The role of cyanide in the multi-component elution of cyanide complexes from activated carbon

J.S.J. van Deventer*, S.P. Liebenberg

Department of Chemical Engineering, The University of Melbourne, Victoria 3010, Australia

Received 6 December 2001; accepted 13 December 2002

ABSTRACT

At high temperature and with cyanide pretreatment the elution of metal cyanides from activated carbon in a column is independent of flow rate. Therefore, an equilibrium model based on the multi-component Freundlich isotherm could be used to simulate the competitive desorption of gold and copper cyanides from activated carbon. The elution profiles of free cyanide and the spectator cation had to be modelled as a precursor to the modelling of elution profiles for the metal cyanides. The dependence of the desorption equilibrium parameters on cyanide pre-treatment also had to be considered. In the model for the removal of free cyanide the rate of the cyanide destruction in the bulk solution was included by combining the hydrolysis and oxidation reactions that revealed first order kinetics. The rate of cyanide decomposition in the carbon pores was assumed to change with the amount of cyanide already decomposed at a specific temperature. It was also important to consider the dependence of equilibrium parameters on the concentration of spectator cations. The introduction of a competition coefficient adequately described the competitive effect of copper on gold elution profiles. © 2003 SDU. All rights reserved.

Keywords: Gold; Copper; Cyanide; Elution; Modelling

1. INTRODUCTION

Internationally the most common technology for the elution of gold from activated carbon is the Anglo American Research Laboratories (AARL) method or modifications thereof. This process consists of a pre-treatment step in which the loaded carbon is soaked with cyanide at a high temperature, followed by a rinsing step using high quality water. Van der Merwe (1991) and Stange (1991) showed that the elution of gold is dependent on the removal of the sodium or potassium introduced in the pre-treatment step. The extent of cyanide decomposition determines the passivation of the carbon surface and the decrease in the equilibrium isotherm for gold loading (Van der Merwe, 1991). The interdependence of factors affecting the elution of activated carbon makes this process difficult to model. Temperature, cation and cyanide concentration, and pH of the solution are the most important factors affecting the elution process (Van Deventer and Van der Merwe, 1994).

Van der Merwe (1991) proposed a generalised model for the simulation of both the Zadra and AARL elution processes, which involves the use of a shifting equilibrium isotherm, due to a change in conditions such as the cation and cyanide concentrations. It was concluded that the mass transfer in the elution stage is very fast at high temperatures. It was shown that under severe desorption conditions (high temperatures and cyanide pre-treatments) the elution of gold is independent of flow rate, and therefore an equilibrium model can be used as a special case of the more complex surface diffusion model.

Van der Merwe (1991) concluded that in the AARL elution procedure the effect of free cyanide from the pre-treatment step in which the loaded carbon is soaked with cyanide at a high temperature, followed by a rinsing step using high quality water. Van der Merwe (1991) and Stange (1991) showed that the elution of gold is dependent on the removal of the sodium or potassium introduced in the pre-treatment step. The extent of cyanide decomposition determines the passivation of the carbon surface and the decrease in the equilibrium isotherm for gold loading (Van der Merwe, 1991). The interdependence of factors affecting the elution of activated carbon makes this process difficult to model. Temperature, cation and cyanide concentration, and pH of the solution are the most important factors affecting the elution process (Van Deventer and Van der Merwe, 1994).

Van der Merwe (1991) proposed a generalised model for the simulation of both the Zadra and AARL elution processes, which involves the use of a shifting equilibrium isotherm, due to a change in conditions such as the cation and cyanide concentrations. It was concluded that the mass transfer in the elution stage is very fast at high temperatures. It was shown that under severe desorption conditions (high temperatures and cyanide pre-treatments) the elution of gold is independent of flow rate, and therefore an equilibrium model can be used as a special case of the more complex surface diffusion model.

Van der Merwe (1991) concluded that in the AARL elution procedure the effect of free cyanide from the pre-treatment step is of little significance. However, the effect of different concentrations of pre-treatment and the resulting influence of the different cyanide profiles on the elution of gold was not investigated. Also, the elution model was developed only for gold cyanide. It is the objective of this paper to extend this work to the case of a dynamic model for multicomponent elution. While Liebenberg (2001) investigated the simultaneous elution of different metal cyanides, only selected data for gold and copper will be presented here. The role of cyanide in the elution process will be explained mechanistically. Although the model assumptions presented here have been verified on the basis of a large set of experimental results, only limited results are presented here for illustrative purposes.

