Zinc-dust cementation of silver from alkaline cyanide solutions — analysis of Merrill-Crowe plant data

J.R. Parga, R.Y. Wan, and J.D. Miller

Abstract — *The direct recovery of precious metals from alkaline cyanide solution is frequently accomplished by the well-established Merrill-Crowe process involving zinc-dust cementation. This is particularly true for silver. Plant data from two operations are presented and analyzed in terms of intrinsic reaction features. In such Merrill-Crowe plants a plate-and-frame filter press acts as a semicontinuous fixed-bed reactor with a distribution of particle retention times. For the plants studied, 99% of the silver is recovered with a solution retention time of less than 2 min. Differences in plant operating conditions and product characteristics can be related to the nature of the surface deposit of silver which forms on the zinc particles. From laboratory experiments and plant samples it has been found that the presence of lead in the system activates a change in the silver deposit morphology to the dendritic state which affects the rate of silver deposition as well as the filter cake porosity. Finally the plate-and-frame press is considered from an engineering perspective as a semicontinuous fixed-bed reactor to describe the behavior of the system.*

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Introduction

The recovery of precious metals from dilute alkaline cyanide solution by zinc-dust cementation has been practiced since the late 19th century. The technology was patented in 1894 by Sulman and Pichard and was first applied at the Deloro mine in Ontario, Canada (Leblanc, 1942). C.W. Merrill improved the process and used this process strategy at the Homestake mine in 1897. Later, in 1916, T.B. Crowe's vacuum deaerator was incorporated to remove oxygen from cyanide leach solution to significantly improve the efficiency of the precipitation reaction (Leblanc, 1942).

Considerable research has been reported on the characteristic features and mechanistic details of cementation reactions, and this literature has been reviewed in terms of electrochemical theory and transport phenomena on several occasions (Wadsworth, 1986; Miller, 1981; Strickland and Lawson, 1971). In most cases, the cementation reactions follow first-order reaction kinetics and generally are limited by diffusion of the noble metal ion through the mass-transfer boundary layer. The structure and morphology of the reaction product have a significant effect on reaction kinetics, either enhancing the rate in some cases or passivating the surface in other cases.

Only modest attention has been paid to the silver cementation reaction in alkaline cyanide solution. Von Hahn and Ingraham (1968) studied the kinetics of silver cementation on a rotating zinc cylinder in

deoxygenated alkaline silver cyanide solution. They found that the rates were dependent on peripheral velocity and the cementation rates obeyed a pseudo-first-order rate at the beginning of the experiments. The deposits were dense and adherent and had little or no influence on the reaction velocity constant except at very low free-cyanide concentration. Ritchie and Staunton (1984) reported their results on the electrochemical study and electron-microscopic features of the silver/copper cementation reaction in cyanide solutions. In this case, the silver deposit appeared to be clustered around anodic areas on the copper surface.

Most recently research in our laboratory has provided further information regarding details of the intrinsic reaction kinetics for the $Ag^+/Zn(CN^-)$ system, and these results are discussed in another publication (Parga, et al., 1987). In this contribution, the plant data on silver cementation from alkaline cyanide solution by zinc dust are analyzed in terms of the intrinsic reaction kinetics and the nature of the surface deposit. Further, an engineering analysis of the plate-and-frame press as a semicontinuous fixed-bed reactor is presented in order to describe the operating characteristics of the system. The Escalante plant operations in Utah and the Silver Peak plant operations in Nevada are considered.

Characteristic features of the cementation reaction

Before evaluating the plant data, it is useful to review recent findings regarding the intrinsic reaction kinetics. The recovery of metallic silver by cementation with zinc dust is an electrochemical process involving the oxidation of zinc and the reduction of silver cyanoanions. The overall stoichiometry for the reaction is as follows:

$$2Ag(CN)_2^- + Zn \rightarrow 2Ag + Zn(CN)_4^{-2} \qquad (1)$$
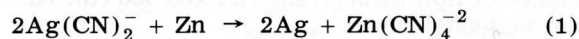
The cementation reaction kinetics were studied by batch reaction of suspended zinc dust in an oxygen-free environment (<0.5 ppm O_2) and generally the results were found to conform to the first-order rate expression to over 99% silver removal as shown in Fig. 1. Further, these rate data have the expected inverse first-order dependence on particle size for a mass-transfer, boundary-layer, diffusion-controlled reaction. The experimental reaction velocity constants are slightly smaller than the expected mass-transfer coefficients as shown in Table 1.

