The absorption of gold cyanide onto activated carbon. I. The kinetics of absorption from pulps

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SYNOPSIS

An account is given of the development of a relatively simple model that describes the kinetics of the absorption of gold cyanide on activated carbon. The model is based on the treatment of the carbon–solution interface as a homogeneous boundary across which gold is transported at a rate determined by the rate of mass transport to and from the interface. Rate equations derived from this model describe the results of various kinetic experiments under continuous or batch conditions in the laboratory and on operating pilot and full-scale plants.

SAMEVATTING

Daar word verslag gedoen oor die ontwikkeling van 'n betreklik eenvoudige model wat die kinetika van die absorpsie van goudsianied op geaktiveerde koolstof beskryf. Die model is gebaseer op die behandeling van die tussenvlak tussen die koolstof en die oplossing as 'n homogene grens waaroor goud vervoer word teen 'n tempo wat bepaal word deur die tempo van massavervoer na en van die tussenvlak. Tempovergelykings wat van hierdie model afgelei is, beskryf die resultate van verskillende kinetiese eksperimente onder kontinue of lottoestande in die laboratorium en in werkende proef- en volskaalse aanlegginge.

Introduction

As a result of developments in the past five years, the carbon-in-pulp (CIP) process has become the preferred route to the recovery of gold from low-grade cyanidation pulps. The use of columns of activated carbon for the recovery of gold and silver from mine waste water and from the clarified solutions resulting from dump leaching is also becoming an established process. In these processes, the most important operation is that of the absorption circuit, since the efficiency of the gold recovery by activated carbon determines the overall recovery rate of the plant, as well as the size of the elution, reactivation, and electrowinning circuits.

Over several years, an empirical but simple approach to the modelling of the absorption process has evolved at the Council for Mineral Technology (Mintek). This approach is being used effectively in the design and optimization of a number of local CIP plants. The basis of the Mintek approach is the realization that the kinetics of the absorption process are the most important factors governing the performance of the absorption circuit. Fig. 1 serves to demonstrate this point: equilibrium between the gold on carbon and that in solution was not reached even after a period of 300 hours when the carbon was isolated in a well-mixed basket in one stage of a continuous CIP plant. The mean residence time of the carbon seldom exceeds 48 hours per stage in an operating plant, so that true equilibrium is never achieved, and any rational approach to the modelling
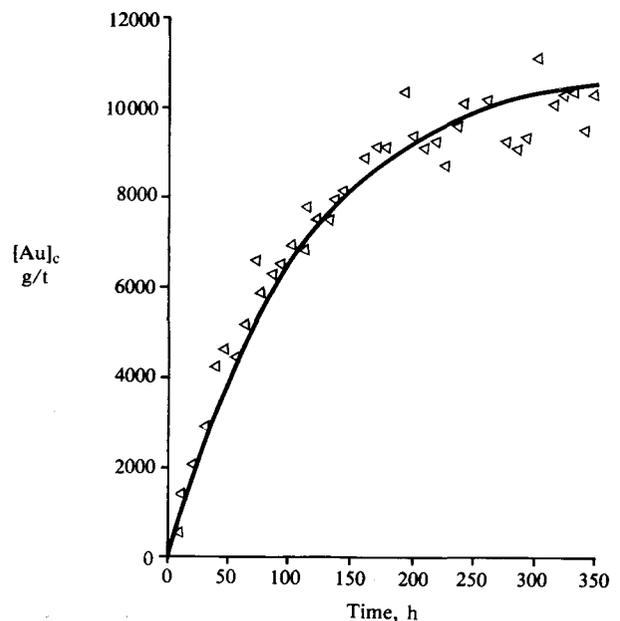

Fig. I—Increase in the concentration of gold on carbon isolated in a basket in the first stage of the Mintek pilot plant at Western Areas Gold Mine

of the absorption process should therefore be based on the kinetics of the absorption reaction.

This paper outlines the factors that led to the development of a simple kinetic model, and demonstrates the use of the model in the derivation of kinetic information from full-scale and pilot-plant operating data and from laboratory experiments. A second paper in this series will outline the use of this model in the design and optimization of a multistage absorption circuit, and a

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third paper will summarize the results of laboratory and plant experiments aimed at the establishment of the factors that influence the kinetics and the equilibrium loading of gold onto carbon.

Criteria for the Model

Any reasonable model should accommodate the following kinetic observations.

