
**CHARACTERIZATION OF THE HIGH TEMPERATURE CAUSTIC CONDITIONING ACTIVATED
CARBON PROCESS FOR OPTIMIZED GOLD RECOVERY FROM DOUBLE REFRACTORY
ORES**

by

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SUMMARY

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Preg-robbing gold ores reduce the gold recovered with conventional aqueous cyanide processing by adsorption of the leached gold onto the ore which is then lost to the residue.

Many ore constituents adsorb gold in the form of aurocyanide, with carbonaceous materials typically, and not unexpectedly, the most troublesome. This problem is addressed by adding the activated carbon used to recover the aurocyanide earlier in the circuit to reduce the concentration of gold in solution available for adsorption on the preg-robbing carbon. Nonetheless, significant gold is still lost to preg-robbing carbon materials. Metso Outotec South Africa developed the HiTeCC (High-Temperature Caustic Conditioning) process through which some of the preg-robbled gold may be recovered. This process entails desorbing gold under high-temperature caustic conditions and then competitively adsorbing the gold onto fresh activated carbon. The success achieved to date with the HiTeCC process to recover gold suggests that preg-robbing is reversible under HiTeCC conditions.

Developmental work has shown that not all preg-robbing ores are equally amenable to the process and the respective roles played by the caustic addition, temperature, and the activity and quantity of activated carbon are, not well understood. The aim with the present investigation was to resolve these issues by applying existing models for the adsorption and desorption of aurocyanide on

activated carbon and preg-robbing materials to the HiTeCC process. A simulation program was developed to support the evaluation of the potential and application of the HiTeCC process to extract additional gold from double refractory ores. As a result of this, the use of experimentally determined preg-robbing sorption isotherms to predict preg-robbing behaviour has been demonstrated. The behaviour of preg-robbing adsorption has further been defined by comparing preg-robbing isotherms at varying temperature and adsorbate compositions.

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LIST OF ABBREVIATIONS / SYMBOLS

Symbol	Description	Unit
Ω	Gold flux	mg/m ² .s
A_i	HiTeCC reactor activated carbon inlet flow	t/h
A_{i+1}	HiTeCC reactor activated carbon outlet flow	t/h
B	Activated carbon Freundlich pre-exponential constant	-
B_1	Activated carbon linear pre-exponential constant	m ³ /t
C_b	Solution gold concentration	g/m ³
C_{bi}	HiTeCC reactor inlet bulk gold solution concentration	g/m ³
C_{bi+1}	HiTeCC reactor outlet bulk gold solution concentration	g/m ³
C_s	Solution gold concentration at the carbon surface	g/m ³
d	Preg-robber particle d50 diameter	m
D	Activated carbon particle d50 diameter	m
F_i	HiTeCC reactor slurry inlet flow	t/h
f_i	HiTeCC reactor bypass slurry inlet flow	t/h
F_{i+1}	HiTeCC reactor slurry outlet flow	t/h
f_{i+1}	HiTeCC reactor bypass outlet flow	t/h
H	Heat of adsorption	kJ/mol
k_a	Activated carbon adsorption mass transfer coefficient	m/s
k_c	Preg-robber adsorption mass transfer coefficient	m/s
M_{AC}	Activated carbon mass flow	t/h
M_{ore}	Preg-robber mass flow	t/h
N	Freundlich exponential constant of preg-robber	-
N	Freundlich exponential constant of activated carbon	-
P	Density of activated carbon	kg/m ³
Q	Preg-robber gold loading	g/t
Q	Activated carbon gold loading	g/t
q_{aci}	HiTeCC reactor activated carbon inlet gold loading	g/t
q_{aci+1}	HiTeCC reactor activated carbon outlet gold loading	g/t
q_{orei}	HiTeCC reactor preg-robber inlet gold loading	g/t
q_{orei+1}	HiTeCC reactor preg-robber outlet gold loading	g/t
R	Universal gas constant	kJ/mol.K
r_{ac}	Activated carbon sorption rate	mg/s
r_p	Preg-robber sorption rate	mg/s
S_i	HiTeCC reactor solution inlet flow	m ³ /h

S_i	HiTeCC reactor solution bypass inlet flow	m^3/h
S_{i+1}	HiTeCC reactor solution outlet flow	m^3/h
S_{i+1}	HiTeCC reactor solution bypass outlet flow	m^3/h
T	Absolute temperature	K
V	Reactor volume	m^3
x	Mass fraction of ore in slurry	-
β	Preg-robber Freundlich pre-exponential constant	-
β_1	Preg-robber Linear pre-exponential constant	m^3/t
ρ	Preg-robber density	kg/m^3

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1 INTRODUCTION

1.1 Background

Gold cyanidation, also known as the MacArthur-Forrest process, is the most widely used extraction process in the mining industry for processing gold ores. The strength of the gold cyanide complex supports effective gold leaching at low cyanide concentrations and highly selective adsorption of the complexed species onto activated carbon. The process involves the oxidation of metallic gold by oxygen and its complexation by cyanide as the soluble aurocyanide complex $[\text{Au}(\text{CN})_2]^-$ indicated in reaction 1.



The resulting slurry is then contacted with activated carbon to adsorb the leached gold. This is commonly referred to as the carbon-in-pulp (CIP) process.

Activated carbon selectively and efficiently adsorbs the gold in solution with process recoveries in excess of 98% for conventional free milling ores. The adsorbed gold is then desorbed (eluted) from activated carbon using hot aqueous caustic cyanide solutions from which gold is precipitated.

Process inefficiencies have been noted when the CIP process is applied to more complex ores which contain refractory and or carbonaceous materials. This is attributed to encapsulation of gold by refractory materials which decreases the leach efficiency and the adsorption of leached gold by carbon compounds in the ore.

Adsorption of soluble gold from the pulp onto ore surfaces is known as preg-robbing and occurs to some extent on all ores. However, naturally occurring carbonaceous materials with surfaces similar to that of activated carbon typically strongly adsorb the aurocyanide complex. Various alternative processes have been used to address this issue, such as blocking adsorption sites with organic compounds, combustion of the carbon, or competitive adsorption by activated carbon. The latter approach is now most commonly used by introducing the activated carbon to the pulp during the leaching of the gold in the so called carbon-in-leach (CIL) process (Dunne *et al.*, 2012). The lowering of the dissolved gold concentration limits adsorption and may even recover some gold already adsorbed by the ore. However, some carbonaceous materials compete so effectively with the added activated carbon that significant gold may be lost to the tailings even when using the CIL process (Van Buuren, 2014).

Metso Outotec took a novel approach in developing a process to recover the residual adsorbed gold from the tailings by applying a low-level desorption process using moderately elevated temperatures and a caustic soda addition in the presence of virgin activated carbon. The so-called high temperature caustic conditioning process (HiTeCC) has been successfully applied to recover some of the gold present in the CIL tailings of highly preg-robbing ores (Van Buuren, 2014). Binks and Wemyss (2012) reported additional gold recoveries up to 14 % at the Fosterville operation in Australia where HiTeCC is implemented.

The process consists of two process stages as indicated in Figure 1, namely a heated desorption stage followed by a cooler adsorption stage. Tailings slurry from the CIL process is conditioned using sodium hydroxide, and then heated to desorb gold in a number of continuously stirred tank reactors (CSTRs) from the ore at temperatures between 50 and 80 °C. The slurry is then cooled and transferred to a second set of CSTRs for the activated carbon adsorption phase. Fresh activated carbon is transferred counter current to the slurry flow and adsorbs the gold desorbed from the ore.

Activated carbon is added at concentrations of between 20 and 40 g/L to the pulp and retained in the reactors by screens. The carbon is transferred up stream at a transfer rate that would allow a 12-hour residence time in both the adsorption and desorption stages of the process. Caustic soda is added at concentrations between 20 and 30 g/L to the feed of the HiTeCC process. No additional cyanide is added to the tailings slurry, but residual cyanide concentrations typically vary between 1 and 2 g/L as NaCN.

Figure 1 shows a typical HiTeCC plant configuration which consists of three heated and three cooled CSTR reactors. Activated carbon is introduced in the cold stage and transferred periodically from reactor to reactor with the final loaded activated carbon leaving the desorption stage of the process.

A better understanding of the process variables and the level to which they affect the gold recovery is key to the optimization and design of the HiTeCC process. The aim of the present work was to develop a model for the HiTeCC process based on the respective gold adsorption characteristics of the ore and activated carbon, and the appropriate mass and energy balances to support the design and optimization of the process. This was done by first determining experimental adsorption isotherms for preg-robbers and testing their accuracy at predicting preg-robbing behaviour in isolation. A combination of preg-robbing and activated carbon adsorption models was then formulated to simulate the HiTeCC process, which can be compared to existing experimental and plant data. Gold adsorption on ores and activated carbon was reviewed to provide a better understanding of the similarities between these processes and how factors like temperature and ionic composition influence the stability, extent and rate of adsorption.

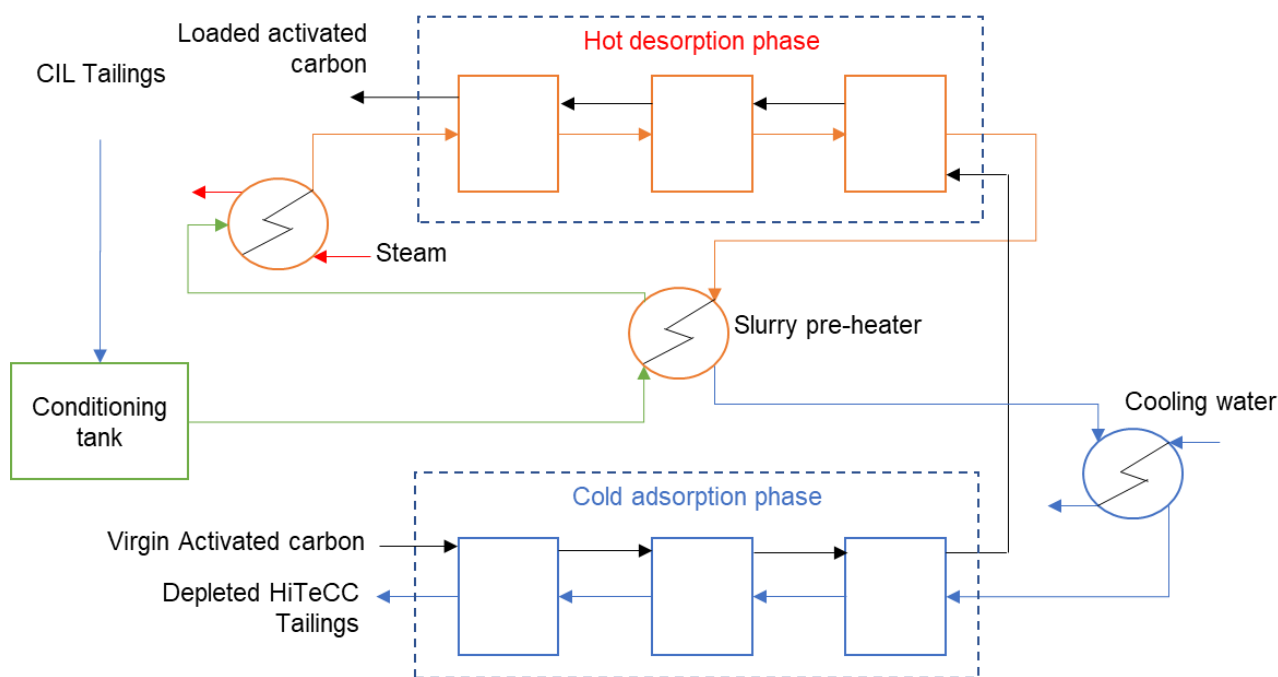


Figure 1 HiTeCC process flow configuration

1.2 Gold adsorption onto activated carbon and carbon substrates

Preg-robbing is defined as the adsorption of soluble gold from cyanide leach slurries onto ore particles within the slurry. Researchers considered multiple components of the preg-robbing ores as possible adsorbents, amongst which are carbon, silicates and sulphide minerals. The main contributor has been identified as finely distributed carbon within the ore, with other components exhibiting weak forms of adsorption, negligible in comparison to that of carbon (Avraamides *et al.*, 2009). Activated carbon is used during gold processing as a strong adsorbent for gold, which explains why carbon native to the ore would pose such a problem.

Various alternative processes to prevent adsorption onto preg-robbing carbon have been considered. Blinding and oxidation of the carbon present in the ore proved partially successful, although blinding reagents led to contamination of the activated carbon used during adsorption while oxidation only lowered the capacity of the preg-robbers (Abotsi and Osseo-Asare, 1986). The most effective measure taken to mitigate the effect of preg-robbing is the addition of activated carbon during the leaching process. This has widely become the standard processing method for preg-robbing ores and is known as the CIL process (Dunne *et al.*, 2012). The addition of activated carbon within the leaching stages provides a competitive adsorbent to the carbon within the ore and reduces preg-robbing by effectively lowering the aurocyanide concentration in the pulp. Even though the CIL process has been effective in reducing preg-robbing, some highly preg-robbing ores are still capable of adsorbing significant amounts of gold even in the presence of activated carbon (Van Buuren, 2014).