The effect of the silver deposition (0.231 mg/cm^2) on the rate of cementation was not significant. Subsequent examination of the cementation reaction product showed that the silver formed a uniform layer around the zinc (see Fig. 2), and it is expected that this layer has sufficient porosity to account for the observed boundary-layer, diffusion-controlled, first-order reaction kinetics.
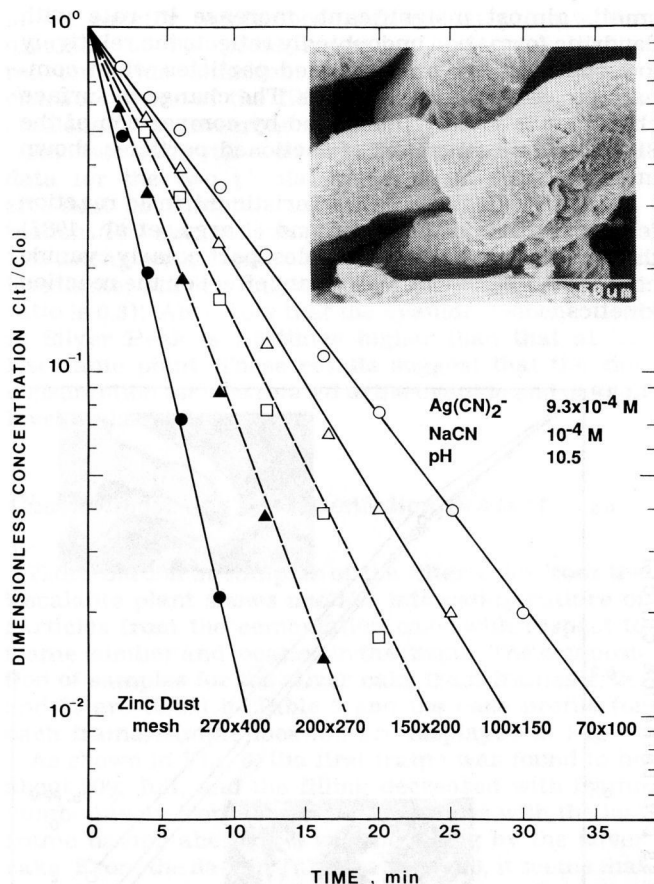

Fig. 1 — First-order reaction kinetics plot for silver cementation from alkaline cyanide solution. Initial silver concentration 100 ppm.
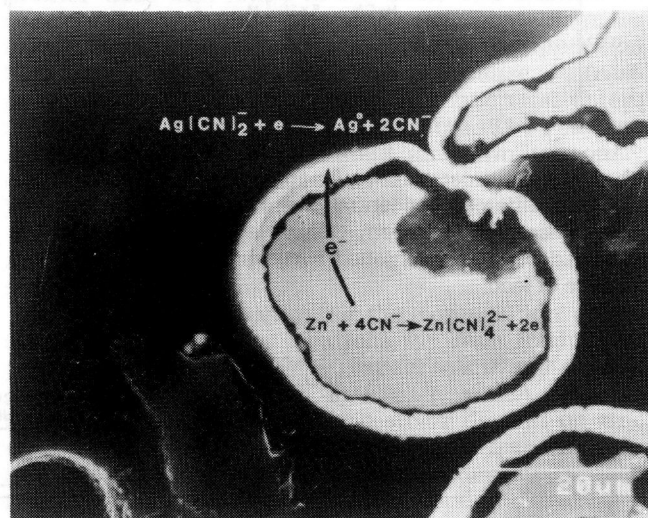

Fig. 2 — SEM photomicrographs of sectioned zinc particles with cemented silver deposited from alkaline cyanide solution.

Further, in this work (Parga, et al., 1987), the structure of the silver deposit was found to be sensitive to small additions of other metal ions, lead in particular. Under these circumstances, a dendritic silver deposit can form (depending on the concentration of lead) as shown in Fig. 3, and the reaction kinetics exhibit a slightly enhanced rate region but significantly less than that observed in other cementation reactions studied with rotating-disk geometry. This rather

Table 1 — Comparison of Experimental Reaction Velocity Constants and Calculated Mass-Transfer Coefficients for Suspended Particles

Particle Size, mesh	Experimental Reaction Velocity Constant, cm/sec	Calculated Mass-Transfer Coefficient, cm/sec
100 × 150	1.88×10^{-2}	2.2×10^{-2}
150 × 200	1.76×10^{-2}	2.4×10^{-2}
200 × 270	1.63×10^{-2}	2.2×10^{-2}
270 × 400	1.62×10^{-2}	3.2×10^{-2}

Source: Parga, et al., 1987.
$Ag = 100$ ppm (9×10^{-4} M), NaCN $= 10^{-2}$ M, pH $= 10.5$.

small, almost insignificant, increase in rate with dendritic formation undoubtedly reflects the relatively low slip velocity for suspended particles when compared to rotating-disk systems. The change in surface character is vividly illustrated by comparison of the SEM photomicrographs of sectioned particles shown in Fig. 3.