(i) Plant tests under steady-state conditions have shown that the increase in the concentration of gold on the carbon in any one stage can be approximated by the simple empirical equation

$$[Au]_c - [Au]_{c,o} = k'[Au]_s t^n, \quad \ldots \ldots \quad (1)$$

where $[Au]_c$ is the concentration of gold on the carbon at time t, $[Au]_{c,o}$ the corresponding quantity at $t = 0$, $[Au]_s$ is the steady-state concentration of gold in solution, and k and n are constants for a particular plant. The value of n has been found to depend on the extent to which the loading of the carbon approaches equilibrium in a particular stage. However, for most practical purposes it can be considered to be constant for a particular set of operating conditions, as will be demonstrated at a later stage.

(ii) Batch adsorption tests have shown that the rate at which gold disappears from solution can be described in terms of an apparent first-order process for short times (less than 12 hours). This is manifest by a linear variation of the logarithm of the gold concentration with time. For longer times, the rate becomes slower than predicted on this basis, and the inclusion of an additional parameter (a) in the expression ln ($[Au]_s - a$) is found to be necessary.

(iii) Both laboratory and pilot-plant tests have shown that, at low concentrations (less than about 10 p.p.m.) of gold in solution, the degree of agitation affects the rate of absorption.

(iv) Pilot-plant and full-scale plant results have revealed that, in the absence of 'poisoning' effects, the fraction of gold extracted per stage is the same for all stages.

A simple model that accommodates these facts is based on the following consideration of the boundary between the activated carbon and 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 supposed homogeneous outer surface, and that mass transport of the gold into the bulk of the carbon particle can be characterized by a single pseudo-mass-transport coefficient (k_c) and a corresponding quantity (k_s) for the solution phase. This is illustrated in Fig. 2.

It is further assumed that the equilibrium between the gold on the carbon and that in the solution at the interface can be described by the simple expression

$$[Au]_c^s = K[Au]_s^s. \quad \ldots \ldots \ldots \ldots \ldots \quad (2)$$

For low concentrations of gold at the interface, this is a reasonable assumption since most absorption processes exhibit linear isotherms at low concentrations.

If the concentration gradients are linear in both phases, the following can be written for the rates of
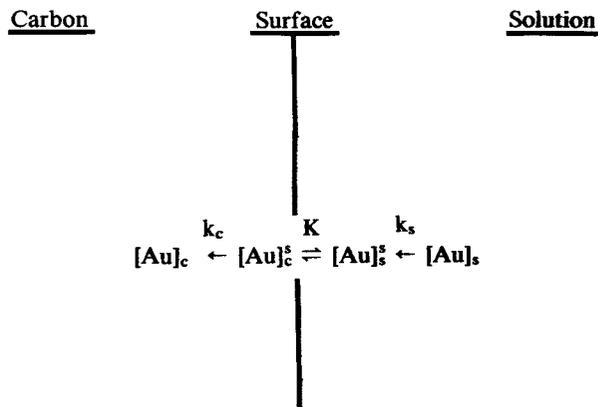

| Carbon | Surface | Solution |

$$[Au]_c \xleftarrow{k_c} [Au]_c^s \underset{}{\overset{K}{\rightleftharpoons}} [Au]_s^s \xleftarrow{k_s} [Au]_s$$

Fig. 2—Schematic diagram of the model

change in gold concentration in each phase:

$$\frac{-d[Au]_s}{dt} = \frac{k_s A M_c}{M_s}([Au]_s - [Au]_s^s)$$

$$\frac{d[Au]_c}{dt} = k_c A([Au]_c^s - [Au]_c),$$

where A is the superficial area per unit volume of carbon, M_c is the mass of carbon, and M_s the mass of solution. Equating of the rates of transfer for a closed system and substitution of equation (2) yield the following expressions:

$$\frac{-d[Au]_s}{dt} = \frac{k M_c}{M_s}(K[Au]_s - [Au]_c) \quad \ldots \quad (3)$$

and

$$\frac{d[Au]_c}{dt} = k(K[Au]_s - [Au]_c), \quad \ldots \ldots \quad (4)$$

where $k = k_s k_c A/(k_c K + k_s)$.

