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The Adsorption of Gold Cyanide onto Porous Adsorbents: Relation between Liquid-Phase Concentration, Suspended Solids, and Mass-Transfer Mechanisms

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ABSTRACT

Much progress has been made during the last decade on carbon-in-pulp and resin-in-pulp technology for the extraction of gold and silver from leached pulps. In this study a systematic investigation was conducted on the mass transfer of gold cyanide to activated carbon and ion-exchange resins in suspended solids under conditions of different gold solution-phase concentrations. The different mass transfer phenomena were studied by measuring the concentration profile of gold in solution. Two distinct mass transfer mechanisms have been identified: 1) at low gold solution-phase concentrations, where the rate of adsorption is controlled by film diffusion, the presence of fine inert particles had no effect on either the rate of adsorption or the equilibrium loading of gold cyanide; 2) at high gold solution-phase concentrations, where intraparticle diffusion becomes rate controlling, the inert particles affected the rate of adsorption of gold cyanide for both the adsorbents. Furthermore, the inert particles did not affect the equilibrium loading of gold at the high solution-phase concentration. It was also found that under certain conditions the silica particles in suspension enhanced the mass transfer of gold cyanide to the adsorbents. This was attributed mainly to the fact that the silica particles act as an adsorbent, thereby increasing the actual loading of gold cyanide onto the adsorbents.

INTRODUCTION

The use of activated carbon has revolutionized the extractive metallurgy of gold. At the same time, resins are being examined as possible alternatives to activated carbon because they have been shown to exhibit a number of significant advantages (1). Although resin-in-pulp technology has been used throughout the world for many years in the processing of ura-

nium ore, it has been applied only recently in pilot-plant tests on gold. Most leached slurries contain various fine particles of silica, shales, or clayey materials. Activated carbon becomes easily fouled by these materials and requires frequent thermal regeneration. Resins are less selective than activated carbon for gold cyanide over base metal cyanides prevalent in cyanide leach liquors.

Fleming and Nicol (2) observed that the presence of inert solids in a pulp reduced the rate of gold extraction by activated carbon. Although numerous authors (3-5) observed the same effect, there are some investigators who claim the opposite (6). The experimental conditions used in the latter case typically entailed solutions containing relatively low gold solution-phase concentrations (conditions atypical of those prevailing in a practical plant situation) whereas, without exception, all the other researchers employed conditions of high gold concentrations. The experiments carried out in this study have indicated that different adsorption mechanisms become operative under conditions of different initial gold concentrations.

Boydell and Haines (7) showed that resin particles could be fouled through silica polymerization inside the resin bead as well as on the outside, and thereby retarded diffusion of species to the resin. Existing studies on the mass transfer of solid particles to adsorbents in agitated systems have included the dissolution of solid particles, whereas entirely inert particles were used in the present study. Jordi et al. (4) found that in the presence of fine silica particles, the gold profile on activated carbon is adversely affected. Although these authors claim that the silica particles were inert, the pH range in which these experiments were performed indicates that dissolution of silica must have taken place.

In spite of the practical importance of both the carbon-in-pulp and resin-in-pulp processes, analysis of the mass transfer phenomena associated with the adsorption of aurocyanide onto these adsorbents in suspended solids has not received adequate attention. Recently, Ahmed et al. (8) modified the homogeneous surface diffusion model to allow for the outside blinding of the macropores of the carbon by fine solid material. However, they failed to distinguish clearly the conditions which would favor blinding of the macropores.

It is the objective of this paper to investigate the different mass transfer phenomena associated with the adsorption of gold cyanide in suspended solids. Furthermore, it will be shown that the kinetic parameters in a film diffusion/intraparticle diffusion model are affected by the presence of inert solids in the case of high gold concentrations, whereas the inert particles have no effect on the parameters if the gold concentrations are low.

