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The simulation of gold adsorption by carbon using a film diffusion model

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2015-04-22
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The same argument may not apply to the fluidized bed tests, as the observed kinetics were slower than for the fixed bed. The mass transfer coefficients obtained from the fixed bed were greater in value than those obtained from the fluidized bed at equivalent Reynolds numbers. Although this was not expected, Kunii[24] reported that the mass transfer coefficients in a fixed bed are twice the value of those obtained in a fluidized bed. This may be due to different flow conditions, e.g. bypassing in fluidized beds or plug flow in packed beds. Rahman[23] and Snowdon[22] reported in their correlations (which hold for both fluidized and fixed beds) that, as the voidage increases, the mass transfer coefficient decreases. Hence, contrary to simple logic, fixed beds provide a better system for mass transfer than fluidized beds.

The dimensionless numbers for each test were calculated and are shown in Table 4.9. All three carbon size fractions were used, and the linear velocity varied from 0,009 to 0,017 m s^{-1}. The voidage remained constant at 0,57. The Reynolds numbers varied from 16,8 to 37,1, and the Sherwood numbers varied from 96 to 181.

To analyse the effects of particle diameter and linear velocity on the mass transfer coefficient, Equations 1-1, 1-2 and 1-5 were used. These are the dimensionless number correlations relating to fixed beds. The plots listed in Table 4.3 were drawn and the slopes and linear regression correlation coefficients obtained. The results appear in Table 4.10.

TABLE 4.9 Dimensionless numbers for fixed bed tests

Test	Particle diameter m	Linear velocity m s^{-1}	Reynolds number	Sherwood number
FA	0,001 85	0,013	23,5	113,9
FB	0,001 85	0,017	31,5	123,1
FC	0,002 18	0,013	27,7	159,7
FD	0,002 18	0,017	37,1	181,4
FE	0,001 55	0,013	20,2	97,4
FF	0,001 55	0,016	25,4	105,6
FG	0,002 18	0,009	20,5	122,5
FH	0,001 85	0,009	16,8	101,9
FI	0,001 85	0,017	32,0	123,1
FJ	0,001 55	0,016	24,6	95,6

NOTE: For all tests -

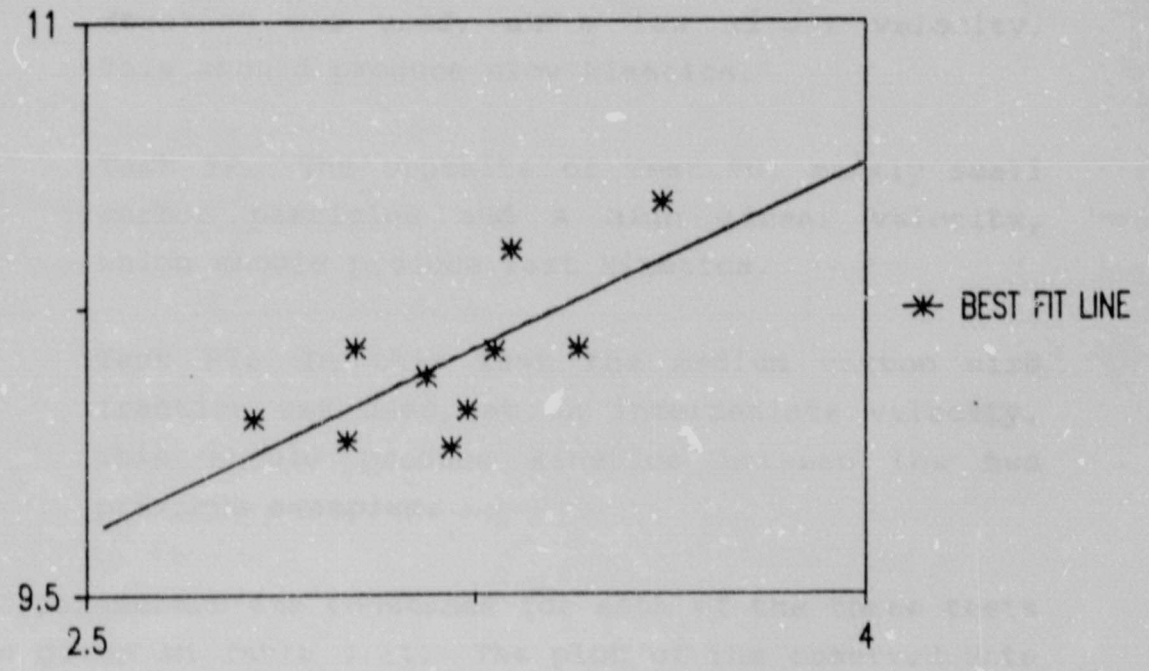
1. The Schmidt number = 1000
2. The density = 1000 kg m^{-3}
3. The viscosity = 0,001 kg m^{-1} s^{-1}
4. The diffusivity = 10^{-9} m^2 s^{-1}
5. The voidage = 0,57

