

# The isotherm shift in carbon-in-pulp adsorption circuits

by L.C. Woollacott\* and G. Nino de Guzman\*

## SYNOPSIS

The isotherms that are usually taken to represent the force 'driving' the adsorption in carbon-in-pulp processes may change from contactor to contactor. This paper reports on an investigation into the extent to which this isotherm shift is influenced by the changes in oxygen and cyanide concentration that occur in operating plants. The impact of the isotherm shift on the reliability of simulation results is examined.

## SAMEVATTING

Die isoterme wat gewoonlik geag word die krag te verteenwoordig wat die adsorpsie in koolstof-in-pulp prosesse 'aandryf', kan van een kontaktor na in ander verander. Hierdie referaat doen verslag oor in ondersoek na die mate waarin hierdie isotermsverskuiwing beïnvloed word deur die veranderinge in die suurstof- en sianiedkonsentrasie wat in bedryfsaanlegte voorkom. Die impak van die isotermsverskuiwing op die betroubaarheid van die simulatiesresultate word ondersoek.

## INTRODUCTION

Almost universally, the isotherm information used in the assessment of adsorption performance in carbon-in-pulp (CIP) plants is obtained from equilibrium tests involving the gold-bearing solution (or slurry) feeding the circuit and samples of the regenerated or fresh carbon used at the plant. Such an isotherm is referred to here as the 'feed/regen isotherm' for the circuit. It is common practice for this single isotherm to be taken as representative of the force driving the adsorption in each of the contactors in the plant. There are a number of potential problems with this practice.

The first is a problem of principle. Nowhere in a CIP operation is feed slurry contacted deliberately with regenerated carbon. Feed slurry comes into contact with carbon that is highly loaded, while regenerated or fresh carbon comes into contact with slurry that is all but barren. The feed/regen isotherm therefore applies to a system that does not occur in practice, and its applicability to the adsorption occurring on a plant is to some extent in question.

The second problem arises because the compositions of the solution and of the carbon in each contactor are complex and change down the adsorption train. It is well known that changes in the adsorption conditions can influence the adsorption isotherms. Fouling of the carbon, if it occurs, decreases the adsorptive capacity of the carbon the longer it remains in contact with the gold-bearing slurry<sup>1,2</sup>. Some of the ions compete with gold for adsorption onto carbon, and the concentrations of these influence the adsorption isotherms for gold<sup>3-5</sup>. In addition, the concentrations of dissolved oxygen and cyanide in the gold-bearing solution influence the loading capacity of the carbon<sup>6-8</sup>.

Table I gives an indication of how the compositions of solution and carbon can change down an adsorption train. The implication of this change is that each contactor should be associated with a different isotherm, and each should be different to a greater or lesser extent from the feed/regen isotherm. The change in the isotherm from contactor to contactor is referred to here as an 'isotherm shift'.

The errors that are introduced by the assumption that the feed/regen isotherm is representative of conditions in all the contactors are generally thought to be small. However, a preliminary investigation<sup>9</sup> carried out in 1988 at the CIP-adsorption circuit at Grootvlei indicated that this might not be so.

The results indicated, firstly, that a significant isotherm shift was evident at Grootvlei, and that the feed/regen isotherm was rather different from the isotherms for the first three contactors. (Those for the fourth and fifth contactors could not be determined reliably.) Secondly, the results suggested that the shift was in an unexpected direction. The loading capacity of the carbon decreased from the first to the third contactor. If the carbon were being fouled in any way, the loading capacity would be expected to increase down the adsorption train.

As a result of these observations, further investigations were undertaken into the nature of the isotherm shift in operating CIP plants. Specifically, the following questions needed to be addressed.

- (1) How significant is the isotherm shift in operating plants?
- (2) What factors most affect the isotherm shift?
- (3) How do these factors change in operating plants?
- (4) In view of the isotherm shift, to what extent does a feed/regen isotherm represent the conditions that exist down an adsorption train?

In the investigations described in this paper, it was decided to concentrate on the influence of oxygen and cyanide. There were several reasons why this was done. Firstly, the concentrations of these two components can, in principle, be manipulated in a CIP operation. Secondly, their synergistic influence on adsorption had not been studied previously.

The investigation began with a careful examination of the combined influence of oxygen and cyanide on synthetic adsorption systems. Thereafter, plant systems were examined. This involved a careful monitoring of plant conditions, coupled with a determination of the associated adsorption isotherms.

## EXPERIMENTAL

In order to determine the combined influence of oxygen and cyanide on the adsorption isotherms, it was necessary

\* University of the Witwatersrand, P.O. Wits, 2050 Transvaal.

© The South African Institute of Mining and Metallurgy, 1993. SA ISSN 0038-223X/3.00 + 0.00. Paper received November 1992; revised paper received May 1993.

**Table I**  
**Adsorption conditions at Grootvlei in 1988**

		Feed solution	Contactor					Regenerated carbon
			1	2	3	4	5	
Solution conditions	Temp, °C pH	12,0	18,6 11,5	18,4 *	17,1 *	17,8 *	17,9 12,0	
Composition of solution, ppm	CN <sup>-</sup>	89	*	*	*	*	*	
	O <sub>2</sub>	*	8,7	7,2	6,0	4,8	1,9	
	Lime	*	46	*	*	*	20	
	Au	3,2	0,72	0,19	0,05	0,009	0,004	
	Ca	438	422	488	499	476	458	
	Ni	7	7	8	6	4	2	
	Cu	6	6	7	7	7	7	
Undissolved gold in the solids, g/t		0,17	*	0,17	*	0,15	0,16	
Carbon loading, ppm	Au		3 180	1 090	320	110	40	10
	Ca		8 093	6 432	5 342	4 225	2 400	768
	Ni		9 794	8 687	7 355	6 594	4 466	962
	Cu		136	170	182	312	482	21

\* Not measured

to refine the procedure usually employed in equilibrium tests. In brief, the technique that was developed<sup>10,11</sup> was as follows. The solution and carbon were contacted in a closed vessel with a controlled oxygen–nitrogen atmosphere that was refreshed continually. The vessel was agitated in a bottle shaker. It was found that mechanical stirring and gas sparging had to be avoided; otherwise, there was excessive destruction of the cyanide in the solution. A further precaution that was adopted to minimize the destruction of cyanide was to powder the carbon so that the duration of the test could be shortened. In all the work reported here, an equilibration time of 50 hours was used.