Applications of the Model

Steady-state Continuous Tests

Under steady-state conditions, the concentration of gold in solution is constant, and equation (4) can be integrated to yield

$$\ln \left[\frac{K[Au]_s - [Au]_{c,o}}{K[Au]_s - [Au]_c} \right] = kt. \quad \ldots \ldots \quad (5)$$

In this equation, $K[Au]_s$ is the equilibrium loading of gold on the carbon for a solution concentration of $[Au]_s$. The results illustrated in Fig. 1 were fitted to this equation by a non-linear least-squares programme, the curve drawn in Fig. 1 being calculated from the best-fit parameters $K = 11055$ and $k = 9,05 \times 10^{-3} \cdot h^{-1}$.

As shown in the Addendum, this equation can be simplified under certain conditions. Thus, if the reaction is far from equilibrium, i.e. $[Au]_c < < K[Au]_s$, then

$$[Au]_c - [Au]_{c,o} = kK[Au]_s t, \quad \ldots \ldots \quad (1)$$

which is of the same form as the empirical equation (1) with $n = 1$. Fig. 3 shows results (obtained during the operation of the Mintek CIP pilot-plant at the Grootvlei Gold Mine) plotted in terms of this relationship. The reasonably good fit to the simple linear model is due to
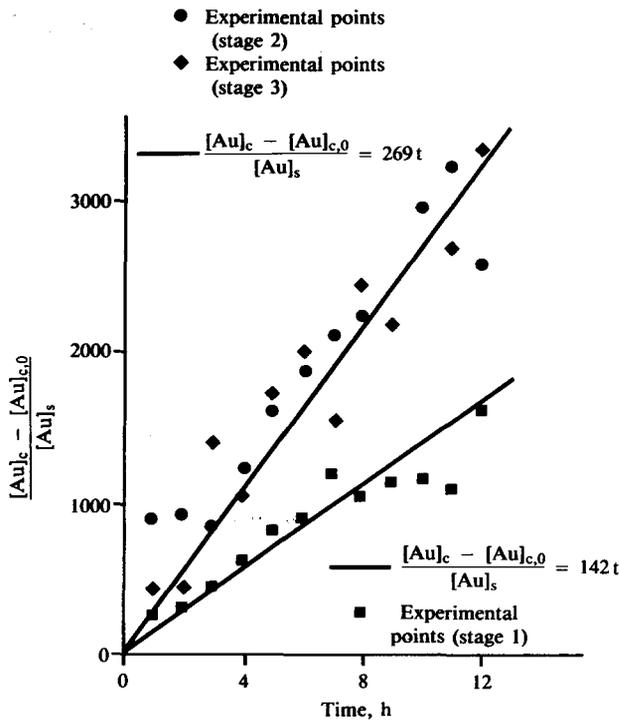
Fig. 3—Rate of loading of gold cyanide onto activated carbon in the first three stages of the CIP pilot plant at Grootvlei Gold Mine

the fact that the operating loading of the carbon is only a fraction (less than 30 per cent) of the equilibrium value in each stage.

On the other hand, if the carbon is loaded to a greater extent, the above simplification is not valid but, as shown in the Addendum, equation (5) can be reduced to the following equation under certain conditions:

$$\frac{[Au]_c - [Au]_{c,o}}{[Au]_s} = k't^n. \qquad \ldots \ldots \ldots (6)$$

Results obtained from basket tests on the Fairview CIP pilot plant are plotted in Fig. 4. It is apparent that the results can be described very well by an equation of this form with a best-fit value of $n = 0{,}52$. A similar analysis of the results from a number of tests on various ores has confirmed the general applicability of this simple equation with values of n that range between about 0,5 and 1.

Batch Absorption Tests

In the batch tests, a quantity of carbon was added to a stirred contactor containing pulp, and the concentration of gold in solution (or on the carbon) was monitored as a function of time. A mass balance of gold in such a system requires that

$$[Au]_c = [Au]_{c,o} + \frac{M_s}{M_c}([Au]_{s,o} - [Au]_s),$$

and substitution in equation (3) and integration yield the relationship

$$\ln\left[\frac{[Au]_{s,o} - B}{[Au]_s - B}\right] = k\left[\frac{KM_c}{M_s} + 1\right] t, \quad \ldots \ldots (8)$$

where $B = \dfrac{(M_s\,[Au]_{s,o} + M_c\,[Au]_{c,o})}{(KM_c + M_s)}$

For $KM_c > > M_s$, i.e. carbon in excess of that required to absorb all the gold in solution, $[Au]_s > > B$ at short times, and equation (8) can be simplified to

$$\ln\left[\frac{[Au]_{s,o}}{[Au]_s}\right] = k\,\frac{KM_c}{M_s}t. \qquad \ldots \ldots \ldots (9)$$