TABLE 4.10 Fitting dimensionless number correlations for the fixed bed

Relationship tested	Correlation coefficient	q
4-1	0,71	0,64
4-2	0,71	0,64
5-5	0,71	0,64

In the review of the dimensionless number correlations (Table 1.1), the power of the Reynolds number is given as 0,5 by all investigators except one. The three different dimensionless correlations tested provided similar values. As Equation 1-2 was derived from work on ion exchange resins in fixed beds[22,23], as well as fitting the fluidized bed data, this equation was used to propose a correlation. Equation 1-2 states that a plot of ln *Re versus* ln $(Sh \cdot \epsilon / Sc^{0,33})$ should produce a straight line. This plot for the fixed bed tests is shown in Figure 4.11. The linear regression correlation coefficient of this plot is 0,71, the low figure probably being due to the occurrence of a change of mechanism, as previously discussed.

FIG 4-11 FIXED BED DIMENSIONLESS NUMBER FIT
BY PLOTTING LN(Re) versus LN((Sh.ϵ)/(Sc**1/3))



The dimensionless number correlation proposed for fixed beds from the above results is:

$$Sh = \frac{0,859}{\epsilon} Re^{0,648} Sc^{0,333} \qquad 4\text{-}2$$

The relationships suggested by Rahman[23] and Snowdon[22], who completed their work on adsorption, were quoted in Section 4.5.2. The relationship proposed above is similar to those suggested previously from ion exchange resin testwork. To illustrate this relationship, a plot of the observed data and the predicted curves for selected tests was drawn. The mass transfer coefficient for each test was calculated from Equation 4-2, and the predicted curves were then calculated by Equation 2-9.

The three batch tests were chosen for the following reasons:

* Test FG. In this test the largest carbon size fraction was used, at a low linear velocity. This should produce slow kinetics.

* Test FF. The opposite of Test FG, namely small carbon particles and a high linear velocity, which should produce fast kinetics.

* Test FI. In this test the medium carbon size fraction was used, at an intermediate velocity. This should produce kinetics between the two previous examples.

The parameters and constants for each of the three tests are given in Table 4.11. The plot of the observed data and the predicted curves is shown on Figure 4.12. As expected, the predicted lines fit the data during the initial stages but, after two to three hours, the

predicted kinetics are faster than the observed kinetics because, as already discussed, after some time the mechanism changes from film diffusion control to intraparticle diffusion control, slowing down the mass transfer. As the model is based purely on film diffusion control, any interaction from particle diffusion control will cause the predicted kinetics to be faster than those observed.

It can be concluded that the effects of particle diameter and linear velocity in a fixed bed can be linked to the mass transfer coefficient via dimensionless numbers, provided the system is under film diffusion control.