Under these conditions, the oxygen level in the solution could be maintained at a level within 0,2 ppm of the target value. The average level of cyanide destruction during a test was 4,9 per cent—the maximum was 14,2 per cent. Without these precautions, the cyanide destruction reached levels that, in some cases, were in excess of 50 per cent. (It should be noted that the cyanide concentrations are reported in parts per million (ppm) of free cyanide, CN<sup>-</sup>.)

The synthetic adsorption systems that were tested consisted of virgin carbon (ANK11) ground to minus 75 µm. The activated carbon had previously been soaked in 5 per cent hydrochloric acid and hot water, followed by a double soaking in de-ionized water and drying at 110°C. The solutions were made up from potassium aurocyanide and potassium cyanide, and were buffered to a pH value of about 10,5 by the use of boric acid and sodium hydroxide. To ensure high ionic strengths in the adsorption system, the solutions were made up from a stock of 0,1 M potassium chloride. Adams<sup>12</sup> has shown how important this is when researchers want to make inferences meaningful to operating plants from work conducted on synthetic adsorption systems.

The tests on plant systems were conducted on samples prepared in the following way. A sample of slurry was taken from the contactor and was immediately screened at 0,42 mm to remove the carbon. This carbon was then rinsed thoroughly with plant water, was dried at 110°C, and was

then ground to minus 75 µm. The slurry was filtered, and the solution retained. The oxygen concentration of the solution was determined from a separate sample of the slurry. Soon after the solution had been filtered, the level of free-cyanide ions in the solution was determined titrimetrically by the use of silver nitrate and potassium iodide. The samples were then transported to the laboratory and were stored in a dark room.

Equilibrium tests were conducted under controlled conditions so that the oxygen levels were the same as those measured at the plant. The procedure described for the control of the oxygen and cyanide levels was again employed. It was not possible to conduct all the equilibrium tests immediately because the gas-control system was able to maintain only one oxygen–nitrogen atmosphere at a time. Consequently, the time taken to complete the determination of the parameters for the isotherms at a given plant was up to two weeks.

The solutions taken from the different contactors had low concentrations of gold. It was expected that, after being equilibrated with carbon, the concentrations would have been reduced well below accurate detection limits. To overcome this problem, the solutions from each contactor were spiked with potassium aurocyanide before each test. In this way, the gold concentration in solution at the beginning of each test was raised to about 5 ppm. As discussed shortly, this practice does not appear to have changed the isotherms. The gold concentrations in the feed solutions showed that the spiking had not been necessary.

In almost all cases, the results were fitted best by the Freundlich expression, equation [1]:

$$C_c = A C_s^n, \quad [1]$$

where  $C_c$  and  $C_s$  are the concentrations of gold on the carbon and in solution respectively,  $A$  is the loading capacity of the carbon in equilibrium with a solution of unit gold concentration, and  $n$  is a parameter.

## TESTS ON SYNTHETIC ADSORPTION SYSTEMS

Previous investigations into the influence of oxygen and cyanide on CIP-adsorption systems had focused on the effect of either oxygen or cyanide in isolation. In this investigation, the combined influence of these two components was studied. Synthetic systems were used. The work has been reported in detail elsewhere<sup>10,11</sup>. A summary of the results is shown in Figure 1, and the relevant conclusions are as follows.

- (a) An increase in the concentration of dissolved oxygen always enhances the loading capacity of the carbon, while an increase in the cyanide concentration is always detrimental.
- (b) The extent to which changes in the concentrations of these two components affect the loading capacity of the carbon depends on their concentrations in the gold-bearing solution. As shown in Figure 1, three composition regimes are important.
  - *Region A: Sensitive region.* In solutions with moderate to high oxygen concentrations (> 5,5 ppm) and low free-cyanide levels (< 100 ppm), the loading capacity is very sensitive to changes in the concentration of either component.
  - *Region B: Insensitive region.* In solutions with moderate to high oxygen concentrations (> 3,6 ppm) and high free-cyanide levels (> 100 ppm), the loading capacity is only slightly sensitive to changes in the concentration of either component.
  - *Region C: Oxygen-sensitive region.* In solutions low in oxygen (< 3,6 ppm), an increase in its concentration will increase the loading capacity significantly.
- (c) In both the insensitive and the oxygen-sensitive regions, the loading capacity decreases to a small extent with an increase in the cyanide concentration. The decrease is linearly proportional to the cyanide concentration.
- (d) The magnitudes of the loading capacities are highest in the sensitive region (Region A).
- (e) A simple model, equation [2], was developed to quantify the influence of oxygen and cyanide on the adsorp-

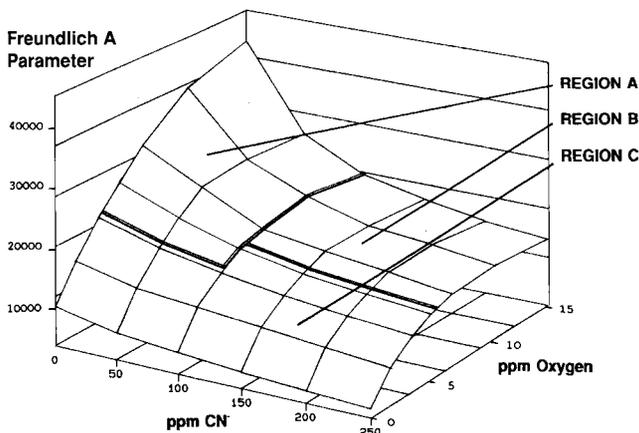


Figure 1—Combined influence of oxygen and cyanide on the loading capacity of carbon (the loading capacity is the Freundlich A parameter in equation [1] in g/t)

tion isotherms. It is valid for the synthetic system investigated, except in the region of low cyanide (< 40 ppm) and high oxygen levels (> 7 ppm), where it tends to under-predict the equilibrium loading on the carbon.

$$C_c = (\alpha - \beta CN) O_2^\gamma C_s^\delta, \quad [2]$$

where  $CN$  and  $O_2$  are respectively the concentrations of cyanide and oxygen in ppm. The respective values of the parameters  $\alpha$ ,  $\beta$ , and  $\gamma$  are 14 709, 25,62, and 0,2495. The influence of oxygen and cyanide on  $\delta$  can be estimated roughly by use of equation [3] or a value of 0,378 can be used.

$$\delta = 0,4257 O_2^{-(0,055 - (1E-4) CN)} \quad [3]$$

## CONDITIONS IN OPERATING PLANTS

The way in which the concentrations of oxygen and cyanide change down an adsorption train was investigated at Grootvlei, Western Deep Levels, and Kinross. The results shown in Table II were obtained from samples taken from each plant over a short period of time.