The amount of gold adsorbed by the preg-robbing is ore dependent and no single property of preg-robbing ores has been identified which correlates with their gold loading capacity. The work done by Avraamides *et al.* (2009) showed that the capacity of preg-robbers to adsorb gold is a function of the carbon content and the crystallinity of the carbon, but no definitive relationship could be established as the extraction of the carbon from the ore altered the carbon characteristics.

The level to which an ore exhibits preg-robbing behaviour is typically characterized by preg-robbing index tests (PRI) which were developed to give a qualitative measure of the level to which an ore adsorbs gold under cyanidation conditions (Miller *et al.*, 2005). The tests typically involve contacting an ore slurry sample with a solution containing a known concentration of soluble gold and then determining the total gold adsorbed from the solution within a specified time, assuming that no leaching of gold occurs from the ore. The percentage of adsorbed gold is then referred to as the preg-robbing index. This allows operations to decide on processing options for a specific ore body, but still does not enable modelling of the preg-robbing behaviour in the CIL process. The Barrick Gold Mines Incorporated PRI test as described by Goodall *et al.* (2005) has become one of the industry standard tests which allows for a larger sample size and longer residence time to be used. This gives a more accurate measure of an ore's adsorptive capacity.

Adsorbents may be further classified by equilibrium isotherms which relate the adsorbate loading on the adsorbent to the concentration of the adsorbate in solution at the surface of the adsorbent. These isotherms can then be coupled with dynamic process models to predict the behaviour of an adsorbent in any process. As preg-robbers are adsorbents, a dynamic model and isotherm to predict their behaviour would aid in understanding their influence on the gold balance within a typical CIL or HiTeCC process.

Rees and van Deventer (2001) and Rees *et al.* (2001) attempted the simultaneous modelling of preg-robbing, leaching and activated carbon adsorption of gold on various minerals. Using the Freundlich isotherm and a simplified boundary layer diffusion mass transfer model, they determined kinetic and isotherm constants by fitting the model to batch CIL data. The exponent of the isotherm was not directly determined but instead the relationship between the pre-exponential and exponential constant, as suggested by Van Deventer and Van der Merwe (1994), was applied.

They did not determine adsorption isotherms for specific preg-robbers but rather compared the adsorptive capacity of different components of the same ore relative to one another and to that of activated carbon. In addition, the effect of varying cyanide concentration on the adsorption capacity and rate was also established.

Unsurprisingly, when comparing different feed materials from the Telfer mine (Australia), they showed that, of the minerals tested, the carbon-rich flotation feed and product streams had higher capacities toward adsorption, in comparison to the oxide ore. The mass transfer coefficients for these minerals were also orders of magnitude greater than that of the oxide ore, as shown in Table 1. The mass transfer coefficients determined vary considerably. As the ore was subject to the same comminution processes, it is fair to assume that the particle size distributions were similar. The difference in mass transfer rate is thus probably related to the affinity of some materials towards gold adsorption.

The cyanide concentration only influenced adsorption onto the sulphide-rich minerals up to a cyanide concentration of 2 g/L, reducing the capacity of the sulphide minerals considerably. This is explained by the formation of base metal cyanide complexes at high cyanide concentrations at the surface of the minerals which inhibit adsorption of gold, as illustrated by the work done by Rees and Van Deventer (2000).

Table 1 Preg-robbing isotherm constants and mass transfer coefficients for Telfer mine product and feed streams (Rees and Van Deventer, 2001; Rees *et al.*, 2001).

<i>Ore tested</i>	<i>Mass transfer coefficient (m/s)</i>	<i>Freundlich pre-exponential constant</i>
<i>Oxide Ore</i>	0.56×10^{-10}	2×10^{-6}
<i>Flotation Feed</i>	1.40×10^{-10}	2.2×10^{-3}
<i>Pyrite Concentrate</i>	4.2×10^{-10}	5.6×10^{-3}
<i>Chalcopyrite Concentrate</i>	330×10^{-10}	30×10^{-3}

Figure 2 illustrates the isotherms determined for activated carbon and the preg-robbing at a cyanide concentration of 2 g/L. Unsurprisingly, the isotherms predict a lower gold loading on the preg-robbing compared to the activated carbon.

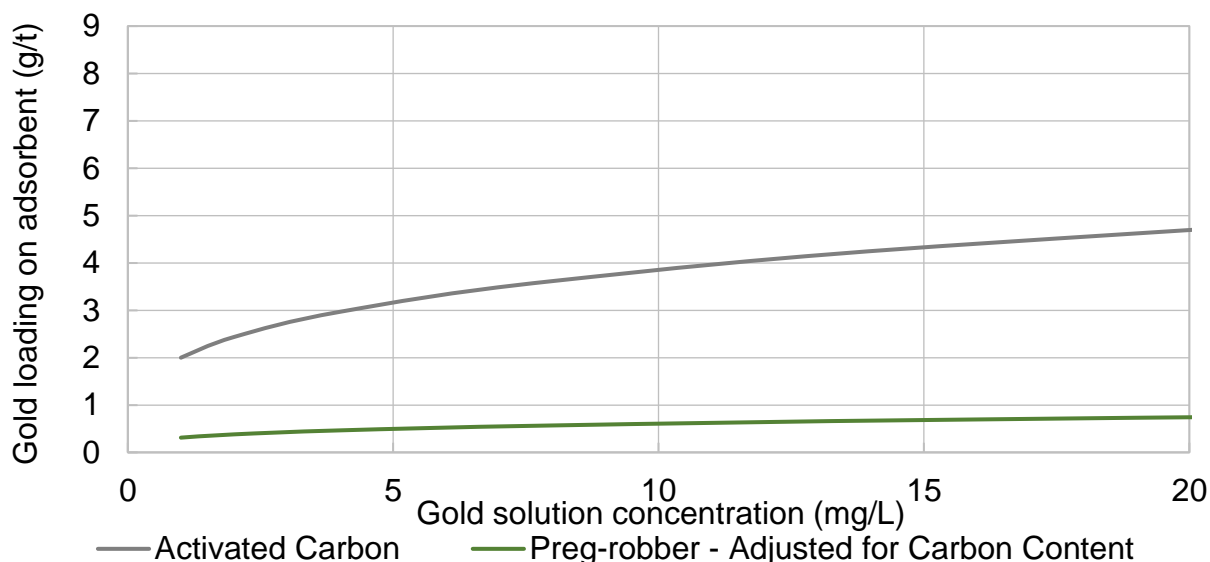
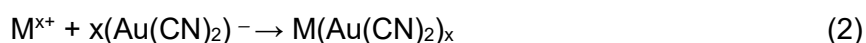


Figure 2 Experimentally determined isotherms for Telfer flotation feed slurry and activated carbon in a CIL experiment (Rees and Van Deventer, 2001; Rees *et al.*, 2001).

Gold adsorption onto activated carbon is exothermic (Groszek *et al.*, 1991) and, although many proposed mechanisms exist, most suggest the adsorption of a cation–aurocyanide complex (Davidson, 1974; McDougall *et al.*, 1980; Yin *et al.*, 2014), with possibly some oxidation of the cyanide to produce aurocyanide (Van Deventer and Van der Merwe, 1993a; 1994) which no longer takes part in the adsorption process. It is likely that adsorption onto preg-robbing carbons will be governed by the same mechanism.

Davidson (1974) proposed that aurocyanide adsorbs on activated carbon as a neutral ion pair formed between an alkali metal or alkali earth metal cation and the aurocyanide anion. The ion pair adsorbs in the ionic double layer at the surface of the carbon, with the cation acting to stabilize the charge at the surface. Davidson (1974) proposed that Ca^{2+} , Mg^{2+} , H^+ , Li^+ , Na^+ and K^+ combine with aurocyanide via reaction 2 to favour gold adsorption in decreasing order.



The cations could be expected to determine the reversibility of adsorption, with the more strongly adsorbed calcium and magnesium ion pairs proving more difficult to desorb compared to the potassium or sodium ion pairs when using demineralized water. The enhancement of elution by the addition of alkali metal salts of potassium and sodium to the eluent suggests that ion exchange at the surface of the carbon is possible, allowing for the less stably adsorbed potassium or sodium ion pairs to be formed and more easily desorbed (Davidson, 1974). The addition of sodium during the HiTeCC process is done based on the premise that the gold is adsorbed on the preg-robbing

material as the calcium–aurocyanide ion pair and that desorption should be favoured by exchanging the calcium in the complex with sodium.

Most commercial operations use lime (CaO) to adjust the pH of the leach slurry. This would invariably lead to the adsorption of the very stable $\text{Ca}(\text{Au}(\text{CN})_2)$ complex on preg–robbing material, which in turn would necessitate the addition of an alkali metal salt (Davidson and Duncanson, 1977).

McDougall *et al.* (1980) and van Deventer (1986) however showed that after adsorption of the ion pair, partial reduction at the surface may occur, with van Deventer (1986) and van Deventer and van der Merwe (1993a; 1994) also identifying rather unpredictable partial oxidation of cyanide to leave AuCN on certain carbon surfaces under similar conditions.

Formation of AuCN on the surface of carbons has been shown experimentally, with free cyanide concentration and the carbon surface itself playing crucial roles in determining the extent to which it occurs. Most operations treating complex gold ores have residual cyanide concentrations in excess of 0.5 g/L (Van Aswegen and van Niekerk, 2004) which would be sufficient to prevent the formation of AuCN. The role of cyanide is however important, as cyanide plays a crucial role in the desorption of some of the gold, silver and base metals (Davidson and Duncanson, 1977). The leaching of relatively high gold contents of the refractory ore concentrates typically justifies the maintenance of high residual cyanide concentrations, e.g., of the order of 1 g/L NaCN, which should be adequate to facilitate the leaching of insoluble adsorbed cyanide complexes on the carbonaceous materials during the HiTeCC process (van Aswegen and van Niekerk, 2004). Cyanide losses due to oxidation and consumption due to leaching need to be monitored however as low concentrations can be detrimental to the recovery of gold (Adams, 1990).

The carbon present in the preg–robber plays a role in determining the stability of the adsorption although this would be difficult to predict as the nature of the carbon varies quite extensively due to the heterogeneous nature of ore bodies (Fuerstenau and Ibrado, 1992). Due to this, it is expected that for any preg–robbing ore, a range of capacities will exist, i.e., multiple isotherms which define its sorption behaviour. The heterogeneous nature of the activated carbon surface leads to variable levels of adsorption, as detailed by the work done by Yin *et al.* (2014). It has also been shown that different carbon substrates have variable adsorption capacities (Kalambaheti *et al.*, 2002; Syna and Valix, 2003). It is expected that the same characteristics of the carbon which affect adsorption onto activated carbon, will affect preg–robbers. Preg–robbing ores contain variable quantities of carbon ranging from 1 % to 8 %, with adsorption capacities ranging between 0.0005 g/t to 0.5 g/t (Avraamides *et al.*, 2009), which further emphasises the need to define the adsorption properties of an ore.

The equilibrium gold adsorption on carbon is therefore determined by the temperature, ionic strength, aurocyanide and cyanide concentrations, pH of the solution, the composition of the aurocyanide complex or ion pair, and the nature of the carbon.

1.3 Adsorption kinetics

Gold adsorption onto carbon involves mass transfer from the adsorbate solution to the surface of the carbon, followed by the adsorption reaction itself. The gold adsorption reaction is much faster than any of the preceding mass transfer processes that take place and will seldom be rate determining. Due to the low concentration of gold slurry solutions, the majority of gold adsorption processes are rate limited by diffusion through the mass transfer boundary layer (Vegter and Sandenbergh, 1996) to the particle surface. Only once the carbon outer surface has become loaded will surface and pore diffusion become rate limiting. CIP processes for gold recovery are typically operated at low gold loadings on the carbon, i.e., far from equilibrium, and the reverse reactions are thus typically not important. The relative contact time for preg-robbing carbon is similar to that of activated carbon and it would be expected that, for this reason, the gold loading on preg-robbers will also be far from equilibrium.

Various adsorption process models have been developed for gold adsorption onto activated carbon. The homogenous surface diffusion model (HSDM) combines the effects of a mass transfer boundary layer (film), surface and pore diffusion in a comprehensive model for predicting the behaviour of gold adsorption (Young *et al.*, 1991). Other models, which ignore the contribution of surface diffusion, are only accurate within the first stages of adsorption, where film diffusion is rate limiting. Due to the relatively short residence time of industrial adsorption circuits, equilibrium is rarely, if ever reached, and film diffusion remains the rate determining step.

The process of adsorption or desorption can therefore be modelled using a simplified HSDM model which only accounts for boundary layer diffusion. Boundary layer diffusion is modelled using Fick's law, which relates the flux of an adsorbate across the boundary layer surface to the concentration difference between the bulk solution and the solution concentration at the surface of a particle as indicated by equation 3.

$$\Omega = k_f \cdot (C_b - C_s) \quad (3)$$

where:

Ω : Gold flux

k_f : Film mass transfer coefficient

C_b : Solution gold concentration of the bulk solution

C_s : Solution gold concentration at the carbon surface

What is further needed is a method by which the gold solution concentration at the particle surface of the preg-rober can be estimated. Adsorption isotherms are extensively used in gold processing metallurgy for the prediction of gold adsorption onto activated carbon (Bailey, 1987). The empirical Freundlich isotherm is commonly used to predict the equilibrium behaviour of gold adsorption onto activated carbon from cyanide leach slurries. The isotherm describes the equilibrium between the adsorbate concentration of the solution on the carbon surface and the concentration of the adsorbate adsorbed onto the carbon itself.

