

A comparison of several kinetic models for the adsorption of gold cyanide onto activated carbon

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SYNOPSIS

Several rate models for the adsorption of gold cyanide from aqueous solution onto activated carbon are given in the literature. The purpose of this study is to critically examine their ability to simulate the adsorption process over a wide range of conditions.

An account is given of a comprehensive set of experimental work on the kinetics of gold adsorption onto a coconut-shell-based activated carbon. Equilibrium isotherms were also determined.

It is concluded that the homogeneous surface-diffusion model fits the experimental data reasonably well and provides a good balance between simplicity and descriptive accuracy. The model contains two parameters: the extra-particle mass-transfer coefficient and an effective intraparticle surface-diffusion coefficient. Both can be evaluated readily from simple adsorption experiments.

SAMEVATTING

Daar word verskeie tempomodelle vir die adsorpsie van goudsianied uit 'n waterige oplossing op geaktiveerde koolstof in die literatuur aangegee. Die doel van hierdie studie is om hul vermoë aan die adsorpsieproses in 'n groot verskeidenheid omstandighede te simuleer, krities te ondersoek.

Daar word verslag gedoen oor 'n omvattende stel eksperimente in verband met die kinetika van goudadsorpsie op geaktiveerde koolstof wat van klapperdoppe berei is. Daar is ook ewewigsisotermes vasgestel.

Die gevolgtrekking word gemaak dat die homogene oppervlakdiffusiemodel die eksperimentele data redelik goed pas en 'n goeie balans tussen eenvoudige en beskrywende akkuraatheid gee. Die model het twee parameters: die ekstrapartikel-massaoordragkoëffisiënt en 'n effektiewe intrapartikel-oppervlakdiffusiekoëffisiënt. Albei kan maklik aan die hand van eenvoudige adsorpsie-eksperimente ge-evalueer word.

INTRODUCTION

The recovery of gold by the adsorption of aurocyanide complexes onto activated carbon is a well-established commercial metallurgical process¹. It has found application in countercurrent stirred-tank systems (the carbon-in-pulp or CIP process), in packed adsorption columns², and in fluidized-bed reactors³. After the gold species has been eluted from the activated carbon with a hot caustic cyanide solution, the gold is recovered by electrowinning or zinc precipitation and, finally, by smelting¹.

The design of such activated-carbon adsorption systems may be based on information gained from pilot-plant test programmes. Although this approach considers many practical aspects of a particular application, the tests are highly specific and time-consuming, and do not readily lend themselves to generalization, and hence to the prediction of system variables other than those employed in the particular test. On the other hand, well-controlled bench-scale laboratory adsorption experiments can be employed for the development of mathematical process models that can be used to elucidate adsorption and adsorber design principles, and will permit the directed use of pilot-scale tests to verify the design of adsorption systems⁴.

Laboratory-scale adsorption studies could typically involve equilibrium or kinetic experiments. Researchers have reported that equilibrium between gold cyanide and activated carbon had not been achieved after three

months⁵ and, in another case, after six months⁶. Since practical retention times in a CIP adsorber are of the order of one hour⁷, it appears reasonable to focus on adsorption kinetics as a means of describing and comparing different gold-adsorption systems². In this regard, many of the rate mechanisms are studied more easily by the use of agitated finite-bath batch adsorption systems⁸.

A major objective of the study reported here was to evaluate and compare a number of adsorption models in terms of their adequacy in describing the adsorption of aurocyanide species from a suitable background solution. Both empirical and fundamental kinetic models of moderate complexity were considered.

KINETIC MODELS

As is the case with all kinetic processes, the rate of adsorption is a function of the state of the system; that is, the rate is dependent on intensive properties only. In some of the models that have been proposed, time is included in the expressions. However, this variable is an extensive property and therefore has no place in such models. In batch experiments, time appears in the model as a consequence of mass balances, and not kinetic expressions.

Rate models can generally be classified as empirical, mechanistic, or a combination of the two. In the first, an attempt is made to fit the experimental data to a simple functional form, which need not possess any theoretical basis. Mechanistic models, on the other hand, attempt to use detailed physicochemical concepts to describe the process. However, this may lead to prohibitively complex models that may be difficult to apply in practice.

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A good model should therefore strike a balance between simplicity and descriptive accuracy.

Empirical Rate Models

The simplest means of linearizing the data from batch kinetic experiments is to plot the concentration of residual adsorbate in the liquid phase against the square root of the time⁹. This method was employed with good results by Weber and Morris¹⁰, who compared the rates of adsorption of a range of alkyl benzene sulphonates over time ranges of several hours. However, the method proved inadequate to linearize kinetic data for p-nitrophenol⁹.

Many of the other empirical rate models that have been used to describe the adsorption of gold from solution have been reviewed, although not exhaustively, by Johns¹¹, La Brooy *et al.*¹², and Van Deventer⁶. The most relevant of these models are listed below.

First-order rate model¹¹:

$$r = k_1 C - k_2 q \dots\dots\dots (1)$$

Model of Dixon *et al.*¹³:

$$r = k_3 C(q^+ - q) - k_4 q \dots\dots\dots (2)$$

Model of Nicol *et al.*²:

$$r = k_5 (K C - q) \dots\dots\dots (3)$$

Model of Fleming *et al.*¹⁴:

$$q = k_6 C_0 t^n \dots\dots\dots (4)$$

Model of La Brooy *et al.*¹²:

$$q = k_7 C t^n, \dots\dots\dots (5)$$

- where r = rate of gold adsorption (mg Au/s·dm³)
 C = concentration of gold in solution (mg Au/dm³)
 q = mass of gold on the carbon (mg Au/g carbon)
 t = time elapsed from start of batch experiment (s)
 C_0 = initial concentration of gold in solution (mg Au/dm³)
 q^+ = mass of gold on carbon when it is completely loaded (mg Au/g carbon)
 $k_1 \dots k_7, K, n$ = characteristic constants.