In addition to these characteristic intrinsic reaction features, it has also been found (Parga, et al., 1987) that solution chemistry variables, particularly cyanide concentration, have a significant effect on the reaction kinetics.
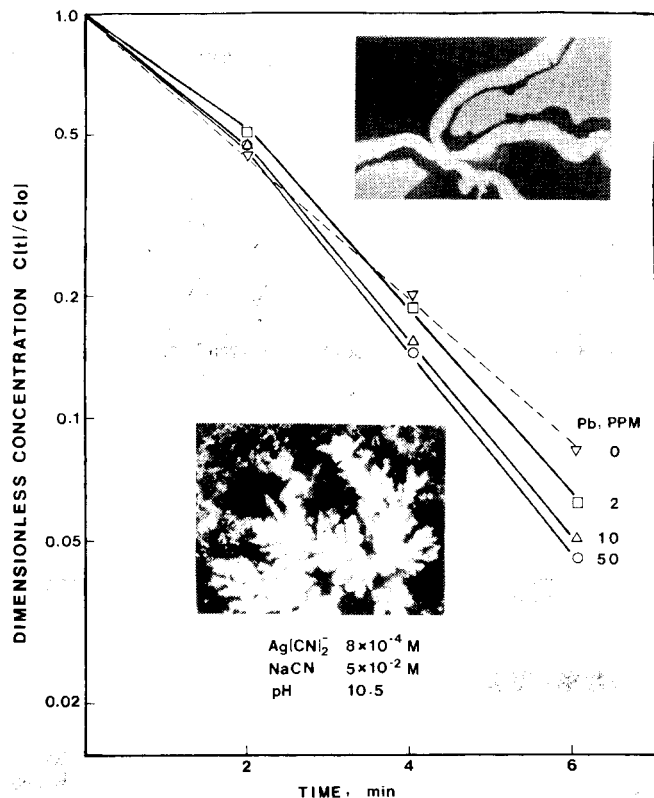

Fig. 3 — First-order reaction kinetics plot for silver cementation with different concentrations of dissolved lead. Initial silver concentration 85 ppm. Comparison of the nature of the surface deposit for sectioned particles in the presence and absence of lead.

Plant operations

The extraordinary efficiency of the zinc-dust precipitation reaction for silver recovery requires that the pregnant leach solution first be clarified and deaerated before reaction initiation. Deaeration decreases the tendency of the silver to redissolve by chemical reaction with oxygen from the atmosphere. A typical flowsheet for silver recovery by cementation is shown in Fig. 4. The pregnant leach solution is clarified by filtration. The clarified solution is deoxygenated in a vacuum tower. In the plant, the zinc dust (99.9% zinc, spherical in shape, and 97% -45 μm) is added to a small mixing cone, through which an auxiliary stream of barren cyanide solution passes, carrying the zinc dust into the feed pipe. The cementation reaction starts at this point and is completed as the zinc particles are collected and held in the filter press. For continuous operation, a process will have three filter presses in parallel so that one filter can be cleaned while the other two are in operation, typically on a seven-day cycle. When a cycle is completed, the cake is blown dry with air, the press is opened, and most of the cake readily falls into a wheeled tray placed beneath the press. The remainder of the cementation cake is removed by scrapers. Normally, the filter cake is soft but sometimes becomes hard as a result of oxidation and the presence of calcium carbonate.

It is evident that the cementation reaction occurs both in the pipe and in the plate-and-frame filter press. The filter press acts as a semicontinuous fixed-bed reactor with accumulation of zinc dust and cemented silver during the plant cycle of approximately one week. Of course, most of the time the zinc particles are stationary in the press as they react. This situation makes detailed analysis of the system somewhat difficult because each zinc particle has a different retention time in the reactor and mass-transfer coefficients for flow through such a fixed bed (the cake) are not well-established.