* Corresponding author. E-mail: jannie@unimelb.edu.au

261
2. EXPERIMENTAL METHODS

Salts of KAu(CN)\textsubscript{2} and CuCN were used for the loading of the activated carbon. The copper complexes were formed by dissolving CuCN and a stoichiometric amount of KCN to form mainly Cu(CN)\textsubscript{2}\textsuperscript{−} and Cu(CN)\textsubscript{3}\textsuperscript{2−}. The activated carbon used was Norit RO 3515 extruded granular carbon with an apparent density of 670 kg/m\textsuperscript{3}, an internal surface area (BET) of 975 m\textsuperscript{2}/g, average particle sieve size of 1.54 mm, a void fraction of 0.285 when packed in a column, and a pore volume of 8.2 \times 10^{-4} m\textsuperscript{3}/kg. The free cyanide concentrations in solution were determined using a Perkin Elmer Optima 3000 ICP-OES. For increased accuracy the potassium levels of the standards were matched with those of the samples analysed.

The carbon was placed in distilled water 24 hours prior to loading to ensure that the air in the pores was displaced. Approximately 20 grams of carbon was loaded with metal cyanide(s) in a 1.0L stirred vessel. Loading took place over 24 hours at room temperature and a pH of 10. The pH was adjusted by the addition of small amounts of diluted KOH or HCl. The stirred vessels were fitted with lids to prevent evaporation and contamination.

The column and the piping used for the elution experiments were made from stainless steel. The column had no lining, due to the fact that no acid wash was necessary. To be able to work at temperatures higher than 100 °C and at pressure, the column was constructed with an enclosing jacket through which silicone oil was pumped. The operating temperature was 110 °C and the column pressure was in the region of 250 kPa (gauge), which was achieved by the use of a pressure regulator at the outlet of the column. The column had a capacity of about 18.5 g of carbon, a height/diameter ratio of 9.1 and a bed volume of 38.5 cm\textsuperscript{3}. Pre-treatment of the carbon was performed in the column with a 20 g or 40 g KCN/L solution. The column was filled with half a bed volume of pre-treatment solution, and then the carbon was dropped into the column to minimise air bubbles. The oil heater was then started and the column sealed. The flow of oil to the column was only opened after 30 minutes of pre-treatment. The heating of the column to operating temperature took about 2 hours. Eluant was pumped upwards through the column by a positive displacement pump at a flowrate of about 3.7-4.0 bedvolumes/hr.

3. MODELLING OF CYANIDE PROFILES

A model describing the cyanide profiles during the elution of the metal cyanides should be incorporated in the overall shifting equilibrium model. This model could also be used for describing the dynamics of cyanide degradation in other systems. Van der Merwe (1991) showed that cyanide undergoes mainly oxidation, hydrolysis and adsorption in the elution environment. The model has to account for mass transfer between the bulk of the solution and the carbon particles, while intraparticle diffusion proved to be of minor importance.

A fundamentally correct model for cyanide will have to account for oxidation and hydrolysis in the bulk solution, film transfer, and oxidation, hydrolysis and adsorption in the pores of the carbon. The oxidation reaction inside the pores will also be a function of the amount of cyanide already decomposed. To simplify the overall model, some assumptions should be made:

1. The oxidation and hydrolysis reactions of cyanide in the bulk solution can be combined and described by a single first-order reaction;
2. Adsorption of cyanide at gold elution temperatures is negligible;
3. The oxidation and hydrolysis reactions of the cyanide in the carbon pores can be combined and described by a single first-order reaction;
4. The cyanide concentration inside the carbon particles is homogeneous;
5. Mass transfer between the bulk solution and the pore liquid occurs via diffusion through a boundary layer surrounding the carbon particles; and
6. The combined reaction rate in the pores of the carbon will change with the amount of cyanide decomposed on the carbon.

