The authors proposed that the reduction, albeit partial reduction, is an important aspect of the loading mechanism. They postulated that the adsorption is a two-step process. The initial stage involves the adsorption of an ion-pair $M^{n+}[Au(CN)_2^-]_n$ onto the carbon. Once the gold complex is on the carbon, they visualize it as being reduced in a second step to some unidentified species.

In conclusion, it can be said that there is much confusion with little agreement. The theories involving complete reduction can be discounted, and there is little chance of the adsorption being electrostatic, but all other theories are possible.

1.3 FACTORS AFFECTING ADSORPTION

The rate of adsorption onto carbon is slow. Nicol[7] showed that carbon isolated in a stage of a carbon-in-pulp plant had not reached equilibrium after 300 hours. It is for this reason that the rate of adsorption is the most important factor governing the design and optimization of the adsorption circuit. The factors affecting adsorption can be broadly split into two:

* those affecting the rate of adsorption, and
* those affecting the gold loading capacity of the carbon.

Literature concerning the factors affecting adsorption dates back to 1914, and Fleming[3,8] provides extensive coverage on the subject.

The factors affecting the adsorption rate are the carbon particle size, the pulp density, and the mixing efficiency. The smaller the particle diameter, the faster the rate of adsorption. The particle size has no influence on the equilibrium loading capacity. Fleming[8] noted an inverse dependence of the rate on the mean particle diameter. An increase in the concentration of inert solids has the effect of decreasing the rate. This could be due to a decrease in the mixing efficiency as a result of increased apparent viscosity, or due to physical "blinding" of the carbon surface by slimes in the pulp. Fleming has shown that, at gold concentrations of 10 p.p.m. and less in solution, the rate of gold adsorption is dependent on mixing speed. At higher gold concentrations in solution, the rate becomes less dependent on mixing speed. This is due to a change of adsorption mechanism from film diffusion control to intra-particle diffusion control.

The factors affecting the equilibrium capacity are the pH value, the ionic strength, the free cyanide and the temperature. The pH value has a marked effect on the equilibrium capacity, this capacity increasing for decreasing pH value. This effect is especially marked at values below 7. The rate also increases slightly in more acid solutions. Fleming's results indicate that the loading rate and equilibrium loading capacity increase with increasing ionic strength. The effect on the loading capacity is much greater than that on the loading rate. An increase in the concentration of free cyanide depresses the rate of loading and the equilibrium capacity, and this feature is also utilized in the elution of gold from activated carbons. Fleming confirmed what other researchers had already noted: that the equilibrium loading is exothermic in nature, that is, the equilibrium loading decreases with an

increase in temperature. This forms the basis of the high-temperature elution procedure adopted on most carbon-in-pulp plants today. The increase in loading rate with temperature is fairly small, in common with most diffusion-controlled processes.

A further factor affecting the adsorption is the presence of other ions in solution, or the presence of certain solids. These are collectively termed the poisons of carbon, and are detailed by Fleming[9]. Calcium carbonate, formed by the reaction of lime and carbon dioxide, precipitates in the pores of the carbon and is detrimental to adsorption. The calcium carbonate can be removed from the carbon by washing with a dilute acid (HCl). Haematite physically adsorbs onto the carbon to form a skin, which is detrimental to the adsorption of gold. During reactivation, haematite is converted to magnetite, which is acid-soluble. Organics (machine lubricants, detergents, polar solvents, flotation reagents) are all known to poison the carbon to varying degrees. If the organics enter the adsorption circuit faster than the carbon withdraws them, the stage efficiency profile will be flat. If the opposite situation occurs, the stage efficiencies will increase down the plant. The organics are removed from the carbon during the reactivation stage.

Lower adsorption efficiencies are obtained when using calcine pulps. The calcine forms a skin which affects the kinetics of adsorption, not the capacity of the carbon. Shales and clay type minerals also decrease the efficiency of adsorption.

Various base metals are usually leached with gold in cyanide solutions, notably copper, nickel, cobalt, iron and zinc. However, with the exception of copper and, to

a lesser extent, nickel, the cyanide complexes of these metals are apparently not loaded onto activated carbon, and their presence in solution has little effect on the extraction efficiency of gold.