Some researchers have shown that a linear isotherm adequately predicts gold adsorption at relatively low gold concentrations (Bailey, 1987; de Andrade Lima, 2007) where the gold in solution is approximately below 30 mg/L (Young *et al.*, 1991).

Preg-robbing adsorption must be characterised in a similar manner. Adsorption onto preg-robers, as has been discussed, is in essence adsorption onto a carbon substrate within the slurry and would therefore be characterised by a sorption isotherm which describes its behaviour in cyanide leach slurries. Preg-robers pose the challenge that they are highly heterogeneous and suspended in complex slurries with highly variable constituents. Preg-robbing isotherms will therefore be specific to the ore they are determined for, as the basic composition of the carbon within the ore will be unique to it. This study examined whether an isotherm can be used to characterise a preg-rober, and if so, how different process conditions affect the equilibrium and kinetic behaviour.

Various isotherms have been used to model the equilibrium of gold adsorption; the Freundlich isotherm has proved to be the most useful and widely used. A kinetic model which describes the adsorption as a function of the rate of film diffusion consists of Fick's law, combined with the Freundlich equilibrium isotherm for the specific adsorbent, equations 3 and 4, respectively.

$$q = \beta \cdot (C_s)^n \quad (4)$$

where:

- q : Carbon gold loading
- β : Freundlich pre-exponential constant
- C_s : Solution gold concentration at the carbon surface
- n : Freundlich exponential constant

The Freundlich isotherm is an empirical isotherm and therefore must be determined experimentally. In instances where the gold loading is low, the exponent of the Freundlich isotherm can be assumed to be one. This then becomes a linear isotherm with a constant defined by β_1 . If the adsorption sites are similar, the heat of adsorption should not vary significantly with degree of adsorption and the

temperature dependence of adsorption is adequately described by the Gibbs–Helmholtz equation (equation 5), where the heat of adsorption is calculated per mole of gold adsorbed.

$$\ln \beta = \frac{-\Delta H}{R.T} \quad (5)$$

where:

β : Freundlich pre-exponential constant

ΔH : Heat of adsorption

R : Universal gas constant

T : Absolute temperature

Adsorption under film diffusion control in a batch process may be described using equation 6; this is the same model used by Rees and Van Deventer (2001) and Rees *et al.* (2001) for comparing the adsorption behaviour of preg-robbbers within a CIL process.

$$\frac{dC_b}{dt} = \frac{-k_c.(C_b - C_s)}{\rho.d.V} \quad (6)$$

where:

V : Volume of the reactor

ρ : Density of adsorbent

d : Diameter of the particle

k_c : Kinetic mass transfer coefficient

C_b : Bulk gold solution concentration

C_s : Solution concentration of gold at the carbon surface

When fully reversible adsorption occurs, the same model can be used to predict the desorption from the activated carbon (van Deventer, 1986). In this study, this principle was extended to preg-robbbers.

Using equation 6 as a departure point, the rate of change of the concentration in solution in a batch reactor can be expressed as a function of the movement of gold from/to the surface of the particle.

The Freundlich isotherm is used to define the sorption behaviour of the preg-robbber adsorbent. Incorporating the isotherm in equation 6 produces the batch gold balance:

$$\frac{dC_b}{dt} = \frac{k_c.(C_b - (q/\beta)^{\frac{1}{n}})}{\rho.d.V} \quad (7)$$

Several properties of the adsorbate solution influence the rate of adsorption by changing the conditions of the boundary layer. These have been studied for activated carbon in simple synthetic

solutions where the effects could be isolated. Preg-robbers occur in complex slurries making it difficult to mimic specific conditions. For activated carbon the rates of adsorption and desorption are influenced by pH, ionic strength and species present, temperature, hydrodynamic conditions, and the size and concentration of the carbon.

The rate of adsorption increases at lower pH values that favour adsorption of the gold as the $\text{H}(\text{Au}(\text{CN})_2)$ ion pair, which is more stable than the alkali metal aurocyanide ionic pairs. This will however not play a role when examining the mechanism of preg-robbing adsorption as for typical aqueous cyanide processes which operate in a higher pH range where the effect of pH on the rate of adsorption is negligible (Fleming and Nicol, 1984).

Both the cation present and its concentration influence the rate and capacity of adsorption onto activated carbon. The more stable alkali earth metal aurocyanide ion pairs favour adsorption by lowering the surface concentration of adsorbed gold, although this has been shown to play a minimal role compared to the concentration of the cation present (McDougall *et al.*, 1980). High ionic concentrations favour adsorption, with desorption only possible with the introduction of hot demineralized water and only to a limited extent for the alkali earth metals (Van Deventer and Van der Merwe, 1994).

The primary differences between preg-robbing carbon and activated carbon influence their relative adsorptive rates. The size of activated carbon used on commercial plants is carefully managed to allow separation from the pulp based on size, with particle sizes ranging from 0.6 to 3.5 mm. Preg-robbing carbons are comminuted and classified with the ore with particle sizes similar to that of the ore, e.g., in the range from 1 – 150 μm , which would inherently lead to higher mass transfer rates defined on a mass basis. Smaller particles have higher specific external areas, which contribute to increased mass transfer and adsorption rates as well as thin boundary layers which improve the rate of diffusion over the boundary layer (Vegter and Sandenbergh, 1996). Goodall *et al.* (2005) indeed reported that the rate of adsorption on preg-robbers is about four times as fast as on activated carbon.

The adsorption reaction is exothermic, with the heat of adsorption for activated carbon a function of the adsorption site and the gold loading (Yin *et al.*, 2014; Groszek *et al.*, 1991).

Reported adsorption energies range from –10 to –50 kJ/mol depending on the gold loading of the carbon, with higher loaded carbons, as expected, having lower heats of adsorption.

Adsorption is favoured at low gold loadings and desorption at high gold loadings as the strength of adsorption decreases. Activated carbon with gold loadings up to 3 kg/t has been shown to have

relatively high rates of adsorption with surface diffusion only becoming rate limiting beyond this point. Below 0.1 kg/t the carbon activity cannot be determined accurately (Pleysier *et al.*, 2008) but would be assumed to be high, congruent with the results of Groszek *et al.* (1991) who showed the heat of adsorption to be higher at lower gold loadings. Increased temperature would improve the overall mobility of the adsorbed gold, leading to faster adsorption kinetics, although at lower equilibrium loadings.

1.4 Objectives

Preg-robbing is a rather wasteful phenomenon as gold is lost at a stage when significant costs have already been incurred to leach the gold from an ore. The aim of the present work is to model the desorption of gold from preg-robbing substances at moderately elevated temperatures to support optimization of the HiTeCC process. The HiTeCC process is an economically viable process for the recovery of gold from preg-robbes. The application of the HiTeCC process will be further enhanced if the effects of temperature and ionic species on desorption from preg-robbes and the activity and loading of the activated carbon on capturing the released gold are better understood and quantifiable.

The specific objectives of this study were to:

- Investigate the influence of temperature and ionic composition on the reversibility of preg-robbing adsorption.
- Develop a method and process model with which future HiTeCC process units can be designed and optimized.
- Determine the effects of temperature, ionic composition, activated carbon concentration and gold loading on the HiTeCC process gold recovery.
- Validate the process model developed using existing HiTeCC operational and test data.

2 EXPERIMENTAL OUTLINE

Gold sorption onto and from carbon is highly sensitive to temperature, ionic composition of the adsorbate solution, and the carbon present. This section aimed to test the sensitivity of preg-robbing adsorbents to these factors using isotherms which were experimentally determined for a known preg-robbing ore. As most preg-robbing ores will differ due to the inherent variability in ore composition, this study aimed to infer general behaviour to specific factors that influence adsorption onto the carbonaceous material. A comparison of isotherms determined for different ores and samples within the same ore body was done to determine how much variability there is between different ores and to gauge the variability within one ore body.

The factors that influence the equilibrium of gold sorption also play a role in the rate thereof. This is important when controlling and designing operations to ensure the best possible set of operating conditions and equipment used to allow for adsorption or desorption during processes like HiTeCC and CIL.

Adsorption experiments performed on activated carbon have shown that the rate of adsorption is highly variable and a function of multiple factors within the leach solution and carbon itself. The same can be expected of preg-robbers.

The sorption rates for activated carbon are affected by the pH, temperature, the ionic composition of the solution from which the adsorption occurs, and particle size and morphology of the carbon.

For the purpose of this study, pH was not considered as HiTeCC operations operate at pH values in excess of 10.5, above which the pH does not play a significant role in determining the rate or equilibrium of the sorption process (Petersen and Van Deventer, 1991).

As discussed earlier, increased temperature favours desorption due to the exothermic nature of the gold adsorption process. The rate of sorption is however always favoured by increased temperature. This is exploited during the elution (desorption) of gold from activated carbon in conventional CIL or CIP processes (Van Deventer and Van der Merwe, 1993b; 1994). The effect of temperature on the HiTeCC process is therefore decidedly important as the temperature will influence both the extent and rate of desorption and adsorption onto both preg-robbers and activated carbon.

The composition of the aurocyanide complex is directly related to the rate and capacity of adsorption, with the alkali earth metal complexes showing a higher rate and capacity of adsorption compared to the alkali-metal complexes (Davidson, 1974). This effect is minimal compared to the influence of the concentration of the ionic elements present in the adsorbate solution, which plays a more significant role. Higher ionic concentrations have been shown to slow the rate of desorption from activated carbon (Davidson and Duncanson, 1977). If preg-robbers are similarly sensitive to this parameter, then addition of caustic soda during the HiTeCC desorption stage could lead to low rates of desorption and suppress the amount of gold that is desorbed.

The particle size of the solids in the slurry also plays a role in determining the kinetic response of sorption. The particle sizes of the preg-robbing carbon are typically significantly smaller than those of activated carbon particles and would therefore, in theory, have a higher rate of sorption. This is due to the much larger specific external surface area compared to that of the activated carbon. The loading of aurocyanide on activated carbon occurs via mass transfer mechanisms, with relative

rates dependent on the relative loading of the carbon as well as the concentration of the gold in solution (Vegter and Sandenbergh, 1996). The contribution of internal surfaces of preg-robbing substances to gold adsorption should be relatively low considering the relatively low surface area per mass of typical preg-robbing carbons of $\sim 40 \text{ m}^2/\text{g}$ (Miller *et al.*, 2005) compared to the $\sim 1000 \text{ m}^2/\text{g}$ of the activated carbons used for gold adsorption (Bailey, 1987). The particle size is however not a controlled parameter and was not considered during this study.

The carbon composition and surface morphology play a role in the adsorption kinetics. This is however difficult to examine for preg-robbers as isolating the carbon from the preg-robbler invariably will lead to changes of the carbon itself. For this reason, it did not form part of this study.

During development of the HiTeCC process, several tests were performed by Metso Outotec, the aim of which was to determine the preg-robbing behaviour of two ore types and the potential to reverse the preg-robbing under high temperature caustic conditions. This was done by subjecting the ores to varying concentrations of caustic soda at a range of temperatures in the presence of activated carbon. The effect of using carbon with varying degrees of gold present on the surface was also examined. The work included PRI tests on the different ores, batch desorption tests under HiTeCC conditions, excluding carbon addition, and batch HiTeCC tests.

The results of these tests indicated the conditions under which preg-robbing adsorption is reversible and demonstrated that the desorption temperature and activated carbon gold loading are important factors in the possible recovery of gold from preg-robbers.

The effect of ionic strength and caustic additions on the recovery of gold was, however, not investigated and is addressed in the present work using bottle roll tests. These tests were designed to match conditions of the tests performed by Metso Outotec, to enable a direct comparison of the results and to use the experimentally determined isotherms to simulate HiTeCC batch and plant models. The specific aims of this work were to:

- Determine isotherms for a specific preg-robbing ore.
- Determine how different operating conditions influence the isotherm.
- Determine whether the isotherm could be used, in combination with a dynamic model, to predict the data generated during the Metso Outotec development tests.
- Further enhance understanding of how the HiTeCC process mechanism works, and how preg-robbing sorption functions within the process.
- Compare the desorption and adsorption properties of an ore, using its isotherm, by relating the preg-robbing behaviour to the desorption behaviour.

A quantity of Ore 3 was supplied by Metso Outotec for further experimental work; this ore was split in five large samples from which the test work was completed. A sample from each of the five split samples was taken and analysed for carbon and gold content, the results of which are summarized in Table 2.

2.1 Preg-robber materials used

All experimental work was performed on preg-robber CIL tailings samples from two operations serviced by Metso Outotec. For ease of reference, Table 2 summarises the gold and carbon contents of the various ores used in the different experiments. Ore 1 was sourced from an operation located in Asia with Ore 2 and 3 originating from the same operation in Australia, samples being taken two years apart.