The elution column is divided into sections with heights \( \Delta h \). Depending on the degree of axial dispersion in the column, different values of \( \Delta h \) could be used. For an ideal plug flow reactor \( \Delta h \) approaches zero. A mass balance of cyanide in the pore liquid is given by:

\[
\rho V_p \frac{\partial C_{\text{CN}}}{\partial t} = \bar{n} a_v - k_{\text{sp}} C_{\text{NP}} \rho V_p
\]

where \( t \) is time, \( C_{\text{CN}} \) is the concentration of cyanide in the pore solution, \( a_v \) is the specific superficial surface area of the carbon, \( \rho \) is the apparent density of the carbon, \( V_p \) is the specific pore volume of the carbon, and...
k_{NP} is the decomposition rate constant (s^{-1}) in the pore liquid. The flux \( \tilde{n} \) of cyanide through the liquid film surrounding the carbon particles can be written as:

\[
\tilde{n} = k_s(C_N - C_{NP})
\]  

where \( k_s \) is the film transfer coefficient for cyanide, and \( C_N \) is the concentration of free cyanide in the bulk phase. When Eq. 2 is substituted into Eq. 1 and spherical carbon particles are assumed, the following is obtained:

\[
\frac{\partial C_{NP}}{\partial t} = \frac{6k_s}{d_p^2} (C_N - C_{NP}) - k_{NP} C_{NP}
\]  

A mass balance in the interparticle solution of a section (i) of the elution column gives:

\[
QC_{i}^N = QC_{i}^N - \tilde{n}(1 - \varepsilon) \Delta h a \Delta h - \varepsilon a \Delta h k_s C_N = \varepsilon a \Delta h \frac{dC_{i}^N}{dt}
\]  

where \( Q \) is the volumetric flow rate of eluant, \( \varepsilon \) is the void fraction in the carbon bed and \( a \) is the cross sectional column area. If Eq. 2 is substituted into Eq. 4 and further simplification takes place by dividing Eq. 4 by \( \Delta h \) and letting \( \Delta h \rightarrow 0 \) for plug flow, Eq. 4 becomes:

\[
\frac{\partial C_{NP}}{\partial t} = -\frac{Q}{a \varepsilon} \frac{\partial C_{NP}}{\partial h} - \frac{6k_s}{ed_p} (C_N - C_{NP}) - k_{NP} C_{NP}
\]  

The rate of the cyanide destruction in the bulk solution (\( k_N \)) was included by combining the hydrolysis and oxidation reactions that revealed first order kinetics (Hoecker and Muir, 1987). Nicol (1986) concluded that the hydrolysis reaction is dominant at high temperatures whereas the catalytic oxidation reaction is more significant at low temperatures. The activation energy of 87143J/mol determined by Van der Merwe (1991) compared favourably with the activation energy of the hydrolysis reaction as determined by Muir et al. (1988). The rate equation used here is:

\[
k_N = 6 \times 10^7 \exp(-\frac{87143}{R_o T})
\]  

where \( T \) is the absolute temperature and \( R_o \) is the universal gas constant. Van der Merwe (1991) showed that the decomposition of the cyanide decreased with an increase in the amount of cyanide decomposed on the carbon, probably because the carbon surface becomes deactivated. The rate of cyanide decomposition in the carbon pores was assumed to change with the amount of decomposed cyanide at a specific temperature. Liebenberg (2001) showed that the following expression could be used to describe the decomposition in the pores:

\[
k_{NP} = \frac{0.1}{(q_{NP} + 1)^2}
\]  

The amount of decomposed cyanide in the pores of the carbon, \( q_{NP} \), is given by:

\[
\frac{\partial q_{NP}}{\partial t} = V_p k_{NP} C_{NP}
\]  

Eqs. 3, 5 and 8 were solved simultaneously by discretising with backward differences in time and column height. The procedure was incorporated in the Pascal program describing the elution of the metal cyanides.

