KINETICS OF AUROCYANIDE LOADING WITH AN

ANION EXCHANGE RESIN

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Abstract

Synthetic ion-exchange resins offer an attractive alternative to carbon for the recovery of gold from alkaline cyanide solutions. This paper describes an investigation of the kinetics of loading gold onto a new weak-base resin (PAZ-4) designed specifically for gold and silver cyano anions. The uptake of gold was determined at temperatures from $25^{\circ}C$ to $45^{\circ}C$, pH's from 8.5 to 11.5, and free cyanide concentrations from 0.20 g/l to 0.80 g/l. The adsorption rate increases strongly with decreasing pH and to a lesser extent with increasing free CN^- concentration. Temperature was observed to have very little effect on the loading kinetics.

The initial loading kinetics obey a shell-progressive (shrinking core) diffusion mechanism and can be explained mathematically by the classical diffusion equation for spherical particles. An exchange mechanism involving reaction between aurocyanide and hydrogen cyanide is proposed to explain the results.

Introduction

Activated charcoal has been used in conjunction with cyanidation for nearly a century to recover gold and silver. Adsorption of gold from alkaline cyanide solution by activated carbon has developed into an extremely efficient and economical method of treating low grade ores and tailings. The advances, especially in carbon-in-pulp (CIP) technology, have been truly remarkable. However, carbon by its very nature has some process limitations: namely, slow loading rates, poor chemical specificity, and difficult desorption characteristics. Synthetic ion exchange resins offer an attractive alternative to carbon for the recovery of gold from alkaline cyanide solutions. Development of an advanced resin-in-pulp (RIP) process for gold is highly desirable and has received considerable attention in recent years. (1,2,3,4)

Probably the most attractive feature of anion-exchange resins is the ability to design and produce superior chemical and structural characteristics. Fleming and Cromberge (1) have listed a few of the advantages of resins over carbon. For aurocyanide extraction, anion-exchange resins typically:

(1) exhibit faster kinetics and higher equilibrium loadings,
(2) can be eluted at low temperatures and pressures,
(3) do not require thermal reactivation, and
(4) are not as sensitive to fouling and poisoning.

Some of the disadvantages that were cited for resins currently available are:

(1) less selectivity
(2) small particle sizes
(3) poor physical strength
(4) low bead density.

The hope for resins is that these limitations can be overcome by the appropriate advances in organic synthesis. Despite these limitations, work is proceeding in application of resins in precious metal processing.

Strong- or weak-base resins can be used to extract gold from cyanide solution. Strongly basic anion-exchange resins exhibit loading behavior which is independent of pH. They are non-selective and are difficult to elute, often requiring complex procedures to obtain gold free of impurity metals. (5) Weak-base resins on the other hand, show extractive characteristics which are dependent on the solution pH. Exchange only occurs in the "acid" form and not in the unionized or "free base" form of the resin. As a consequence, exchange of aurocyanide can be considered a two step process:

$$|-NR_2 + HX = |-NR_2H^+X^- \qquad [1]$$

$$|-NR_2H^+X^- + Au(CN)_2^- = |-NR_2H^+ Au(CN)_2^- + X- \qquad [2]$$
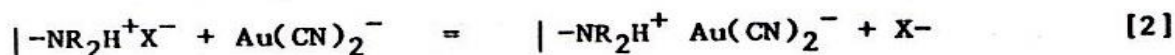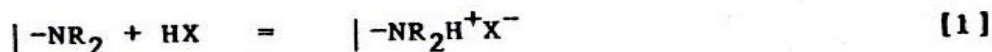
where $|-$ represents the polymeric resin matrix.

Anion exchange behavior of weak-base resins is approximately equivalent to strong-base resins when they are in the protonated form or when the solution pH is sufficiently low to cause protonation. When the resin is not protonated (neutral solutions), weak to moderately strong complexes are not adsorbed. Very strong complexes, on the other hand, can be extracted by a hydrolysis mechanism which is shown here for aurocyanide:

$$|-NR_2 + Au(CN)_2^- + H_2O = |-NR_2H^+ Au(CN)_2^- + OH^- \quad [3]$$

The simple acid-base properties of weak-base resins make them more attractive for gold recovery because of their straight forward elution. However, most weak-base resins have active groups with pK values at pH between 6 and 8. Whereas, most gold cyanide leach operations have solution with pH values ranging from 10 to 11.

Adsorption under slightly acidic conditions followed by elution with alkaline solutions would be one possibility, but this approach would be expensive and may impose safety problems. Therefore, the pK of the active groups is critical in the application of weak-base type resins in ion exchange processes to recover aurocyanide. In this regard, there has been interest in developing new weak-base resins with higher pK values. It is conceivable that an efficient ion-exchange process could be developed with a resin having pK's in the range pH 8 to pH 10. The objective of the current investigation is to examine a new resin that fits into this category.

Since one of the most important advantages of resins over activated carbon is faster loading rates of aurocyanide, this study was carried out in an attempt to elucidate the kinetics of gold cyanide adsorption. Adsorption rates are reported for various pH's, temperatures, and free cyanide concentration.

Experimental

The anion exchange resin (PAZ-4) used in the experimental work was obtained from SELA, Inc., New York. The as received resin had the size distribution shown in Table I. Monosized samples of resin used in the loading experiments were prepared by standard sieving methods. Unless specified otherwise, the resin size used was 14x20 mesh (1190x840 μm). Prior to use, the samples of resin were converted to the chloride form by treatment with hydrochloric acid.