Table 2 Gold loading and carbon content of CIL tailings from two operations employing the HiTeCC process, supplied by Metso Outotec.

Ore	Preg-robber gold content (g/t)	Total carbon con- tent (%)
Ore 1	6.1 – 8.7	2.86
Ore 2	27.9	3.8
Ore 3	29.3	3.17

2.2 Chemicals

All chemicals used during this study were of analytical grade and were supplied by Merck South Africa. Sodium cyanide was used to adjust the cyanide concentration throughout all experiments to concentrations of 1 g/L, expressed as NaCN, except where specified otherwise. The pH was adjusted to a value greater than 11 by the addition of CaO prior to cyanide and ore additions. Solutions of different cation salts used were diluted to give equal molarity concentrations (0.75 M) in the resulting solution of the cation being tested. Two cations were introduced, namely, potassium and sodium, of which the carbonate, chloride and hydroxide salts were used.

2.3 Ore characterization

A quantity of Ore 3 was obtained from Metso Outotec for experimental work. The sample was split by combining and quartering into five representative samples from which the isotherm test work was completed. In addition to this, samples were analysed for gold and carbon content and a cyanide leach was performed to determine whether free gold was present. Samples of the ore was

suspended in cyanide solutions at varying solid-to-liquid ratios to determine whether free gold could be leached which would not re-adsorb onto the ore.

2.4 Metso Outotec preg-robbing experiments

Exploratory preg-robbing experiments were performed by Metso Outotec on samples from two different ores, as indicated in Table 3. Masses of 200 g of dried CIL tailing sample were suspended in 600 mL of a 20 mg/L potassium aurocyanide solution. The solution gold concentrations were measured over a period ranging from 3 to 30 hours, to allow for comparison the gold concentration at 180 minutes was used. A PRI value was calculated from the results which, in addition, provided a kinetic adsorption curve for the specific sample tested. The tests were performed in duplicate. As these were known preg-robbing ores the gold content as reported by Metso Outotec was used as the initial gold loading for each experiment.

Table 3 Summary of PRI tests performed on known preg-robbing ores, including the preg-robbler gold content.

<i>Test</i>	<i>Ore</i>	<i>Preg-robbler gold content (g/t)</i>
<i>PRI – Test 1 and 2</i>	Ore 1	8.7
<i>PRI – Test 3 and 4</i>	Ore 2	27.9
<i>PRI – Test 5 and 6</i>	Ore 3	29.8

2.5 Metso Outotec desorption experiments

Metso Outotec performed desorption tests on samples from two different ores, namely, Ore 1 and Ore 3. The emphasis of the desorption tests was to determine the effect of temperature on the desorption phase of the HiTeCC process and therefore the experiments were performed at temperatures ranging between 50 and 80 °C.

Dried and filtered samples of CIL tailings of these ores were pulped with potable water to a solid-to-liquid ratio of 1:3 and heated to different temperatures to induce desorption. Prior to addition of the ore to the solution, the pH was adjusted to above 11 and sodium cyanide added to adjust the cyanide concentration to greater than 1 g/L, expressed as NaCN. To mimic HiTeCC desorption conditions caustic soda was added to a concentration of 30 g/L. The gold concentration of the solution was measured periodically to produce a desorption kinetic curve. The gold loading of the ore was measured before and after desorption.

2.6 HiTeCC batch experiments

HiTeCC batch experiments were performed by Metso Outotec using samples from Ore 1 and Ore 3. The purpose of the HiTeCC tests was to determine the effect of activated carbon concentration and gold loading on the recovery of gold from the preg-robber.

Table 4 and Table 5 summarise the HiTeCC experimental test conditions.

HiTeCC tests were performed at temperatures of 70 and 80 °C. Dried and filtered CIL tailings samples of the respective ores was suspended in 2 g/L cyanide solutions at a pH of 11 with solid to liquid ratios of 1:3. Caustic soda was added to a concentration of 30 g/L, which is typically used in most HiTeCC operations.

The desorption and adsorption process stages of the HiTeCC process were simulated by first heating and then cooling the pulp. The duration of the heating and cooling stages was varied between 6 and 12 hours to determine whether either of the stages was kinetically constrained. Activated carbon concentrations were varied between 10 and 30 g/L to determine the effect this would have on gold recovery and the rate of adsorption.

The effect of adding multiple activated carbon additions was tested by conducting single and double addition tests. During the single addition tests, a single batch of activated carbon was introduced during the desorption phase and retained in the slurry throughout the experiment, while double additions of activated carbon involved a first addition during the desorption stage, which was then removed prior to cooling, and then a second addition during the adsorption stage.

Table 4 HiTeCC batch experiment summary using virgin activated carbon as adsorbent performed on samples of Ores 1 and 3.

Test	First carbon addition concentration (g/L)	Second carbon addition concentration (g/L)	Initial preg- robbing ore gold content (g/t)	Temperature (°C)
<i>HiTeCC Test - 1*</i>	30	20	29.8	80
<i>HiTeCC Test - 2</i>	30	20	8.7	70
<i>HiTeCC Test - 3</i>	30	20	8.7	80
<i>HiTeCC Test - 4</i>	30	20	8.3	70
<i>HiTeCC Test - 5</i>	30	20	8.3	70
<i>HiTeCC Test - 6</i>	30	0	8.7	70
<i>HiTeCC Test - 7</i>	20	0	8.7	70
<i>HiTeCC Test - 8</i>	20	10	8.1	70

*Ore 3 used for HiTeCC test

Table 5 HiTeCC batch experiments using regenerated or eluted activated carbon as adsorbent performed on samples of Ore 1.

HiTeCC Test	First activated carbon addition concentration (g/L)	Second activated carbon addition concentration (g/L)	Initial preg-robber gold content (g/t)	Initial activated carbon gold content (g/t)	Temperature (°C)
<i>HiTeCC Test - 10</i>	30	20	8.3	45.0	70
<i>HiTeCC Test - 11</i>	40	20	8.3	45.0	70
<i>HiTeCC Test - 12</i>	30	20	8.3	224.0	70
<i>HiTeCC Test - 13</i>	40	20	8.3	224.0	70

2.7 Preg-robbing isotherm bottle roll experiments

The addition of caustic soda during the HiTeCC process and its effects on the gold recovery from preg-robbers was investigated with the aim of simultaneously determining the isotherms required for the simulation of the HiTeCC process.

As part of this study a range of bottle roll adsorption tests were designed to test the effect that the concentration and specific cation present in the adsorbate and temperature have on the equilibrium

loading of preg-robbers. Table 6 outlines the experimental conditions used during the tests, all solutions were prepared prior to contact with the ore.

A standard starting solution was prepared with a pH greater than 11 and a sodium cyanide concentration of 1 g/L to which different alkali metal salts were added to give equal molarity concentrations of the various cations at a concentration of 0.75 mol/L.

The ore was split into five different samples containing varying masses and volumes of solution and ore in solid to liquid ratios ranging from 1:1 to 1:8. The prepared samples were mixed and then bottle rolled for a period of 24 hours after which they were filtered at temperature, and the solution and solids analysed for gold concentration.

The carbon content of the samples was measured to determine whether a relationship exists between the total carbon content and the gold loading of the ore sample.

Table 6 Experimental preg-robber isotherm bottle roll test conditions performed on samples of Ore 3.

<i>Test</i>	<i>NaCN</i> (g/L)	<i>Temperature</i> (°C)	<i>NaOH</i> (mol/L)	<i>K₂CO₃</i> (mol/L)	<i>Na₂CO₃</i> (mol/L)	<i>KCl</i> (mol/L)
Isotherm Test 1	1	40	–	–	–	–
Isotherm Test 2	1	40	0.75	–	–	–
Isotherm Test 3	1	40	–	–	–	0.75
Isotherm Test 4	1	80	0.75	–	–	–
Isotherm Test 5	1	40	0.25	–	–	–
Isotherm Test 6	1	60	–	0.37	–	–
Isotherm Test 7	1	60	–	–	0.75	–
Isotherm Test 8	1	60	–	–	–	–

2.8 Kinetic experiments

The effect of cation concentration on the kinetic behaviour of preg-robbing desorption was not investigated as part of the Metso Outotec test work; therefore sets of kinetic desorption experiments were performed at varying temperatures and caustic soda concentrations to determine the effect this would have on the rate of desorption. The experiments consisted of suspending a sample of Ore 3 in solutions with varying concentrations of sodium hydroxide and then adjusting the temperature.

The solution temperature was increased to the set point prior to the ore addition to reduce the delay in reaching set point. Table 7 outlines the conditions for each test. Ore 3 was used in all experiments;

the pH was adjusted to greater than 11 using CaO prior to cyanide addition. The desorption experiments were performed over a 3-hour period as this is representative of the average residence time of a single HiTeCC desorption reactor.

Table 7 Kinetic desorption test experimental conditions using Ore 3.

<i>Test</i>	<i>NaCN Concentration (g/L)</i>	<i>Temperature (°C)</i>	<i>NaOH (g/L)</i>
<i>Kinetic Test 1</i>	1	40	–
<i>Kinetic Test 2</i>	1	80	30
<i>Kinetic Test 3</i>	1	40	10

2.9 Analytical methods

Analyses for the preg-robbing, desorption and HiTeCC batch experiments were done by Metso Outotec. All other chemical analyses were done by SGS South Africa. A Metrohm 827 pH probe was used to determine the pH of the solutions. The gold content of all solids was analysed using fire assay combined with atomic adsorption analysis, LECO analysis was used to analyse for carbon content. Solution samples were analysed for gold concentration using mass spectrometry on a Varian AA-1275 spectrophotometer.

Samples were submitted for X-Ray diffraction (XRD) and particle size distribution analysis (PSD) analysis to determine the mineralogical composition of the ore treated during the isotherm bottle roll tests, the samples were analysed using a PANalytical X'Pert Pro powder diffractometer.

3 RESULTS AND DISCUSSION

The aim of this work was to establish a method through which preg-robbing sorption could be modelled within the context of the HiTeCC process. To that extent two separate sets of data were used; first, experimental data generated during development of the HiTeCC process by Metso Outotec, and secondly, data generated specifically to determine isotherms and kinetic responses for a specific ore. Both sets of data were used in combination with process models to illustrate the behaviour of preg-robbers and evaluate the accuracy of a potential HiTeCC process model.

3.1 Ore characterization

The initial gold loading of the preg-robbler was higher than that reported by Metso Outotec, which speaks to the variable nature of the preg-robbing capacity of the ore. An average gold loading of 98.95 g/t was calculated for Ore 3 from the analysis of the five split samples (Table 8). To ensure the gold loading could be attributed to adsorbed and not un-leached residual gold, a cyanide leach was performed on the split samples. These samples were contacted with a pH 11, 2 g/L sodium cyanide solution at solid to liquid ratios ranging from 1:1 to 1:8. The slurries were agitated at room temperature for 24 hours, filtered and analysed for gold concentration in solution, with the results reported in Table 9. Minimal amounts of gold were leached from the ore; therefore, it was assumed that the gold adsorbed onto the preg-robbler in the ore. The carbon content of the ore was relatively low, with an average content of 2.7 % by mass.

A sample of the ore was analysed for its mineralogical composition, the results of which are detailed in Table 10, and particle size distribution is shown in Figure 3. The ore did not contain any known gold adsorbents and it was therefore concluded that the carbon present would be the only adsorbent responsible for preg-robbing.

The particle size of adsorbents plays an important role in determining the rate of adsorption when mass transfer is rate limiting. It is therefore crucial that when adsorption test work is performed, the sample particle size be as representative of the adsorbent being studied as possible. For preg-robbing ores, it was assumed that the preg-robbing carbon has a particle size distribution that closely matches that of the remainder of the ore. The Ore 3 sample was found to have a d₅₀ of 10 µm and d₈₀ of 30 µm, which aligned well with similar processes in industry. The particle size forms part of the mass transfer model used to simulate gold adsorption; in this instance, the d₅₀ of the preg-robbler was used as it best represented the particle size of the ore sample and therefore the preg-robbler.

Table 8 Ore 3 carbon and gold assay results.

Sample	Carbon analysis (mass %)	Gold content (g/t)
Sample 1	2.37	97.9
Sample 2	2.73	98.5
Sample 3	2.80	99.4
Sample 4	2.73	99.4
Sample 5	2.90	99.5

Table 9 Ore 3 cyanide leach test experimental results.

Sample	Au in solution (mg/L)
Sample 1	0.823
Sample 2	0.149
Sample 3	0.153
Sample 4	0.200
Sample 5	0.314

Table 10 Mineralogical composition of preg-robbed ore, excluding carbon.