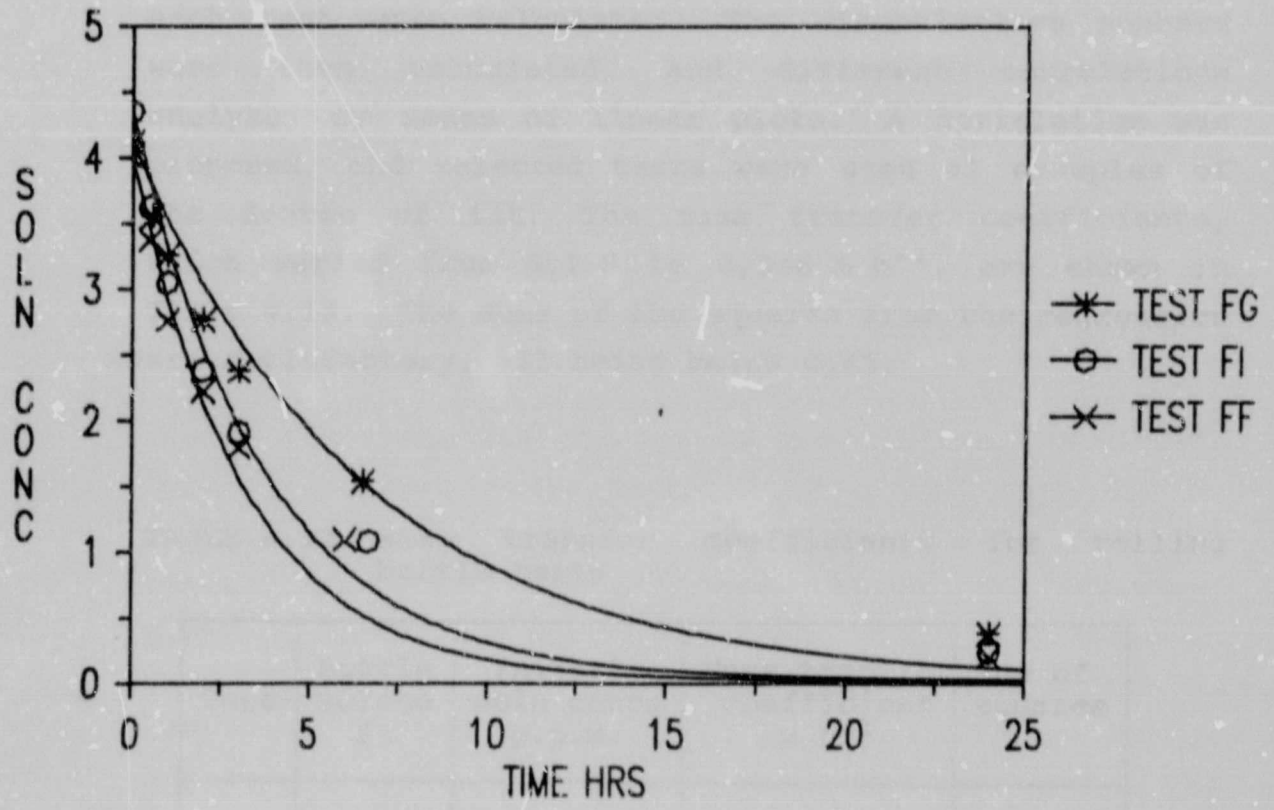
TABLE 4.11 Fixed bed examples for predicted curves against observed data

Test	FG	FI	FF
Particle diameter m	0,002 18	0,001 85	0,001 55
Linear velocity m s^{-1}	0,009 4	0,017 3	0,016 4
Mass of carbon kg	0,007 95	0,007 68	0,007 73
Reynolds number	20,5	32,0	25,4
Sherwood number	106,7	142,2	122,5
Mass transfer coefficient m h^{-1}	0,176	0,277	0,285
Voidage	0,57	0,57	0,57

NOTE: For all tests -

Mass of solution	=	20 kg
Schmidt number	=	1000
Initial carbon concentration	=	0 mg kg^{-1}
Diffusivity	=	10^{-9} m^2 s^{-1}
Viscosity	=	0,001 kg m^{-1} s^{-1}
Density	=	1000 kg m^{-3}
Freundlich *a*	=	8,812 x 10^{-21}
Freundlich *b*	=	4,538

