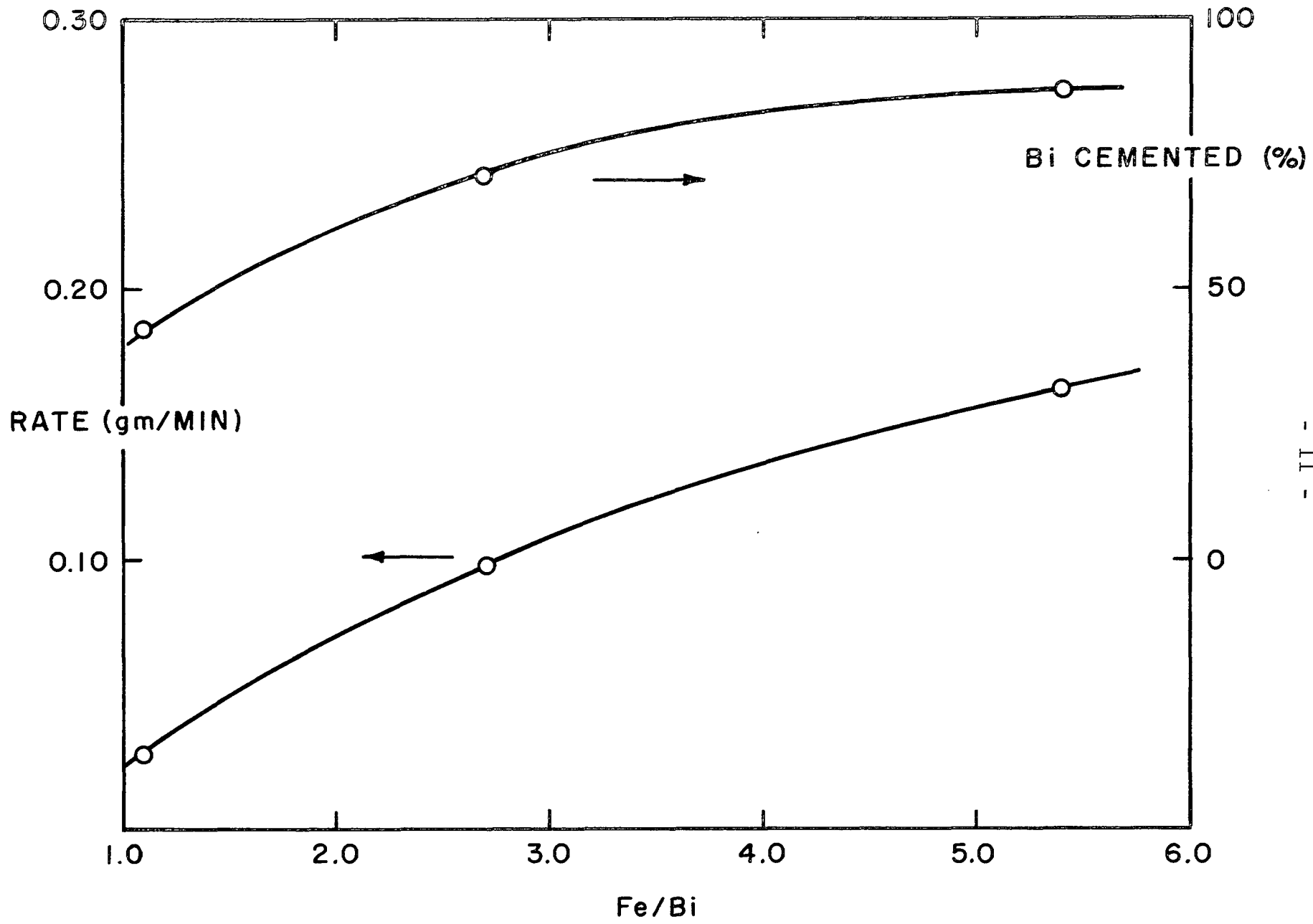prepared by hydrogen reduction would also have a beneficial

Figure 2. Plot Showing the Cementation Rate and the Per Cent Bismuth Cemented as a Function of the Fe/Bi Ratio.

effect on the reaction rate because this is an often-used method for surface activation.

The efficiencies of the various types of iron as cementing agents for bismuth are compared in Table 2. These results are based on the per cent bismuth cemented after 20 minutes from a leach liquor containing 1.4 g Bi/l.