Table I. Particle Size Analysis of PAZ-4 Resin

Size Range Mesh	μm	Wt%
-10 + 14	-1651 + 1168	1.1
-14 + 20	-1168 + 833	38.3
-20 + 28	-833 + 589	38.8
-28 + 35	-589 + 417	16.5
-35 + 48	-417 + 295	4.0
-48 + 65	-295 + 208	.6
-65	-208	.3

The PAZ-4 resin is reported to be an improved version of A-7. (6) Common A-7 is classified as a weak-base resin containing secondary amine functional groups and a pheno-formaldehyde matrix. PAZ-4 is synthesized in an ultrasonic chamber which imparts a high degree of surface porosity and a large internal capillary network. Figure 1a shows 14x20 mesh resin particles which are typically of irregular shapes and Figure 1b reveals the extremely porous nature of the particle surface.
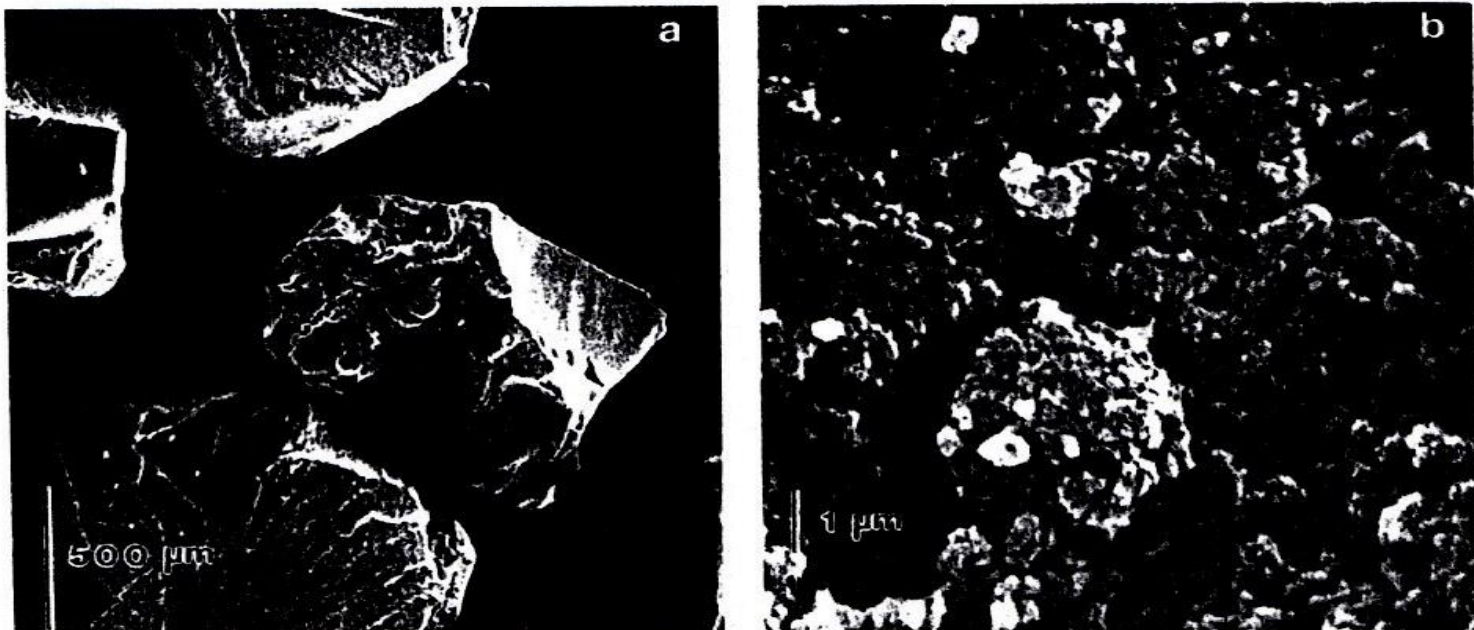
Figure 1 - Scanning electron micrographs: (a) typical 14x20 mesh PAZ-4 resin particles, and (b) surface features of the PAZ-4 resin.

A 1000 g/ml gold cyanide stock solution was prepared by dissolving gold powder (supplied by D. F. Goldsmith Chemical & Metal Corp., Evanston, Illinois) in a sodium cyanide solution. Gold cyanide solutions for each experiment were prepared by diluting the stock solution to the appropriate concentration and using the appropriate sodium cyanide additions to establish the free cyanide concentration. Sodium hydroxide and hydrochloric acid were used to adjust the pH values. All reagents used were of reagent-grade quality and the water used was distilled and deionized.

Kinetic Tests

All experiments were performed in a four neck one-liter glass reactor with a clamp-held lid containing openings for a stirrer, thermometer, solution sampler and a pH electrode. Constant temperatures were maintained with a Cole-Palmer Immersion Heater Circulator. Loading experiments were conducted by charging a weighed portion of prepared resin into 0.5 l of solution at the desired temperature, stirring with a 3-blade impellor at 500 rpm, and withdrawing solution samples of about 5 ml at periodic intervals. Solutions were analyzed for gold on a Perkin Elmer Model 2380 atomic adsorption spectrophotometer. Gold loading on the resin was determined from solution depletion as measured by AA analysis and reported per unit weight of dry resin.

Equilibrium Tests

In some instances equilibrium data were obtained from kinetic tests which were allowed to run for extended times. Other eqilibrium tests were carried out in 250 ml Erlenmeyer flasks containing 1 gram of resin in 0.1 l of aurocyanide solution. A wrist-action shaker was used to agitate the system. The time allowed for equilibration was 24 hours. The equilibrium concentration of gold was determined by atomic adsorption spectrophotometry. There was no attempt to analyze the gold content of the resin directly.