It is evident that the concentrations of both oxygen and cyanide in the gold-bearing solution can change very significantly down the adsorption circuit. The pH value of the solution appears to have a significant effect on this change. If the pH value is very high (11,5 at Kinross), the cyanide is very stable<sup>12</sup> and the oxygen concentration decreases only to a moderate degree from stage to stage. At lower pH levels (10 at Grootvlei and 9 at Western Deep Levels), both the cyanide and the oxygen concentrations can change dramatically. The effect is most significant in the first stage, where about 60 per cent of the cyanide is destroyed and between 20 and 70 per cent of the oxygen is removed from solution. Thereafter, the destruction of cyanide and the removal of oxygen are more moderate.

Table II  
Adsorption conditions at three CIP plants

CIP plant	Stage	Cyanide ppm	Oxygen ppm	pH
Grootvlei	Feed	64	9,0	9,9
	1	26	5,9	10,0
	2	32	5,2	10,0
	3	32	4,7	10,1
	4	26	4,1	10,2
	5	22	3,7	10,1
Western Deep Levels	Feed	82	8,2	9,0
	1	31	2,5	9,4
	2	32	2,3	9,3
	3	28	2,1	9,2
	4	21	1,3	9,1
	5	17	1,1	9,1
	6	15	1,6	9,1
7	15	1,0	9,0	
Kinross	Feed	139	10,4	11,9
	1	142	10,6	11,7
	2	138	9,7	11,7
	3	138	9,3	11,7
	4	137	9,1	11,6
	5	138	8,1	11,7
6	137	6,2	11,6	

It is well known that activated carbon is an oxygen scavenger, and it was noticed that the dissolved oxygen decreased when regenerated carbon was added to the circuit. As shown in Table III, a decrease of up to 30 per cent can occur within an hour of such additions, but the effect disappears within a short period (within 2 hours at the plant where the measurements were conducted). In the other contactors, the oxygen concentration was found to be relatively stable and to fluctuate primarily in sympathy with the conditions in the leach slurry feeding the circuit.

The concentrations of various ionic species in the different contactors at Grootvlei were determined in the preliminary investigation in 1988. These are shown in Table I. The loading of nickel, copper, and calcium on the carbon in loaded and eluted carbons at Kinross are shown in Table IV, where they are compared with the loadings found at Grootvlei.

Table IV shows that the levels of competing ions are higher at Grootvlei than at Kinross—seventeen times higher in the case of nickel. In addition, the loading of species other than gold on the carbon changes more dramatically at Grootvlei than at Kinross. The loading of nickel and calcium increases by a factor of 10 at Grootvlei but by only a factor of 2,7 at Kinross.

### TESTS ON SAMPLES FROM OPERATING PLANTS

The Freundlich parameters associated with each of the plant isotherms measured are shown in Table V.

**Table III**

Effect of the addition of activated carbon on the oxygen concentration in solution (Grootvlei, stage 5)

Elapsed time min	Oxygen reduction, %
0	0
1,5	2,8
2,0	14,3
2,5	11,4
3,0	22,8
3,5	22,8
49,0	31,4
120,0	0

**Table IV**

Loadings of various ions on carbon (Grootvlei results dated 1988 and Kinross results dated 1990)

Item	Ni		Cu		Ca	
	Loaded carbon	Eluted carbon	Loaded carbon	Eluted carbon	Loaded carbon	Eluted carbon
Carbon loadings, g/t at Grootvlei	9794	962	136	21	8093	768
at Kinross	574	214	54	2	2400	900
Ratio of carbon loadings (Grootvlei/Kinross)	17,1	4,5	2,5	10,5	3,4	0,85
Ratio of carbon loadings (loaded/ eluted) at Grootvlei	10,2		6,5		10,5	
at Kinross	2,7		27,0		2,7	

### Isotherm Shift at Grootvlei

The feed/regen isotherm for Grootvlei was measured on three occasions. The first was measured by Dew<sup>13</sup> in 1987 and involved open rolling bottles and equilibration times of 3 days. The average of three replicates is shown in Figure 2a. The second was conducted by Draper and Woollacott<sup>9</sup> in 1988 using a very similar procedure. The pH value of the solution in that test was about 12. The third was in the current work (1991), in which the oxygen and cyanide concentrations were closely controlled and the pH value was about 10. In addition, the carbon was powdered to  $-75 \mu\text{m}$ . The carbon had not been powdered in the two previous tests.

Figure 2a shows the agreement between the three determinations, an agreement that is remarkable considering that the tests were carried out by independent workers under different conditions using sets of samples taken from the plant on three occasions over a span of four years.

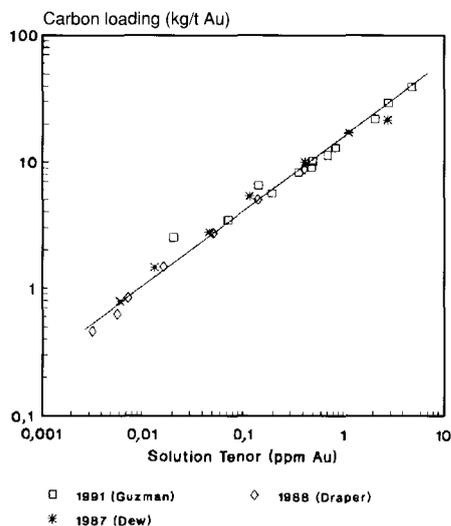
Figures 2b, c, and d compare the isotherms measured for the first three contactors in 1991 with those measured in the preliminary investigation in 1988. The two sets of determinations for each contactor are similar. This confirms the measurements made previously by Draper.