Attempts were also made to cement bismuth by using zinc and lead powders. Both these metals proved ineffective for this purpose when used with the actual leach liquor. This lack of reactivity is probably related to the presence of ferric ion in the leach liquor, a conclusion supported by the fact that zinc powder proved to be a very effective cementing agent for synthetic bismuth solutions that did not contain Fe^{+++}.

5. Effect of Temperature and Stirring Velocity

The effect of temperature on bismuth cementation on iron filings was also investigated. The results are summarized in Figure 3, which includes a plot of per cent Bi cemented against temperature, in °C, and an Arrhenius plot from which the apparent activation energy was determined. These tests were done using iron filings such that the Fe/Bi ratio was 1.1. Figure 3 indicates that the Bi cemented increases linearly with temperature up to 58°C. At this point, 97% of the Bi has been removed from solution.

TABLE 2

PER CENT BISMUTH RECOVERED AS A FUNCTION OF THE

TYPE OF IRON

Type of Fe	Weight of Fe (gm)	Surface Area (cm^2)	Bi Cemented after 20 min (%)
Hydrogen-reduced powder	1.5	22.5×10^3 *	97
Filings (40-mesh)	1.5	--	43
Cold-rolled sheet		22.9	30

*The surface area of the iron powder was determined by the BET (krypton gas) absorption method.

A plot of log rate against $10^3/T$ ($°K^{-1}$) (also shown in Figure 3) yields an apparent activation energy of about 7.8 kcal/mole. This value, together with the fact that the reaction rate did not change with an increase in stirring velocity, indicates that the rate-determining step in the cementation reaction is probably a chemically controlled reaction.

6. Nature of the Deposit

The Bi deposit was the same for the three types of iron used in the test work. It was gray-black and easily removed from the surface of the iron strip. In fact, rapid stirring aided the removal of the deposit from the iron surface during the course of the reaction. The cement bismuth was recovered by vacuum filtration. Excess iron could be washed-out of the deposit by treatment with a 2% HCl solution. A typical product was analysed as follows, in per cent: 69 Bi, 7 Pb, 0.54 Fe, and 0.2 Cu. Other metals, e.g., Sn, In, Mo, As, and W were not determined.

7. Conclusions

Bismuth cementation on iron from leach liquors containing 100 g HCl/l is very rapid at room temperature. The acid consumption is 10 to 15 g/l and iron consumption increases in the presence of ferric ions, requiring excess iron metal to be added to prevent the cement bismuth from redissolving.
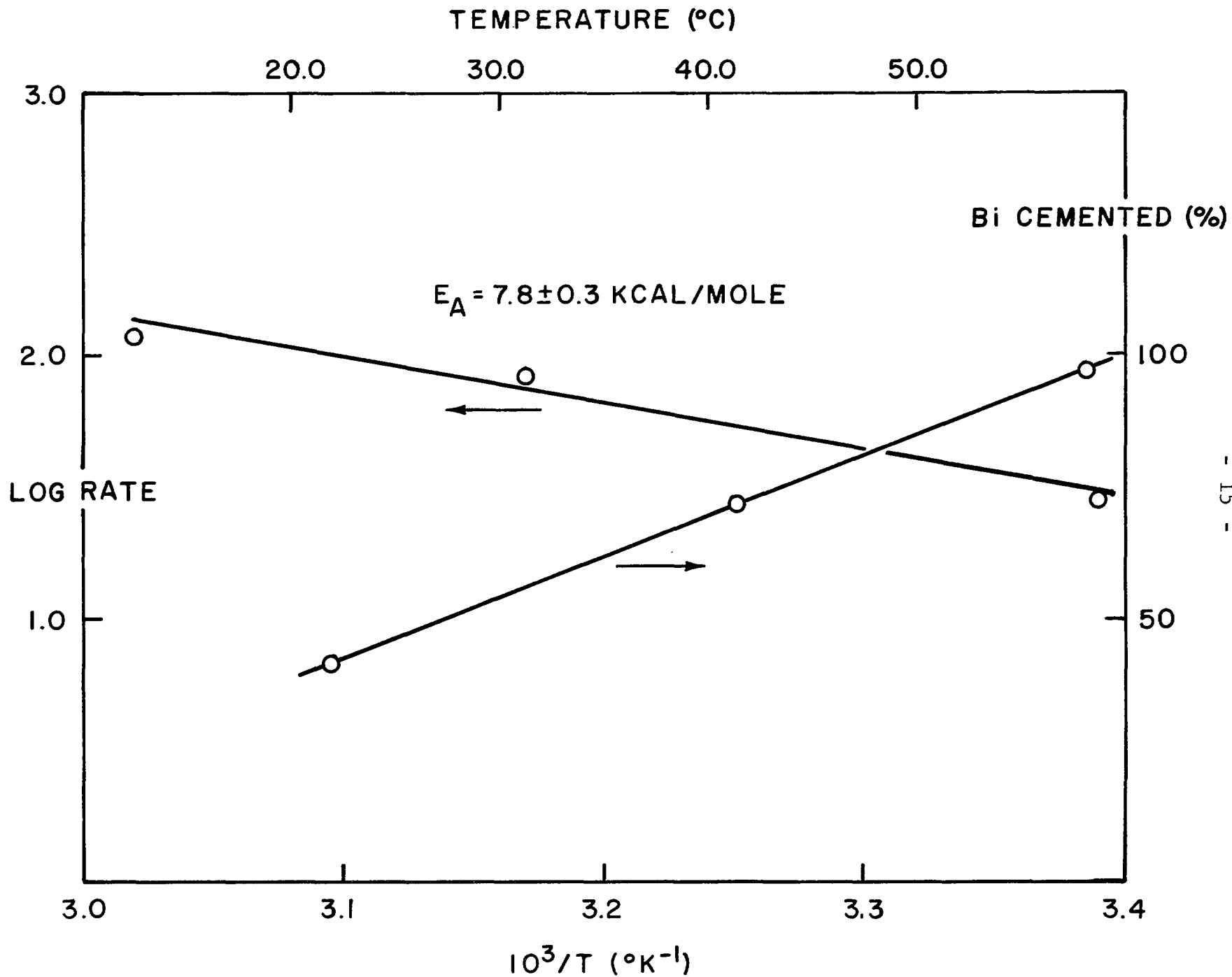
Figure 3. Plot Showing the Effect of Temperature on Bismuth Cementation on Iron