FIG 4-12 FIXED BED MODEL FITS



4.5.4 The rolling bottle

The purpose of these tests was to link the angular velocities of the bottles to the mass transfer coefficient, using the following procedure: the equilibrium constants and the mass transfer coefficients for each test were calculated. The dimensionless numbers were then calculated, and different correlations analysed by means of linear plots. A correlation was proposed, and selected tests were used as examples of the degree of fit. The mass transfer coefficients, which varied from 0,178 to 0,336 m h^{-1}, are shown in Table 4.12. The sums of the squares from the regression are satisfactory, all being below 0,03.

TABLE 4.12 Mass transfer coefficients for rolling bottle tests

Test	Bottle volume ℓ	Initial soln concn p.p.m.	Mass transfer coefficient m h^{-1}	Sum of squares
AE	2	4,65	0,205 3	0,022
AC	2	4,62	0,249 3	0,004
AI	2	4,86	0,262 9	0,017
AA	2	4,89	0,325 3	0,009
AG	2	4,57	0,311 7	0,002
AF	5	4,65	0,178 3	0,005
AD	5	4,62	0,214 8	0,005
AJ	5	4,86	0,257 4	0,026
AB	5	4,89	0,356 4	0,008
AH	5	4,57	0,335 8	0,008

NOTE: For all tests - Mass of solution = 0,5 kg
Mass of carbon = 0,000 77 kg
Freundlich *a* = 3,686 x 10^{-12}
Freundlich *b* = 2,596

Dimensionless numbers are required to link the speed of rotation of the bottles to the mass transfer coefficient. A variable for speed is included in the Reynolds number. For the column tests, this variable is the linear velocity of the solution through the column, but a different definition of velocity is required for the rolling bottle tests. The options open to define this term are

* the angular velocity - rad s^{-1}
* the speed of rotation - rev s^{-1}
* the velocity of the bottles past the rollers, that is, tip speed - m s^{-1}

During the testwork, bottles of two different diameters were used. When these bottles are placed on a set of rollers rotating at a set speed, the bottle with the smaller diameter has a higher speed of rotation, although their tip speeds are identical. At low speeds of rotation, the method of agitation in the bottle is the shear caused by the moving interface. At higher speeds of rotation, the major cause of agitation in the system is centrifugal force. The motion of the bottle causes a mixing pattern in the bottle similar to that encountered in milling.

For the system studied, centrifugal force was the major factor agitating the system. Hence, a bottle of a smaller diameter would have a greater degree of agitation, and the use of tip speed in the Reynolds number would be incorrect. Either of the other options would be correct, as they define the degree of agitation. Angular velocity was the term used in calculating the Reynolds number for rolling bottles. The dimensionless numbers for the tests undertaken are listed in Table 4.13.

TABLE 4.13 Dimensionless numbers for rolling bottle tests

Test	Angular velocity rad s^{-1}	Reynolds number	Sherwood number
AE	0,86	1 591	105,3
AC	2,18	4 033	128,0
AI	3,99	7 381	135,0
AA	6,48	11 988	167,2
AG	9,33	17 260	160,0
AF	0,70	1 295	91,3
AD	1,62	2 997	110,0
AJ	2,93	5 420	132,2
AB	4,82	8 917	183,1
AH	7,25	13 412	172,5

NOTE: For all tests -

1. The Schmidt number = 1000
2. The density = 1000 kg m^{-3}
3. The viscosity = 0,001 kg m^{-1} s^{-1}
4. The diffusivity = 10^{-9} m^2 s^{-1}
5. The voidage = 0,99
6. The particle diameter = 0,001 85 m

The angular velocities ranged from 0,7 to 9,3 rad s^{-1}, producing Reynolds numbers ranging from 1300 to 17 300. The Sherwood numbers varied from 91 to 173

The dimensionless correlations 1-1, 1-2 and 1-5 were used to analyse the effect on the mass transfer coefficients of changing the angular velocity. The linear plots associated with these equations were drawn and the slopes and linear regression coefficients obtained. The results are given in Table 4.14. As all three equations yielded identical results, Equation 1-2 was used for the rolling bottle tests, in keeping with the equation proposed for the fluidized and fixed beds.