These models are all subject to limitations, either in regard to adequacy of fit or in terms of the time span over which they accurately describe the gold concentration in solution. Thus, the first-order rate model when tested by Johns⁷ was rejected in favour of a more sophisticated non-linear model (to be considered later) on the grounds that the rate constants are dependent upon the particle size of the activated carbon, and are also difficult to calculate accurately since they differ by some five orders of magnitude.

La Brooy *et al.*¹² found both the model of Fleming, equation (4), and that of Nicol *et al.*, equation (3), to be adequate for only the first hour of batch adsorption. They consequently adapted the former model by replacing the initial concentration, C_0 , by the time-dependent concentration, C (equation (5)), and reported a good fit over the first 4 hours of their kinetic batch adsorption

experiments.

The simplicity and apparent usefulness of this two-parameter model over an extended adsorption period make it attractive for describing the rate of gold adsorption. As with all empirical models, its value is limited to the range of experimental variables used. In addition, time appears in equation (5) and, as pointed out earlier, this expression is valid only for batch systems.

Mechanistic Models

Possible Transport Mechanisms

From a mechanistic point of view, the rate of adsorption of an adsorbate onto activated carbon can be described by the following series of transport mechanisms^{15,16}:

- (1) film diffusion, i.e. diffusion from the bulk liquid phase through a hypothetical hydrodynamic boundary layer or film surrounding the particle;
- (2) pore diffusion, i.e. diffusion within the pore fluid of the particle;
- (3) surface diffusion, i.e. migration of adsorbed molecules along the internal pore wall; and
- (4) adsorption onto the internal surface of the carbon.

These steps each represent a resistance in the transport mechanism. Adsorption step (4) is considered to be so rapid as never to constitute the rate-limiting step and, for strongly adsorbed molecules, the pore-diffusion flux has been shown to be orders of magnitude lower than that of surface diffusion¹⁷. These two steps can consequently be neglected in most adsorbate-adsorbent systems¹⁵ without undue loss of accuracy. Thus, the rate of adsorbate removal from a liquid can often be adequately described by the assumption of initial film-transfer dominance, eventual surface-diffusion dominance, and a transition period during which both mechanisms influence the adsorption rate¹⁸. Van Lier⁸, comparing the surface-diffusion and pore-diffusion models, showed that they have very similar characteristics, and that it is therefore difficult to separate the two mechanisms. He ultimately showed that it is adequate to combine the effects of intraparticle diffusion by means of an effective surface-diffusion coefficient. This coefficient is therefore not necessarily the true surface-diffusion coefficient, but rather a measure of intraparticle diffusion.

Film transfer can be assumed to determine the adsorption rate in the early stages of a batch adsorption experiment, and the film theory postulates a linear concentration gradient from the bulk liquid to the surface of the adsorbent particle. If diffusion through the film is described by Fick's first law, and if spherical-particle geometry is assumed, the flux, Ψ , of the diffusing species is given by

$$\Psi = k_f (C_b - C_s), \dots\dots\dots (6)$$

where k_f is the film coefficient, C_b is the concentration of the bulk liquid phase of the adsorbate species, and C_s is the concentration of the species at the interface between the bulk liquid and the particle surface. The film-transfer model assumes equilibrium between C_s and the average adsorbent loading or solid-phase concentration, \bar{q} , of the adsorbate species. This effectively means that intraparticle diffusion is assumed to be rapid. From a mass balance over the batch reactor on the basis of spherical-particle

geometry, the batch rate equation for film-diffusion control is found to be

$$\frac{dC_b}{dt} = -k_f \beta (C_b - C_s), \dots\dots\dots (7)$$

where

$$\beta = \frac{3m}{V \rho_p r_p} \dots\dots\dots (8)$$

and ρ_p is the density of the dry adsorbent in air (i.e. the density of the adsorbent particle), r_p is the radius of the particle, m is the mass of the adsorbent, and V is the volume of the batch reactor.

Linear Film-transfer Model

The linear film-transfer model assumes that the concentration of the adsorbate at the particle surface, C_s , is negligible at small values of time in a batch reactor, compared with the concentration of the bulk liquid, C_b . Thus, equation (8) can be integrated to yield

$$\ln\left(\frac{C_b}{C_{b0}}\right)\Big|_{t \rightarrow 0} = -k_f \beta t \dots\dots\dots (9)$$

Experimentally k_f is determined from the initial slope of a plot of $\ln C_b/C_{b0}$ against t for a given adsorbent-particle diameter since β is a function of r_p .