Figure 3 shows the isotherm shift that occurred at Grootvlei. (In the figure, the results from the investigations in 1988 and 1991 are combined.) It can be seen from Table V that the loading capacities of the carbon decreased from the first to the third contactor and then increased.

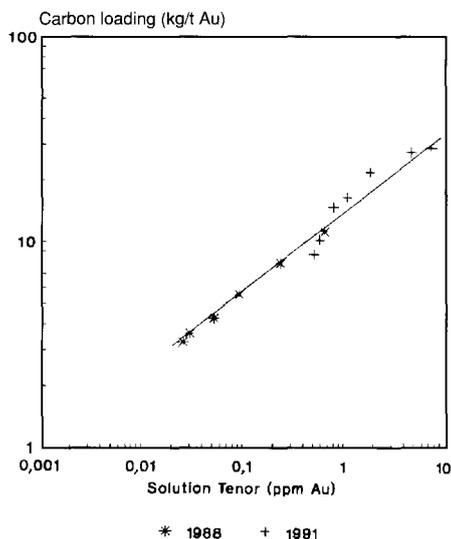
**Table V**

Freundlich isotherm parameters—plant-adsorption systems

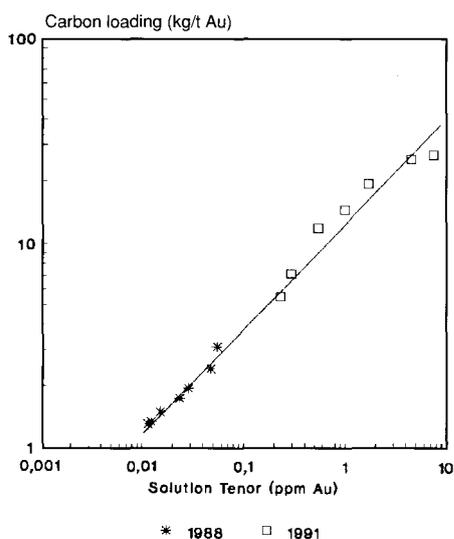
Contactor	A ppm	n	Correlation coefficient
<i>Grootvlei, 1988 (preliminary study)</i>			
Feed/regen	16 865	0,601	
1	13 733	0,385	
2	12 308	0,509	
3	7 170	0,468	
<i>Grootvlei, 1991</i>			
Feed/regen	15 096	0,507	
1	14 656	0,422	0,939
2	13 307	0,451	0,966
3	8 360	0,577	0,951
4	15 524	0,691	0,951
5	13 389	0,695	0,948
<i>Western Deep Levels</i>			
Feed/regen	13 720	0,502	
1	20 030	0,783	0,919
2	24 501	0,940	0,973
3	37 159	1,452	0,916
4	33 698	1,301	0,853
5	35 895	0,616	0,950
6	23 741	0,581	0,987
7	20 514	0,556	0,999
<i>Kinross</i>			
Feed/regen	12 853	0,602	
1	12 942	0,608	0,980
2	13 453	0,534	0,965
3	11 434	0,670	0,908
4	13 003	0,634	0,953
5	10 517	0,821	0,835
6	10 989	0,790	0,906



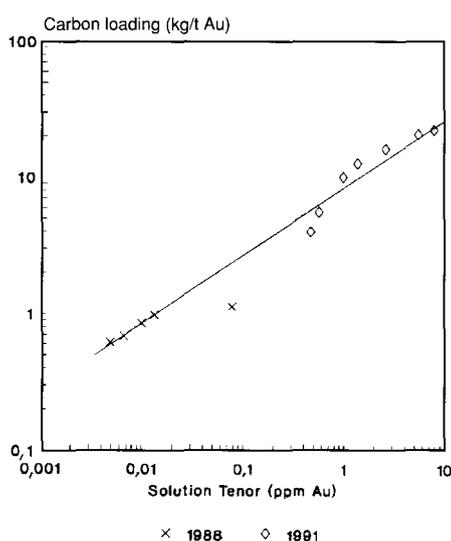
**a Feed/regen isotherms**



**b Isotherms for contactor 1**



**c Isotherms for contactor 2**



**d Isotherms for contactor 3**

**Figure 2—Adsorption isotherms for Grootvlei tests**

### Isotherm Shift at Western Deep Levels

The isotherm results obtained from the samples from Western Deep Levels show considerable scatter. Also, the values for  $n$  are abnormally high. The reason for the scatter and for the results being dubious is not known.

The results are shown in Table VI, however, because they indicate that there was a significant isotherm shift at the plant. The observed shift is opposite to that found at Grootvlei: the loading capacity increased from contactors 1 to 5, followed by a decrease in contactors 6 and 7.

### Isotherm Shift at Kinross

As can be seen from Figure 4, no significant isotherm shift was found at Kinross. The similarity of the feed/regen isotherm and the isotherms in each contactor demonstrates two additional things. Firstly, it demonstrates the reproducibility of the experimental procedure that was used. Secondly, it indicates that the addition of aurocyanide to the contactor solutions before the equilibrium tests did not alter the isotherm. Although this practice was not followed

in the determination of the feed/regen isotherm, the isotherm was similar to those in each contactor.

### THE REPRESENTIVITY OF FEED/REGEN ISOTHERMS

Where no isotherm shift occurs, it would be expected that the feed/regen isotherm would be essentially the same as those for each contactor. As already noted, this was found to be the case at Kinross. The representivity of the feed/regen isotherm is in question only in those plants where an isotherm shift occurs.

Figure 3 highlights the difference between the feed/regen isotherm and the isotherms in the first three contactors at Grootvlei. In the case of the fourth and fifth contactors, the isotherms are very similar to the feed/regen isotherm—at least, over the range of values measured.