To date a large number of batch absorption tests have been carried out on various local ores on a scale that has varied from small laboratory contactors to large full-scale plant units. The results obtained from these tests generally conformed very well to the above relationships, and this is illustrated by the results shown in Fig. 5 for Grootvlei pulp in various contactors. The lines drawn were calculated by the use of best-fit parameters derived from a non-linear least-squares fit of the results to equation (8). It is interesting to note that the effective rate constant (kK) has values of 548, 127, and 126 h^{-1} for the 5-litre, 400-litre, and 600 m^3 contactors respectively. The significantly higher value for the 5-litre contactor is due to the superior mixing of the mechanically agitated small vessel as compared with the air-agitated 400-litre vessel or the large mechanically agitated contactor. This aspect will be discussed more fully in the second paper. The simplified expression (9) was generally found to describe well the results from batch extraction tests for the first 6 to 12 hours of reaction. For longer periods, the more rigorous equation (8) has to be used. It should be pointed out that the ratio of pulp to carbon in the batch test should be such that significant deviations from the simple equation (9) will enable both k and K to be estimated with reasonable confidence.

Non-steady-state Continuous Tests

Typical current operational practice on CIP plants involves the periodic (varying from hours to days) transportation of the carbon in a countercurrent mode. The conditions in a contactor never therefore reach a true steady-state condition, and it is desirable for the performance of the absorption circuit to be described in terms of a model that involves periodic changes to the carbon inventory of a contactor. With this in mind, several
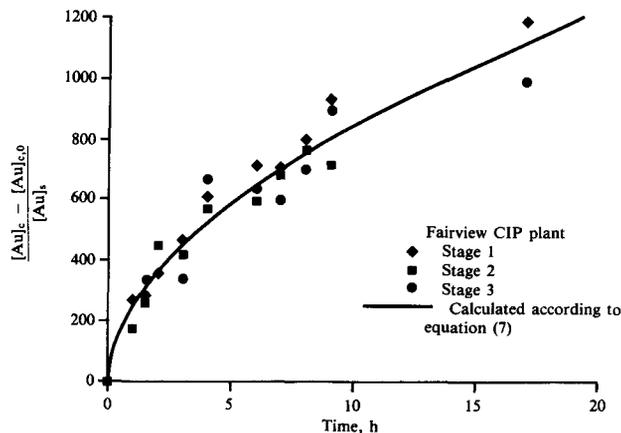

Fig. 4—Rate of absorption of gold in three stages of the Fairview CIP pilot plant

Batch tests on Grootvlei pulp

◆ 5 litre
■ 400 litre
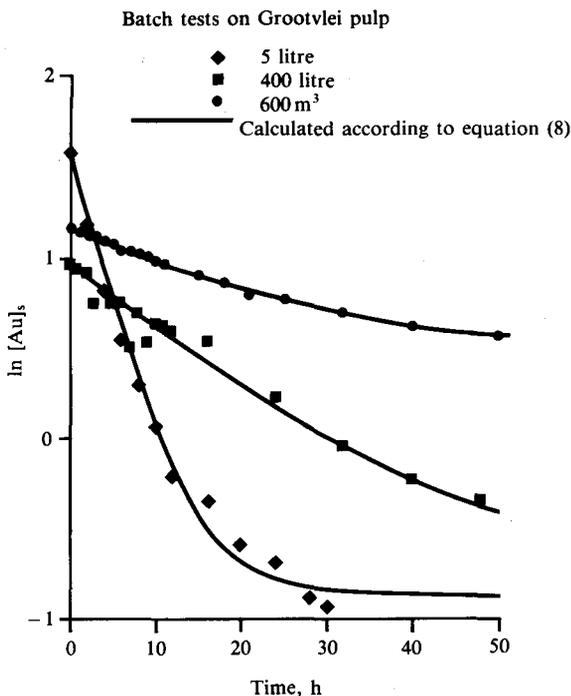● 600 m^3
—— Calculated according to equation (8)

Fig. 5—Rate of disappearance of gold from solution in batch tests carried out on pulp from the Grootvlei Gold Mine

tests were carried out on the Mintek five-stage pilot plant at Western Areas in which both the carbon and the solution were sampled and analysed at relatively short intervals over a number of carbon-transfer cycles in three stages of the plant. (The complete inventory of each stage was transferred every 48 hours.) After the plant had reached a pseudo-steady-state condition (five transfers), the rate of loading in each stage was examined in more detail by a more intensive sampling procedure of both the carbon and the solution over a 48-hour period.