Results and Discussion

The ion exchange properties of weak-base resins are influenced primarily by the pH value of the solution in contact with the resin. To examine this effect for the PAZ-4 resin and to compare the loading behavior of PAZ-4 with that of A-7, equilibrium loading of aurocyanide was determined as a function of pH. The results for PAZ-4 from this work and A-7 from the work of Fleming and Cromberge (1) are shown in Figure 2. It can be seen that the percentage of gold adsorbed is very high (~97%) for both resins at solution pH values of 7 and below. Furthermore, both resins exhibit good elution characteristics at pH values 13 and above. In the pH range 10 to 11, typical for most gold cyanide leach solutions, the loading of the A-7 resin is noticeably less than that of the PAZ-4. The PAZ-4 exhibits from 40 to 45% higher aurocyanide adsorption than A-7 in the pH range 10 to 11.
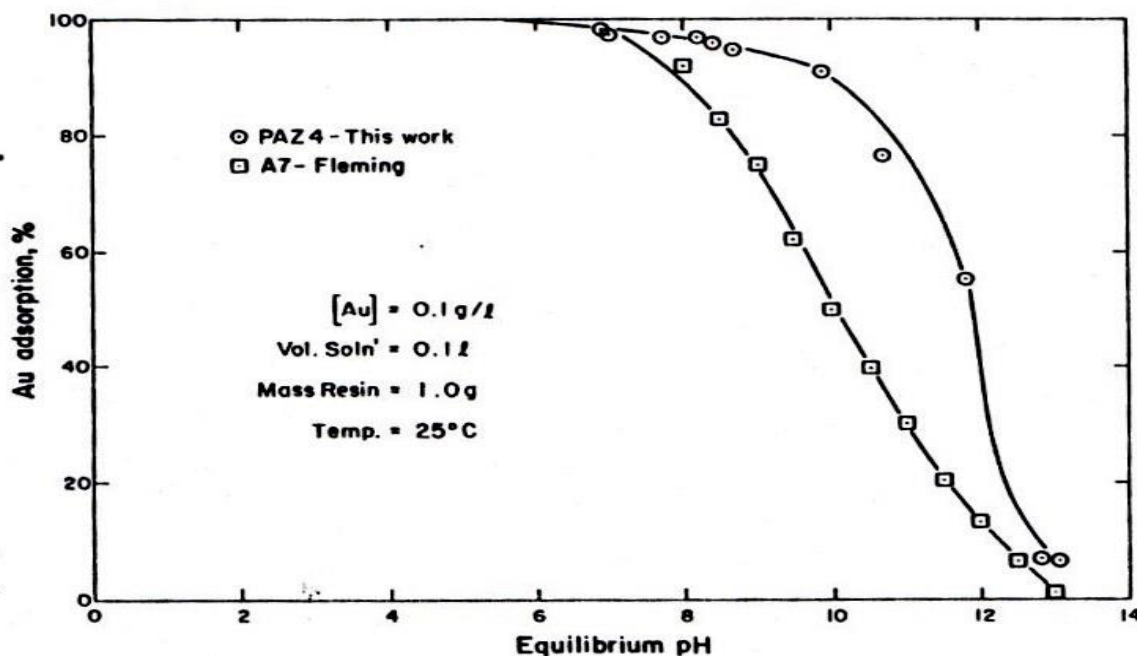

Figure 2 — Equilibrium adsorption curves for aurocyanide loading onto PAZ-4 and A-7.

Palmer (4) studied the loading of aurocyanide on A-7 in the presence of mercury (II) cyanide complex (500 ppm Au, 500 ppm Ag, 0.5 g/l NaCN). Typical weak-base behavior was observed for both $Au(CN)_2^-$ and $Hg(CN)_4^{2-}$. However, the presence of mercury depressed the adsorption of gold which was only about 80% at pH 7. Furthermore, the A-7 resin under these conditions exhibited approximately 20% gold adsorption at pH 13. A-7 did not exhibit any selectivity of gold over mercury.

Adsorption Isotherms

Adsorption isotherms were determined using solutions containing 0.40 and 0.80 g/1 free cyanide, $[CN^-]$, and at different initial gold cyanide concentrations. Isotherms were determined for 35 and 45°C. The results of this work are shown in Table II.

Initial [Au] g/l	$[CN^-]_f$ g/l	Temp °C	Solution [Au] g/l	Resin [Au] kg/t
0.40	0.80	35	0.168	58.0
	0.80	45	0.169	57.8
0.20	0.40	35	0.096	26.0
	0.80	35	0.053	36.8
	0.40	45	0.142	14.5
	0.80	45	0.069	32.8
0.10	0.40	35	0.050	12.5
	0.80	35	0.016	21.0
	0.40	45	0.066	8.5
	0.80	45	0.021	19.8
0.05	0.40	35	0.020	7.5
	0.80	35	0.006	11.0
	0.40	45	0.027	5.8
	0.80	45	0.009	10.3
0.025	0.40	35	0.007	4.5
	0.40	45	0.012	3.3

The Langmuir adsorption equation is given by

$$\theta = \frac{K\,C}{1+K\,C} \qquad [4]$$

where θ is the fraction of surface occupied (Q/Q_m), K is the equilibrium constant for the process, Q_m is the maximum quantity of gold which can be adsorbed, Q is the equilibrium quantity of adsorbed gold and C is the equilibrium concentration of gold cyanide in solution. The two constants (Q_m and K) are conveniently evaluated by rearranging equation [4] in the form