This equation states that the plot of ln *Re versus* ln ($Sh \cdot \epsilon / Sc^{0,33}$) should produce a straight line. This plot for the rolling bottle tests is shown in Figure 4.13. The linear regression correlation coefficient of this plot is 0,93.

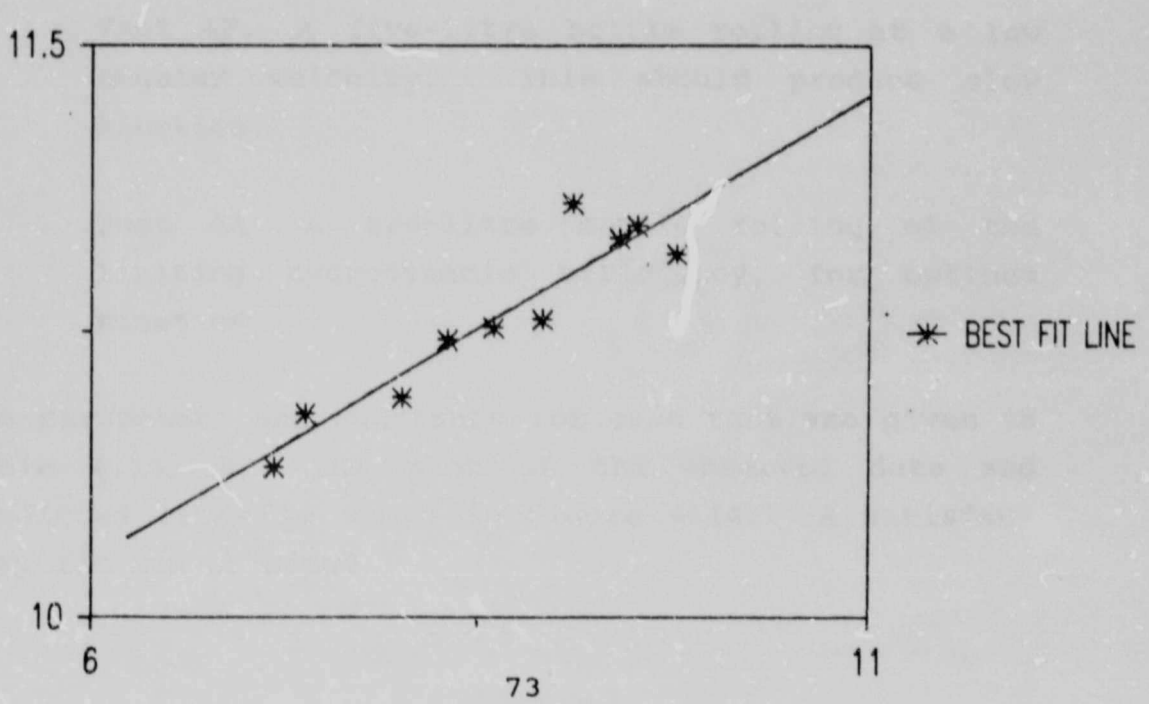
The dimensionless number correlation proposed for rolling bottles, based on the above results, is

$$Sh = \frac{1,64}{\epsilon} Re^{0,244} Sc^{0,333} \qquad 4\text{-}3$$

TABLE 4.14 Fitting dimensionless number correlations for the rolling bottle tests

Relationship tested	Correlation coefficient	q
1-1	0,93	0,244
1-2	0,93	0,244
1-5	0,93	0,244

FIG 4-13 ROLLING BOTTLE DIMENSIONLESS NUMBER FIT
BY PLOTTING LN(Re) versus LN((Sh.ε)/(Sc**1/3))