Non-linear Film-transfer Model

The linear film-transfer model is applicable only over the initial portion of the kinetic curve, insofar as it is linear and can be described by equation (9). The film-transfer model can be refined by the introduction of an expression to describe the concentration of the adsorbate at the particle surface, C_s in equation (7). The concentration of the liquid phase at the particle-liquid interface is assumed to be in equilibrium with the concentration of the solid adsorbate at the interface, and can therefore be described by an appropriate isotherm model. In the present study, the Freundlich isotherm was found to adequately describe the experimental equilibrium data. This isotherm has the form

$$q = A C^\gamma, \dots\dots\dots (10)$$

where A is the Freundlich constant and γ is the Freundlich exponent. The combination of equations (7) and (10) with the batch reactor mass-balance equation yields the following differential rate equation in the variable C_b :

$$\frac{dC_b}{dt} = -\beta k_f \left[C_b - \left(\frac{V(C_{b0} - C_b)}{mA} \right)^{1/\gamma} \right], \dots\dots (11)$$

which, upon integration, results in

$$\int_{C_b}^{C_{b0}} \frac{dC_b}{[C_b \zeta (C_{b0} - C_b)^{1/\gamma}]} = \beta k_f t = \tau, \dots\dots\dots (12)$$

where

$$\zeta = \left(\frac{V}{mA} \right)^{1/\gamma} \dots\dots\dots (13)$$

Equation (12) is a relation between C_b and dimensionless time, τ , which is uniquely described for the constants β , k_f , A , C_{b0} , and γ . The history of the batch-reactor

concentration is easily obtained by numerical integration. The parameters β , A , C_{b0} , and γ are determined *a priori*, and it therefore remains to shift the time scale of the experimentally determined concentration history so that it lies on top of equation (12). This formulation of the model is a significant simplification of the formulation proposed by Johns⁷ since one can determine the concentration history in dimensionless variables without knowing the film-transfer coefficient. If film transfer is the operative mechanism, then the entire history of the experimental concentration should be superimposable on the theoretical curve. Since k_f is the only parameter in the system, it can be approximated by a value selected to minimize the sum of squared errors between the experimental bulk liquid concentrations, $C_b'(t)$, and the concentrations, $C_b(t)$, calculated according to equation (13) at corresponding times in order to satisfy the relation

$$\frac{d}{dk_f} \left(\sum_{n=1}^J [C_b'(t) - C_b(t)]^2 \right) \rightarrow 0, \dots\dots\dots (14)$$

where J is the number of experimental points.

This has the effect of giving a 'smoothed' value of the film coefficient k_f that best fits the data up to the experimental point J . In a system that is controlled not only by film-diffusion, the value of k_f can be expected to remain constant for the first data points and to decrease at increasing times as the effect of intraparticle diffusion increasingly influences the rate of adsorption and the model becomes inadequate. This means that the model will be unable to describe the shape of the batch curve and will deviate from the experimental results. The dimensionless concentration-time profiles for different initial gold concentrations are shown in Fig. 1.

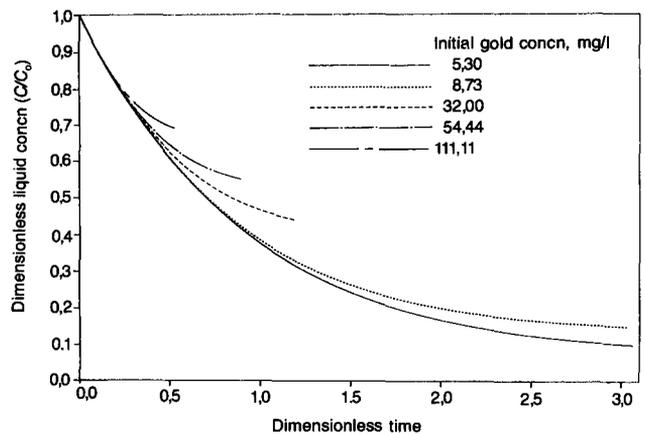


Fig. 1—Non-linear film-diffusion model: Dimensionless time-concentration profiles for different initial gold concentrations

Homogeneous Surface-diffusion Model (HSDM)

A mechanistic model of the rate of adsorption of an adsorbate onto activated carbon must incorporate, or at least consider, the rate of the adsorption reaction, and of the mass-transfer mechanisms within the adsorbent particle (the micro-environment). These are then related to the adsorption reactor or contacting mode employed (the macro-environment). The present study is concerned with the description of the fate of a target adsorbate, the

aurocyanide species, as adsorbed by a particulate adsorbent in a stirred batch reactor or finite bath. In the construction of an adsorption model for this system, the micro- and macro-environments are considered separately, and the concentrations of the solid and liquid phases are then associated by a suitable equilibrium relationship.

The following initial assumptions were made:

- spherical geometry is assumed for the adsorbent particles¹⁹
- the particles of adsorbent are considered to be isotropic or uniform¹⁶
- adsorption is considered to take place under isothermal conditions
- diffusion of the adsorbate in the bulk liquid is assumed to have a negligible influence¹⁶.

As discussed earlier, in this study intraparticle diffusion is regarded as a single mechanism. It is referred to as surface diffusion, and is characterized by the effective surface-diffusion coefficient.

General expositions of the HSDM are given elsewhere^{15,20}. A detailed derivation of the form of the model used in this study has been given by Le Roux²¹. The governing equations in dimensionless form are as follows:

The particle mass-balance equation is

$$\frac{\partial \Phi}{\partial \tau} = \frac{1}{\zeta^2} \frac{\partial}{\partial \zeta} \left(\zeta^2 \frac{\partial \Phi}{\partial \zeta} \right) \dots\dots\dots (15)$$

with initial condition

$$\Phi(\zeta, \tau = 0) = 0 \dots\dots\dots (16)$$

and boundary conditions

$$\frac{\partial \Phi}{\partial \zeta} \Big|_{\zeta=0} = 0, \dots\dots\dots (17)$$

and

$$\frac{\partial \Phi}{\partial \zeta} \Big|_{\zeta=1} = Sh_b (X - X_s) \dots\dots\dots (18)$$

$$Sh_b = \frac{k_f r_o C_{bo}}{\rho_p D_s q_o} = Bi \left(\frac{C_{bo}}{\rho_p q_o} \right) \dots\dots\dots (19)$$

$$Bi = \frac{k_f}{\rho_p D_s} \dots\dots\dots (20)$$

The dimensionless variables are

$$\Phi = \frac{q}{q_o} \quad \chi = \frac{C_b}{C_{bo}} \quad \tau = \frac{t D_s}{r_o^2}$$

$$\chi_s = \frac{C_s}{C_{bo}} \quad \zeta = \frac{r}{r_o} \dots\dots\dots (21)$$

Sh_b is the Sherwood number based on the surface-diffusion coefficient (D) for a batch reactor system, and Bi is the Biot number, which represents the ratio between the film- and the surface-diffusion coefficients for a specific particle radius¹⁵; q_o is the solid concentration in equilibrium with the initial liquid concentration C_{bo} .

The reactor mass-balance equation is

$$\chi(\tau) = 1 - \alpha \int_0^1 \zeta^2 \Phi(\zeta, \tau) d\zeta, \dots\dots\dots (22)$$

where

$$\alpha = \frac{3 m q_o}{V C_{bo}}$$

The Freundlich isotherm in dimensionless form becomes

$$\Phi = X^\gamma \dots\dots\dots (23)$$

The HSDM equations were solved numerically. Equation (15) was solved by use of the NAG FORTRAN software-library routine D03PGF, while the integration of equation (22) was performed by the IMSL software-library routines DCSINT and DCSITG.

EXPERIMENTAL

Activated carbons made from coconut shell are considered to be well-suited to the recovery of gold^{6,11,22}, and the brand G210 AS, which is manufactured by Pica SA (France), was consequently selected for the present study. An analysis of some of the properties of this activated carbon is given in Table I. The skeletal density was determined by use of a Micromeritics Autopycnometer Model 1320, the BET internal-surface area was measured with a Micromeritics Rapid Surface Area Analyzer Model 2200A, and the pore-volume distributions and particle densities were determined by mercury porosimetry on a Micromeritics Autopore Model 9200. The iodine numbers, methylene blue numbers, and caramel decolorizing index are standard analyses for adsorbents²³, and are performed with molecules of progressively increasing molecular masses (iodine = 254 amu and methylene blue = 373,9 amu). Thus, they give an indication of the pores accessible to these molecules.

TABLE I
PROPERTIES OF ACTIVATED-CARBON ADSORBENT

Property	G210 AS (Pica)
Iodine number	1345
BET surface area (m ²)	981
Methylene blue number	262
Caramel decolorizing (%)	77,8
Particle density (g/cm ³)	0,818
Skeletal density (g/cm ³)	2,151
Apparent density (g/cm ³)	0,431
Total pore volume (cm ³ /cm ³)	0,620
Macro-pore volume (cm ³ /cm ³)	0,186
Meso-pore volume (cm ³ /cm ³)	0,130
Micro-pore volume (cm ³ /cm ³)	0,304
Ash content (%)	1,77

The aurocyanide complex $Au(CN)_2^-$ has a molecular mass of 246 amu, which corresponds closely to the mass of the iodine molecule.

A sample of commercially available G210 activated carbon was dry-sieved, and the particle-size fraction plus 1,4 mm minus 1,7 mm was selected for the study. The arithmetic average of 1,55 mm was used for all the model calculations.

Properties of the Adsorbate

The gold solution was prepared according to the method of AARL²⁴ for the determination of the gold-adsorption rate of activated carbon. All the reagents were

of analytical grade, and distilled deionized water was used throughout. The following buffer solution was employed for all the studies:

- Borate buffer (H_3BO_3) at 3,1 g/l
- Calcium chloride ($CaCl_2 \cdot H_2O$) at 3,2 g/l
- Sodium cyanide (NaCN) at 200 mg/l.

The solution pH was adjusted to approximately 10 by the addition of sodium hydroxide (NaOH), about 1,75 g/l usually being required. To this background solution, potassium aurocyanide, $KAu(CN)_2$ (obtained from Johnson Matthey Chemicals Ltd), at a gold content of 68 per cent was added to produce the desired gold concentration.

Adsorption Experiments

All the equilibrium adsorption experiments were conducted using G210 activated carbon of the fraction plus 1,4 minus 1,7 mm from a single batch. For the adsorption isotherms, known amounts of background solution containing aurocyanide were added. To increase the accuracy and range of the isotherms, different ranges of initial gold concentrations were employed. After the closed flasks had been agitated in a tumbler for the required period, samples of the liquid were filtered through 45 μ m membrane filters (Millipore SA), and the concentrations were determined by atomic-absorption spectroscopy. On the basis of preliminary experiments, an equilibrium time of 7 days was selected. The carbon loadings were determined by batch-reactor mass balance, and the Freundlich isotherm parameters were fitted by means of non-linear regression.

The objective of the kinetic experiments was to determine the rate at which the target adsorbate, i.e. gold in the form of an aurocyanide complex, is adsorbed from solution in a laboratory-scale agitated batch or finite-bath reactor. These experimental results were then used in a comparison of the various kinetic models.