The loading of copper cyanides onto carbon is influenced by the chemical conditions in the solution. The two parameters affecting the loading of copper are the free cyanide content and the pH value of the solution. Fleming's results[8] showed that the $Cu(CN)^-$ complex loads well, whereas the $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ species do not load appreciably. At a cyanide to copper ratio of 1 to 4, the copper complexes are loaded more strongly than gold and actually "squeeze" gold cyanide off the carbon. At higher ratios, the copper complexes do not load and have no effect on the adsorption of gold.

1.4 LITERATURE REVIEW ON APPROACHES TO MODELLING

In this section, the literature is reviewed with respect to the following topics:

* the rate of the reaction and the rate controlling step
* the different models written to simulate the adsorption of gold by carbon
* the mathematical description of the equilibrium isotherm, and
* dimensionless number correlations.

McDougall[5] lists both Feldtmann (1914) and Gross (1927) as stating that the adsorption of gold cyanide by carbon is slow. As mentioned, Nicol[7] showed that, even after 300 hours, carbon isolated in a stage of a CIP circuit had not yet reached complete equilibrium. It is for this reason that the rate of adsorption is the most important factor governing the modelling and simulation of the adsorption of gold onto carbon.

Fleming[10] observed that the rate of mass transfer is about an order of magnitude slower than would be expected if simple mass transfer through the bulk was rate-controlling. He concluded that either film diffusion, intraparticle diffusion, or reaction at the carbon surface is rate-controlling. Cho[11] stated that adsorption of gold by carbon in a solution concentration of 100 to 200 p.p.m. is controlled by pore diffusion. Fleming[8] completed a detailed investigation on the rate controlling step, and his conclusions are noted below:

1 Under film diffusion control the mixing efficiency (stirring speed) influences the rate of gold adsorption by carbon. At gold concentrations of 1 p.p.m., the rate of gold extraction is strongly dependent on stirring speed, which is consistent with film diffusion. At higher concentrations (±100 p.p.m.) the stirring speed still has an effect on the rate, but this effect is not as marked as in the 1 p.p.m. solution concentration.

2 During testwork on the effect of carbon particle size on the rate of adsorption, an inverse dependence of the rate on the mean particle diameter was detected. This is generally

believed to be indicative of a reaction that is controlled by film diffusion (Helfferich[12]), an inverse squared dependence pointing to control by intraparticle diffusion.

3 Under conditions of control by intraparticle diffusion, the rate of extraction should be virtually independent of the concentration of gold in solution. Fleming's results showed that intraparticle diffusion is significant at gold concentrations of 100 p.p.m.

4 Fleming undertook interruption tests to distinguish between film and intraparticle diffusion control, and concluded that film diffusion control is dominant at loadings of up to 50 per cent of the equilibrium value.

Peel[13], on whose work van Deventer's work[14] is based, assumes in his model that a surface diffusion mechanism is responsible for the transport in the pores. He bases his assumption on the conclusion of several researchers, that, when working with strongly adsorbed solutes, surface diffusion gives a more rational description of transport than is given by a pore diffusion mechanism.

It can therefore be concluded that the rate controlling step for adsorption is initially film diffusion control. As the carbon nears its equilibrium gold loading value, intraparticle surface diffusion starts to play an integral part. The contribution from intraparticle diffusion increases with mixing efficiency, gold concentration in solution, and the degree of gold loading on the carbon from its equilibrium value.

Hence, to model the adsorption of gold by activated carbon, several pertinent points must be considered. They are:

1 that the rate of adsorption is slow, and hence the rate is the most important step governing the modelling of adsorption;

2 that the fundamental mechanism of adsorption is unknown, and, since a single incontrovertible rate expression is not available, semi-empirical rate expressions based on experimental verification are used;

3 that, because the rate controlling mechanism is dependent on conditions, at low concentrations and away from equilibrium, the system is under film diffusion control, and that factors such as gold concentration, agitation rate, pulp density, type of carbon and carbon particle size, affect the transition from film diffusion control to intraparticle diffusion control;

4 that, since certain factors affect the rate and others the equilibrium, any rate expression should have terms for the rate and the equilibrium;

5 that the adsorption, if viewed as a reaction, is reversible.

Although there are many models relating to the adsorption of adsorbates other than gold (Peel[13]), only those relating to gold adsorption by activated carbon will be discussed here. As stated, the modelling of the adsorption process should be based on the kinetics of the adsorption reaction.