The power of the Reynolds number for the rolling bottle tests was less than that obtained for the column tests - 0,24, compared with 0,59 and 0,65. When a system is under film diffusion control, provided the limiting hydrodynamic efficiency has not been reached, the liquid side mass transfer coefficient is dependent on the degree of agitation. The degree of agitation is contained in the Reynolds number, and, if the degree of agitation is close to the limiting hydrodynamic efficiency, the Reynolds number will have less effect on the Sherwood number (the term containing the mass transfer coefficient). In the bottle rolling tests, rolling at an angular velocity greater than 6,5 rad s^{-1} had no effect on the kinetics of adsorption. It can therefore be concluded that the degree of agitation in the bottles had reached the limiting efficiency, and hence it would be reasonable to expect the power of the Reynolds number to be low.

Two examples were chosen to illustrate equation 4-3, the correlation of which was used to calculate the mass transfer coefficient, and equation 2-9 was used to predict the rate of adsorption. The reasons for the choice of the examples were

* Test AF. A five-litre bottle rolling at a low angular velocity. This should produce slow kinetics.

* Test AA. A two-litre bottle rolling at the limiting hydrodynamic efficiency, for optimum kinetics.

The parameters and constants for each test are given in Table 4.15, and the plot of the observed data and predicted lines is shown in Figure 4.14. A satisfactory fit was obtained.

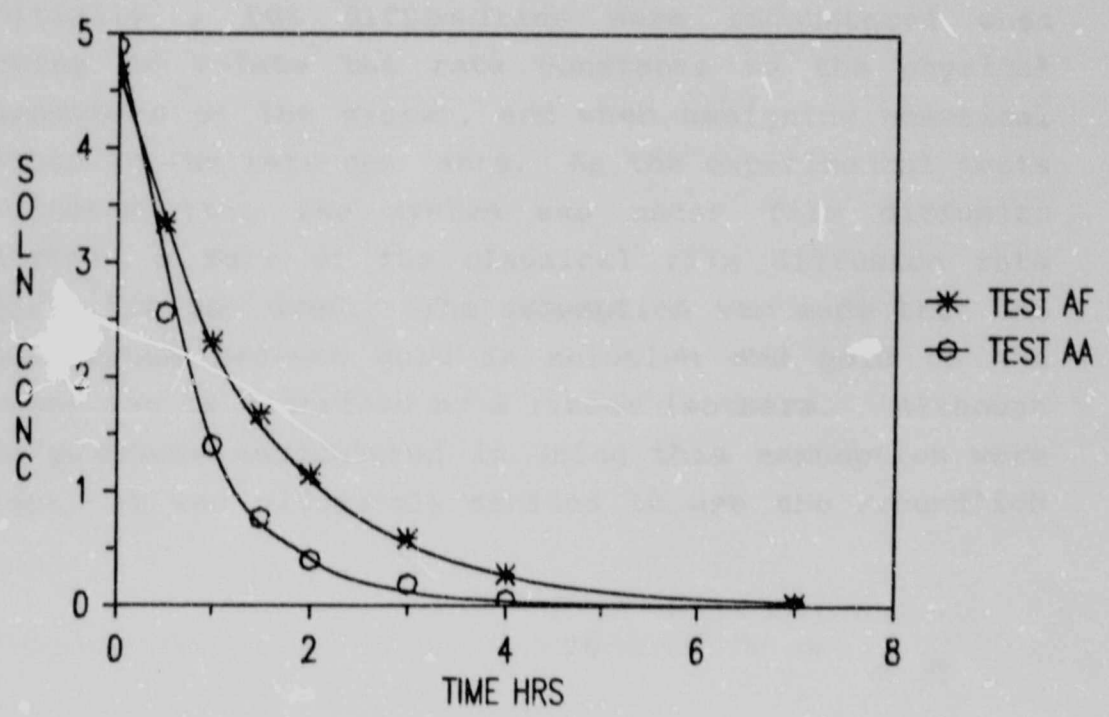
TABLE 4.15 Rolling-bottle examples for predicted curves against observed data