Compound	Composition (mass %)
Gypsum	18.8
Microcline	5.8
Muscovite	38.8
Plagioclase	1.9
Quartz	34.7

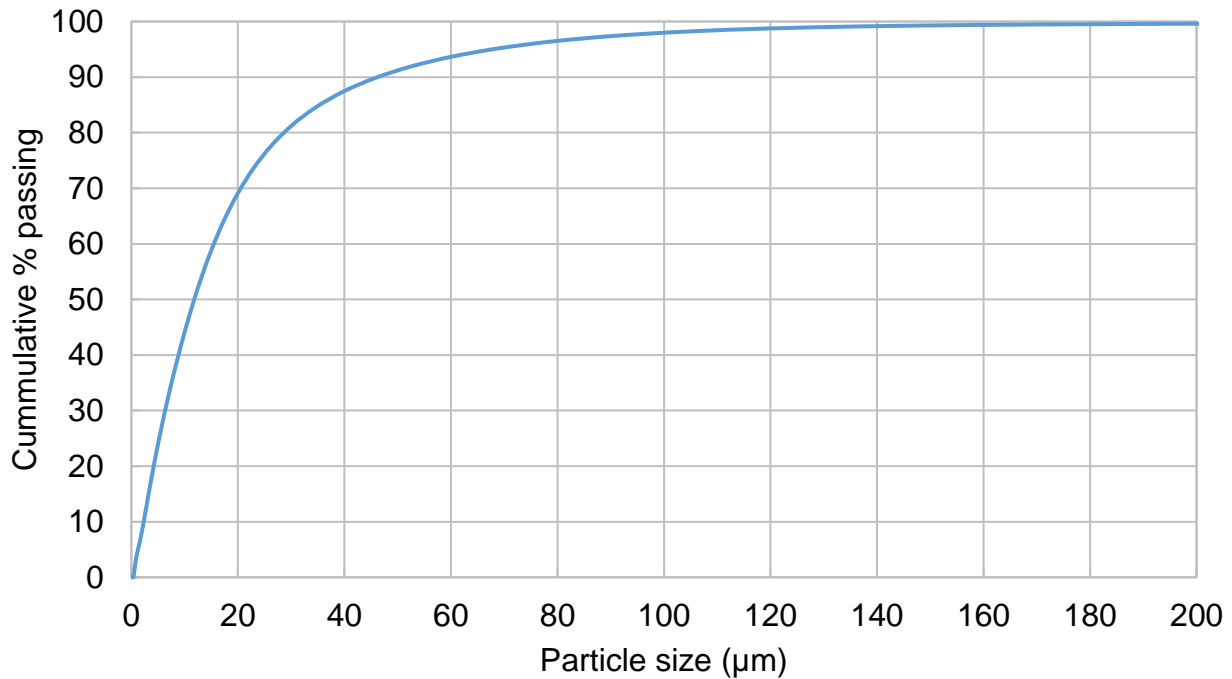


Figure 3 Particle size distribution of Ore 3.

3.2 Effect of temperature on desorption of gold from preg-robbers

The results of the bottle roll tests shown in Figure 4 showed that higher temperatures consistently led to increased desorption from the preg-robber when comparing the isotherm data for the same ionic composition. Temperature also had the largest effect on the level of desorption. As mentioned in section 3.1 virtually no desorption was achieved at room temperature under normal leaching conditions. When comparing the results of Table 9 (Cyanide leach 15 °C) with the results of the baseline isotherm (Isotherm Test 1) performed at 40 °C under similar leaching conditions, the gold released from the ore was nearly twelve times higher; this is a significant improvement which highlighted the temperature sensitivity of the process.

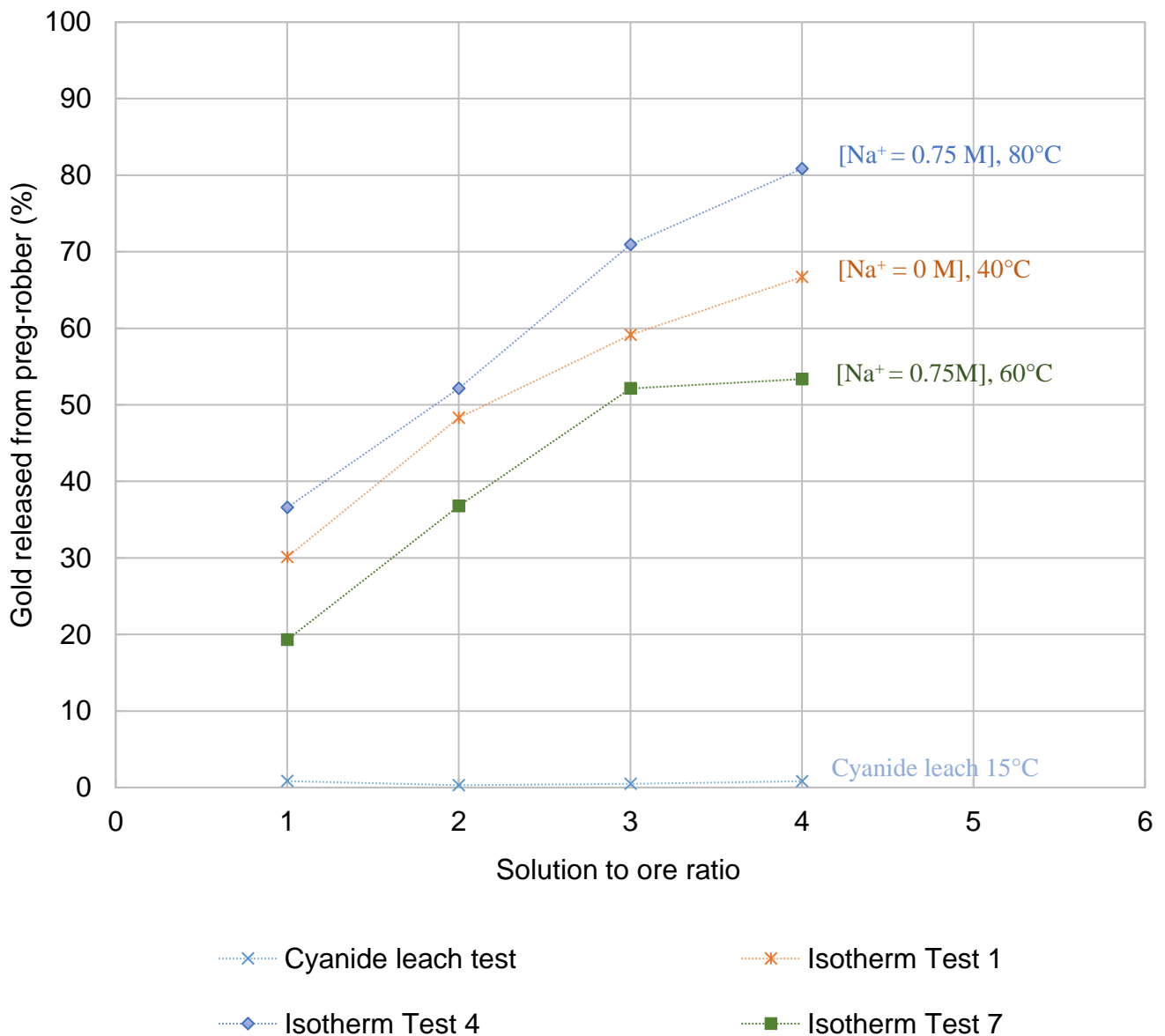


Figure 4 Gold recovery as a function of temperature under similar desorption conditions.

Figure 5 shows the isotherms determined for different temperatures and ionic conditions. The concentration of gold on the preg-robbing ore decreased at higher temperatures and increased with increasing ionic strength and with sodium, as expected, favouring adsorption more than potassium. The effect of temperature on the recovery of gold from the ore makes the HiTeCC process possible and is also one of the largest cost components, as heating slurries at plant scale is energy intensive.

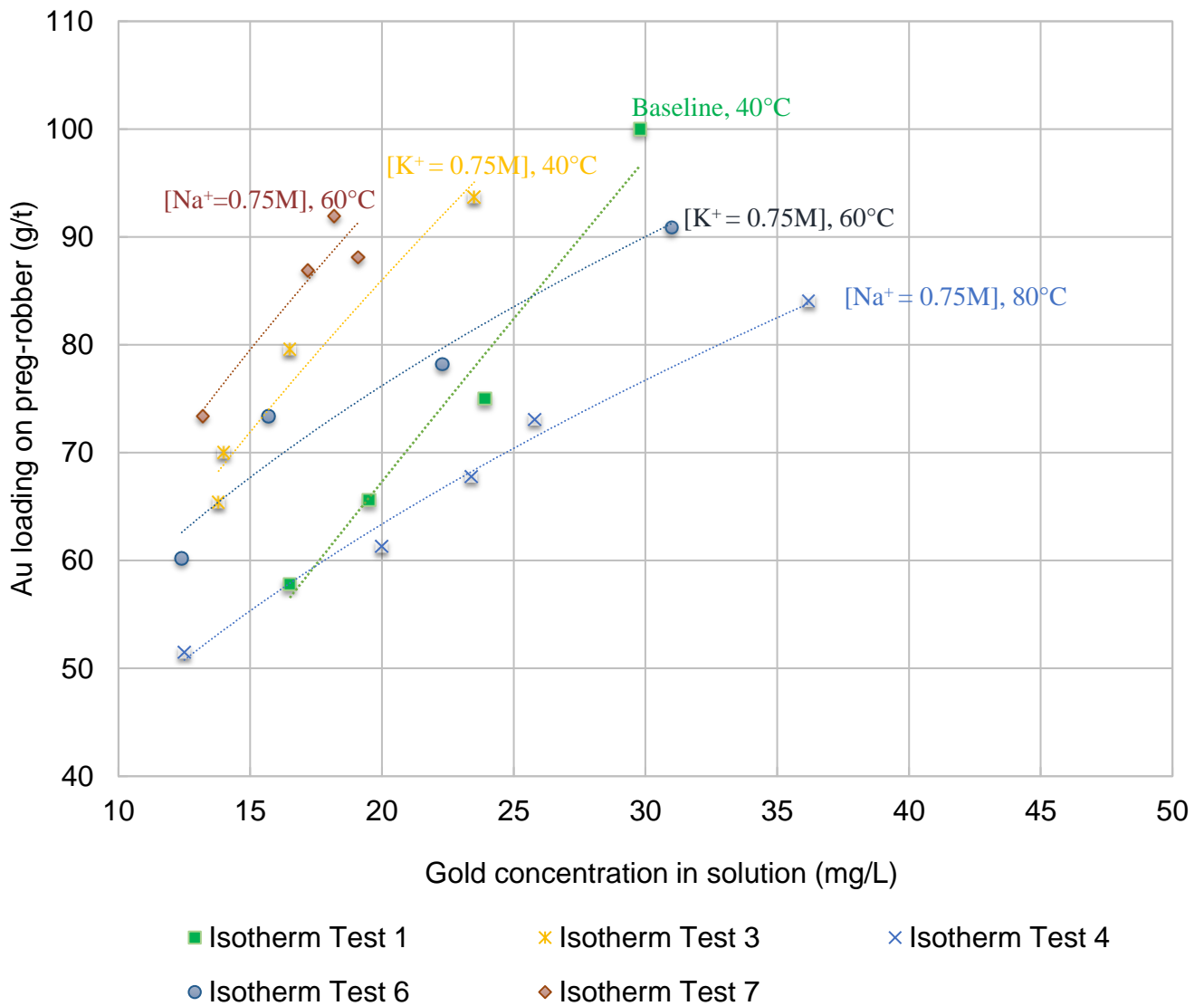


Figure 5 Preg-robbing isotherms determined for Ore 3 using bottle roll experiments with a standard NaCN concentration of 1 g/L at a pH of 11.

The results of the Metso Outotec desorption test work further emphasized the role that temperature plays in the HiTeCC process. Figure 6 shows the results of desorbing gold from Ore 1 at different temperatures under HiTeCC conditions with a caustic concentration of 30 g/L. In the temperature range between 50 and 80 °C, the gold desorbed from the preg-robbing increased as the desorption temperature increased. In the HiTeCC process the desorbed gold could potentially be recovered by activated carbon.

Using data supplied by Metso Outotec (Figure 6), isotherms for Ore 1 could be determined. This was done by fitting the sorption model, equation 6, to the desorption experimental data, to determine the sorption isotherm constants. This eliminated the need to do extensive bottle roll test work. As Ore 1

had a relatively low gold loading, the isotherm was assumed to be linear leaving only the pre-exponential constant to be determined.

By applying a sum of errors minimization program, equation 6 was fitted to the experimental data, producing a range of linear isotherms for the different temperatures at which the experiments were performed, as detailed in Table 11. The results from desorption test 4 was omitted as the large variance in the initial data points did not allow for a satisfactory fit.