What is important, however, is not so much the differences between the isotherms but the impact of such differences on the prediction of adsorption rates. To investi-

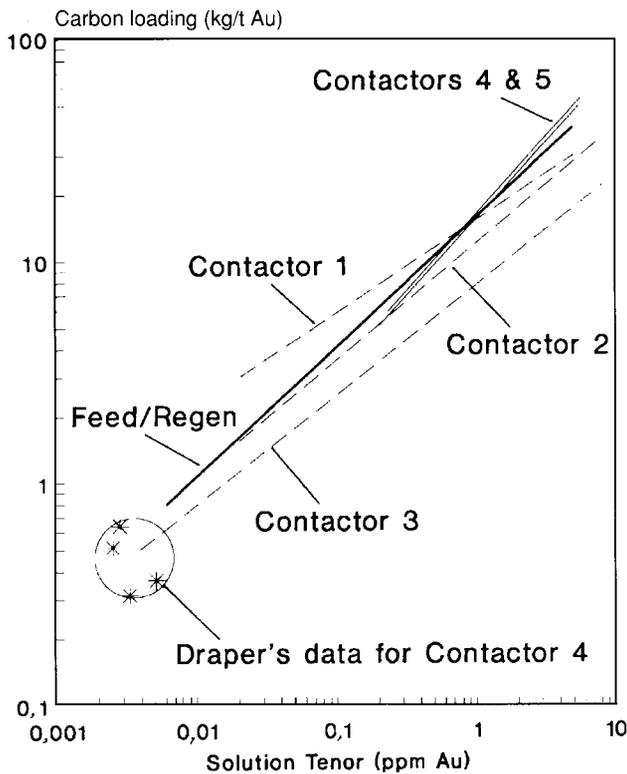


Figure 3—The isotherm shift at Grootvlei

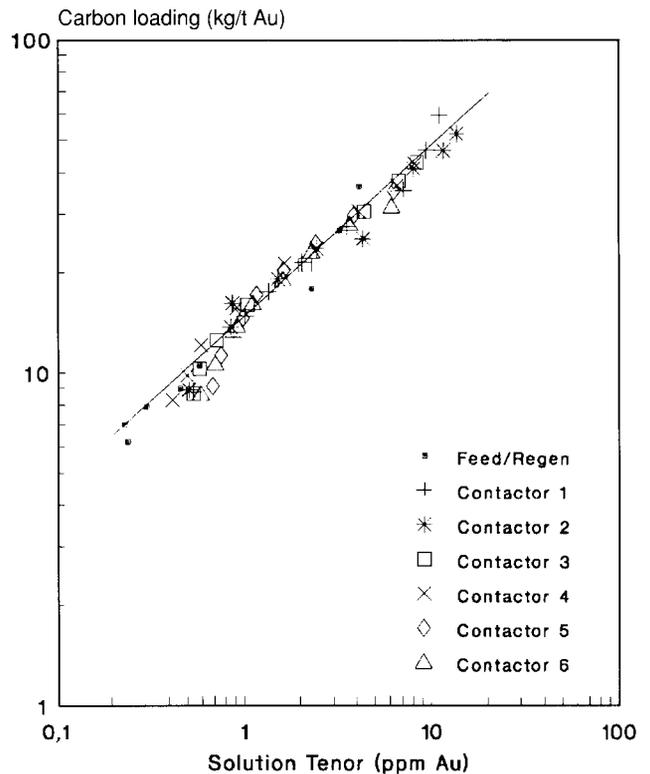


Figure 4—Adsorption isotherms at Kinross

Table VI  
The magnitude of the isotherm shift at Grootvlei

Item	Tank 1	Tank 2	Tank 3	Tank 4	Tank 5
Oxygen, ppm	5,9	5,2	4,7	4,1	3,7
Cyanide, ppm	26	32	32	26	22
Parameter A (loading capacity)	Percentage change from Contactor 1				
Measured, ppm	14 656	91%	57%	106%	91%
Predicted, ppm	14 656	97%	94%	92%	91%
Parameter n	Percentage change from Contactor 1				
Measured	0,422	107%	137%	164%	165%
Predicted	0,422	101%	101%	102%	103%

gate this impact, the adsorption rate,  $R$ , of gold onto carbon was estimated in each contactor (Table VII). The estimates were obtained from the Johns rate expression<sup>14</sup> (equation [5]), either the feed/regen isotherm or the actual isotherm applicable to the contactor in question, and the results applicable to Grootvlei<sup>15</sup>:

$$R = k (C_s - C^*), \quad [4]$$

where  $C^*$ , the tenor of the solution in equilibrium with a carbon loading of  $C_c$ , is given by

$$C^* = \left( \frac{C_c}{A} \right)^{\frac{1}{n}}. \quad [5]$$

Table VII indicates that, where there is a significant isotherm shift, the feed/regen isotherm will give an incorrect indication of  $C^*$  in each contactor. However, in the first two contactors, where more than 90 per cent of the gold is ex-

tracted<sup>14</sup>, the impact of this on  $R$  is not large. In the third contactor, where the isotherm is very different from the feed/regen isotherm, the impact on the prediction of  $R$  is significant. However, the rate of adsorption in this contactor is low, less than one-tenth of the rate in the first contactor.

In the last two contactors, the extrapolation of the measured isotherms to low solution tenors makes the prediction of both  $C^*$  and  $R$  unreliable. These isotherms were measured over a limited range of solution tenors and, when extrapolated, give rather different values for the feed/regen isotherm. However, if Draper's results<sup>9</sup> are taken into account, it appears that the isotherms in these contactors are very similar to the feed/regen isotherm over a wider range of values than those indicated by the isotherm measured in 1991 (Figure 3).

The calculations suggest that, where accurate predictions of adsorption rates are needed, the systems are so far from equilibrium that the difference between the feed/regen

**Table VII**

**Errors in the prediction of adsorption rates introduced by the use of feed/regen isotherms instead of the actual isotherms for each contactor (results from Grootvlei)**

Contactor	Isotherm used	A ppm	n	C* ppm	R <sup>†</sup> g/t/h
1	Feed/regen	15 097	0,51	0,042	115
	Actual	14 656	0,42	0,023	117
Error in R	2% low				
2	Feed/regen	15 097	0,51	0,0082	35
	Actual	13 307	0,45	0,0057	35
Error in R	0% error				
3	Feed/regen	15 097	0,51	0,0032	9,2
	Actual	8 360	0,58	0,0176	7,5
Error in R	21% high				
4	Feed/regen	15 097	0,51	0,00032	1,16
	Actual	15 524	0,69	0,00025	0,96
Error in R	21% high				
5	Feed/regen	15 097	0,51	0,00014	0,60
	Actual	13 389	0,695	0,00032	0,56
Error in R	7% high				

† R is the adsorption rate (in grams of gold per tonne of carbon per hour) calculated by use of the Johns rate expression, equation [5]. The following conditions were assumed to apply:

Rate constant,  $k = 120 \text{ g/t/h}$

Contactor	Carbon loading, g/t	Solution tenor, ppm
1	3000	1
2	1300	0,3
3	800	0,08
4	250	0,01
5	50	0,005

isotherm and the correct isotherms are not significant enough to affect the prediction of adsorption rates very much. However, the example also shows that some caution should be exercised and that, to be more confident about the reliability of a simulation, the nature of the isotherm shift should be established.