Test		AF	AA
Particle diameter	m	0,001 85	0,001 85
Angular velocity	rad s^{-1}	0,70	6,48
Mass of carbon	kg	0,000 77	0,000 77
Reynolds number		539	4 990
Sherwood number		95,5	164,4
Mass transfer coefficient	m hr^{-1}	0,186	0,32
Voidage		0,99	0,99

NOTE: For all tests -

Mass of solution	=	0,5 kg
Schmidt number	=	1000
Initial carbon concentration	=	0 mg kg^{-1}
Diffusivity	=	10^{-9} m^2 s^{-1}
Viscosity	=	0,001 kg m^{-1} s^{-1}
Density	=	1000 kg m^{-3}
Freundlich *a*	=	3,686 x 10^{-12}
Freundlich *b*	=	2,596

FIG 4-14 ROLLING BOTTLE MODEL FITS



It can therefore be concluded that the angular velocity of a rolling bottle in which gold adsorption by carbon is taking place can be linked to the mass transfer coefficient by means of dimensionless numbers.

4.6 *CONCLUSIONS*

The rate-controlling step was tested by means of interruption tests. A gold-bearing solution (made up by dissolving potassium gold cyanide in demineralized water buffered by borax) was contacted with virgin Le Carbone G210 AS carbon, and the interruption tests showed that the adsorption was under film diffusion control until the carbon reached 60 to 70 per cent of its equilibrium loading value, after which indications of intraparticle control were noted. The assumption that the system was under film diffusion control was further verified by rolling bottle tests at different rates of agitation.

A first order reversible type rate expression was used initially , but difficulties were encountered when trying to relate the rate constants to the physical parameters of the system, and when assigning numerical values to the rate constants. As the experimental tests indicated that the system was under film diffusion control, a form of the classical film diffusion rate expression was used. The assumption was made that the equilibrium between gold in solution and gold on the carbon can be described by a linear isotherm. Although the problems encountered in using this assumption were minor, it was ultimately decided to use the Freundlich

isotherm to describe the equilibrium. The rate expression had the form

$$r = (A_c/V_s)\ \rho_s\ k_1\ (C_s - a\ (C_c)^b)$$

Five rolling bottle tests at different ratios of carbon mass to solution volume were completed. The equilibrium constants and the mass transfer coefficients were calculated. It was shown that the observed data can be accurately predicted by the use of the component mass balance and the rate expression developed.

Some of the factors influencing the extent of adsorption affect the rate of the reaction, while others affect the equilibrium loading capacity of the carbon. The kinetics of the reaction between gold and carbon are slow, and therefore most practical systems operate away from equilibrium.

A rate expression, based on film diffusion control, was proposed, and the factors affecting the rate, namely carbon particle size and agitation rate, were investigated. After reviewing the literature on dimensionless number correlations, six forms of correlation were tested on three agitation systems, namely, fluidized bed, fixed bed and rolling bottles. The best-fitting correlation was then derived for each system. The correlations linked the Sherwood number (containing the mass transfer coefficient) to the Reynolds number (containing the particle size and agitation rate) and the Schmidt number. At equivalent Reynolds numbers, the fixed bed provided the optimum system for mass transfer.

5 CONCLUDING CHAPTER

5.1 GENERAL SUMMARY OF WORK COMPLETED

It has been known since 1894 that carbon adsorbs gold, and this knowledge has been used on a commercial scale since the 1970s. The actual mechanism of the adsorption still confuses and perplexes investigators to the present day. It is for this reason that no fundamental rate expression has been developed. Models available are either empirical or based on experimental observation.

The reaction of the adsorption of gold onto carbon is slow, taking hundreds of hours to approach equilibrium, and for this reason the kinetics of the reaction are the most important aspect in modelling the simulation of the adsorption. The factors affecting the adsorption can broadly be split into those affecting the rate and those affecting the equilibrium capacity.