For gold loaded onto a batch of carbon (M_c) transferred into a contactor containing a mass M_s of solution through which pulp containing gold at a concentration of $[Au]_s^{in}$ is passed at a flowrate of V_s, the loading rate can be derived if the following expression for a mass balance of gold across the contactor is combined with equation (4) to yield an expression for the concentration of gold in solution:

$$M_c \frac{d[Au]_c}{dt} = ([Au]_s^{in} - [Au]_s).$$

$$V_s - M_s \frac{d[Au]_s}{dt}. \qquad \ldots \ldots \ldots (10)$$

This procedure can be considerably simplified if it is recognized that, under normal operating conditions, $M_c\, d[Au]_c/dt >> M_s d[Au]_s/dt$, and the latter term can be neglected. Under these conditions

$$[Au]_s = \frac{M_c k[Au]_c + V_s[Au]_s^{in}}{M_c kK + V_s}.$$

Substitution in the simplified form of equation (10) yields the following expression for the rate of loading:

$$\frac{d[Au]_c}{dt} = \frac{V_s k}{M_c kK + V_s} \left[K[Au]_s^{in} - [Au]_c \right].$$

This relationship can be further simplified because, under normal operating conditions, $[Au]_c << K[Au]_s^{in}$. This is apparent if it is recalled that the carbon is seldom loaded to more than 50 per cent of the equilibrium value, and that $[Au]_s/[Au]_s^{in}$ is generally less than 0,5. Under these conditions, the above equation can be simplified and integrated to yield

$$[Au]_c = [Au]_{c,o} + \frac{V_s kK[Au]_s^{in}}{M_c kK + V_s}.t.$$

It can similarly be shown that

$$[Au]_s = [Au]_{s,o} + \frac{V_s M_c k^2 K[Au]_s^{in}}{(M_c kK + V_s)^2} t.$$

In a multistage absorption process, these relationships are valid only for the first stage since $[Au]_s^{in}$ is constant for the feed to the first stage, and varies periodically in subsequent stages. The linear increase in both $[Au]_c$ and $[Au]_s$ in the first stage of the pilot plant after the carbon had been transferred from the second stage is shown in Fig. 6. A value of $kK = 293$ h^{-1} compares favourably with that of 371 h^{-1} obtained from a batch absorption test in a contactor of the same size. The superior mixing in the 5-litre laboratory contactor is apparent in the value of 555 h^{-1} obtained in a batch test in this vessel with the same ore. It should be pointed out that the slopes of both lines in Fig. 6 can be used in the calculation of k and K, and the value of 10 850 thus obtained for the latter compares favourably with the equilibrium loading observed for the carbon in the basket in Stage 1 (Fig.1). The application of these equations to the cyclic perform-ance of a multistage process will be described in a later paper.

Plant Operational Data

In multistage absorption circuits, the amount of carbon transferred periodically is generally a fraction of the total carbon inventory of each stage. Under these conditions, each stage soon attains a pseudo-steady-state condition in which the concentration of gold in the pulp entering and leaving the stage can be regarded as con-stant. It is convenient for the performance of a stage to be described in terms of the percentage of gold extracted, i.e.

$$E = \frac{100 ([Au]_s^{in} - [Au]_s)}{[Au]_s^{in}}.$$

The assumption has been made that the concentration of gold in the pulp leaving the stage is the same as that in the stage, i.e. that the contactor is a perfectly mixed reactor.

The combination of this relationship with equation (4) and a mass balance across the stage yield the following expression for the extraction efficiency of the stage:

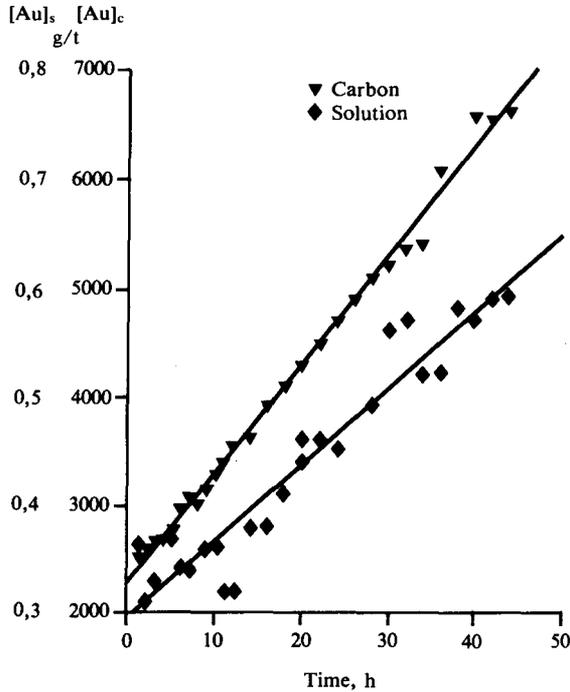$$E = \frac{100k(K - [Au]_c/[Au]_s)}{V_s/M_c + k(K - [Au]_c/[Au]_s)}.$$