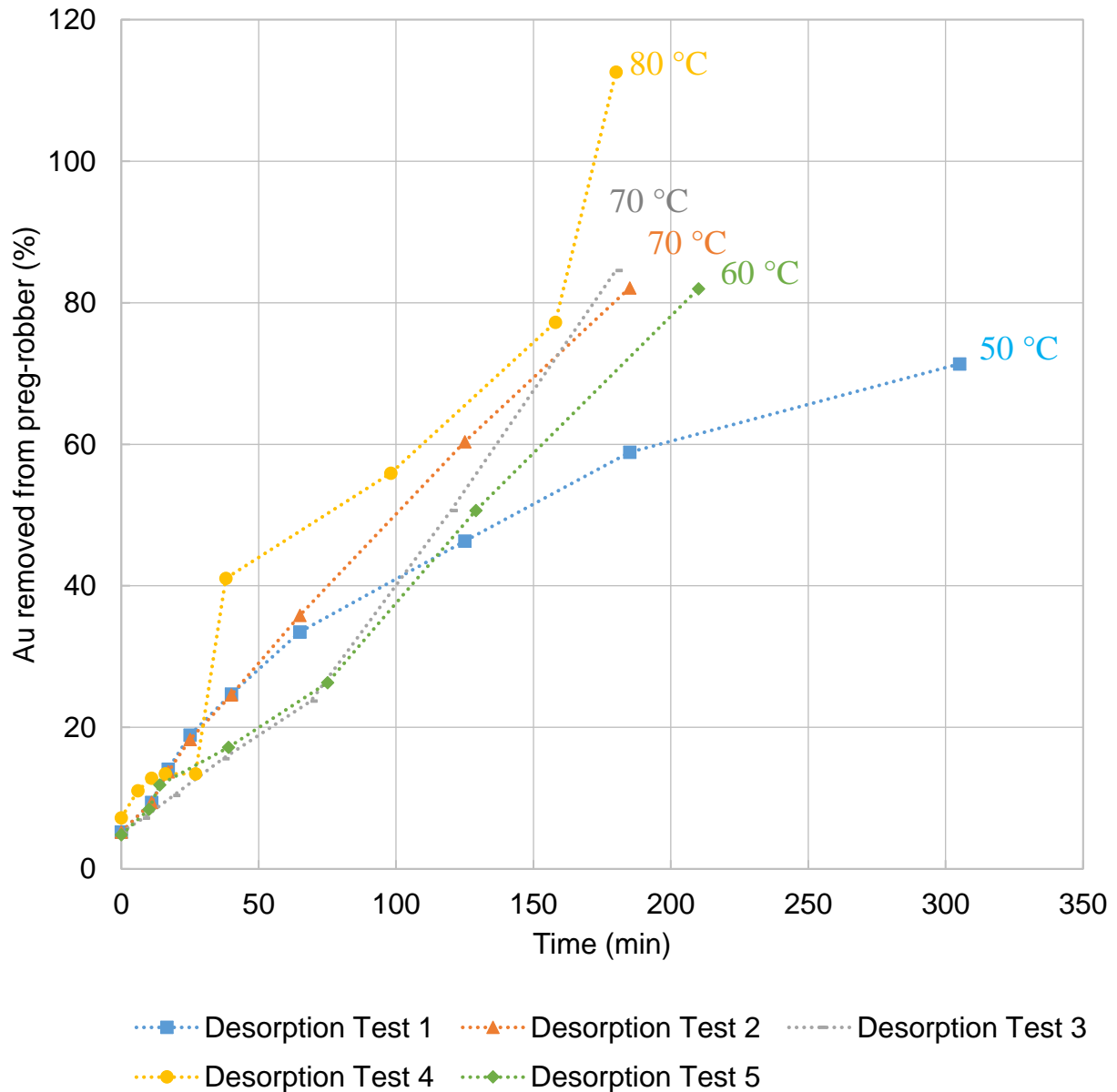


Figure 6 Results of Metso Outotec desorption experiments with 30 g/L NaOH and 1 g/L NaCN performed at temperatures between 50 and 80 °C.

Table 11 Linear adsorption isotherm constants for preg-robbing Ore 1 derived from the gold desorption results shown in Figure 6.

<i>Desorption test</i>	<i>Isotherm constant (m³/t)</i>	<i>Temperature (°C)</i>
<i>Desorption Test 1</i>	0.01499	50
<i>Desorption Test 2</i>	0.00738	60
<i>Desorption Test 3</i>	0.00314	70
<i>Desorption Test 5</i>	0.00412	70

The isotherm constants were used to determine a heat of gold adsorption with the Gibbs–Helmholtz plot shown in Figure 7. The high heat of gold adsorption of -50 kJ/mol found for Ore 1 indicates a very low gold loading. This is in line with similar findings for adsorption onto activated carbon (AC) Groszek *et al.*(1991) and it is therefore assumed to also hold for preg-robbers as a carbon substrate.

Due to the exothermic nature of gold adsorption, the greater the heat of adsorption the greater the energy required for desorption, which in processes like HiTeCC invariably means higher temperatures would be required to release the gold from the preg-robbler. This is especially important for the HiTeCC process and the sensitivity of the process to temperature will affect the possible gold recovery and costs associated with operating the circuit. The temperature also impacts on the capacity of the activated carbon used. It is important for the process activated carbon concentration to be managed to prevent conditions where the activated carbon gold loading reaches a level which at elevated temperature could lead to desorption from the activated carbon.

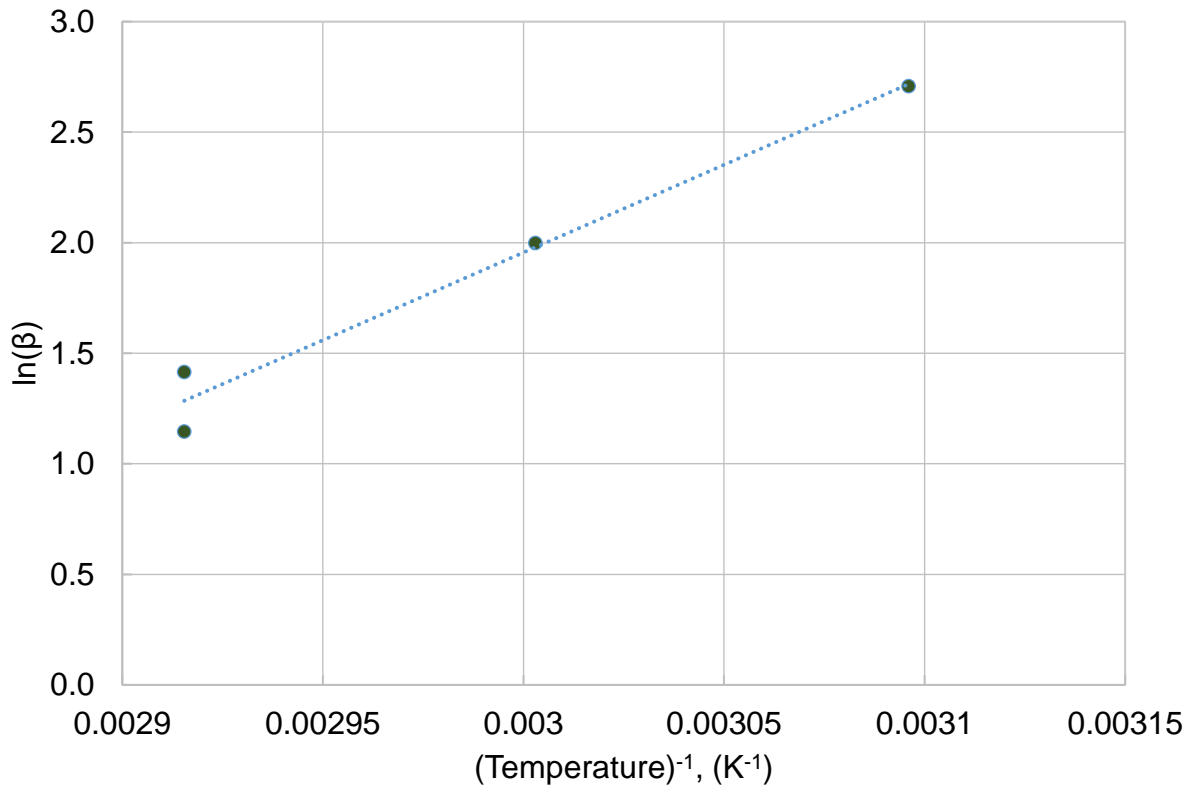


Figure 7 Gibbs-Helmholtz plot of the temperature dependence of the linear Freundlich isotherm constants for gold adsorption by Ore 1 as determined from the Metso Outotec desorption tests.

The present work indicates that, for preg-robbers, temperature has the greatest influence on the equilibrium when comparing different adsorption-desorption conditions and would play a crucial role in determining the amount of gold that can be recovered from the preg-robbler under HiTeCC process conditions. The relatively high heat of adsorption calculated for Ore 1, i.e. -50 kJ/mol, further shows the affinity that preg-robbers have toward gold adsorption, which explains why adsorption onto preg-robbers occurs in the presence of activated carbon in CIL processes.

The rate of desorption is not strongly affected by the temperature as would be expected for a mass transfer-controlled process for which the activation energy is typically in the range of 10 to 20 kJ/mol. The desorption test results shown in Figure 6 confirm, this with only a relatively small increase in the rate of desorption as temperature increases.

The results of the HiTeCC batch tests performed on Ore 1 and 3, shown in Figure 8 and Figure 9 compare the influence of variable desorption/adsorption phase times, multiple additions of activated carbon and varying concentrations of activated carbon. Figure 8 specifically shows a comparison of the effect carbon activated carbon concentration has on the rate and extent of desorption. Figure 9 compares the effects of having multiple activated carbon additions, and how this affects the gold

recovery of the process. Both these figures further illustrate that temperature does not play a significant role in the rate of desorption. The change in the heats of adsorption when temperature changes are made to the tests should be instantaneous, equilibrium however is seldomly reached due to slow adsorption kinetics observed for adsorption onto activated carbon at ambient conditions (Bailey, 1987).

However, the rates of mass transfer should be faster for preg-robbers compared with activated carbon, considering their generally smaller particle sizes and high specific surface areas.

This does, however, imply that the respective rates of desorption and adsorption, although mass transfer controlled, are fast and probably due to the small particle size of preg-robbers.

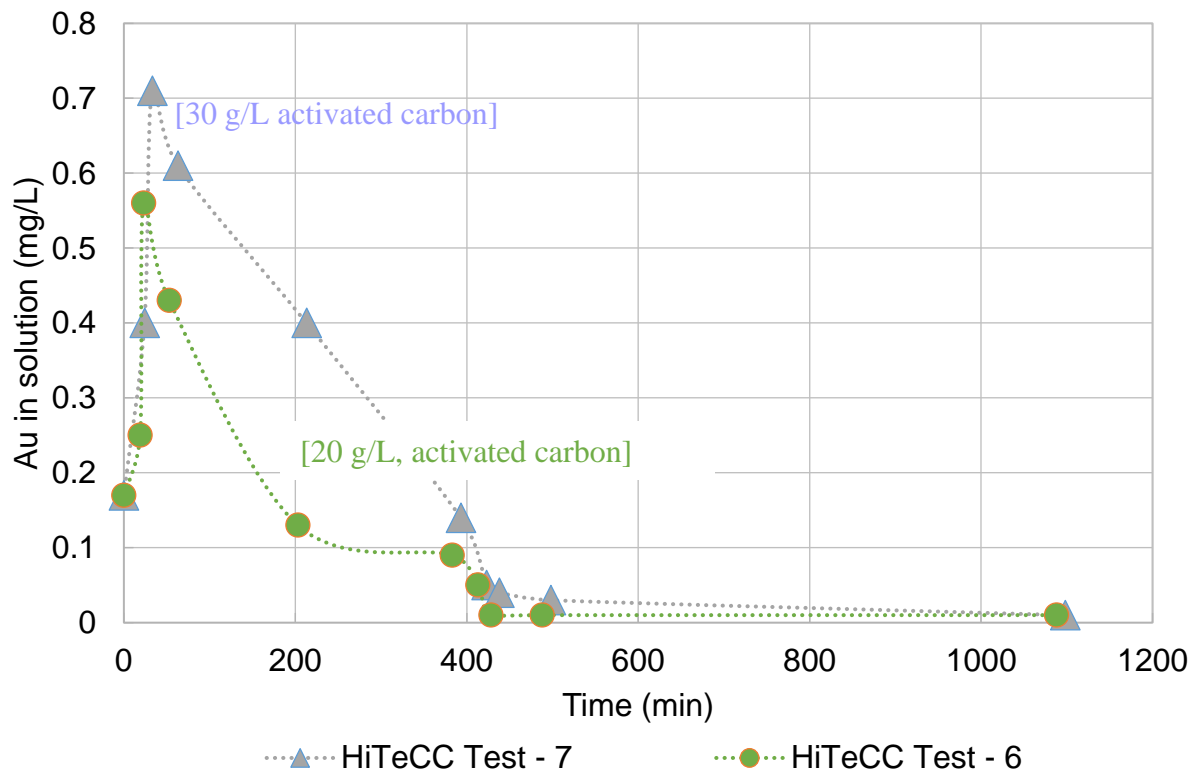


Figure 8 Metso Outotec single carbon addition HiTeCC experiment results conducted at 70 °C.