$$\frac{1}{Q} = \frac{1}{Q_m K\,C} + \frac{1}{Q_m} \qquad [5]$$

It follows that a plot of 1/Q vs 1/C should give a straight line having a slope of $1/Q_m K$ and an intercept of $1/Q_m$. Plots of this type are shown in Figures 3 and 4 for 0.40 and 0.80 g/l $[CN^-]_f$, respectively. From these plots it is apparent that there is an excellent fit of the experimental data and that the adsorption of gold on the PAZ-4 resin is explained by the Langmuir adsorption isotherm. The values of Q_m and K were determined from these plots, and are presented in Table III.
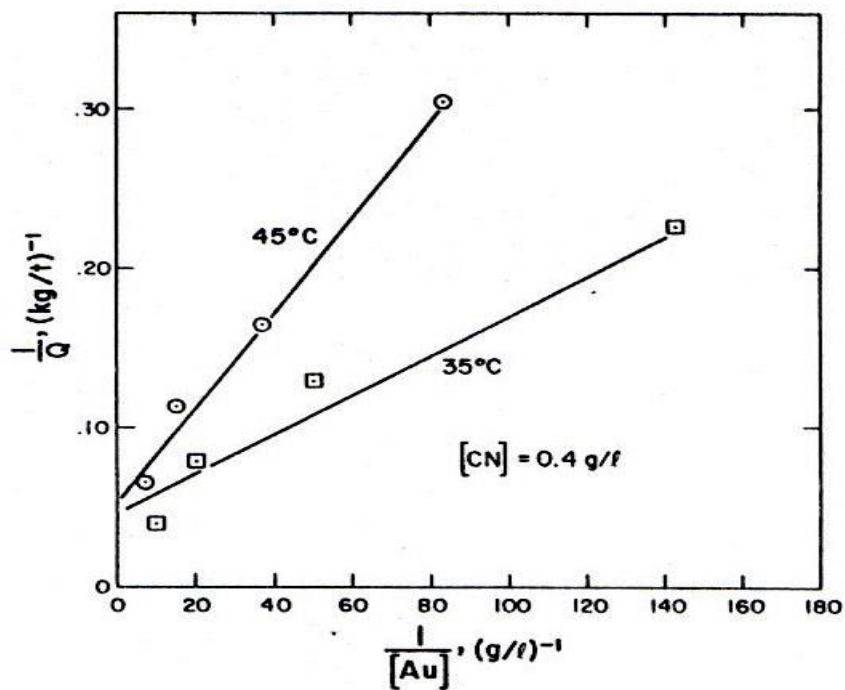
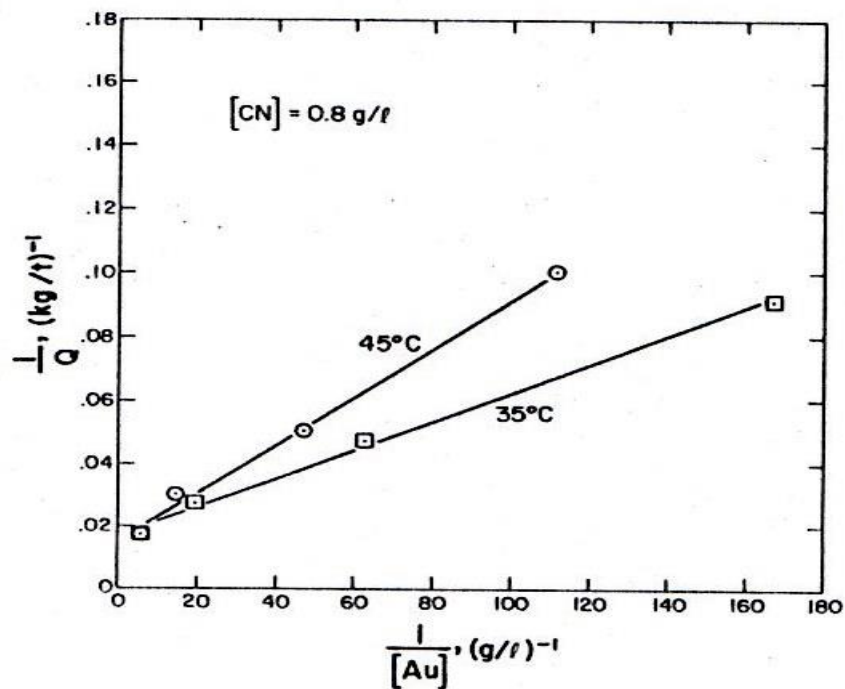Figure 3 — Linearized Langmuir plots for the adsorption of aurocyanide onto PAZ-4 at 0.4 g/l free cyanide.

Figure 4 — Linearized Langmuir plots for the adsorption of aurocyanide on PAZ-4 at 0.8 g/l free cyanide.

Table III. Langmuir Isotherm Parameters for Gold Loading on PAZ-4 Resin

Temp, $^{\circ}$C	$[CN^-]$ g/l	Q_m kg/t	K 1/g
35	0.40	21.5	37.8
45	0.40	18.5	18.0
35	0.80	58.8	38.0
45	0.80	66.1	19.8

Increasing the temperature had little if any effect on the value of Q_m. However, as expected, the equilibrium constant for the adsorption process was found to be sensitive to temperature. The net enthalpy of adsorption calculated from these values was 56.1 and 49.0 kJ/mole for 0.40 and 0.80 g/l $[CN^-]_f$, respectively. It was observed that the concentration of the free cyanide ion had a substantial effect on the amount of gold which was adsorbed on the resin. There was an increase in loading capacity with increasing free cyanide. Unlike strong-base resin where CN^- may compete with $Au(CN)_2^-$ for exchange sites, cyanide ion appears to enhance exchange of the aurocyanide complex based on the limited data available.

The competition between free cyanide and the metal-cyano complex with strong-base resins is illustrated quite nicely by the work of Riveros and Cooper.(7) They observed that the loading of $Ag(CN)_2^-$ is strongly influenced by the concentration of free cyanide. Silver loadings on Dowex MSA-1 was approximately 350 kg/t when the solution contained no free cyanide. With 0.51 g/l free cyanide present, the loading decreased about 33% to a value near 240 kg/t.

Adsorption Kinetics

Figure 5 depicts a typical rate curve for the adsorption of aurocyanide onto the PAZ-4 resin. It is evident from this curve that for all practical purposes equilibration is achieved in 3 hours, and that kinetic effects are only important during the initial stages of loading. Therefore, the rate of gold adsorption was normally examined for times up to about 1 hour.