4. MODEL FOR COMPETITIVE ELUTION OF METAL CYANIDES

The fitted parameters of an equilibrium model are only applicable at the specific elution temperature used. For the simulation of single component elution, the Freundlich isotherm could be used to describe the equilibrium conditions:

\[
q = AC^n
\]  

where \( q \) is the equilibrium loading of a metal on the carbon, and \( C \) is the equilibrium solution concentration of the metal. Van der Merwe (1991) showed that with an increase in \( A \) there is a linear decrease in \( n \).
with \( b \) and \( B \) being empirical parameters. Liebenberg (2001) showed that this approach was applicable to the competitive elution of metal cyanides. This approach simplifies the equilibrium model, because changes in the equilibrium can be described by changes in \( A \). Eqs. 9 and 10 give:

\[
q = A_C^{bA-B}
\]

(11)

During the elution process the carbon surface becomes reactivated towards the gold cyanide and the degree of reactivation is dependent on the temperature at which the pre-treatment has been conducted. If the pre-treatment is performed at elevated temperature no reactivation of the carbon surface has to be considered (Van der Merwe, 1991). The pH stays fairly constant at a specific elution temperature and is therefore incorporated with elution temperature in the reference \( A_0 \)-value of the Freundlich isotherm. The \( A \)-value can therefore be approximated by the following expression:

\[
A = A_0(C_K + 50)^p(C_N + 1)^f
\]

(12)

where \( C_K \) is the solution concentration of potassium or sodium, which is called the spectator cation forming an ion-pair with \( \text{Au(CN)}_2^- \), and \( C_N \) is concentration of cyanide. \( A_0 \) is a constant which includes all the conditions, such as temperature and pH, that are constant during the elution process. A constant value of 50 was added to the potassium concentration to lower the sensitivity of the elution model to low concentrations of potassium. Parameter \( p \) indicates to which degree the metal cyanide species are dependent on the removal of the cation during the elution process and will be referred to as the cation dependency. The cation dependency is determined by fitting the model to elution data with different concentrations of potassium in the feed (Liebenberg, 2001). The horizontal position of the elution curve and the initial experimental metal cyanide concentrations give an early indication of the expected value of \( p \). In the experiments presented below \( p = 0.22 \) for gold and \( p = 0.18 \) for copper. Parameter \( f \) gives the dependency of the metal cyanide elution on the removal of free cyanide (\( f \leq 0 \), i.e., cyanide enhances elution). The \( A_0 \)-value is determined by fitting the model to data. Eq. 12 should be determined for each metal cyanide in a competitive system.

Figure 1 presents an example of the elution sequence, with an ‘early’ elution of potassium and cyanide. The shift in equilibrium conditions is clear from especially the sharp decrease in the potassium concentration. The cyanide profile in Figure 1 has been simulated by the model outlined above. The potassium profiles are modelled by an adapted non-ideal flow model with two deadwater regions which represent the macropores and micropores (Van der Merwe, 1991). The gold profile has been calculated using the elution model outlined below.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Sequence of elution of potassium, cyanide and gold from carbon with a loading of 4.11 g Au/kg}
\end{figure}

It is assumed that the elution process is controlled by equilibrium considerations at high temperature and severe cyanide pre-treatment. Therefore,

1. The adsorption or desorption reaction is instantaneous and equilibrium exists between the adsorbate in the liquid phase and that in the adsorbed phase.
2. The concentration in the pore liquid is equal to that in the bulk solution.
3. No concentration gradient exists within the liquid or adsorbed phases at a specific position in the column.

Nieuwoudt (1989) and Liebenberg (2001) showed that the Freundlich-type multicomponent isotherm gives a reasonable approximation of the competitive equilibrium adsorption of metal cyanides. Parameter
estimation of this multicomponent isotherm is simple compared to that of other isotherms and can be of practical use in industry. The effects of the different sorbates are introduced by the use of competition coefficients \((b_{jj})\) as follows:

\[
q_{s,j} = A_j C_{s,j} \left( \sum_{j' \neq j} b_{jj'} (C_{s,j'}) \right)^{n_{jj}-1}
\]

(13)

where \(C_{s,j}\) and \(C_{s,jj}\) are the equilibrium solution concentrations of the reference and competitive metals respectively, and \(q_{s,j}\) is the equilibrium loading of the reference metal. Where copper and gold are eluted simultaneously the bi-component expressions are:

\[
q_{Cu} = A_{Cu} C_{Cu} \left( C_{Cu} + b_{Cu,Cu} C_{Cu} \right)^{n_{Cu}-1}
\]