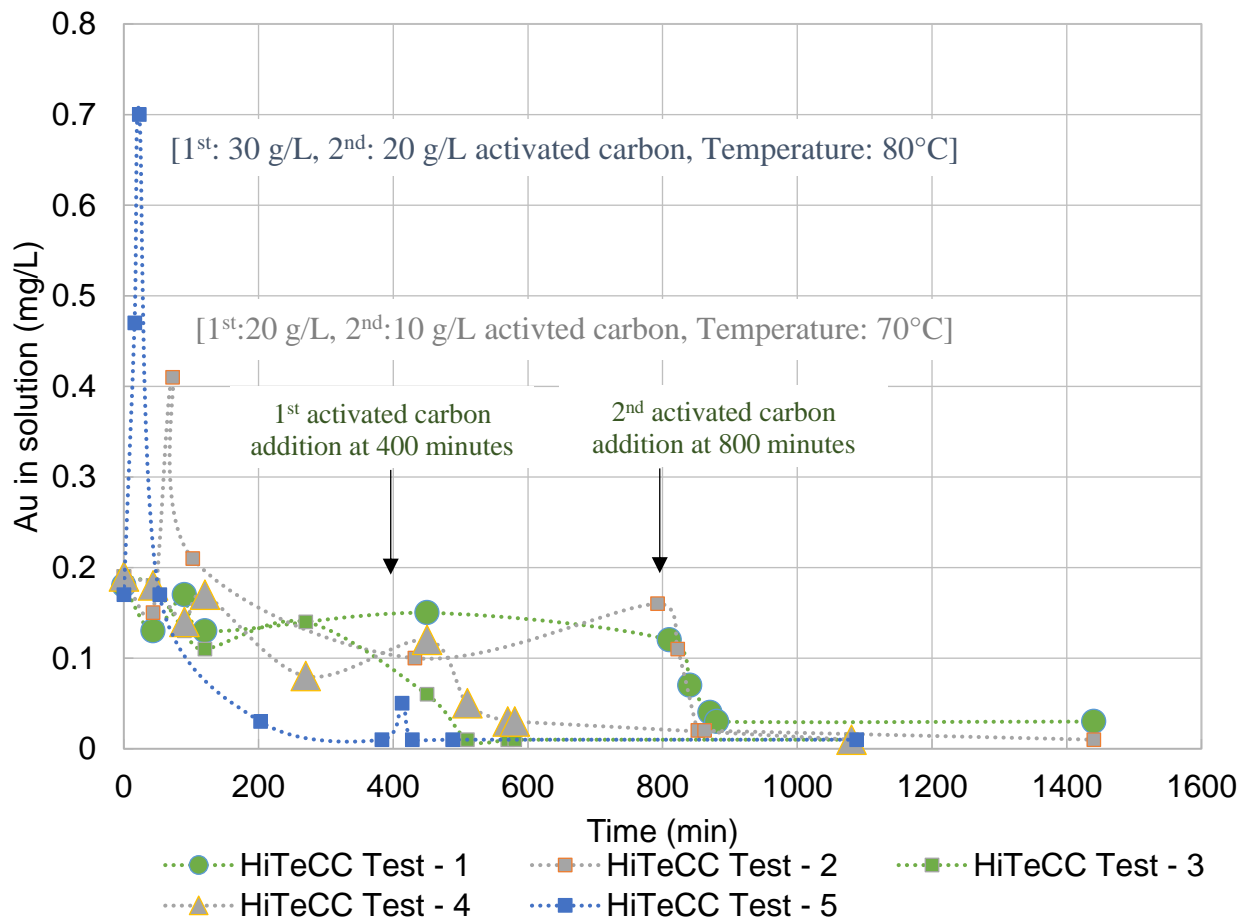


Figure 9 Metso Outotec HiTeCC double carbon addition test results, conducted at 70 °C with 30 and 20 g/L activated carbon concentrations except where indicated otherwise.

It can be concluded that the preg-robbing sorption processes are rather sensitive to temperature and that the direction of the sorption/desorption process will change rapidly. However, equilibrium conditions will take much longer to achieve due to the lower temperature sensitivity of mass transfer-controlled processes. However, the rate of desorption from preg-robbars should be favoured by comparatively higher mass transfer kinetics compared with these of the larger size and more extensive internal surface area of activated carbon particles.

3.3 Effect of ionic composition and concentration of adsorbate on gold desorption from preg-robbars

The bottle roll test work, aimed at determining the effect that concentration and type of cation had on the desorption of gold from preg-robbing ores, was performed on a sample of Ore 3. The isotherms determined from the bottle roll tests for Ore 3 involved tests in which the concentration of sodium in the adsorbate was varied. Increased ionic concentration has been shown to favour adsorption onto activated carbon although to a lesser extent than the cation present itself, for

instance calcium (Davidson, 1974). It has also been shown that ion exchange occurs at the surface of activated carbon within the aurocyanide complex pair, which may be used to favour desorption by exchanging of the alkali earth aurocyanide complex pairs with those with alkali metal cations (Davidson and Duncanson, 1977). To test whether this also applies to preg-robbing adsorption, bottle roll tests were performed using fresh CIL tailings samples, without the addition of alkali metal salts, thereby assuming calcium aurocyanide pairs would be present due to the leaching conditions of the plant. In addition, tests where potassium and sodium were introduced to the samples in equal molar concentrations were performed to test whether ion exchange occurs.

The results reported in Figure 10 and Figure 11 indicate that sodium additions rather favoured adsorption than desorption, as indicated by the higher degree of desorption achieved at a lower temperature in the absence of added sodium. However, significant sodium was already introduced by the sodium cyanide used to adjust the cyanide concentration to what would be present within the CIL tailings slurry. The increased ionic strength resulting from the additional addition of sodium should favour adsorption and is thus a possible reason for the decreased desorption of the gold from the preg-robbars.

Increasing the sodium concentration further suppressed desorption from the ore as is evident from the lower gold solution concentrations as compared to the standard test (Isotherm Test 1), by a factor ranging between 4 and 38, where no additional species was introduced. This should affect the HiTeCC process two-fold. During the desorption phase, the increased ionic strength will suppress the desorption of gold from the ore, lowering the concentration of gold in solution thereby limiting the amount of gold available for adsorption onto activated carbon.

During the cooled adsorption stages, however, this could drive adsorption onto the activated carbon, but will also promote re-adsorption onto the ore. This could also explain the high heat of adsorption calculated for Ore 1 during the desorption test work. The desorption tests were performed under HiTeCC conditions, i.e. with sodium hydroxide concentrations of 30 g/L, which should favour adsorption and possibly, explaining the higher heat of adsorption measured.

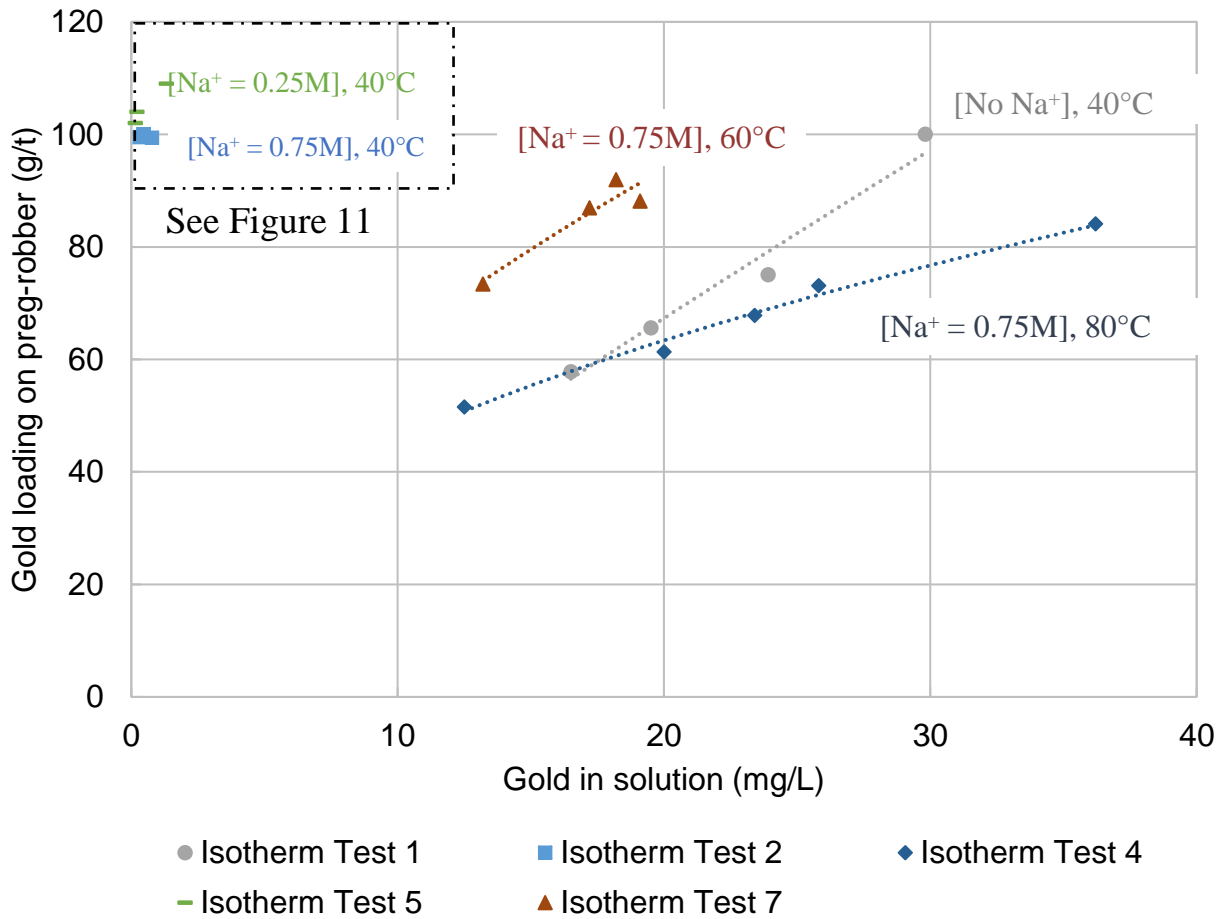


Figure 10 Bottle roll test isotherm results of Ore 3 at varying sodium concentrations I.

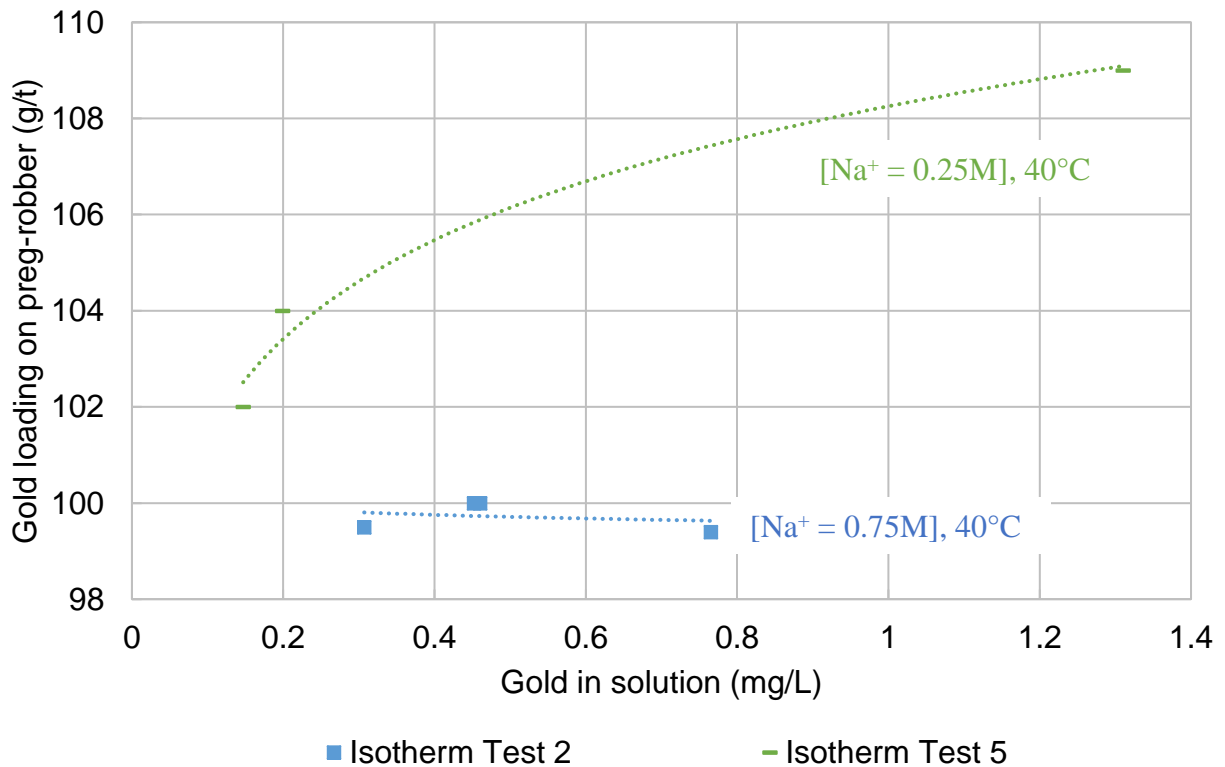


Figure 11 Bottle roll test isotherm results of Ore 3 at varying sodium concentrations II.

When operating at high sodium concentrations, the temperature required to facilitate desorption was much higher than under conditions where no sodium was added. This would have a direct cost implication for the HiTeCC process. Table 12 indicates the steam requirements for operating the desorption circuit of the HiTeCC process for different sodium additions, assuming all gold released during desorption can be recovered. A reduction in the steam requirement of 54% per percentage gold recovered is possible when not operating the desorption phase at high sodium concentrations. This is assuming that no preheating of the slurry is done.