The batch rate experiments were carried out in an un-baffled cylindrical glass reactor vessel containing 2000 ml of gold-bearing solution. The activated carbon was boiled twice in distilled-deionized water and oven-dried overnight at 110°C. The adsorbent was then soaked for at least 12 hours in a small amount of adsorbate-free background solution to remove all the air entrapped in the pores. The gold-containing solution was made up the previous day to ensure adequate formation of the aurocyanide complex. After the withdrawal of the first sample, the adsorbent was added and 10 ml samples were withdrawn periodically by syringe and filtered into the sample bottles through an attachable 45 μ m membrane filter (Millipore SA) to remove any carbon fines that might be present. Agitation was carried out at 250 r/min by means of a rectangular flat-paddle stirrer with a radial dimension slightly smaller than that of the vessel diameter and set close to the bottom of the vessel. Thus, the adsorbent was always completely suspended, and the absence of baffles minimized the formation of fines through inter-particle shearing and abrasion action.

A number of batch experiments were performed and five typical batch experiments, at different initial gold concentrations, were selected for the comparison of the various models.

RESULTS AND DISCUSSION

Determination of Isotherm Parameters

Non-linear regression yielded a Freundlich constant of 28,4 (based on a solid loading expressed in milligrams of gold per gram of activated carbon) and a Freundlich exponent of 0,393, with a correlation coefficient of 0,976. The Freundlich isotherm is illustrated in Fig. 2. These isotherm parameters were employed in the solution of the non-linear film-transfer kinetic model and the HSDM.

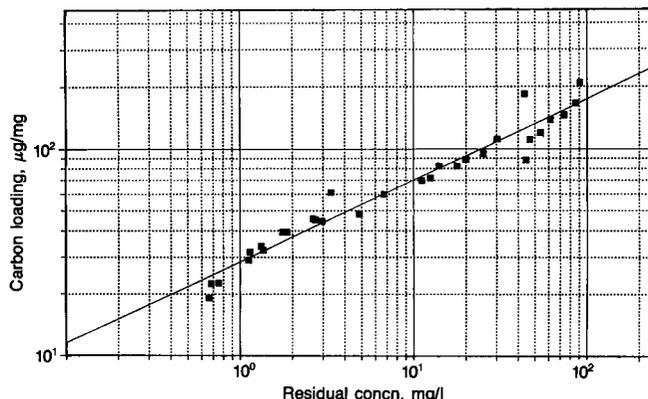


Fig. 2—Freundlich isotherm for aurocyanide

Linear Film-transfer Kinetic Model

The linear film-transfer model is given by equation (10), and the film coefficient k_f is determined from the initial slope of a plot of $\ln(C_b/C_{b0})$ against time for the fixed carbon-particle size fraction of 1,4 to 1,7 mm used in all kinetic experiments. This was done by the fitting of a linear regression model to the data and then eliminating all but the first number of data points until an adequate correlation coefficient had been obtained. This usually corresponded to what appeared visually to constitute a straight line. Fig. 1 illustrates this method for an initial gold concentration of 8,7 mg/l, and the resulting film coefficients for different initial gold concentrations are listed in Table II.

TABLE II
LINEAR FILM-TRANSFER MODEL: FILM COEFFICIENTS FOR DIFFERENT INITIAL GOLD CONCENTRATIONS

Initial gold concentration (C_{b0}) mg/l	k_f 10^{-4} cm/s	Degrees of freedom	Correlation coefficient
5,30	7,97	4	0,9595
8,73	4,85	5	0,9929
32,00	5,66	3	0,9904
54,44	5,44	3	0,9785
111,11	4,88	3	0,9952

It is apparent that this model can be applied only to the first three to five data values (in other words, at low gold loadings), and it appears to describe the data better at lower initial concentrations than at higher concentrations. Since the concentrations were measured every 15 minutes initially, the film coefficient was determined from only two degrees of freedom at higher gold concentrations, and this cannot be expected to yield very reliable

results. Johns⁷ also considered the linear film-transfer model to be inadequate, and La Brooy *et al.*¹² found it to be accurate only up to adsorption times of 1 hour. The latter finding was confirmed in the present study for the initial gold concentrations of 5,3 and 8,7 mg/l.

Non-linear Film-transfer Model

The non-linear film-transfer model is considered to be more sophisticated than the linear film-transfer model since the former does not neglect the gold concentration of the intraparticle solid phase.

The model was applied using dimensionless concentration-time profiles that give the solution for each value of C_{bo} of equation (3). The profiles for the different initial concentrations are depicted in Fig. 1. It is noteworthy that the initial portions of the profiles are almost linear and independent of the initial liquid concentration, C_{bo} , and that this region constitutes an increasing portion of the profile as C_{bo} decreases.

The application of the non-linear film-transfer model to the kinetic data for an initial gold concentration of 8,73 mg/l is illustrated in Fig. 3, and the results for all the initial concentrations employed are given in Table III.

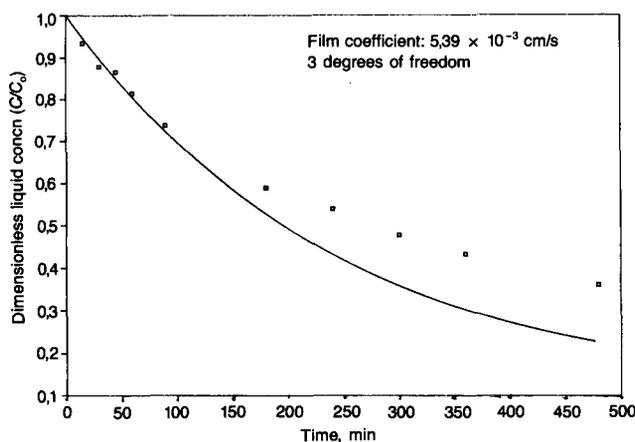


Fig. 3—Non-linear film-diffusion model for an initial gold concentration of 8,73 mg/dm³