A typical plate-and-frame press is shown in Fig. 5. The pregnant solution with the zinc dust is pumped under pressure into the filter cavities. Typically diatomaceous earth is used as a precoat for the chambers and the zinc dust particles covered with silver are captured at this surface or by the cake while permitting the clarified barren solution to pass through. Filtration generally proceeds until the chambers are filled with the cementation product. By releasing and shifting the plates, the cementation reaction product is removed as cake, and the filter is ready for reuse.
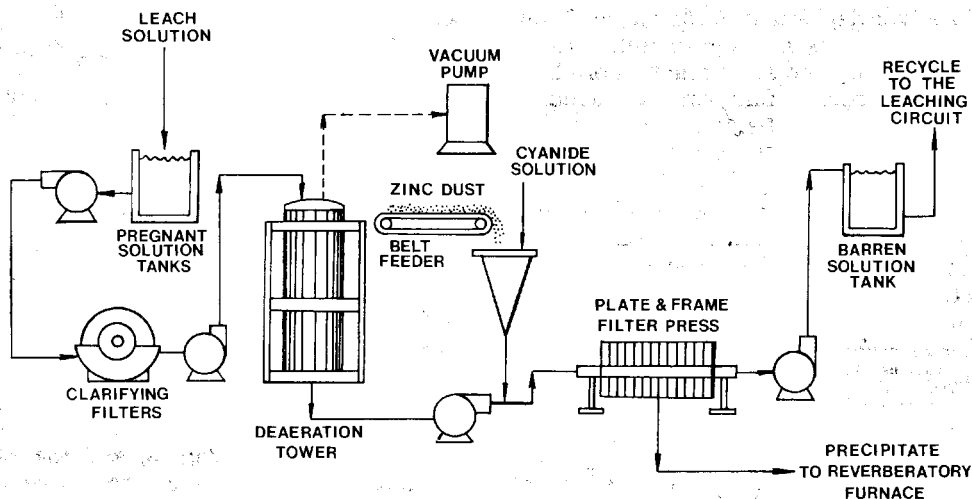

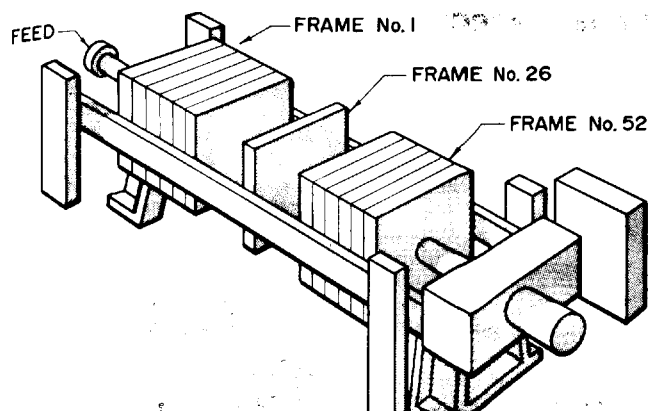Fig. 4 — Typical Merrill-Crowe flowsheet for silver cementation.

Fig. 5 — Typical plate-and-frame press, a semicontinuous fixed-bed reactor for cementation.

Data were collected from two Merrill-Crowe plants to evaluate the plant performance and to determine the characteristic features of the cementation reaction product. The two Merrill-Crowe plants examined were Escalante Silver mine, Redco Silver Inc., Enterprise, UT, and Silver Peak operations, Sunshine Mining and Minerals, Silver Peak, NV. Both plants have a Merrill-Crowe process similar to that described previously. The silver cementation reaction begins as the particles are transported through a pipe leading to the filter press. The plate-and-frame filter press collects the particles and acts as a semicontinuous fixed-bed reactor. The operating conditions for zinc-dust cementation at the two plants are presented in Table 2.

Table 2 — Plant Data for Zinc-Dust Cementation at Different Merrill-Crowe Plants

	Escalante	Silver Peak
Solution		
Flow rate, gpm	330	265
Ag, pregnant, oz per ton	2.87	2.4
Ag, barren, oz per ton	0.02	0.02
NaCN, lb per ton	6.0	10.0
Solution Retention Time		
Pipe, sec	7.0	12
Filter press, sec	112	168
Zinc Dust		
Zn/Ag by weight	0.5	1.85
Zn/Ag by stoichiometry	0.82	2.86
Filter Press		
Number of units	3	3
Units per cycle	2	2
Number of frames per unit	52	45

It is evident from Table 2 that the retention time of the solution in the press is approximately 14 times greater than the retention time in the pipe. As can be imagined from the flowsheet presented in Fig. 4, some reaction may occur passing through the pipe. Analysis of samples taken from the entry to the filter press at the Escalante plant indicates that 10% of the silver reacted in the pipe. The remaining 90% of the silver is removed in the filter press as the solution passes through the cake, giving an overall recovery in excess of 99% for a total solution retention time of approximately 2 min. Based on laboratory data (Parga, et al., 1987), it is expected that such a retention time is sufficient to remove over 99% of the silver as was observed in both plants. Of course, for this semi-continuous fixed-bed reactor, the retention time of the reacting zinc dust varies significantly. Zinc-dust particles that enter early in the cycle spend seven days

in the reactor, while those added just prior to the breaking of the press spend only minutes in the reactor. This situation leads to some interesting characteristics of the filter cake and provides for a challenging engineering analysis.