EXPERIMENTAL

Potassium aurocyanide was used as an adsorbate. All reagents were of analytical grade, and distilled water was used throughout. The 1.0 to 2.0 mm size fraction of a commercial coconut shell activated carbon, Le Carbone G210 AS, with an apparent density of $835 \text{ kg}\cdot\text{m}^{-3}$, was used. The resins used in this study were Duolite A161 (macroporous) and DU A101 (microporous) with an average bead diameter of 0.9 mm. Atomic absorption was used for the analysis of gold cyanide in solution. Precipitated silica and alumina with particle sizes smaller than $15 \mu\text{m}$ were used. A pH of 9.5 was maintained in all experiments by manually adding small amounts of potassium hydroxide solution or hydrochloric acid.

Equilibrium and batch adsorption tests were both conducted in a stirred tank with an internal diameter of 11 cm, a height of 15 cm, and three evenly spaced baffles of 1-cm width. Agitation was provided by a flat blade impeller of 6-cm width and 5-cm height, driven by a Heidolph variable speed motor.

MATHEMATICAL MODEL

A dual resistance model involving both external film diffusion and intra-particle surface diffusion was applied to the profiles for the uptake of gold cyanide by activated carbon or ion-exchange resins in a stirred batch reactor in order to estimate kinetic parameters. It is further assumed that:

The carbon and resin particles can be treated as equivalent spheres for modeling purposes.

The radial transport of gold cyanide into the pores can be ascribed to a surface diffusion mechanism.

Pore diffusion is assumed to be negligible.

Accumulation of metal cyanide in the liquid phase within the pores of the carbon or resin is negligible.

The adsorption reaction on the carbon, and the ion-exchange reaction on the resin, occur instantaneously, so that equilibrium exists at the solid-liquid interface.

The liquid-phase material balance for a batch stirred tank reactor yields

$$-\partial c/\partial t = (C - C_s)k_f A \beta \quad (1)$$

where $A = 6M/\sigma d_p$ for carbon and $6\epsilon V_R/d_p$ for resin.

The mass balance for surface diffusion inside the pores is

$$\frac{\partial q}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial q}{\partial r} \right] \quad (2)$$

If no accumulation occurs at the external surface of the carbon or resin, the boundary condition becomes

$$k_f(C - C_s) = \frac{D\phi}{\beta} \frac{\partial q}{\partial r} \Big|_{r=R} \quad (3)$$

The phase conversion factor $\phi = \sigma$ for carbon and $1/\epsilon$ for resin.

Equilibrium expressions were used to relate q_s and C_s at $r = R$. In general, these expressions can be written as

$$q_s = f(C_{s,1}, C_{s,2}, \dots, C_{s,n}) \quad (4)$$

where n is the number of solutes.

It was found that a Freundlich isotherm gave the best fit for the equilibrium of activated carbon, while a Langmuir isotherm gave the best fit for ion-exchange resin.

Equation (2) was transformed to an ordinary differential equation by the use of average metal loadings in the pores. The value of C_s in Eq. (4) is guessed at each step, and the calculation of Eq. (2) was repeated with a 4th-order Runge-Kutta method until Eq. (3) was satisfied. By approximating the loading gradient at the external particle surface by a quadratic driving force (9), Eq. (4) was written as a normal algebraic equation. The value of the film transfer coefficient k_f can be estimated from the initial rate of a batch experiment as explained by Van Deventer (10), while the surface diffusivity D can be estimated by using the model in a least-squares routine.

RESULTS AND DISCUSSION

Effect of Solids in Low Aurocyanide Concentrations

Solutions of low gold concentration are those typically found in the practical plant situation. In these tests the adsorbent particles were pretreated with silica or alumina, rinsed with water, and then contacted with a clear 8 ppm gold cyanide solution. In the pretreatment step the adsorbents were soaked in 2 g/L of either silica or alumina at room temperature. Figure 1 indicates clearly that the intrusion of fine silica particles did not affect either the rate of adsorption or equilibrium loading of gold cyanide