Effect of pH. As shown in Figure 2, the ion exchange performance of weak-base resins like PAZ-4 is extremely sensitive to pH in alkaline solutions. Experiments to determine the effect of pH on the rate of loading were performed using 0.20 g/l initial gold and 0.40 g/l $[CN^-]_f$. The rate of adsorption of gold was examined at pH values ranging from 8.5 to 11.5. The adsorption of gold for the various pH values is plotted as a function of time in Figure 6. As indicated by these results, the rate of gold loading on PAZ-4 increases with decreasing pH in the range studied. Fleming and Cromberge (1) examined the influence of pH and the rate of loading of aurocyanide on to A-7 and MG-1 (Ionac-Polyamine), both being weak-base resins. They observed that the rate of adsorption was independent of the solution pH at values below about 8. However, the rate dropped off markedly between pH 8 and 10 a trend similar to that depicted in Figure 6.
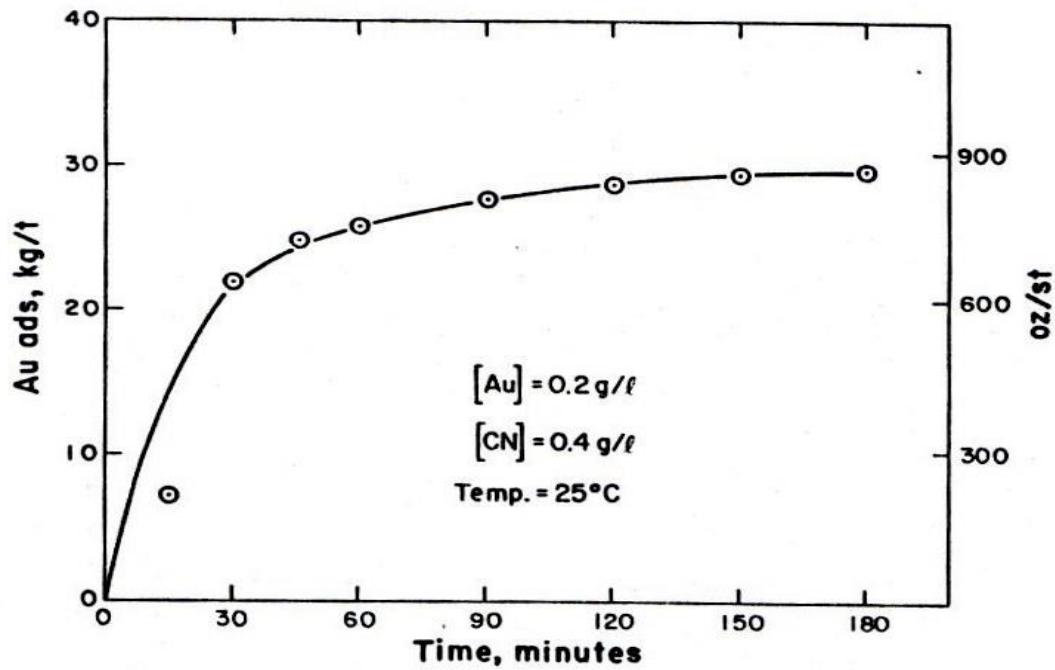
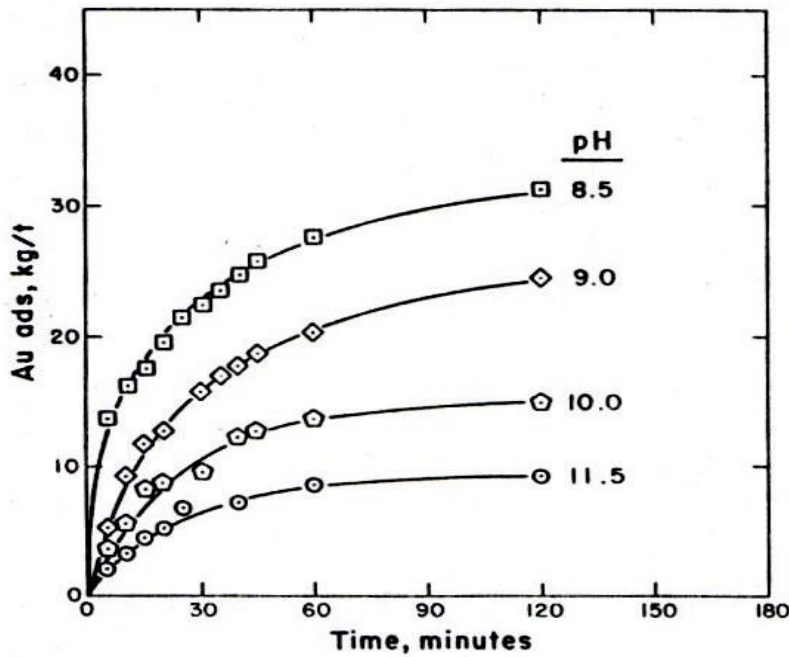Figure 5 – Typical curve showing the rate of adsorption of aurocyanide onto PAZ-4.

Figure 6 – Effect of pH on the rate of aurocyanide adsorption at 25°C, $[Au]_o$ = 0.20 g/1, and $[CN]_f$ = 0.40 g/1.

There is an obvious trend for the curves in Figure 6 to attain an adsorption plateau which is sensitive to pH. The observed increase in adsorption with increasing acidity is expected if one considers that protonation of the resin is required for anion exchange (see Equation 1). Kinetic trends associated with solution pH are not as easily explained.

Simple ion exchange processes typically follow a particle diffusion mechanism that can be described according to either Fickian diffusion, homogeneous diffusion, or shell-progressive (shrinking core) diffusion. Figure 7 illustrates the three situations for diffusion in an ion exchange resin. Helfferich and Hwang (9) and Rao and Gupta (10) observed that weakly basic resins exhibit a well-defined shrinking core type adsorption similar to that depicted in (c) of Figure 7. The shrinking core model for diffusion in spherical particles is described by the following expression.

$$1 - 2/3\alpha - (1-\alpha)^{2/3} = \frac{k}{r_o^2}t = k_o t \qquad [6]$$

For the resin system, α is the fractional loading of aurocyanide at time t, r_o is the initial particle radius, and k is a rate constant which contains apparent diffusivity, bulk phase activity of the diffusing species, and physical parameters for the resin.
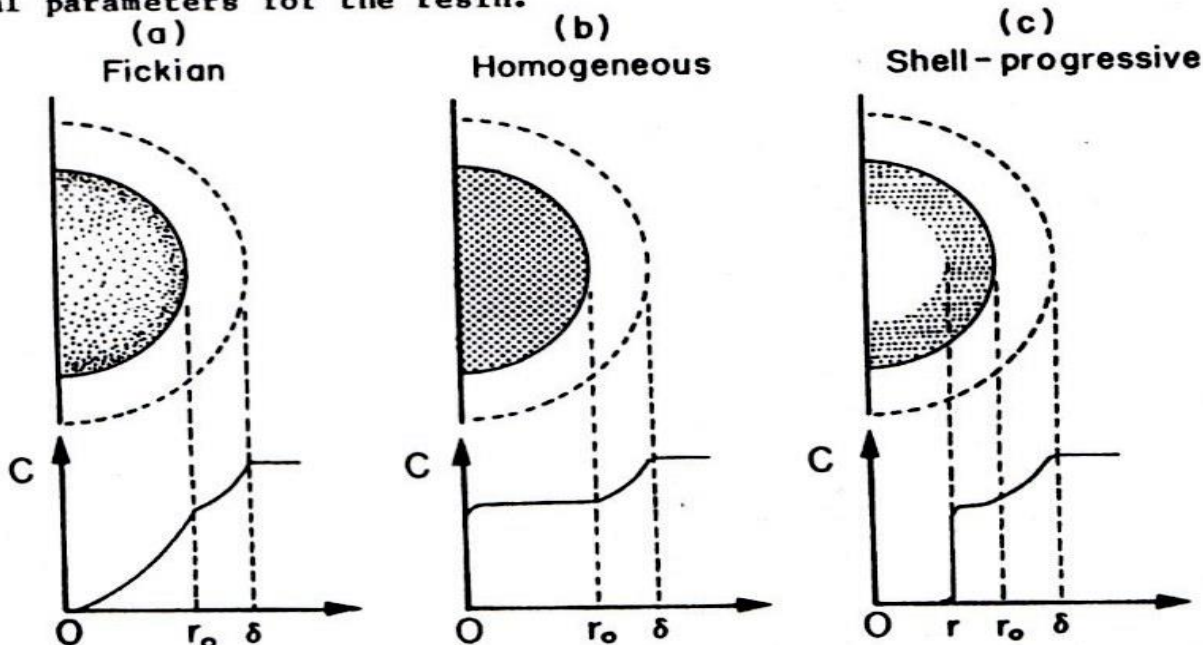

Figure 7 - Representation of different diffusion mechanisms for ion exchange and the corresponding concentration profiles (After Ref. 7).