### CAUSES OF AN ISOTHERM SHIFT

The following six important factors affect gold adsorption isotherms.

- (1) **Fouling by organic or inorganic poisons.** If fouling of the carbon occurs to any significant degree, the loading capacities of the carbon should increase markedly from the first to the last contactor. This constitutes an isotherm shift that is opposite in direction to that found at Grootvlei. Clearly, no fouling is discernable at Kinross.
- (2) **Temperature.** An increase in temperature decreases the loading capacity<sup>5</sup>. However, the temperature changes that occur down an adsorption train are not very significant (Table I).
- (3) **Ionic strength.** An increase in ionic strength causes an increase in loading capacity<sup>5</sup>. However, the ionic strengths of solutions in commercial CIP plants are

very high, and are not likely to change appreciably down the adsorption train.

- (4) **pH value.** An increase in pH value will increase the loading capacity of the carbon<sup>5</sup>. Changes in pH, however, cannot explain the observations that have been made. In the first place, the variation in pH down an adsorption train is generally negligible (Tables I and II). In addition, the two sets of isotherms measured at Grootvlei suggest that pH may have little effect on the isotherm shift. In 1988, when the plant was operating at a pH value of 12, the isotherm shift that was measured was virtually the same as that measured in 1991, when the plant was operating at a pH value of 10.
- (5) **Competing ions.** Various ions compete with gold for adsorption onto activated carbon<sup>3-5</sup>. The concentrations of these ions, both in solution and on carbon, can have a significant effect on the gold adsorption isotherm. Table I indicates that the concentrations of competing ions change very significantly at Grootvlei, primarily on the carbon. Even at Kinross, where the levels of competing ions are fairly low, there is a significant change in concentration from one contactor to the next (Table IV). In general, changes in the concentrations of competing ions may affect the gold-adsorption isotherms to a greater or lesser extent, and can cause an isotherm shift.

- (6) **Oxygen and cyanide.** Changes in the concentrations of oxygen and cyanide can affect adsorption isotherms. Table II indicates that these concentrations change at the plants investigated and could therefore cause isotherms to shift. The work on synthetic systems suggests that the nature of the impact of such changes can be assessed by reference to three sensitivity regions. Plant results have been obtained for systems that fall into each of these regions.

It is apparent that the factors most likely to cause an isotherm shift are fouling and changes in the concentrations of oxygen, cyanide, and competing ions.

### Factors Affecting Isotherms at Grootvlei

The work on synthetic systems suggests that the adsorption systems at Grootvlei fall into the sensitive region, and that the isotherms should be sensitive to changes in both oxygen and cyanide concentrations. In view of the changes in concentration that occur (Table II), an isotherm shift is expected in which the loading capacities decrease down the train as the oxygen levels decrease. This is what was found. However, the increase in loading capacities that was found in the last two contactors cannot be explained on the basis of changes in oxygen or cyanide concentrations.

On closer examination of the magnitude of the isotherm shift in the first three contactors, it becomes apparent that the shift is greater than expected. If oxygen and cyanide affect the plant system in a way that is similar to their influence on the synthetic systems tested, then that influence can be estimated by use of equation [2] in a suitably modified form.

What needs to be done is to introduce two calibration factors,  $FA$  and  $FN$ , as indicated in equation [6]. The values of these can be chosen so that, at some reference level of oxygen and cyanide, the equation yields the correct values for the Freundlich parameters  $A$  and  $n$ . The equation in this

form will then suggest how the isotherm might shift when the oxygen and cyanide levels change from the reference composition

$$C_c = FA(\alpha - \beta CN) O_2^\gamma C_s^{FN\delta} \quad [6]$$

In Table VI, the conditions in the first contactor were taken as the reference point. This yielded values of 0,6777 and 1,099 for  $FA$  and  $FN$  respectively. The table indicates that the plant isotherms shift to a significantly greater extent than the synthetic system would be expected to shift as a result of the changes in the oxygen concentrations that occur.

It is entirely possible that the plant system is far more sensitive to such changes in concentration than is the synthetic system. However, other evidence indicates that oxygen and cyanide may not be the prime factors affecting the isotherm shift. This arises from a consideration of the conditions under which Draper's investigation<sup>9</sup> was carried out. Those tests were conducted in 1988 in open rolling bottles. Under such conditions, the oxygen level in all the tests would have been more or less the same, namely at the value associated with air saturation. In the 1991 tests, the oxygen concentrations were controlled at levels significantly lower than that. Further, the cyanide levels were a little higher in 1988 than in the 1991 tests. (In 1988 the cyanide level in the feed solution was 89 ppm, as opposed to a level of 64 ppm in 1991.) Although the concentrations of both oxygen and cyanide were rather different in the two series of tests, the isotherms were similar as Figure 2 indicates.

What this suggests is that the Grootvlei isotherms are not very sensitive to oxygen and cyanide. There are two significant consequences to this observation. Firstly, the sensitivity regions identified by the work on synthetic adsorption systems are different from those that apply in plant systems. The findings of Davidson *et al.*<sup>7</sup> suggest that, in plant systems, the boundary between the sensitive and the insensitive regions occurs somewhere between 10 and 50 ppm of cyanide. This would explain the relative insensitivity found with the Grootvlei isotherms. The second consequence of the insensitivity of the Grootvlei systems to oxygen and cyanide is that some other factor must be responsible for the observed isotherm shift. The only other candidate is the variation in the concentrations of the competing ions.