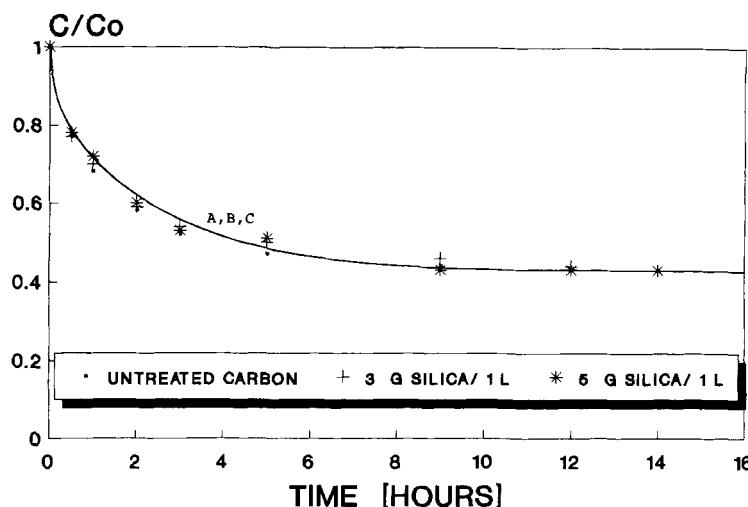


FIG. 1 Inhibited mass transfer of gold cyanide to activated carbon owing to fouling by silica particles. $C_0 = 8 \text{ mg/L}$; $V = 1.0 \text{ L}$; $N = 250 \text{ rpm}$; $M = 1.0 \text{ g}$.

on the adsorbents. From Table 1 it can be seen that the film transfer coefficient is independent of solids concentration.

Microscopy revealed that the inert silica and alumina were evenly distributed throughout the resin and carbon beads. Therefore, one would expect that the intrusion of fines should influence the diffusion of gold cyanide into the pores of the adsorbents. The results presented here, how-

TABLE 1
Sensitivity of Mass-Transfer Parameters to Fouling of Adsorbents by Silica Slurry

No.	Conditions	$k_f \times 10^5$ (m/s)	$D \times 10^{12}$ (m^2/s)
A	Untreated carbon	3.81	4.6
B	Carbon pretreated with 3 g silica/L	3.81	4.6
C	Carbon pretreated with 5 g silica/L	3.81	4.6
D	Untreated resin	3.08	4.2
E	Resin pretreated for 15 min	2.95	3.1
F	Resin pretreated for 60 min	2.95	2.5
G	Carbon pretreated for 15 min	3.78	3.2
H	Carbon pretreated for 60 min	3.78	1.5
I	Carbon pretreated with 3 g <i>untreated</i> silica/L	3.84	4.8

ever, indicate the opposite. In this case, the relative low gold solution concentration favored conditions for film diffusion. This implies that if the adsorption process is controlled by film diffusion, the effect of fine solids on the concentration profile of gold in solution is negligible.

Effect of Solids in High Aurocyanide Concentrations

The tests performed here were conducted in a similar manner as previously, except that the gold cyanide concentration used was 20 ppm. From the results illustrated in Figs. 2 and 3, it is evident that the fine solid material affected the rate of adsorption for both the adsorbents. Whereas only slight differences were observed in the k_f values for the untreated and pretreated adsorbents, the surface diffusivity D was largely affected, as depicted in Table 1. It was interesting to note that the equilibrium conditions were not affected for both the adsorbents. Figure 4 clearly shows a decrease in the value of the surface diffusivity D with an increase in the pretreatment period for both the ion-exchange resin and activated carbon. This means that if the adsorption process is controlled by intraparticle diffusion, such as in calcine treatment plants where the concentration in solution and the loadings on the adsorbents are high, the effect of fine solids on the mass transfer of gold cyanide can be quite significant. These fouling tests were repeated with a gel resin (DU A101), and as could be