Another important observation in comparing the data for the two plants is the large difference in zinc-dust consumption and cyanide-solution concentration. The zinc consumption at Silver Peak is about 1.85 Zn/Ag weight ratio, 3.7 times the consumption at Escalante, which is only 0.5 (the stoichiometric weight ratio is 0.3). Also, note that the cyanide concentration at Silver Peak is 1.5 times higher than that at the Escalante plant. These results suggest that the zinc consumption may be related to the cyanide and oxygen level in the system.

Characterization of cementation product

Examination of samples of the filter cake from the Escalante plant shows another interesting feature of particles from the cementation cake with respect to frame number and location in the frame. The composition of samples for the silver cake from frames 1, 26, and 52 are listed in Table 3 and the cake profile for each frame/sample location are displayed in Fig. 6.

As shown in Fig. 6, the first frame was found to be about 90% full, and the filling decreased with frame number away from the front of the press with the last frame having about 20% volume filling by the silver cake. From the data in Table 3 and Fig. 6, it seems that there is only a small variance in average composition from frame to frame. Specifically the silver analysis systematically decreases from the first frame (No. 1) to the last frame (No. 52); further, it is evident that the copper content in the last frame is significantly greater than that found in the other two frames. In each frame the middle part of the cake contains more impurities with less silver compared to the upper and bottom portions of the cake. This is because the fresh pregnant leach solution mixed with zinc dust enters from the top on one side of the frame. The reacting zinc particles become sediment and simultaneously collect on the plates, creating the profiles shown in Fig. 6. Of course, the particles in the middle are those that have been in the press the shortest period of time and hence have not reacted to the same extent as those at the top and bottom.

In addition to determining the composition of the silver cake at various locations for each frame, the product was examined with respect to surface-deposit characteristics as shown in Fig. 7, which presents SEM photomicrographs of the silver deposit on zinc dust particles for the Escalante plant, frames 1, 26, and 52. The structure of the silver deposit in each frame was found to have a distinct dendritic character that is expected to increase the cathodic surface area and enhance the cementation reaction rate. This deposit morphology is similar to that observed in the laboratory when lead was added to the cementation system. This lead effect may, in fact, account for the dendritic growth. Note from Table 3 that a substantial amount of lead, typically 3%, is found in the Escalante cake. This natural lead content in Escalante's pregnant solution (±0.8 ppm Pb) is probably responsible for the dendritic morphology of the silver deposit. For such a particle structure, a faster reaction rate should be realized, and the pressure drop across the press should be minimized because of increased cake porosity.

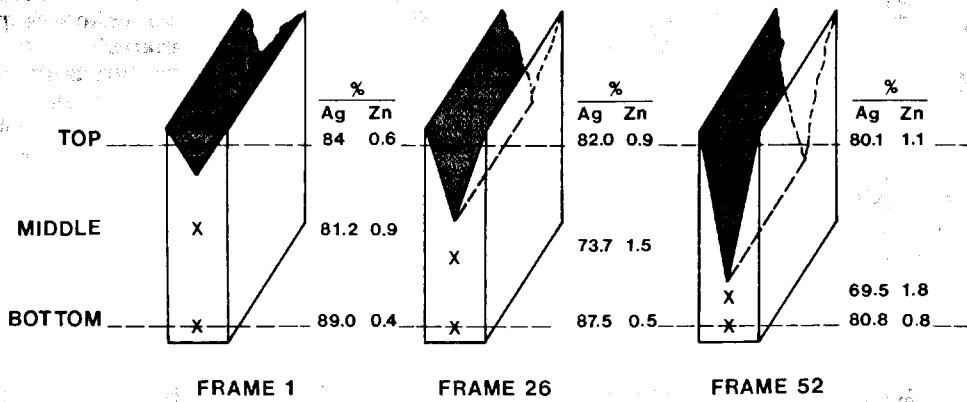# CHEMICAL COMPOSITION ANALYSIS ACROSS THE CAKE

		% Ag Zn			% Ag Zn			% Ag Zn
TOP		84 0.6			82.0 0.9			80.1 1.1
MIDDLE	X	81.2 0.9		X	73.7 1.5			69.5 1.8
BOTTOM	x	89.0 0.4		x	87.5 0.5	X x		80.8 0.8

FRAME 1   FRAME 26   FRAME 52

Fig. 6 — Cake composition for various locations in frames 1, 26, and 52 for the plate-and-frame press at the Escalante operation.