In 1979, Fleming[10] suggested an empirical rate expression which took the form:

$$C_c - C_c^o = k\, C_s\, t^n$$

where k and n are constants.

The continuous process was solved by defining t as the mean residence time of carbon, and using the gold mass balance. The expression is purely empirical and not based on any theoretical reasoning. Time also appears as an independent variable, which is unsuitable.

Hussey[15] determined that the equilibrium concentrations between carbon and solution can be described by the Freundlich isotherm. To model a batch counter-current operation, Hussey used a McCabe-Thiele approach to estimate reasonable carbon loadings in each stage. Using these estimates, the McCabe-Thiele diagram was constructed, using the Freundlich isotherm to describe the equilibrium. He then proceeded to calculate the residence time of carbon in each stage via a complex procedure. The procedure used will not be discussed in this report, as the method predicts a plant requiring different carbon residence times in each stage. This can only be achieved in a counter-current situation by having different carbon concentrations in each stage, or by having different contactor volumes. Operating plants do not follow this strategy.

In 1982 Lenne[16] used a rate expression originally suggested by Dixon[17]. This rate expression is based on the reversibility of the reaction and contains a term which allows for the capacity loading of the carbon, that is, a driving force term. No theoretical discussion or experimental evidence is provided by either of the authors as to how the rate expression was obtained.

The rate expression used had the form:

$$r = k_1 C_s (C_c^* - C_c) - k_2 C_c$$

where k_1 and k_2 are the forward and reverse rate constants and C_c^* is the maximum capacity of the carbon for gold. Dixon[17] showed that, at equilibrium, the rate expression can be simplified to the Langmuir isotherm, which fairly satisfactorily represents the equilibrium loading behaviour of gold out of real pulps. The use of the maximum loading capacity instead of the equilibrium loading capacity, as in ion-exchange models, can lead to errors. In a CIP plant, the gold loading on the carbon decreases down the train, and therefore the model will predict better extractions down the train due to the driving force term, an observation not detected on operating plants.

Williams[18] used the same rate expression as Menne and Dixon. Although he did not include the mathematics of the batch test, he modelled the continuous process by using a CSTR mass balance, ignoring the accumulation in the solution phase. He did not include any experimental verification of predicted results, nor discuss the effects of the system parameters, such as agitation rate or particle size, on the rate constants. Work by the author of this dissertation shows that the rate constants do vary as the mentioned parameters are varied. Hence, Williams provides an accurate method of mathematically describing the process, but his procedure has not yet been verified through experimental work.

In 1984, Nicol[7,19] and Fleming[8] proposed a new rate expression based on the consideration of the boundary between the activated carbon and the solution as an interface across which gold is transferred in the form of the aurocyanide ion. The assumption is made that

equilibrium is established at the supposedly homogeneous outer surface, and that mass transfer of the gold into the bulk of the carbon particle can be characterized by a single pseudo mass transfer coefficient and a corresponding quantity for the solution phase. A further assumption is that the equilibrium between the gold on the carbon and that in the solution at the interface can be described by a linear expression. If the concentration gradients are linear in both phases, the rate expression can be derived. The rate expression suggested was

$$r = k\ (K\ C_s - C_c)$$

where k is the rate constant and K an equilibrium constant. This rate expression, integrated when the system is far from equilibrium, yields the rate expression first proposed by Fleming. The rate expression suggested by Dixon[17] includes a driving force term $(C_c^{\dagger} - C_c)$. if the system is away from equilibrium, that is, $C_c^{\dagger} \gg C_c$, Dixon's expression condenses to a form identical to the expression suggested by Nicol and Fleming. They showed that their suggested rate expression fitted experimental data from batch tests. Using a CSTR mass balance without the term for accumulation in the solution phase , they were able to model the continuous process and show good fits between observed and predicted data from a pilot plant rig. As discussed in Section 1.3, Fleming identified the factors influencing the adsorption. He determined that the system parameters affecting the rate are the carbon particle size, the pulp density and the mixing efficiency. The factors affecting the equilibrium capacity of carbon are the pH value, the ionic strength, the free cyanide level and the temperature. Hence, Fleming and Nicol developed a rate expression and showed

reasonable fits in both the batch and continuous processes. However, due to the assumption that the equilibrium between the gold in solution and the gold on the carbon can be described by a linear isotherm, this rate expression cannot be used if high solution concentrations are encountered, as the linear isotherm will predict higher carbon loadings than those encountered in the real situation. Although the factors affecting the rate were identified, no attempt was made to describe the rate constant in terms of these factors.