(14)

\[
q_{Au} = A_{Au} C_{Au} \left( C_{Au} + b_{Au,Au} C_{Au} \right)^{n_{Au}-1}
\]

(15)

Similar to the model for the cyanide profile, the elution column is considered here as a series of \(N\) continuous stirred tank reactors (CSTR's) each of height \(\Delta h\). A mass balance over a height section takes the flow from the previous section \((i-1)\) into account, as well as the changes that take place on the carbon, in the pore liquid of the carbon and in the interparticle solution. A mass balance for a single component over the \(i\)'th section gives (variables refer to \(i\)'th section) the following:

\[
Q(C^{i-1} - C) = a_\Delta h \rho (1 - \varepsilon) \frac{dq}{dt} + [a_\Delta h \rho V_p (1 - \varepsilon) + a_\Delta h \varepsilon] \frac{dC}{dt}
\]

(16)

In order to simplify and apply this mass balance, the time derivative of the multicomponent Freundlich isotherm (Eq. 13) must be determined. The result is complicated, because \(A\) and \(n\) will change with time due to equilibrium changes in the column (continuous changes in solution composition):

\[
\frac{dq_j}{dt} = \frac{dA_j}{dt} C_j (C_j + \sum_{j' \neq j} \sum_{j'' \neq j'} b_{jj'} C_{jj'}^{n_{jjj}-1}) + \frac{dA_j}{dt} A_j (C_j + \sum_{j'' \neq j'} b_{jj'} C_{jj'}^{n_{jjj}-1}) + \frac{dC_j}{dt} A_j (C_j + \sum_{j'' \neq j'} b_{jj'} C_{jj'}^{n_{jjj}-1}) -
\]

\[
A_j C_j (C_j + \sum_{j'' \neq j'} b_{jj'} C_{jj'}^{n_{jjj}-1}) (\frac{1}{(C_j + \sum_{j'' \neq j'} b_{jj'} C_{jj'}^{n_{jjj}-1})^{n_{jjj}}} \frac{dC_j}{dt} + \sum_{j'' \neq j', j'' \neq j''} b_{jj'} b_{jj''} C_{jj''}^{n_{jjj}-1}) \frac{dn_{jjj}}{dt} \ln(C_j + \sum_{j'' \neq j', j'' \neq j''} b_{jj'} b_{jj''} C_{jj''}^{n_{jjj}-1})
\]

(17)

where \(j\) = specific component, \(jj\) and comp = number of components.

Eq. 17 can now be substituted back into Eq. 16. The result is a complicated set of differential equations equal to the number of components taken into account. All the differential equations have non-linear terms, as indicated by Eq. 17. These equations are solved simultaneously using linear algebra. To use matrices, Eq. 16 must be rewritten in a structured manner to simplify the solution of the set of differential equations. The result is the following equations:

\[
X_1 = A_j s_j^{n_{jjj}-1} + A_j C_j s_j^{n_{jjj}-2} (n_j - 1) + z_1
\]

(18)

\[
X_2 = A_j C_j s_j^{n_{jjj}-2} (n_j - 1)
\]

(19)

\[
X_3 = z_2 (C_j^{i-1} - C_j) - \frac{dA_j}{dt} C_j s_j^{n_{jjj}-1} - A_j C_j s_j^{n_{jjj}-1} \frac{dn_j}{dt} \ln(s)
\]

(20)

where

\[
z_1 = V_p + \frac{\varepsilon}{\rho (1 - \varepsilon)}
\]

(21)

\[
z_2 = \frac{Q}{a_\Delta h \rho (1 - \varepsilon)}
\]

(22)
\[ s_j = (C_j + \sum_{j=1, j\neq j}^{comp} b_{j,j} C_{j,j}) \]  

(23)

On combining Eqs. 18, 19 and 20 the following generalised matrix equation is obtained for each component:

\[ X_j \frac{dC_j}{dt} + \sum_{j=1, j\neq j}^{comp} (X_j b_{j,j}) \frac{dC_{j,j}}{dt} = X_j \]  

(24)

where \( j \)-specific component and [comp]=number of components. The derivative term \( dC_j/dt \) refers to the competing metal cyanides. For [comp] components, [comp] matrix equations are obtained, which are solved by matrix inversion using programmed units in Turbo Pascal 7.0. This calculation involves the calculation of the matrix determinant and the multiplication of the different matrices. The result is a number of simple differential equations. The simple differential equations are solved using the fourth order Runge-Kutta method. In each step of the Runge-Kutta method the calculated concentration of each component is substituted back into Eq. 24 which must again be solved by matrix inversion before calculation of the following Runge-Kutta step. Liebenberg (2001) explains the complete numerical solution of this model, including the determination of time derivatives of \( A \) and the initial pore solution concentrations.