The aim of this project was to develop a simple mathematical model, based on experimental verification, to simulate the adsorption of gold by carbon. Virgin carbon was used, and the gold solution was potassium gold cyanide dissolved in demineralized water. The simulation included two of the factors affecting the rate, namely carbon particle size and agitation rate. Three different systems were studied - rolling bottles, fixed beds and fluidized beds.

It was assumed that the rate controlling step was film diffusion, and interruption tests in a fluidized bed on solutions of 5 p.p.m. gold concentration verified this assumption. When the carbon had reached 60 to 70 per cent of its equilibrium gold loading capacity, however, indications of intraparticle diffusion control were noted. Confirmation of the film diffusion control of the system was shown by varying the agitation rate in rolling bottles, and, as the rate was increased, the kinetics increased, until a "limiting hydrodynamic efficiency" was reached.

A rate expression, based on the classical film diffusion rate expression, was developed, namely

$$r = (A_c/V_s)\ \rho_s\ k_l\ (C_s - a\ (C_c)^b)$$

The equilibrium constants a and b were derived from the Freundlich isotherm. The mass transfer coefficient (k_l) was obtained from experimental results by a non-linear regression method. After developing the mathematical model for the batch tests from the rate expression and associated mass balance, experimental work was carried out on different ratios of carbon mass to solution volume. The model was shown to hold for these experimental tests.

In order to examine the effect of carbon particle size and agitation rate on the mass transfer coefficient, experimental testwork was undertaken whereby these two factors were varied in the three agitation systems (fluidized bed, fixed bed and rolling bottle). After reviewing the literature, six methods of linking the Sherwood number (containing the mass transfer coefficient) to the Reynolds number (containing the particle diameter and agitation rate) were selected.

Subsequent analysis of the experimental data resulted in the proposal of three dimensionless number correlations, namely

Fluidized bed : $Sh = \frac{0,75}{\epsilon} Re^{0,59} Sc^{0,33}$ $20 < Re < 50$

Fixed bed : $Sh = \frac{0,86}{\epsilon} Re^{0,65} Sc^{0,33}$ $15 < Re < 40$

Rolling bottle : $Sh = \frac{1,64}{\epsilon} Re^{0,24} Sc^{0,33}$ $1300 < Re < 17\ 000$

The literature was reviewed for similar relationships. The power of the Reynolds number varied from 0,33 to 0,60. The value of the constant varied from 0,8 to 1,1. The relationships proposed from this investigation are similar to those encountered in the literature for similar systems.

These correlations and the mathematical model developed from the rate expression were shown to fit the experimental data for selected tests. It was found that the fixed bed was the system which yielded the best mass transfer at equivalent Reynolds numbers.

5.2 *LIMITATIONS*

The aim of this project was to develop a simple model capable of simulating the adsorption of gold by carbon, including the factors affecting the rate. During the development, assumptions were made, and various points noted, that might put limitations on the use of the model. The limitations are as follows:

* The experimental work showed that the rate controlling step was film diffusion. However it was established that, when the carbon had reached 60 to 70 per cent of its equilibrium loading value, indications of intraparticle diffusion control began to show. As the rate expression is based on film diffusion control, the model can only be used if the carbon loading is away from its equilibrium loading capacity. This is not a serious limitation, because, in the real situation (CIP plants), equilibrium is only approached after hundreds of hours. The residence time of carbon per stage in plants varies from 8 to 48 hours.

* During the testwork it was noted that the rate of adsorption increased with increasing agitation rate, until a limiting hydrodynamic efficiency was reached, after which point any further increase in the agitation rate had no effect on the kinetics. According to the dimensionless number correlations developed, the mass transfer coefficient is a function of the agitation rate. Therefore, if these correlations are used, it must be ascertained that the system under consideration has not reached its limiting

Author Johns Mark William
Name of thesis The Simulation Of Gold Adsorption By Carbon Using A Film Diffusion Model. 1987

PUBLISHER:
University of the Witwatersrand, Johannesburg
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