The latest published model is that of van Deventer[14]. He bases his work on Peel's branched pore model[13]. This model assumes that the carbon consists of macropores, in which the initial rapid adsorption takes place, and micropores, in which restricted diffusion occurs. In the van Deventer model, the mechanism of the adsorption of gold is not a single step, but a multi-step mechanism, as follows:

* transfer across the liquid boundary layer surrounding the carbon particle, the rate of transfer across the film being described by a linear driving force expression;

* adsorption at the solid-liquid interface, assuming that local equilibrium exists, and that the transfer from the dissolved state to the adsorbed state is reversible, not rate-controlling, and can be described by the Freundlich isotherm;

* transport of gold in the macropore network by a surface diffusion mechanism, the accumulation in the liquid phase within the pores being negligible;

* diffusion from the macropores to the micropores, the rate being described by a linear driving force, and no transfer of gold from the external liquid film to the micropores taking place.

The model produces six constants, namely, the liquid mass transfer coefficient, the two constants in the Freundlich isotherm, the surface diffusion coefficient, the rate coefficient for transfer, and the fraction of macropores. Although van Deventer shows a good fit between his predicted results and observed results, there is a problem in determining the model's constants independently. The mathematics of his proposed model are also complex, requiring large computational facilities. The effects of the system parameters on the constants are also not mentioned.

It can therefore be said that the approaches of Fleming[10] and Hussey[15] seem to be inadequate. The models suggested by Menne[16], Williams[18], Nicol[7,19], Fleming[8], and van Deventer[14], all show good fits when compared with observed data. As the rate controlling mechanism does change, using a single rate expression (Dixon[17] and Nicol[7]) can cause errors when trying to describe the whole spectrum of adsorption. Van Deventer's model, on the other hand, does describe the change in mechanism, but the complexity of the mathematics limits its use. As a suitable theoretical rate expression has not yet been established, semi-empirical rate expressions based on experimental verification will have to suffice for the present.

To describe the equilibrium between the gold in solution and the gold loaded on the carbon, McDougall[5],

Cho[11], Peel[13], van Deventer[14], and Hussey[15] all successfully use the Freundlich isotherm. Menne[16], on the other hand, shows that his rate expression at equilibrium is equivalent to the Langmuir isotherm, which he quotes as representing the equilibrium loading behaviour of gold from real pulps.

If the system under study is in the film diffusion control regime, then the liquid side mass transfer coefficient can be linked to the system parameters via dimensionless numbers. Gilland[20] uses this concept, by relating the mass transfer coefficient in his rate expression to the system parameters by use of the Reynolds number. As was discussed in Section 1.3, the particle size and agitation rate affect the rate of adsorption. Both these system parameters affect the Reynolds number. The liquid side mass transfer coefficient is included in the Sherwood number. The literature was reviewed for correlations linking the Sherwood number to the Reynolds number for fluidized and fixed beds. Numerous correlations were found, resulting from testwork on ion exchange, crystallization, particulate electrodes, and other systems. A summary of the correlations found in the literature is given in Table 1.1. Basically, these correlations take on six different forms, namely:

$$Sh = 2 + p\, Re^{q}\, Sc^{0,33} \qquad 1\text{-}1$$

$$Sh = p/\epsilon\, Re^{q}\, Sc^{0,33} \qquad 1\text{-}2$$

$$Sh = p/\epsilon\, [Re\ (1 - \epsilon)]^{q}\, Sc^{0,33} \qquad 1\text{-}3$$

$$Sh = 2 + [Re\ (1 - \epsilon)]^{q}\, Sc^{0,33} \qquad 1\text{-}4$$

$$Sh = p\ Re^{q}\ Sc^{0,33} \qquad 1\text{-}5$$

$$Sh = p\ [Re\ (1 - \epsilon)]^{q}\ Sc^{0,33} \qquad 1\text{-}6$$

where p and q are constants, q normally 0,5.

Equations 1-1 to 1-6 hold for fluidized beds, while for fixed beds Equations 1-1, 1-2 and 1-5 hold.

Therefore, if the system is under film diffusion control, the liquid side mass transfer coefficient can be linked to the system parameters via one of the dimensionless number correlations.