5. EVALUATION OF CYANIDE PROFILE PREDICTIONS

Van der Merwe (1991) concluded that the effect of cyanide carried over from the pre-treatment step is negligible. However, those elutions were performed at high KCN pre-treatment levels and the effect of different strengths of cyanide pre-treatment was not investigated. The elution experiments in the present investigation were evaluated with 2% and 4% KCN solutions. The elution column took approximately 2 hours to reach operating temperature. This led to significant cyanide destruction. In the modelling of the elution profiles it became apparent that the inclusion of the cyanide profiles, in addition to the potassium profiles, was necessary for simulating the 2% KCN pre-treatment elution experiments. The cyanide profiles were simulated using a packed height of 0.16 m, \( \Delta t = 20 \text{s} \) and \( \Delta h = 0.016 \).

The only parameters that were changed for the different simulations were: initial cyanide pore concentration (\( C_{Npo} \)), initial interparticle cyanide concentration (\( C_{Nip} \)) and amount of decomposed cyanide (\( q_{No} \)). Analytical deviations and slightly different levels of cyanide destruction meant that \( C_{Npo} \) and \( C_{Nip} \) differed between experiments. (Copper was also eluted during these experiments, and the AgNO₃ titration reports both the free cyanide and some of the cyanide associated with the copper.) For the 2% KCN pre-treatment \( q_{No} \) was approximated to be 5 g/kg, while for the 4% KCN pre-treatment \( q_{No} \) was 10 g/kg. As expected, Table 1 shows that the film transfer coefficient \( k_s \) increased with increasing flow rate \( Q \).

Table 1
Model parameters for the simulation of the cyanide profiles

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Figure 2</th>
<th>Figure 3</th>
<th>Figure 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_s ) (m.s⁻¹)</td>
<td>( 0.1 \times 10^{-6} )</td>
<td>( 0.12 \times 10^{-6} )</td>
<td>( 0.12 \times 10^{-6} )</td>
</tr>
<tr>
<td>( C_{Npo} ) (g.m⁻³)</td>
<td>280</td>
<td>450</td>
<td>1400</td>
</tr>
<tr>
<td>( C_{Nip} ) (g.m⁻³)</td>
<td>60</td>
<td>180</td>
<td>800</td>
</tr>
<tr>
<td>( q_{No} ) (g.kg⁻¹)</td>
<td>5</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>( Q \times 10^8 ) (m³.s⁻¹)</td>
<td>4.167</td>
<td>4.306</td>
<td>4.333</td>
</tr>
</tbody>
</table>

Figure 2. Simulation of the cyanide profile during the elution of gold with 2% KCN pre-treatment
Liebenberg (2001) showed that the inclusion of the cyanide profiles was necessary for the effective modelling of the metal cyanide elution profiles conducted with 2% KCN pre-treatment. When a 4% KCN pre-treatment was used, the effect of cyanide seemed to be negligible and the inclusion of the cyanide profiles was omitted. Predictions of three free cyanide profiles are shown in Figures 2-4. The parameters used for the simulations are given in Table 1. All the cyanide profiles were fitted successfully with the cyanide model. While only selected cyanide profiles are presented here, Liebenberg (2001) simulated numerous cyanide profiles for other conditions.