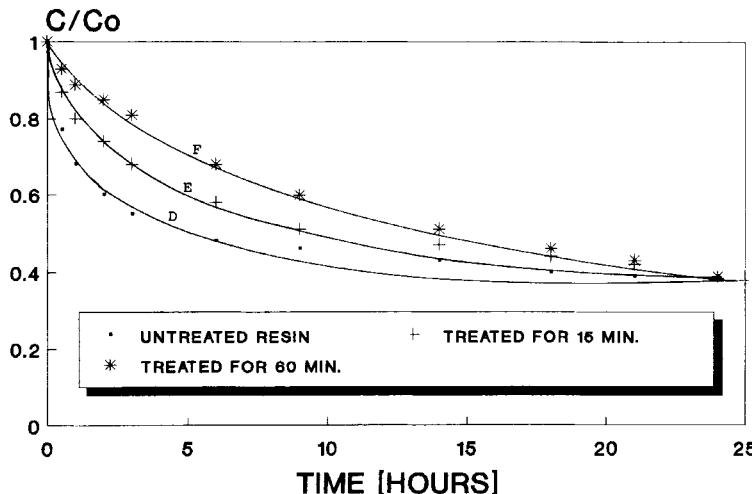


FIG. 2 Inhibited mass transfer of gold cyanide to activated carbon owing to fouling by silica particles. $C_0 = 20 \text{ mg/L}$; $V = 1.0 \text{ L}$; $N = 250 \text{ rpm}$; $M = 1.0 \text{ g}$.

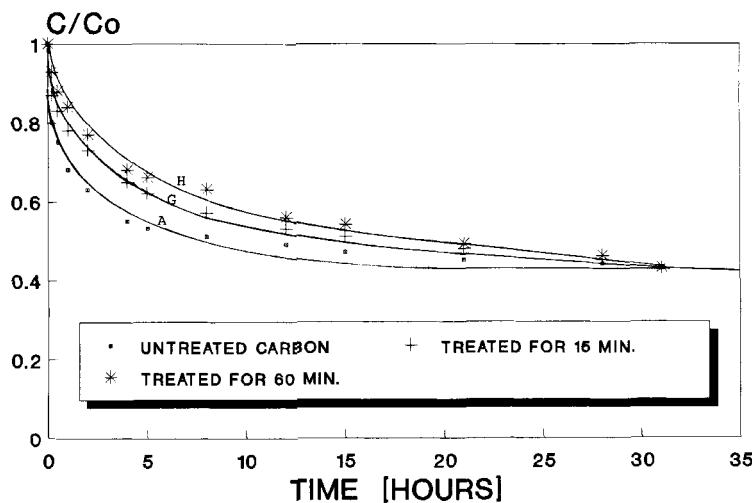


FIG. 3 Inhibited mass transfer of gold cyanide DU A161 owing to fouling by silica particles.
 $C_0 = 20 \text{ mg/L}$; $V = 1.0 \text{ L}$; $N = 250 \text{ rpm}$; $V_R = 2.0 \text{ mL}$.

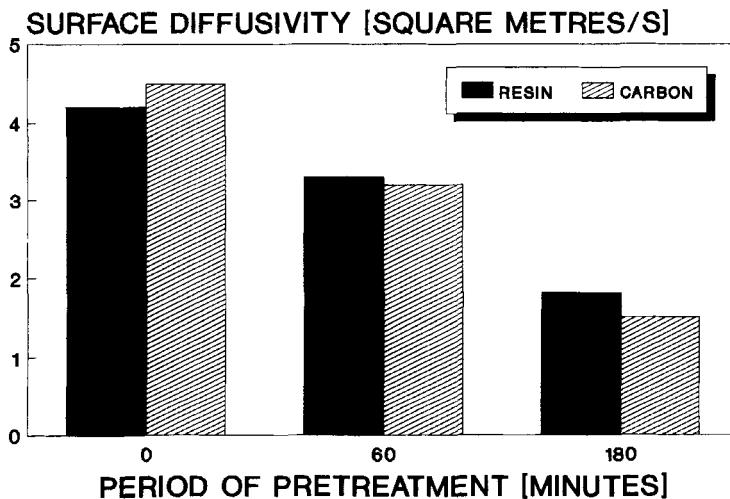


FIG. 4 The effect of pretreatment on the diffusivity (pretreated with fine silica particles).

expected, the silica or alumina had no influence on the concentration profile of gold in solution.