The following observations provide further evidence suggesting that changes in the concentrations of the competing ions are the primary factor behind the trends observed at Grootvlei. Where the adsorption systems are most similar in terms of their levels of competing ions, the isotherms are very similar, as shown by a comparison of the feed/regen isotherm with the isotherms for contactors 4 and 5 (Figure 3). In these systems, the levels of oxygen and cyanide differ most. Where the adsorption systems are most different in terms of their levels of competing ions, the isotherms are differ most, as shown by a comparison of the feed/regen isotherm and the isotherms in contactors 1 to 3. In these systems, the differences in the concentrations of oxygen and cyanide are less extreme than in the previous comparison.

### Factors Affecting Isotherms at Kinross

The work on synthetic systems and the findings of Davidson suggest that the adsorption systems at Kinross fall into the insensitive region. The changes in the concen-

tration of oxygen that occur at the plant are therefore not expected to cause an isotherm shift at this plant, and none was found.

The concentrations of competing ions change down the adsorption train but, clearly, these changes do not affect the isotherms. Either the levels of competing ions are too low to have any effect, or the changes in these levels down the adsorption train are too small. Both possibilities are quite feasible. Alternatively, it may be that the adsorption systems are insensitive to changes in the levels of competing ions, just as they are insensitive to changes in the levels of oxygen and cyanide. However, the results available are insufficient to warrant any firm conclusions in this regard.

### The Isotherms at Western Deep Levels

The work on synthetic systems suggests that the adsorption systems at Western Deep Levels fall into the oxygen-sensitive region and that the isotherms should therefore be sensitive to changes in the concentrations of oxygen but not of cyanide. As already mentioned, the nature of the isotherm results obtained does not lend itself to close scrutiny. All they can show is that these adsorption systems are very sensitive to some unknown factor.

## CONCLUSIONS

For a reliable simulation of the performance of CIP circuits, information is required on the isotherms representing the force that drives the adsorption. To date, simulators have employed a single isotherm, usually the feed/regen isotherm, to describe this driving force. The possibility that the isotherm may change down the adsorption train can undermine the confidence that can be placed in the results of such simulations. The work reported here has addressed this problem, and has clarified the situation in the following ways.

- (1) Three factors are important to the determination of whether an isotherm shift is likely to occur and what its nature is likely to be. The most obvious is fouling, but this was not a discernable factor at the three plants investigated. The second involves the compositions of the solutions in each contactor, specifically the concentrations of oxygen and cyanide. The third involves the loadings of competing ions on the carbon in each contactor.
- (2) The isotherms will change down an adsorption train if the adsorption systems are sensitive to the changes in the concentrations of oxygen and cyanide that occur. The measurements made on three South African plants indicate that the concentrations of oxygen and cyanide can change very significantly down a CIP-adsorption train and so can cause isotherms to shift. The nature of the change is strongly dependent on the pH value in the circuit. This is in agreement with the current understanding of the influence of pH on the stability of cyanide<sup>12</sup>. At high pH (above 11,5), where cyanide destruction catalysed by carbon is very low<sup>12</sup>, the cyanide level changes little down the adsorption train. The oxygen level, however, does decrease somewhat. At lower pH levels, the cyanide destruction is very significant, and is accompanied by a decrease in the level of dissolved oxygen. The effect is very marked in the first contactor, where the con-

centrations of both oxygen and cyanide may drop by up to 60 per cent. Thereafter, both the cyanide and the oxygen decrease steadily, the levels dropping by about 10 per cent from one contactor to the next.

To assess the sensitivity of the isotherms to such changes in concentration, work was done on both synthetic and plant adsorption systems. This sensitivity is composition-dependent, and three composition regions must be considered. If the oxygen concentrations are low, the isotherms are likely to be sensitive only to changes in oxygen levels. Tests on synthetic systems suggest that the boundary of this region is about 3,6 ppm of oxygen. If the concentration of cyanide is low, the isotherms are likely to be very sensitive to changes in both cyanide and oxygen. Tests on synthetic systems suggest that the boundary in this case is about 100 ppm of cyanide, but work on plant systems suggests that it is much lower, probably somewhere between 10 and 50 ppm. Systems in the third region, high cyanide and moderate-to-high oxygen levels, are insensitive to changes in the concentrations of either cyanide or oxygen.

- (3) The isotherms change down an adsorption train if the adsorption systems are sensitive to the changes in the concentrations of competing ions that occur. Although this study did not investigate the influence of competing ions directly, it showed that, where the carbon loadings of the competing ions change significantly down an adsorption train, a significant isotherm shift is likely to occur. The isotherm shift observed at Grootvlei can be explained only on this basis. At Kinross, where the levels of competing ions were relatively low (and the adsorption systems fell into the composition region that is not sensitive to oxygen and cyanide), no isotherm shift was found.

To assess the impact of an isotherm shift on the prediction of a circuit's performance, calculations were made for the results from one plant. From these, it appears that, when an isotherm shift does occur, satisfactory predictions of circuit performance can be obtained by use of the feed/regen isotherm to describe the equilibrium condition in each contactor. Where accurate predictions of adsorption rates are most important, i.e. in the first two contactors, the predictions were not found to be sensitive to errors in the prediction of the equilibrium condition.

Despite the previous conclusion, it is a fact that isotherms can shift. In current simulation approaches, this may lead to errors in the prediction of adsorption rates; an error of 21 per cent was found in one case where the adsorption rate was low. Clearly, caution should be exercised. To improve the confidence that is placed in simulations, the likelihood and nature of an isotherm shift should be investigated.

From the work reported here, it is apparent that such an investigation could be conducted very easily. What needs to be tested is the impact on the isotherms of the carbon loading. Unless adsorption is to be conducted at very low oxygen or cyanide levels, the influence of oxygen and cyanide on the adsorption systems could be neglected, at least in the first instance. Further, it is the loadings of competing ions on carbon, rather than their concentrations in

solution, that change most markedly down the adsorption train. Therefore, the nature of any isotherm shift that may develop can be assessed through standard equilibrium tests on feed solutions and on carbons loaded to the levels expected in each contactor. If suitable samples of carbon are not available, these could be prepared by the soaking of samples of virgin or regenerated carbon in appropriate volumes of feed solution. The isotherms determined on these carbons would not only indicate the nature of the isotherm shift that might be expected, but could also be used for simulation purposes.