TABLE 1.1 Mass transfer dimensionless number relationships

Investigator	Ref. No.	Relationship	Fixed bed	Fluidized bed	System studied	Reynolds No. range	Other
Frössling	21	$Sh = 2 + 0,6\ Re^{0,5}\ Sc^{0,33}$	-	-	Evaporation	-	
Budz	21	$Sh = 2 + 0,9\ Re^{0,5}\ Sc^{0,33}$	No	Yes	Crystallization	10 to 80	
Helfferich	12	$Sh = 2 + 0,37\ Re^{0,6}\ Sc^{0,33}$	-	-	-	<20	
Snowdon	22	$Sh = 0,81/\epsilon\ Re^{0,5}\ Sc^{0,33}$	Yes	Yes	Ion exchange	±10	
Rahman	23	$Sh = 0,86/\epsilon\ Re^{0,5}\ Sc^{0,33}$	Yes	Yes	Ion exchange	2 to 25	
Fan	24	$Sh = 2 + 1,5\ [(1 - \epsilon)\ Re]^{0,5}\ Sc^{0,33}$	No	Yes	-	5 to 120	
Fleischmann	25	$Sh = (1 - \epsilon)^{0,5}/\epsilon\ Re^{0,5}\ Sc^{0,33}$	No	Yes	Particulate electrodes		ϵ <25
Akselrud	20	$Sh = C\ Re^{0,5}\ Sc^{0,33}$	-	-	Dissolution	-	
Budz	20	$Sh = 0,93\ Re^{0,5}\ Sc^{0,33}$	No	Yes	Crystallization	10 to 80	
Yip	25	$Sh = 1,09/\epsilon\ Re^{0,33}\ Sc^{0,33}$	Yes	No	-	<0,1	
Ranz	24	$Sh = 2 + 1,8\ Re^{0,5}\ Sc^{0,33}$	Yes	No	Evaporation	>80	

where $Sh = k_l\ d_p/D$ $\quad Re = d_p\ u\ \rho/\eta$ $\quad Sc = \eta/D\rho$

1.5 OBJECTIVES OF THE PRESENT STUDY

It has often occurred during the development of a process, that its engineering and process design advance far more rapidly than the mathematical description of the process; this is the case in the development of gold adsorption by activated carbon. As discussed earlier, because the reaction comes to equilibrium slowly, the rate of adsorption is the most important factor governing the simulation of gold adsorption by carbon. Rate expressions to describe the adsorption have been suggested, as have mathematical models to describe the batch and continuous processes. It has been detected and noted that certain parameters influence the rate and others influence the equilibrium loading capacity. Those affecting the rate are carbon particle size, pulp density and mixing efficiency, as discussed in Section 1.3. It is not certain whether pulp density is an independent factor or whether it is interlinked with mixing efficiency. In the mathematical descriptions available, no attempt has been made to link these physical parameters to the rate. Hence, one of the primary objectives of this study is to link the rate to the system parameters. The ability to quantify the rate in terms of the rate-affecting factors makes available a method to permit the use of laboratory tests in the design of plants.

The aim of the project can be defined as an endeavour to develop a mathematical model to simulate the rate of adsorption of gold cyanide onto carbon in clear solutions for different agitation systems (fluidized bed, fixed bed and rolling bottles). The simulation must include the physical parameters of the sytem that affect the rate.

The hypothesis tested is that, when adsorption occurs at low concentrations of gold in solution, the controlling mechanism is film diffusion. On this basis, a rate expression incorporating a liquid side film diffusion coefficient can be written. The physical parameters of the system can then be incorporated into the simulation by means of dimensionless number correlations.

The work to be outlined in this project proceeds in the following order:

1 A rate expression based on film diffusion is developed. The model for the batch test is discussed, and the method of obtaining the constants outlined.

2 The procedure followed for the experimental work is presented.

3 On the basis of an interruption test and a test using a varying agitation rate, it is verified experimentally that the rate controlling step in the adsorption range which is of practical interest is film diffusion control.

4 From tests completed at different solution volume to carbon mass ratios, it is shown that the proposed model is capable of simulating the adsorption of gold.

5 From batch adsorption tests done at different carbon particle sizes and agitation rates, dimensionless number correlations are developed for fluidized beds, fixed beds and rolling bottles.

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