Table 3 — Chemical Composition of Silver Cake Samples from the Escalante Plant (see Fig. 6 for Sample Location)

Frame	Position	Ag	Cu	Zn	Fe	Pb
1	Top	84.0	2.2	0.6	0.1	3.0
	Middle	81.2	3.0	0.9	0.1	3.4
	Bottom	89.0	0.3	0.4	0.1	3.0
26	Top	82.0	2.2	0.9	0.1	3.7
	Middle	73.7	6.8	1.5	0.2	4.2
	Bottom	87.5	0.5	0.5	0.2	2.7
52	Top	80.1	3.1	1.1	0.1	2.4
	Middle	69.5	12.4	1.8	0.1	3.5
	Bottom	80.8	3.3	0.8	0.1	2.3

The particle surface morphologies and the chemical compositions of silver-cake samples from the Escalante and Silver Peak operations are compared in Fig. 8. From the SEM photomicrographs, it is evident that the surface deposit at Silver Peak is smooth and produces a dense layer of silver on the zinc dust particles, which is different from the dendritic product formed in the Escalante plant. The retention time for the leach solution in the filter press at Silver Peak is 1.5 times greater than the retention time for Escalante (see Table 2), and the surface deposit morphology may account for the longer retention time due both to its effect on the electrochemical reaction kinetics and its effect on the cake porosity.

Engineering analysis

In Merrill-Crowe plants, the plate-and-frame filter press acts as a semicontinuous fixed-bed reactor with accumulation of zinc dust and cemented silver. It is expected that, during the initial stage of the cycle, the reacting zinc particles are suspended in the silver cyanide solution, but most of the time the particles are stationary in the filter press as the packed bed grows. Study of the intrinsic reaction kinetics for the Ag/Zn(CN⁻) cementation system confirms that the cementation reaction follows diffusion-controlled first-order reaction kinetics. The experimental mass-transfer coefficient for this cementation reaction with suspended zinc-dust particles is estimated to be 1.6×10^{-2} cm/sec (or 0.9 cm/min) as indicated in Table 1.

The mass-transfer coefficient for reaction in a packed-bed reactor can be calculated from the following equation (Hines and Maddix, 1985):

$$J_d = k^* (N_{SC})^{2/3} V^{-1} \qquad (2)$$

where k^* is the packed-bed mass-transfer coefficient, N_{Sc} is the Schmidt number, V is the velocity of the flow, and J_d is the mass-transfer flux in the packed bed.

The flux for a packed bed can be estimated for very low Reynolds' numbers according to the equation (Hines and Maddix, 1985),

$$\varepsilon J_d = 1.09 \, N_{Re}^{-2/3} \qquad (3)$$

where ε is the porosity of the packed bed, and N_{Re} is the Reynolds' number.

In this regard, from Eqs. 2 and 3, the packed-bed mass-transfer coefficient for the Escalante operation can be estimated to be 3.5×10^{-2} cm/sec, or 2.07 cm/min (Parga, 1987).

Now, consider a particular cycle of the cementation operation. The mass balance for silver at any particular time in this semicontinuous fixed-bed reactor (filter press) can be expressed by the following general expression for a first-order reaction,

$$-Q \frac{dC}{dx} - Ak'C = A \frac{dC}{dt} \qquad (4)$$

where Q is the flow rate, cm³/min; A is the cross-sectional area of the reactor, cm²; C is the concentration of $Ag(CN)_2^-$, mol/cm³; and k' is the apparent rate constant, min⁻¹.

If the concentration gradient of the $Ag(CN)_2^-$ is considered to be a linear relationship with the transport distance x into the filter cake, then

$$\frac{dC}{dx} = -\frac{C_i - C_o}{\delta} \qquad (5)$$

where C_i is the inlet concentration of silver, C_o is the outlet concentration of silver, and δ is the filter-cake thickness at time t.