In the development of Equation 6, it is assumed that the steady state approximation applies and that other steps are faster than pore diffusion within the resin particle. It is hoped that this treatment will lend insight into the exchange kinetics, however a more rigous formulation is planned for the future. Future models will not be limited to initial kinetics and will represent a more general treatment.

Figure 8 shows the correlation of aurocyanide loading kinetics plotted according to the shrinking core model for various pH values. There is excellent agreement with the pore diffusion shrinking core model for these results, except the initial portion of the pH 8.5 does not pass through the origin. It is possible that the initial part of the exchange at these conditions is controlled by another mechanism.
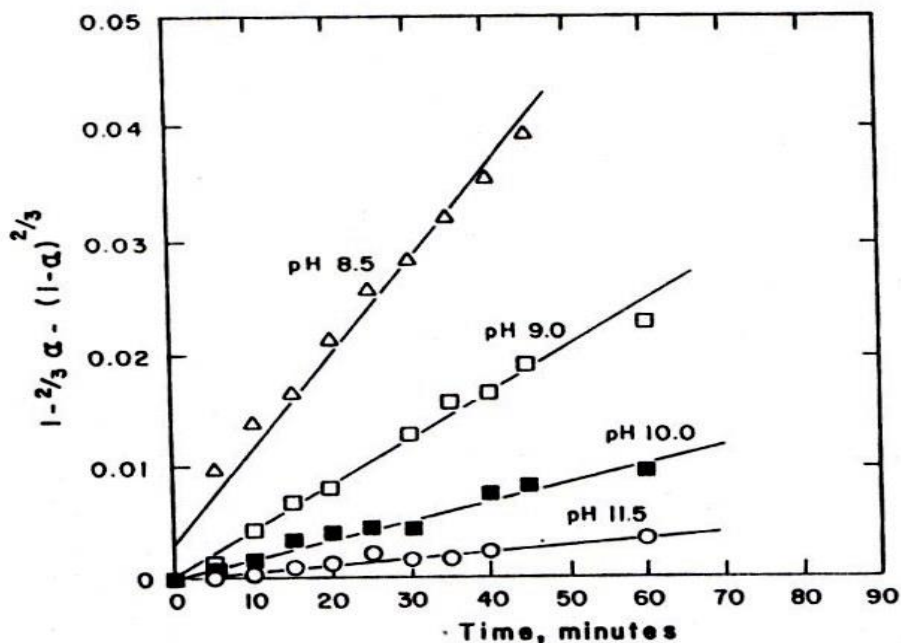
Figure 8 – Initial exchange kinetics plotted according to the shrinking core (shell-progressive) model for various pH values.

The reaction order with respect to hydrogen ion concentration was determined by plotting the log k_o versus log $[H^+]$ as shown in Figure 9. The ion exchange reaction for aurocyanide loading exhibits a 0.38 order with respect to hydrogen ion. Hydrogen concentration (pH) controls the distribution of hydrogen cyanide and free cyanide ion with a pKa for the system equal to 9.32 at $25^\circ C$.
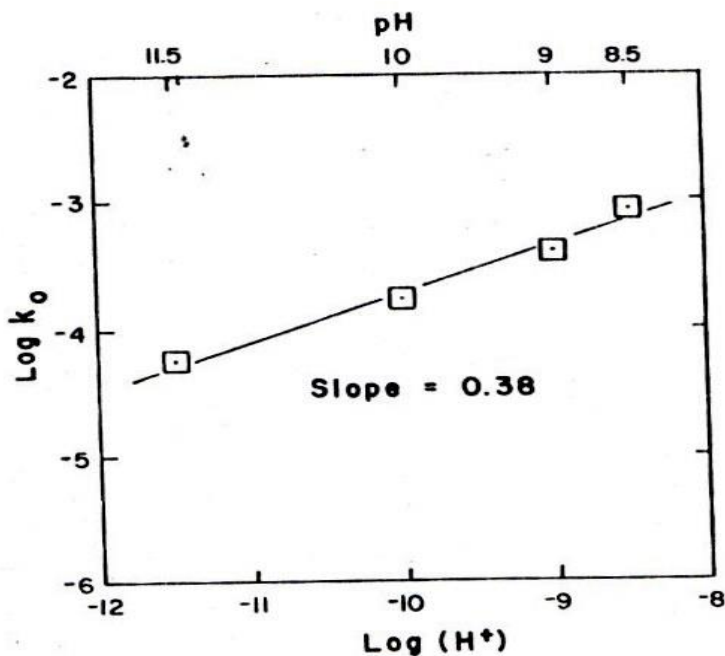

Figure 9 – Reaction order plot for pH dependence on the initial exchange kinetics.