TABLE III

NON-LINEAR FILM-TRANSFER MODEL: FILM COEFFICIENTS FOR DIFFERENT INITIAL GOLD CONCENTRATIONS

Initial gold concentration (C_{bo}) mg/l	k_f 10^{-4} cm/s	Degrees of freedom	Minimum sum of squared errors
5,30	5,40	10	$2,48 \cdot 10^{-2}$
5,30	8,10	3	$1,08 \cdot 10^{-3}$
8,73	5,39	3	$3,95 \cdot 10^{-4}$
32,00	5,42	3	$5,87 \cdot 10^{-4}$
54,44	5,26	3	$8,33 \cdot 10^{-4}$
111,11	4,18		$7,70 \cdot 10^{-4}$

Fig. 4 illustrates the inadequacy of the model at the most favourable C_{bo} value of 5,3 mg/l by comparing the application of the model to the whole range of kinetic data over 480 minutes with the application over the initial 60 minutes only. The inadequacy of the model became considerably more pronounced as the initial concentra-

tion of gold increased. This inadequate performance of the model is at variance with the results of Johns⁷ since he used such a high ratio of carbon to solution that the concentration of the gold solution was reduced to unmeasurably low levels before intraparticle diffusion became relevant. Therefore, the results of the present study do not support the assumption of film-transfer control of the adsorption rate over the range of gold concentrations considered.

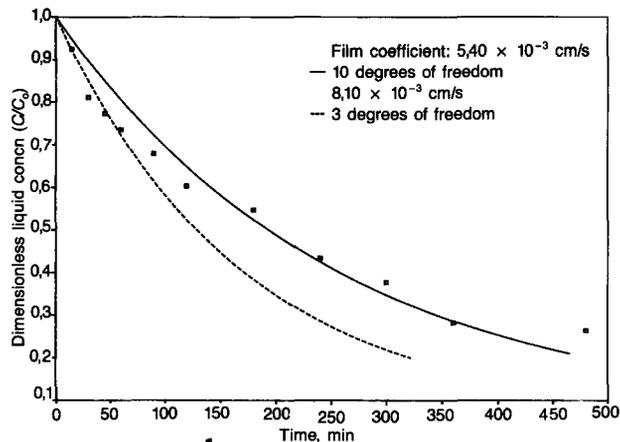


Fig. 4—Non-linear film-transfer model: Determination of the film coefficient at different degrees of freedom from either the initial or all the data values (initial gold concentration 5,3 mg/dm³)

The results obtained from the linear and non-linear film-transfer models are compared graphically in Fig. 5, from which it appears that the k_f values for the two models are substantially similar. For this comparison, it should be borne in mind that the methods of determining k_f in both models are insensitive, i.e. the number of degrees of freedom is small, and on this basis no significant relationship appears to exist between the values obtained from the two models. Thus, the more sophisticated non-linear film model does not appear to represent a significant improvement over the simpler, linear film model.

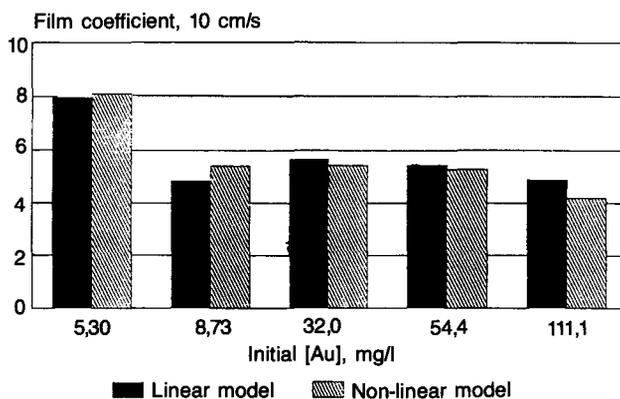


Fig. 5—Linear and non-linear film-transfer models: Comparison of film-transfer coefficients for rate studies at different initial gold concentrations

Empirical Rate Model of La Brooy *et al.*

The empirical model suggested by La Brooy *et al.*¹² as described by equation (5) was applied to test its adequacy

at describing the available kinetic data. The equation was linearized by the plotting of $\ln(q/C)$ against $\ln t$ and the fitting of a linear regression model to the modified data to obtain a slope n and an intercept $\ln k_f$. The resulting values of n and k_f are given in Table IV, and the model equations are compared in Fig. 6.

TABLE IV
EMPIRICAL RATE MODEL OF LA BROOY *et al.*¹²: MODEL PARAMETERS FOR DIFFERENT INITIAL GOLD CONCENTRATIONS

Initial gold concentration (C_{bo}) mg/l	k_f [min]m ^{1/2}	n (slope)	Correlation coefficient
5,30	0,327	1,229	0,9580
8,73	1,052	0,935	0,9985
32,00	2,189	0,742	0,9988
54,44	3,177	0,640	0,9985
111,11	—	—	—

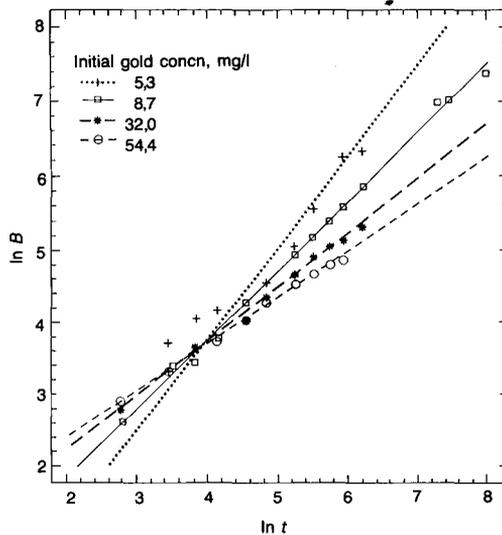


Fig. 6—Comparison of La Brooy model curves for different initial gold concentrations