## ACKNOWLEDGEMENTS

This study was partially funded by a grant from Mintek, which the authors gratefully acknowledge.

## REFERENCES

1. LA BROOY, S.R., BAX, A.R., MUIR, D.M., HOSKING, J.W., HUGHES, H.C., and PARENTICH, A. Fouling of activated carbon by circuit organics. *GOLD 100*. Johannesburg, The South African Institute of Mining and Metallurgy, 1986. vol. 2. pp. 123-132.
2. LE ROUX, J.D. Modelling of the effect of organic fouling on the adsorption of gold cyanide by activated carbon in a batch reactor. Johannesburg, University of the Witwatersrand, M.Sc. thesis. 1992.
3. VAN DEVENTER, J.S. Kinetic models for the adsorption of metal cyanides on activated charcoal. Stellenbosch, University of Stellenbosch, Ph.D. thesis. 1984.
4. DIXON, S., CHO E., and PITT, C. The interaction between gold cyanide, silver cyanide and high surface area charcoal. *AIChE Symposium series 74*, vol. 74, no. 173. 1978. pp. 75-83.
5. MCDUGALL, G.L., and FLEMING, C.A. The extraction of precious metals on activated carbon. *Ion exchange and sorption processes in hydrometallurgy*. Streat, M., and Naden, D. (eds.). London, Society of Chemical Industry, 1987. pp. 56-126.
6. VAN DER MERWE, P., and VAN DEVENTER, J. The influence of oxygen in the adsorption of metal cyanides on activated carbon. *Chem. Eng. Comm.*, vol. 65, no. 121. 1988. pp. 121-138.
7. DAVIDSON, R.J., DOUGLAS W.D., and TUMILTY, J.A. Aspects of laboratory and pilot plant evaluation of CIP with relation to gold recovery. XIV International Mineral Processing Congress. Toronto (Canada), CIM, 1982.
8. TSUCHIDA, N., RUANE, M., and MUIR, D. Studies on the mechanism of gold adsorption on carbon. *MINTEK 50*. Randburg, Mintek, 1984. vol. 2, pp. 647-656.
9. DRAPER, C., and WOOLLACOTT, L.C. Private communication.
10. WOOLLACOTT, L.C., and NINO DE GUZMAN, G. The combined influence of oxygen and cyanide on adsorption isotherms in carbon-based gold-extraction systems. *Minerals Engng.*, vol. 6, no. 3. 1993. pp. 251-265.
11. NINO DE GUZMAN, G. Modelling the influence of dissolved oxygen and free cyanide concentrations on gold adsorption systems. Johannesburg, University of the Witwatersrand, M.Sc. thesis. 1992.
12. ADAMS, M.D. The mechanism of adsorption of aurocyanide onto activated carbon. I. Relation between the effects of oxygen and ionic strength. *Hydrometallurgy*, vol. 25. 1990. pp. 171-184.
13. DEW, D. Gold adsorption isotherms for Grootvlei Mine. Genmin internal report.
14. JOHNS, M.W. The simulation of gold adsorption by carbon using a film diffusion model. Johannesburg, University of the Witwatersrand. M.Sc.(Eng.) thesis 1987.
15. STANGE, W., WOOLLACOTT, L.C., and KING, R.P. Towards more effective simulation of CIP and CIL processes. 3. Validation and use of a new simulator. *J. S. Afr. Inst. Min. Metall.*, vol. 90, no. 12. 1990. pp. 323-331.

## Johannesburg Branch—Annual General Meeting

While increased demands are being put on mining companies to assist in the upliftment of communities in which they operate, emphasis should be placed more on encouraging self-reliance than financial hand-outs.

This view was expressed by Mr Gary Maude, chairman of Gengold, when he addressed the Annual General Meeting of the Johannesburg Branch of The South African Institute of Mining and Metallurgy in July, 1993.

Mr Maude said these demands could be countered by limiting the expenditure of shareholders' money to those matters seen clearly to benefit shareholder's wealth. He added that it would be better to concentrate on helping communities to organize themselves, and said that areas of legitimate spending should be spelled out publicly to avoid raising false expectations. Contact with local communities should also be strengthened to assist in identifying the needs that those communities hold most important.

While Mr Maude stated that education was primarily the responsibility of the state, he advocated the mining industry to play an important role in education and the training of its employees. He commented: 'If we want to make the best of the people in our industry, we must give them the tools to go to the limit of their ability.' This, he maintained, was in the interest of the company and its shareholders, and that the industry could not wait on the state to attend to all the education and training requirements.

Environmental issues, he contended, were a legitimate responsibility of the mining industry and needed continued attention.

While Mr Maude accepted that the Institute tended to concentrate on more technical and technological advances within mining and metallurgy, he asked whether perhaps more attention could be focused on social responsibility in the coming year.

Response from the floor indicated that several members felt that this matter should be addressed.

The President, Mr Hannes Hoffman, thanked Mr George Lee, the outgoing chairman for his excellent leadership during the past year, and presented him with an Institute tie. The new chairman of the Johannesburg Branch is Mr K.A. van Gessel.



**Mr Gary Maude, chairman of Gengold**



**Mr Hannes Hoffman, Immediate Past President of the SAIMM, presenting the traditional tie to Mr George Lee, following his successful term of office as Branch Chairman 92/93**

## XXIV APCOM—31st October to 3rd November 1993

Computer graphics, 'virtually reality', computer-generated animation, and their applications in the minerals industries will be on display when the world comes to Montreal from 31st October to 3rd November 1993, for the 24th International Symposium on the Applications of Computers and Operations Research in the Minerals Industries (APCOM), attracting delegates from the private and public sectors in North and South America, Europe, Asian, Africa, Australia, and the Commonwealth of Independent States.

The Symposium will feature a trade show with 28 booths from international exhibitors. This will include

computer mine simulations and access to a worldwide data base on minerals industry information. Delegates will also be able to tour mining and metallurgical operations in Eastern Canada, and enjoy a social programme with their companions.

All attendees are encourage to register in advance. For information contact:

Chantal Murphy, XXIV APCOM Registration, c/o CIM, Suite 1210, 3400 de Maisonneuve Boulevard West, Montreal, Quebec, H3Z 3B8.

Tel.: (514) 939-2710, Fax: (514) 939-2714.