<u>Effect of Free Cyanide Ion.</u>   Since pH was observed to have a pronounced effect on loading kinetics and pH controls the distribution cyano species, one would expect free cyanide to have an effect on the rate of adsorption of gold.   Experiments to determine the effect of free cyanide ion concentration on the loading kinetics were performed at $[CN^-]$ values of 0.20, 0.40, and 0.80 g/l.   Figure 10 shows the gold adsorption curves as a function of time for the different cyanide concentrations. The initial rate of loading increases with increasing cyanide concentration and was found to obey the diffusion equation. From initial kinetics data, a reaction order for free cyanide was calculated to be 0.30 which is very close to the reaction order obtained for the hydrogen ion (0.38). It is concluded that HCN has a kinetic role in the ion exchange of gold on weak-base resins that are similar to PAZ-4.
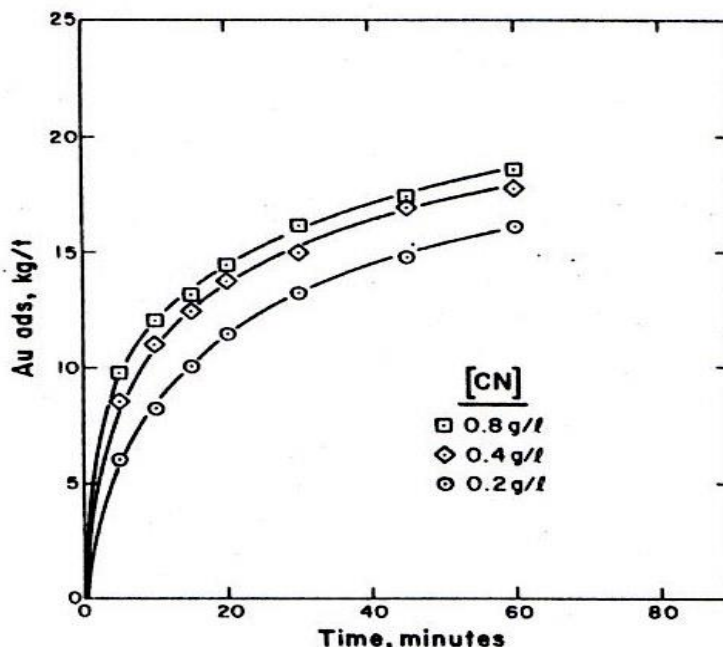

Figure 10 — Effect of cyanide concentration on the rate of aurocyanide adsorption at $25^\circ C$, pH 8.5, and $[Au]_o = 0.10$ g/l.

<u>Effect of Temperature.</u>   Loading of gold onto the PAZ-4 resin was investigated at 25, 35 and $45^\circ C$ using an initial gold concentration of 0.10 g/l and free cyanide at 0.20 g/l.   The results are shown in Figure 11.   The data at 60 minutes show a trend towards higher loading capacities at lower temperatures.   This trend is in agreement with the exothermic nature of aurocyanide adsorption.   On the other hand, the initial loading kinetics appear sensitive to temperature, increasing with increasing temperature. The initial portion has an experimental activation of approximately 8.7 kJ/mol.   This low value is characteristic of a pore diffusion mechanism where the physical properties (i.e. porosity, tortuosity, etc.) are not effected by temperature.

<u>Effect of Particle Size.</u>   Initial kinetics are plotted in Figure 12 according to the diffusion model for three size fractions, 14x20, 35x48, and 48x65 mesh.   According to the Equation 6 a plot of $1-2/3\alpha -(1-\alpha)^{2/3}$ versus time should yield a straight line with a slope of k/r_o^2. The insert in Figure 12, shows a plot of the slopes against $1/r_o^2$ for the three sizes investigated.   There is a fairly good fit for this data which lends additional support to contention that the initial kinetics obey a diffusion model.
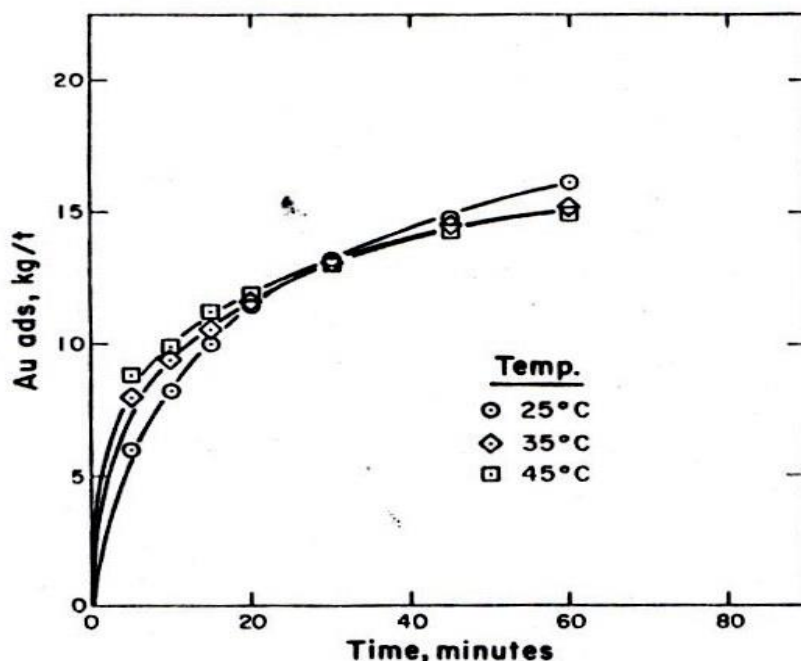
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Figure 11 – Effect of temperature on the rate of aurocyanide adsorption at pH 8.5, $[Au]_o$ = 0.10 g/l, and $[CN]_f$ = 0.20 g/l.
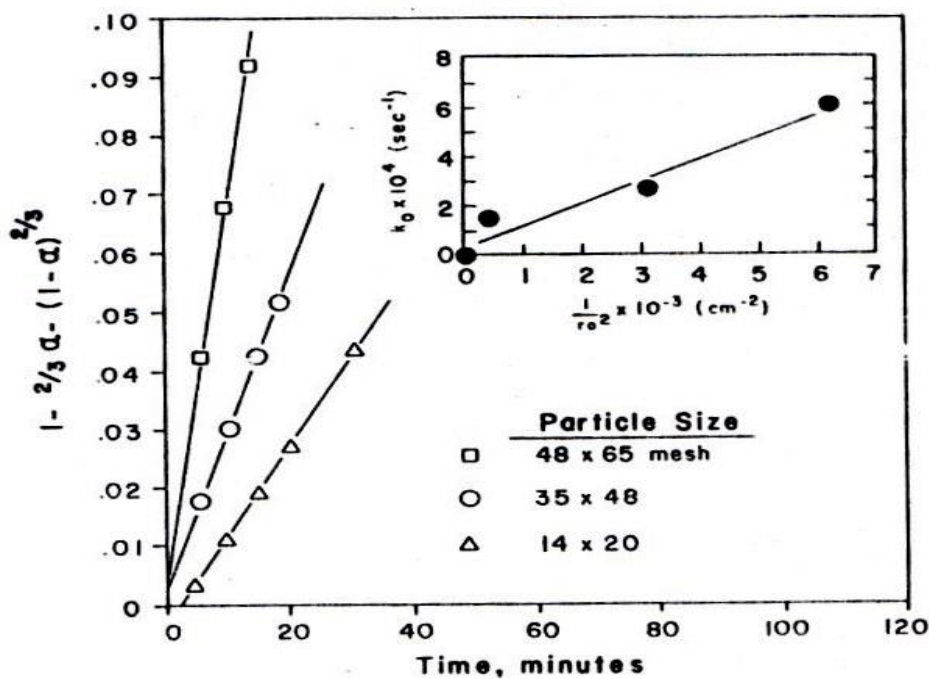