It is apparent that the model fits the data well over the full time range for all the initial gold concentrations studied except 111 mg/l, where the transformation was totally non-linear. Unlike the findings of La Brooy *et al.*, the present study did not yield n values close to unity in all cases. However, their study was conducted at an initial gold concentration of 10 mg/l, and the n value in Table IV for $C_{bo} = 8,73$ mg/l is slightly below unity. It appears therefore that their observation is a special case at the initial concentration they had selected.

Homogeneous Surface-diffusion Model

The homogeneous surface-diffusion model (HSDM) was derived in a form that assumed constant diffusivity. This assumption was made to limit the number of model parameters to two, since recognition of the concentration dependence of D_s would introduce a third parameter into the HSDM equations²⁵ to describe the increase in the effective surface diffusivity with increasing surface loading. In this regard, Van Deventer⁶ success-

fully applied a three-parameter gold-adsorption model in which he assumed that the surface concentration was dependent on the surface diffusivity. A residence time of about 1 hour in a typical CIP reactor underlies the assumption of the present study that the two-parameter model is justified when applied to kinetic data that have been collected at relatively low loadings. If the gold loading approaches the equilibrium loading, a more sophisticated model is required, as shown by Van Deventer⁶.

The application of the HSDM to the experimental kinetic data is illustrated in Fig. 7 for an initial gold concentration of 8,73 mg/l. The values of the fitted parameters for the other initial concentrations are provided in Table V and illustrated in Fig. 8. The results indicate a good fit of the HSDM over the time range studied. Fig. 8 shows an increase in D_s with increasing initial gold concentration, but no particular trend for the k_f values.

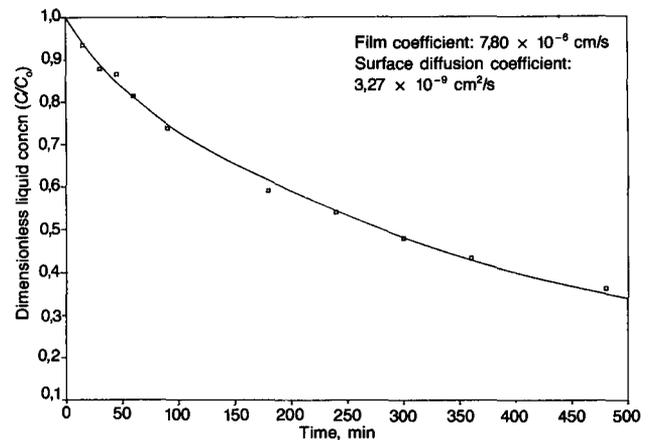


Fig. 7—Homogeneous surface-diffusion model for an initial gold concentration of 8,73 mg/dm³

TABLE V
HOMOGENEOUS SURFACE-DIFFUSION MODEL: MODEL PARAMETERS FOR DIFFERENT INITIAL GOLD CONCENTRATIONS

Initial gold concentration (C_{bo}) mg/l	HSDM parameters		Model fit: minimum sum of squared errors 10^{-3}
	k_f 10^{-4} cm/s	D_s 10^{-9} cm ² /s	
5,30	3,70	2,10	6,67
8,73	0,11	3,04	1,11
32,00	4,40	9,81	1,64
54,44	1,62	15,2	1,02
111,11	0,54	22,6	1,60

The absence of a simple relation between $[Au]_0$ and k_f may be attributable to a combination of two factors, viz the relative inaccuracy of the analytical determination of the residual-gold concentration as discussed above, and the insensitivity of the HSDM to variation in the k_f value. Since the film coefficient is determined mainly from the initial portion of the rate curve, small variations in the analytical accuracy of the first few data points could have a significant impact on its magnitude. On the whole, the model can be considered to be satisfactory for a time range of about 300 minutes for initial gold concentrations of up to about 110 mg/l.

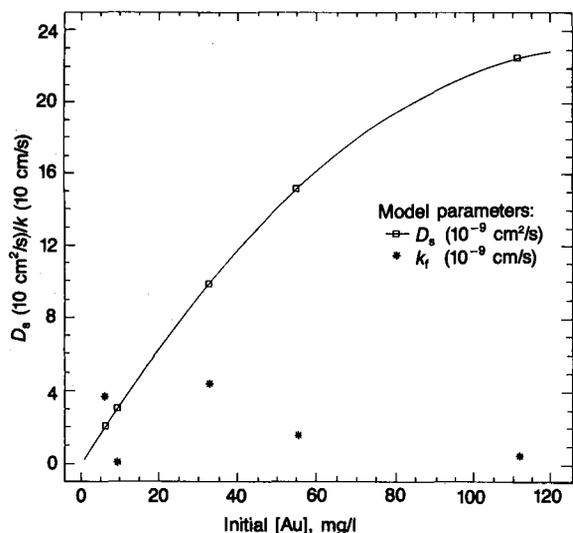


Fig. 8—Comparison of k_f and D_s for different initial gold concentrations

HSDM Sensitivity Analysis

The sensitivity of the HSDM was analysed at an initial gold concentration of 8,73 mg/l since that case gave a good description of the experimental data and has some practical significance.