Thus, the concentration of $Ag(CN)_2^-$ can be solved as a function of time:

$$C_o(t) = \frac{QC_i}{Q + k'A\delta} + \frac{C_i k'A\delta}{Q + k'A\delta} \exp\left(-\left[\frac{Q}{A\delta} + k'\right]t\right) \quad (6)$$

The distance δ can be calculated from the packed-bed volume per unit cross-sectional area,

$$\delta = \frac{mt}{\varrho_{Zn} A(1 - \varepsilon)} \quad (7)$$

where m is the zinc-dust mass flow rate, g/min; ϱ_{Zn} is the density of zinc dust, g/cm³; A is the reactor cross-sectional area, cm²; and ε is the porosity of the packed bed.

FRAME 1

FRAME 26

FRAME 52

Fig. 7 — SEM photomicrographs of the silver deposit on zinc dust for the Escalante filter press.

By combining Eqs. 6 and 7, the concentration of silver during the reaction period can be expressed as a function of time,

$$C_o(t) = \frac{C_i}{1 + \dfrac{k'mt}{Q\varrho_{Zn}(1 - \varepsilon)}} +$$

$$\frac{C_i}{1 - \dfrac{Q\varrho_{Zn}(1 - \varepsilon)}{k'mt}} \exp\left(-\left[\frac{Q\varrho_{Zn}(1 - \varepsilon)}{m} + k't\right]\right) \quad (8)$$
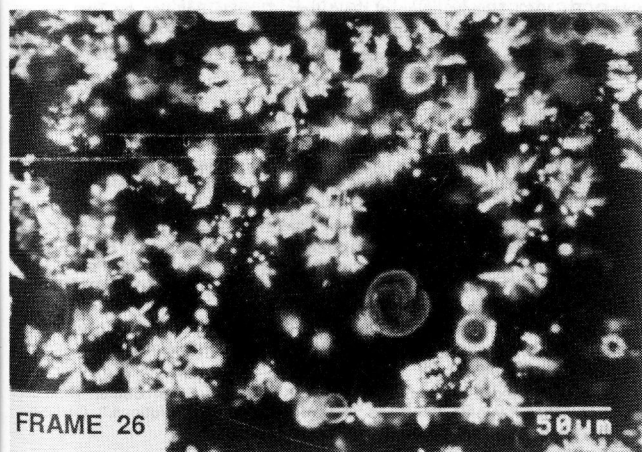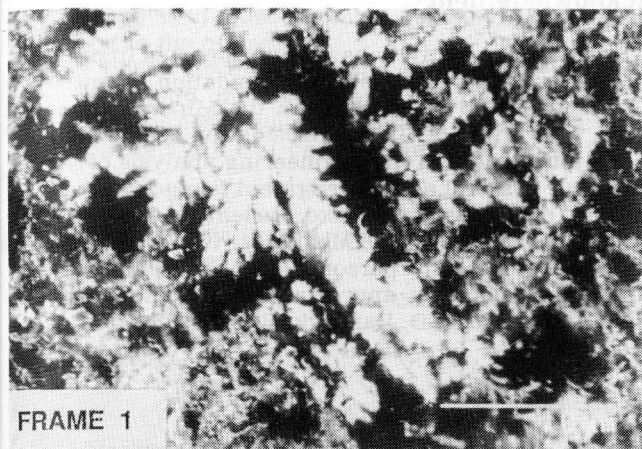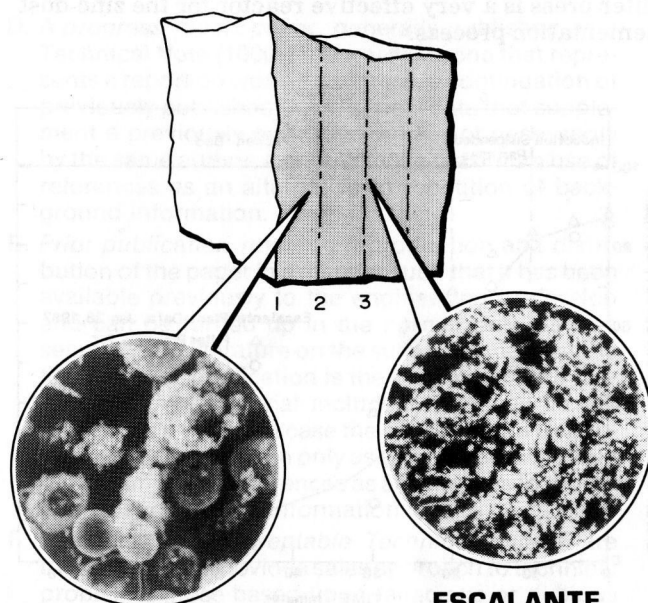

Fig. 8 — Comparison of the surface morphologies and the chemical composition of the silver cementation product for the Silver Peak and Escalante plants.