Figure 12 – A plot of $1-2/3\alpha - (1-\alpha)^{2/3}$ for different resin sizes as a function of time. Insert shows the squared dependence on particle size.

Kinetic Model

The results of this investigation suggest that the initial kinetics for aurocyanide adsorption onto the PAZ-4 weak-base resin are controlled by a pore diffusion model.

The kinetic role of pH in the exchange of gold cyanide is difficult to resolve. Intraparticle diffusion depends upon the degree of resin swelling which in turn depends in part upon the solution concentration. Dilute solution enhances the degree of resin swelling thus increasing the exchange rate. In this work the ionic strength was controlled primarily by the cyanide concentration and was nearly constant for the pH values investigated. Therefore, decreasing pH does not have a pronounced effect on resin swelling in this system and cannot explain the increased loading kinetics.

The pH behavior can only be explained when one assumes that the ion diffusion is influenced by the nature of the exchange site. It is proposed that cyanide ion replaces chloride as the counter ion because it possesses a slightly larger ionic radius and is more polarizable than chloride ion. With cyanide in the resin phase diffusion of the aurocyanide is enhanced. It is assumed that the gold is transported by a bridging and billiard-ball type mechanism similar to that proposed by Liberti and Passino (7). In this mechanism, the cyanide ion is already in place and the Au atom bridges between sites by coordinating with the adsorbed cyanide. Gold advances into the resin when an aurocyanide ion collides with a bridged gold atom, as depicted in Figure 13.
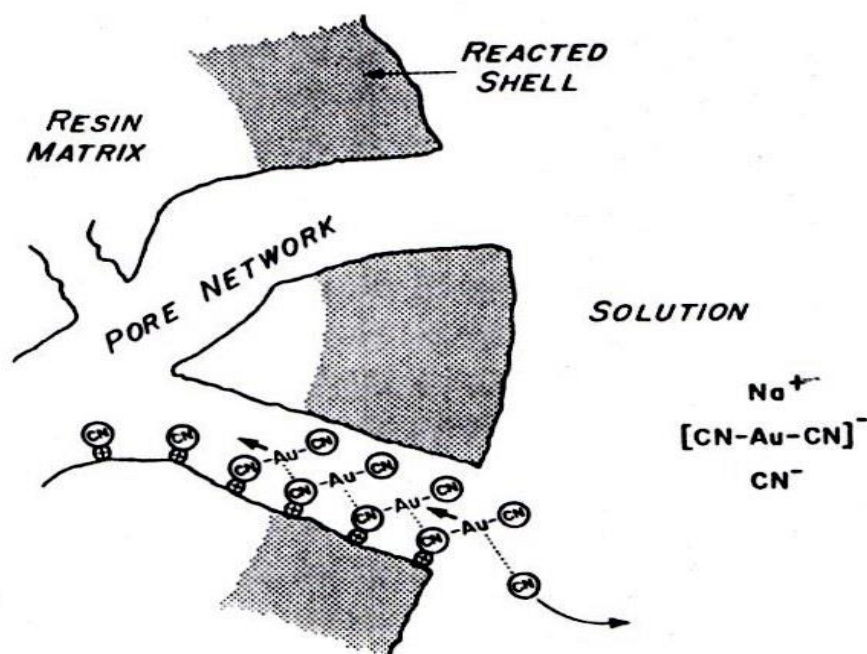

Figure 13 - Schematic depicting the proposed mechanism for aurocyanide loading onto weak-base resins similar to PAZ-4.

According to this mechanism, the loading of gold proceeds according to the following reaction

$$|-NR_2 + HCN + Au(CN)_2^- = |-NR_2H^+ Au(CN)_2^- + CN^- \qquad [7]$$

The gold moves toward the inner core of the resin by continually advancing and not by permanently "parking" on a site. Direct exchange would not be required since the cyanide in its counter ion position can bond with the approaching gold atom. Charge neutrality is maintained by CN^- exchange at the pore exterior. This would require that the exchange of CN^- between the aurocyanide complex and labelled cyanide in aqueous solution to occur at a relatively fast rate. According to Sharpe (11) the aurocyanide complex is classified as labile while other cyano complexes like those of Cr(III), Co(III), Fe(II), Fe(III), and Mo(IV) are considered kinetically inert.

Summary

Preliminary experiments showed that the equilibrium adsorption of aurocyanide onto the PAZ-4 weak-base resin fits a Langmuir type isotherm. The adsorption rate of aurocyanide on PAZ-4 was found to be sensitive to solution pH. The rate constant at pH 8.5 was 8.4×10^{-4} min^{-1} compared to pH 11.5 value of only 5.8×10^{-5} min^{-1}. A pore diffusion model based on a shell-progressive (shrinking core) rate equation provided excellent correlation of the adsorption rate data. It was determined that increases in the free cyanide concentration in the range of 0.20 to 0.80 g/l increased the rate of adsorption. The rate depended on the square of the resin particle size which provided additional support for the diffusion mechanism. Temperature had little effect on the initial adsorption kinetics, with an experimental activation energy of only 8.7 kJ/mol.

An exchange mechanism involving transport via a bridging and billiard-ball type process has been proposed. According to this hypothesis, it is critical that cyanide occupy exchange sites on the resin. Gold then advances into the resin by collision and formation of coordinating (CN-Au-CN) bridges. This conclusion is consistent with the observed experimental finding and the shrinking-core model. However, it is recognized that additional experimental work is necessary to completely verify this conclusion.

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