6. EVALUATION OF COMPETITIVE ELUTION PROFILES

Liebenberg (2001) showed that the elution of gold, silver and copper is independent of flow rate. Therefore, the elution of gold and copper could be simulated with the equilibrium model. The linear relationship between $n$ and $A$ in Eq. (9) can be determined experimentally, but involves tedious experimental work at different temperatures. Equilibrium adsorption data for the metal cyanides are scarce and there are not sufficient data available in the literature to perform a regression analysis. It was therefore decided to treat parameters $b$ and $B$ in Eq. 11 as empirical constants and to determine them from fitting the model to 30 sets of experimental elution data (Liebenberg, 2001). From a modelling point of view it became clear that it was possible to approximate realistic values for $b$ and $B$ from the experimental data. The following linear relationships between $n$ and $A$ were used for gold and copper in the simulations:

$$Au: \quad n = -0.003A + 0.31$$
$$Cu: \quad n = -0.006A + 0.3$$

An interesting fact that surfaced during the modelling was the increase of the $A_0$-value with an increase in the gold loading. The $A_0$-value is there to incorporate the various factors that remain constant during the process, such as temperature and pH. However, from Figure 5 it is evident that there is a linear increase in the $A_0$-value with an increase in the gold loading. The close correlation indicates that the elution of gold becomes more difficult with an increase in loading. This observation might be due to one or a combination of the following factors:

1. With an increase in the gold loaded, more clusters of the gold compound might form which exhibit stronger adsorption characteristics, or
2. With an increase in the gold loading the elution process might shift from having typical equilibrium conditions to a more mass transfer controlled process that leads to slower elution of the gold.

![Figure 5. Effect of gold loading on the Ao-value determined from the equilibrium model](image)

This complex problem has not been addressed elsewhere in research on the surface interactions and possible changes that might occur on the carbon surface.

The same operating parameters as used for the cyanide profiles were used here for competitive elution of gold and copper. Liebenberg (2001) also showed results for single species and competitive elution of gold and silver. The competitive effect of the metal cyanides on each other is described by a competition coefficient $b_{AB}$ which represents the effect of metal B on metal A. For the gold and copper profiles shown below $b_{Au,Cu} = 0.001$, $b_{Cu,Au} = 0.01$, $f = 0$, $p_{Au} = 0.22$, $p_{Cu} = 0.18$, $A_oAu = 0.11$ and $A_oCu = 0.03$.

![Figure 6. Simulation of simultaneous elution of gold and copper with 4% KCN pre-treatment](image)

![Figure 7. Simulation of elution of gold during the simultaneous elution of gold and copper using a 4% KCN pre-treatment](image)
Copper has arguably the most detrimental effect on the elution of gold. A high copper loading leads to a decrease in the gold recovery during the elution process. The competitive effect of copper on gold was investigated by loading gold together with varying levels of copper and subjecting the carbon to different KCN pre-treatments.

Liebenberg (2001) demonstrated that the pre-treatment conditions change the level of competition. Very low levels of competition from copper on gold existed when a 4% KCN pre-treatment was used. However, the competitive effect of copper on gold increased substantially when a 2% KCN pre-treatment was used. The simulations of the elution profiles for a 4% KCN pre-treatment are shown in Figures 6 and 7.

The effect of pre-treatment was further investigated by subjecting the gold and copper loaded carbon to a 2% KCN pre-treatment. The copper loading was varied to quantify the effect of copper on the elution and recovery of gold. The decrease in gold recovery in Figure 8 clearly shows the detrimental effect of copper on the elution of gold when a lower level of pre-treatment is used.

Figure 8. The effect of copper loading on the recovery of gold calculated after 15 bed volumes

8 CONCLUSIONS

A dynamic plug flow model for the removal of free cyanide from an AARL type elution column was validated on the basis of experiments using different levels of cyanide pre-treatment. In this model the effects of flow rate, temperature and initial values were considered. The competitive elution of gold and copper cyanides at different levels of pre-treatment and with different initial loadings was simulated by incorporating multi-component Freundlich expressions in a dynamic plug flow model, solved in conjunction with models for the removal of free cyanide and spectator cations. When severe pre-treatment conditions were used, it was not necessary to take the cyanide profile into consideration. In view of the assumption of equilibrium conditions, flow rate does not have a significant influence on kinetics, except for its effect on the film transfer coefficient for cyanide removal. In related work not reported here, it was shown that the proposed modelling approach is also applicable to more complex systems of metal cyanides. The kinetic model for cyanide decomposition could also be used for other operational systems where cyanide degradation is considered.

REFERENCES