Fig. 6—Concentration of gold on carbon and in solution as a function of time after the carbon had been transferred from Stage 2 to Stage 1 of the Mintek pilot plant at Western Areas Gold Mine

This can, in most cases, be further simplified because the gold concentration on the carbon is only a fraction of the equilibrium value, i.e. $K > > [Au]_c/[Au]_s$, and therefore

$$E = \frac{100 \; kK}{V_s/M_c + kK} \; .$$

It can be seen that the kinetic constant (kK) can be derived from plant operational data. The practical implications of this relationship will be discussed in a second paper, but it should be pointed out at this stage that, as observed in plants where carbon poisoning is not severe, the same fraction of gold is extracted in each stage. Table I serves to illustrate this point.

Summary and Conclusions

It has been demonstrated that a relatively simple two-parameter model can be used to describe the kinetics of the absorption of gold onto activated carbon from pulps containing the aurocyanide ion. This model is based on a

TABLE I

OPERATION OF THE MINTEK PILOT PLANT AT GROOTVLEI GOLD MINE

Average gold concentration in solution, mg/l	Feed	1	2	3	4	5
	2,77	0,99	0,36	0,12	0,047	0,017
Extraction in stage E, %	—	64	64	67	61	64
Constant kK, h^{-1}	—	117	117	133	102	117

semi-empirical treatment of the carbon–solution interface as a homogeneous boundary across which gold is transported with rate-determining mass transfer to and from the interface. The rate equation derived from this model adequately describes the kinetic results that were derived from absorption tests in the laboratory, and on a pilot-plant and a full-scale plant. Methods for the analysis of data obtained from batch, steady-state, and non-steady-state continuous operation have been developed and tested.

The second paper in this series will describe the use of the rate equations in the description, design, and optimization of multistage absorption processes.

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Addendum: Simplification of Equation (5)

Under the steady-state operation of a CIP contactor, equation (5) can be used to describe the rate of loading of gold onto the carbon in any one stage:

$$\ln \left[\frac{K[Au]_s - [Au]_{c,o}}{K[Au]_s - [Au]_c} \right] = kt \quad \ldots \ldots (5)$$

This equation can be written in the form

$$\ln \left[1 - \frac{[Au]_{c,o}}{K[Au]_s} \right] - \ln \left[1 - \frac{[Au]_c}{K[Au]_s} \right] = kt.$$

If equilibrium is not reached, $[Au]_c/K[Au]_s < 1$ and the corresponding term involving $[Au]_{c,o}$ is even smaller. This equation can therefore be simplified by use of the expansion

$$\ln(1 - x) = -x + 1/2 \; x^2 - 1/3 \; x^3,$$

with higher-order terms becoming more significant as the reaction approaches equilibrium, i.e. $x \rightarrow 1$.

The inclusion of only the first two terms and rearrangement yield the equation

$$\frac{1}{2K^2[Au]_s^2}([Au_c - Au]_{c,o})^2 + \frac{1}{K^2[Au]_s^2}(K[Au]_s$$
$$- [Au]_c)([Au]_c - [Au]_{c,o}) = kt.$$

This equation can be further simplified under two limiting conditions.

(i)   The reaction is far from equilibrium, i.e.
      $K[Au]_s - [Au] > > [Au]_c - [Au]_{c,o},$
      and the first term can be ignored. Under these conditions
      $[Au]_c - [Au]_{c,o} = kK \; [Au]_s t,$
      i.e. equation (6)

(ii) Under intermediate loading conditions, i.e. when $[Au]_c - [Au]_{c,o} > > K[Au]_s - [Au]_c$, then the second term can be neglected and the following expression is obtained:
      $[Au]_c - [Au]_{c,o} = K \; [Au]_s \; (2kt)^{1/2},$
      i.e. of the form of the empirical equation (7).