Hydrogen-reduced iron powder was found to be most effective for cementing bismuth from these solutions. The effectiveness of 40-mesh iron filings as a cementing agent was enhanced by increasing the temperature and by increasing the amount used.

The metallic impurities contained in the leach liquor, with the exception of Fe^{+++}, had little or no effect on the cementation rate or on the reaction stoichiometry. The Fe^{+++} in the leach liquor was found to be detrimental to bismuth cementation.

ACKNOWLEDGEMENTS

REFERENCES

1. Mellor, J.W., "Inorganic and Theoretical Chemistry" Vol. IX, Longmans, Green and Co., New York, 1947, p. 595.

2. Ripan, R., and Liteaner, C. "A New Procedure for the Preparation of Bismuth from Sulfide Ores", Acad. Rep. Populare Romane, Bul. Stiint., Ser. Mat., Fiz., Chim. 2, 257-68 (1950).

3. Kovalenko, P.N., "Reduction of Bismuth and Copper with Metallic Cadmium and their Polarographic Determination", Uchenye Zapiski Rostov.-na-Donu Univ. <u>40</u>, 3-21 (1958) C. A. 54:8464c.

4. Gulevitskaya, I.A., and Epshtein, L.A., "Production of Copper-Free Bismuth from Copper Concentrate", Tsvetn. Metall. <u>40</u>, 49-51 (1967). C. A. 66:117946s.

5. Gulevitskaya, I.A., "Hydrometallurgical Extraction of Bismuth from Beneficiation Products", Tr. Nauch.-Tekh. Sess. Inst. "Mekhanober" (Vses. Nauch.-Issled. Prockt. Inst. Mekh. Obrab. Polez. Iskop.), 5th <u>1965</u> (Pub 1967), 1, 792-9. C. A. 70: 21989q.

6. von Hahn, E.A., and Ingraham, T.R., "Kinetics of Pd (II) Cementation on Sheet Copper in Perchlorate Solutions", Trans. AIME, <u>236</u>, 1098-1103 (1966).

7. Ingraham, T.R., and Kerby, R., "Kinetics of Cadmium Cementation on Zinc in Buffered Sulphate Solutions," ibid., <u>245</u> 17-21 (1969).

8. Rickard, R.S., and Fuerstenau, M.C., "An Electrochemical Investigation of Copper Cementation by Iron", Trans. AIME <u>242</u>, 1487 (1968).

9. Welcher, F.J., and Hahn, R.B., "Semimicro Qualitative

    Analysis" (D. Van Nostrand Co. (Canada) Ltd.,

    1955), p. 253.

10. Nadkarni, R.M., and Wadsworth, M.E., "A Kinetic Study of

    Copper Precipitation on Iron· Part II",

    Trans. AIME $\underline{239}$, 1066 (1967).