Enhanced Mass Transfer of Aurocyanide by Fine Particles in Suspension

In the previous two sections the silica particles were oven-dried at 200°C prior to the adsorption tests. In these tests, however, the silica particles were not preheated prior to adsorption, so that these particles were directly transferred into the reactor together with the adsorbents for the pretreatment step. From the results illustrated in Fig. 5 and Table 1, it is evident that the intrusion of silica into the carbon matrix enhanced the mass transfer of gold cyanide, which is manifested in the increase in the value of D . The only way in which this phenomenon could be explained was by assuming that the silica particles "adsorbed" gold from solution, diffused into the carbon pores, thereby enhancing the effective mass transfer of gold cyanide.

Although not investigated here, one would expect that if the particle size of the silica is large compared to the pore size of the adsorbent, *pregrubbing* of gold cyanide would take place. This would in turn affect the model equations, as an additional term should be added to the mass balance for gold cyanide in the liquid phase, and the same accumulation

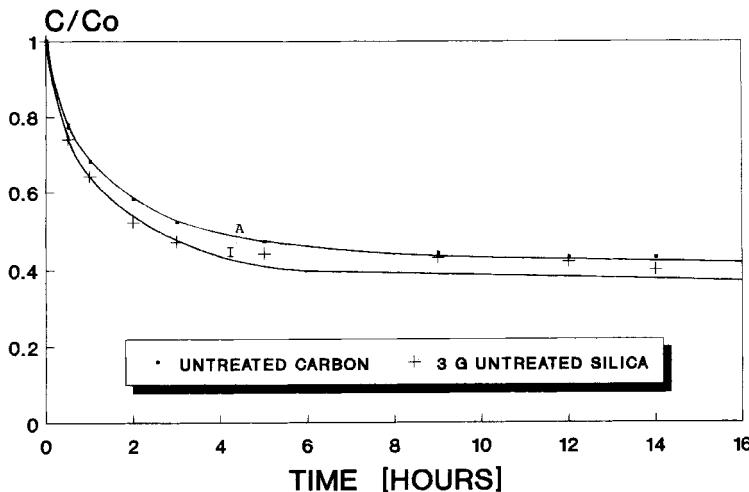


FIG. 5 Enhanced mass transfer of gold cyanide by fine silica particles. $C_0 = 20 \text{ mg/L}$; $V = 1.0 \text{ L}$; $N = 250 \text{ rpm}$; $M = 1.0 \text{ g}$.

term should be added to the material balance equation for gold in the solid ore phase.

CONCLUSIONS

In the present study, two distinct mass transfer mechanisms for the adsorption of gold cyanide onto adsorbents have been identified: 1) at low gold solution-phase concentrations, where the rate of adsorption is controlled by film diffusion, the presence of fine inert particles had no effect on either the rate of adsorption or the equilibrium loading of gold cyanide; 2) at high gold solution-phase concentrations, where intraparticle diffusion becomes rate controlling, the inert particles affected *only* the rate of adsorption for both the adsorbents. Furthermore, it was found that under conditions of no preheating, the silica particles in solution enhanced the mass transfer of gold cyanide to the adsorbents. This was attributed to the fact that these particles "adsorb" the gold, diffused into the pores of the adsorbent, and thereby increasing the actual gold loading.

SYMBOLS

C	solution phase concentration (mg/L)
D	surface diffusion coefficient (m^2/s)
d_p	particle diameter (m)
k_f	external film transfer coefficient (m/s)
M	mass of carbon (kg)
N	rotational speed
q	gold loading on carbon (g Au/kg carbon) or resin (g Au/ m^3 wet-settled resin)
r	radial variable (m)
R	radius of adsorbent particle (m)
t	time variable (s)
V	volume of liquid in batch reactor (m^3)
V_R	volume of wet-settled resin (m^3)

Greek

σ	apparent density
Φ	phase conversion
ϵ	volumetric fraction of wet-settled resin
β	availability factor

Subscripts

e equilibrium
0 initial condition
s surface of adsorbent

ACKNOWLEDGMENT

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