SILVER PEAK PLANT

Ag	Zn	Cu	Pb
%			
95.2	0.6	0.1	0.1
94.9	0.7	0.1	0.4
94.5	0.9	0.1	0.1

ESCALANTE PLANT

Ag	Zn	Cu	Pb
%			
86.3	0.6	0.8	2.2
82.1	0.8	1.1	2.2
60.5	1.7	12.3	4.9

Using this approach, data from the plant operations was examined to determine if the engineering analysis could be confirmed. The parameters such as filter-cake porosity ($\varepsilon = 0.60$) and zinc-dust density ($\varrho_{Zn} = 5$ g/cm³) for the Escalante plant were measured in our laboratory. The average zinc-dust particle size of the Escalante plant is 8×10^{-4} cm, and the specific surface area of the zinc dust as measured by air permeametry was found to be 867 cm²/g. Generally, the second term of the right side of Eq. 8 can be neglected, since $Q\varrho_{Zn}(1 - \varepsilon)/m \gg 1$. A plot of silver concentration vs. reaction time for Escalante plant data is compared in Fig. 9 with the predicted response according to Eq. 8. The flow rate of solution to this semicontinuous fixed-bed reactor is an important variable which has the greatest influence on the performance of the system.

The data analysis suggests that there are three periods during the operation of the plate-and-frame filter press:

- Induction Period — Suspension of zinc-dust particles flows into and fills up the filter-press chambers.
- Suspended-Particle Reaction Period — Reaction continues with suspended zinc-dust particles.
- Packed-Bed Period — Reaction with stationary zinc-dust particles in the packed bed of the filter press.

It is evident that the engineering analysis adequately explains the plant data. Though the filter press acts as a semicontinuous fixed-bed reactor with accumulation of zinc dust and cemented silver during the plant cycle of approximately seven days, the periods of induction time and suspended zinc particle reaction account for only 20 min of the total cycle time. The cementation reaction for silver recovery reaches 95% after only 1 hr of operation. It is evident that the plate-and-frame filter press is a very effective reactor for the zinc-dust cementation process.
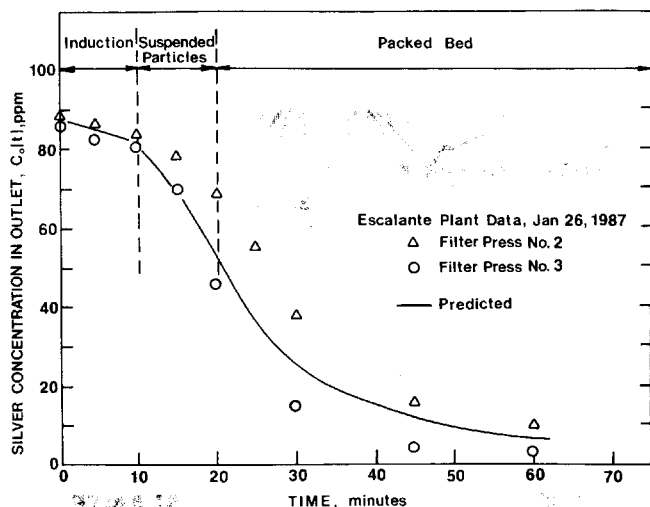

Fig. 9 — Plot of silver concentration vs. reaction time for Escalante plate-and-frame press data during cycle start-up compared with the predicted behavior.

Summary

The zinc-dust cementation reaction of silver from alkaline cyanide solution is controlled by mass-transfer processes as has been established in laboratory investigations. Plant data for silver recovery from cyanide solution by the zinc-dust cementation process using a plate-and-frame filter press as a semicontinuous fixed-bed reactor have been presented and analyzed. Data

were collected from two Merrill-Crowe plants: the Escalante Silver mine, Redco Silver Inc., Enterprise, UT, and the Silver Peak operations, Sunshine Mining and Minerals, NV, and include operational details, plant performance, retention-time calculations, and product filter-cake characterization. The presence of lead in the system has a marked effect on the silver deposit morphology as evidenced by comparison of the dendritic product from the Escalante Silver mine with the product from the Silver Peak operation.

In addition, engineering analysis of the plate-and-frame filter press operation as a semicontinuous fixed-bed reactor adequately explains the plant data obtained during start-up of a particular cycle. ∎

Acknowledgment

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