Fig. 9 contains the model curves for film coefficients of 50, 75, 125, 150, and 200 per cent of the optimum parameter value, and compares these responses with that of the model that best fits the data. It appears that fairly large increases in k_f have only a slight effect on the model up to times of 200 minutes, but that a reduction in k_f has more marked effects. This shows that the accurate determination of k_f is not possible from the present experiments. Generally, the effect of variation in k_f is to change the initial slope of the model curve up to about 100 minutes. Fig. 10 shows the effect of variations in the surface-diffusion coefficient, D_s , by 50, 75, 125, and 150 per cent. The effect is smoother than when the film coefficient is varied, and it is notable that decreases in D_s had the effect of decreasing the gold adsorption rate over the entire period of the experiment.

CONCLUSIONS

Kinetic-rate models based on film-transfer resistance were found to be of limited applicability in describing the rate of gold adsorption in the adsorbent-adsorbate systems studied. Although these models tend to describe the rate data better at lower initial gold concentrations, both models were found to be useful only for the first hour, representing a low gold loading.

Both two-parameter models investigated in the study, viz the empirical model of La Brooy *et al.*¹² and the homogeneous surface-diffusion model (HSDM), were found to adequately describe the experimental kinetic data over the period of 480 minutes selected for this study. The former model was found to be most suitable at lower initial gold concentrations, and could not be applied at the highest concentration of 111 mg/l. However, concentrations such as this would not be encountered in practice. A shortcoming of this model is its empirical basis, which makes it suitable as a descriptive, rather than as a predictive or mechanistic, tool. Both from a fundamen-

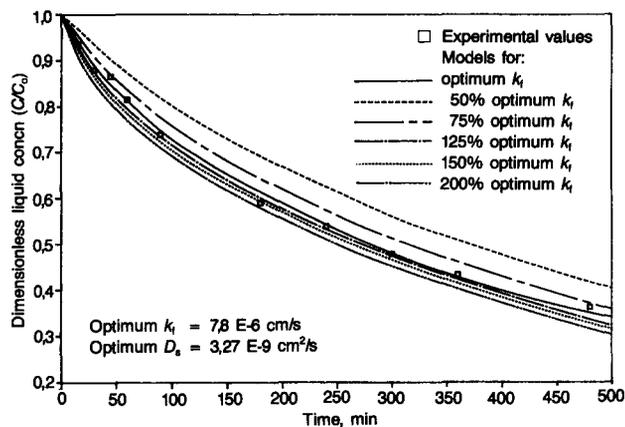


Fig. 9—HSDM: Sensitivity of the model to variations in the film coefficient k_f (initial gold concentration 8,73 mg/dm³)

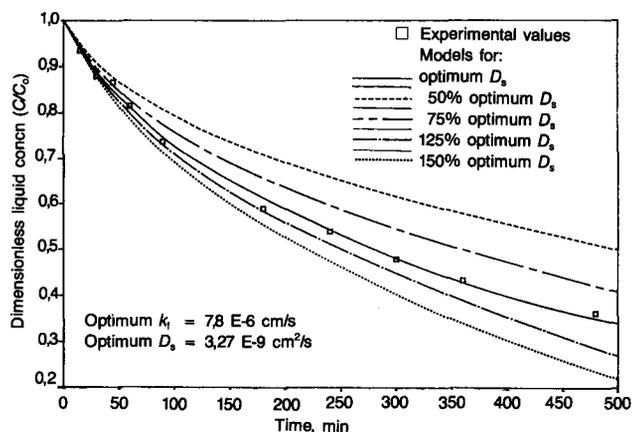


Fig. 10—HSDM: Sensitivity of the model to variations in the surface-diffusion coefficient D_s (initial gold concentration 8,73 mg/dm³)

tal and a descriptive point of view, the two-parameter HSDM was found to be adequate for the purpose of describing the rate of adsorption of gold cyanide in a batch reactor.

It is worth noting that these experiments and most of the other experiments conducted to date have used clear solutions. The effect of slurries on the adsorption performance have been studied by Jordi *et al.*²⁶.

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Comminution processes

The South African Institute of Mining and Metallurgy will be holding a 3-day school devoted to the **Practical Design of Comminution Processes**. The School is scheduled for 14th to 16th May, 1991, in Johannesburg.

Objective

The objective of the School is to provide a wide insight into the modern theory and practices employed in the selection of comminution rates especially, but not exclusively, for those whose experience has previously been mainly confined to Witwatersrand gold ores.

The curriculum will be specifically biased towards North American practice, and Derek Barratt of Wright Engineers, Vancouver, Canada, has agreed to accept the role of principal lecturer. Support will be given by Jens Lichter and other local experts, who will provide a South African perspective.

Who Should Attend

The School will be structured to cater for all actively involved in the many facets of the design and operation of comminution plants.

The Curriculum

Because of the logistical problems involved in assembling a timetable for a school where the lecturers are situated at opposite sides of the world, it is not possible to publish a timetable at this stage. However, the topics that will be covered include the following:

- Work indices
- Testwork on impact crushing
- Effect of mineralogy on test results
- Interpretation of drill-core results
- Batch-scale tests
- Structuring of pilot-plant testwork
- Interpretation of results and scale-up
- Comparison of alternative comminution routes
- Pulp rheology and its effect on grinding efficiency
- Classification
- Mill geometry
- Choice of ancillary equipment
- Financial analysis
- Control and optimization
- Simulation.

Social Events

The programme includes a barbecue on 14th May and a half-day technical visit on 16th May.

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