Table 12 Energy requirements of operating HiTeCC desorption process at different ionic conditions.

<i>Additional sodium hydroxide concentration (g/L)</i>	<i>Temperature (°C)</i>	<i>Possible recovery (%)</i>	<i>Energy requirement (MJ/t)</i>	<i>Steam required (kg/t)</i>	<i>Steam requirement per % recovered Au (kg/%)</i>
30	80	70	272	123	1.74
30	60	52	188	85	1.64
No additional [Na]	40	59	104	47	0.80

*Calculation based on heating 1 t of water (heat capacity, 4.187 kJ/kg.K) with 200 kPa saturated steam (enthalpy, 2706 kJ/kg). Recovery results from isotherm test at an ore to solution ratio of 1:3.

The addition of potassium similarly to sodium favours adsorption. The gold solution concentration for bottle roll tests performed with potassium salts was lower at the same temperatures when compared with desorption tests performed in the absence of potassium addition (Figure 12).

When comparing the levels to which potassium and sodium inhibit desorption from the ore (Figure 13), it becomes clear that sodium has a stronger stabilizing effect on the gold adsorbed onto the preg-rober. Under the same ionic concentration and temperature, the isotherms performed with potassium in solution had higher gold solution concentrations. This is in line with the findings of Davidson (1974) who showed similar behaviour for activated carbon. This by extension also implies that some ion exchange occurs with preg-robers.

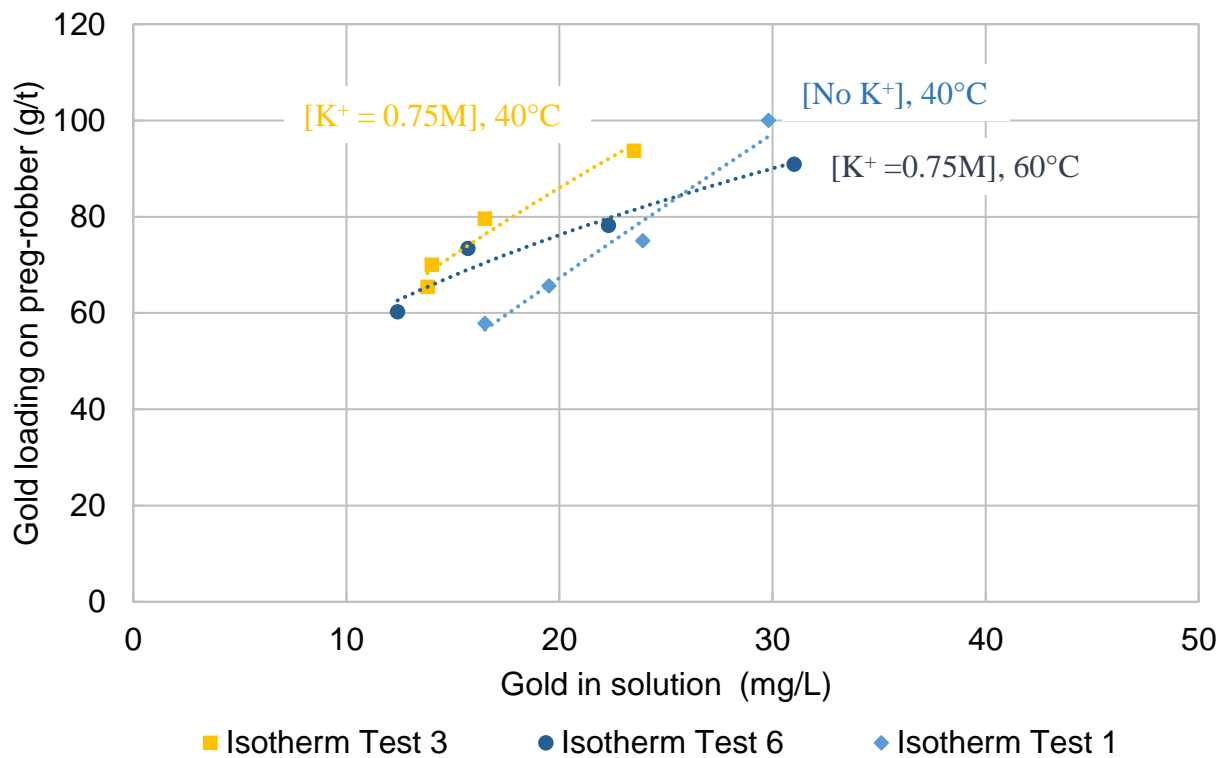


Figure 12 Bottle roll test isotherm results of Ore 3 at varying temperatures with the addition of potassium salts.

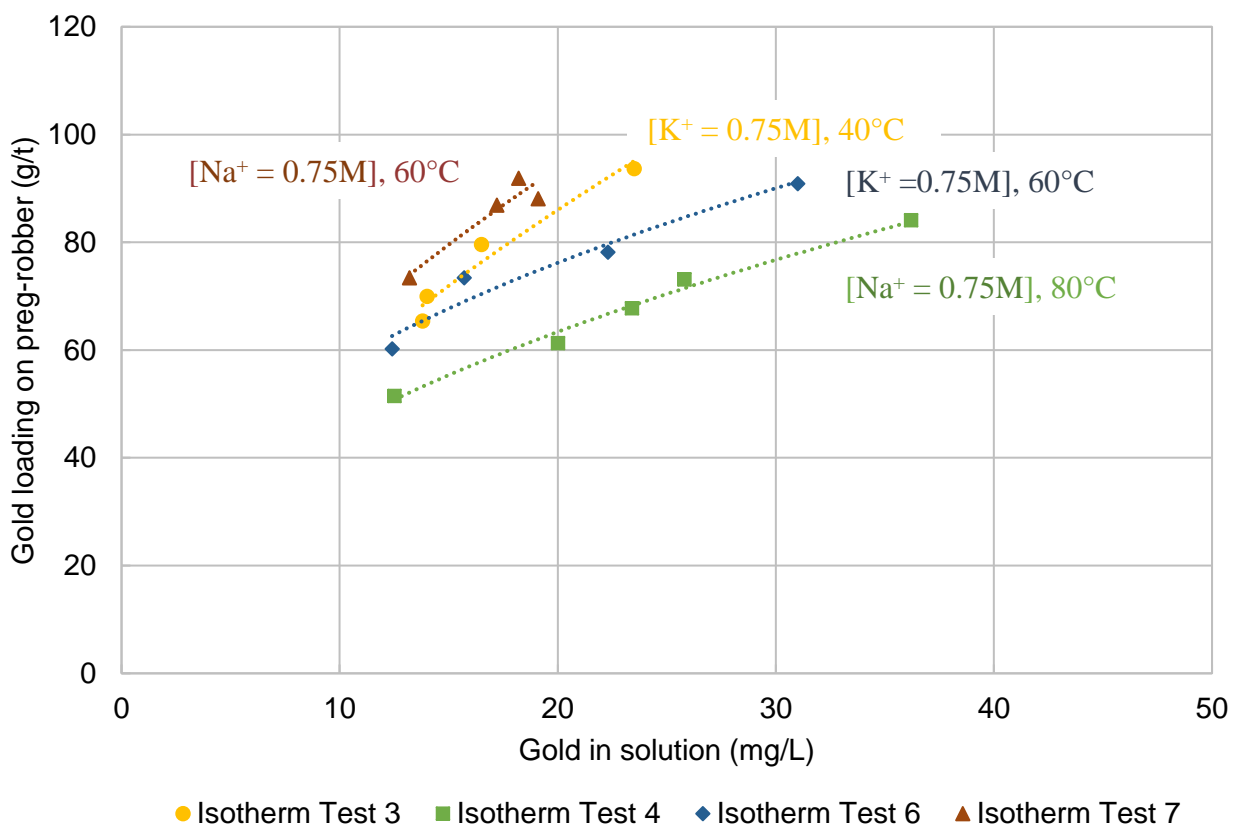


Figure 13 Bottle roll test isotherm results of Ore 3 at varying temperatures comparing the effect that sodium and potassium salts have on the adsorption capacity.

Figure 14 shows the results of the kinetic desorption tests performed at varying sodium hydroxide additions on Ore 3. The introduction of sodium hydroxide during the kinetic experiments on Ore 3 suppressed desorption of gold to a large extent. At higher temperatures gold was released but either re-adsorbed or precipitated as the gold concentration in solution decreased over time.

The kinetic test results indicate that, in the absence of the sodium hydroxide addition, higher quantities of gold can be desorbed and potentially recovered.

The rate similarly decreases at increased concentrations of sodium hydroxide. It would therefore be advisable not to introduce sodium hydroxide during the desorption phases of the HiTeCC process, as it would slow the release of gold from the preg-robbing.

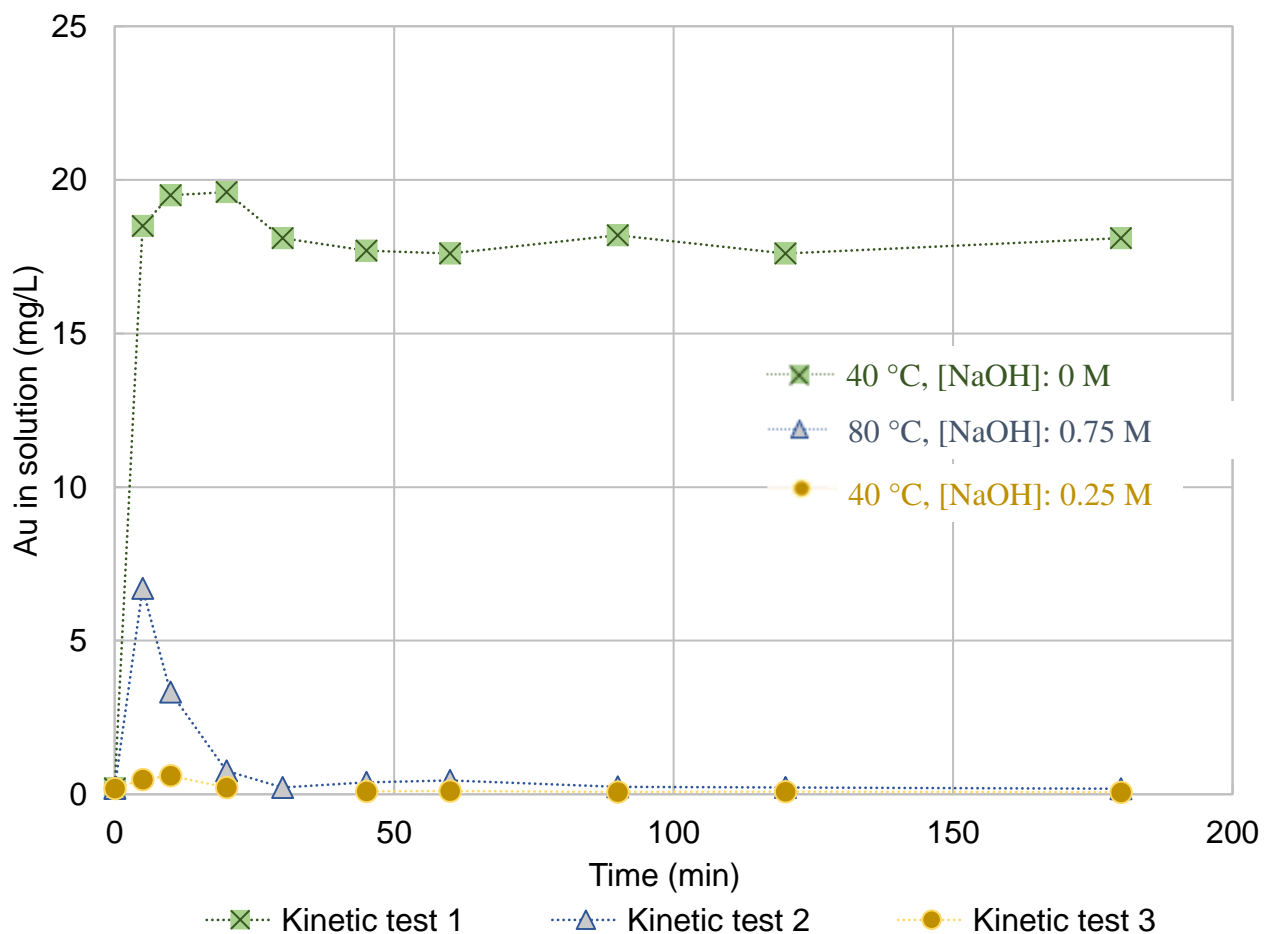


Figure 14 Kinetic desorption test results for Ore 3 at varying sodium hydroxide concentrations and temperature.

The addition of ionic species to the process will suppress desorption during the desorption stages of HiTeCC which would be detrimental to gold recovery. Furthermore, operating at higher ionic

concentration necessitates the need to operate at high temperatures and will also require careful management of effluent streams as many operations recycle tailings water.

3.4 Influence of activated carbon on HiTeCC gold recovery

During the HiTeCC experiments, the adsorption capacities of regenerated and eluted carbon were compared with that of fresh carbon as adsorbent during the HiTeCC process. Regenerated carbon adsorbed less gold with increased gold lost to the preg-robbing.

The desorption of gold from preg-robbing ore will mostly be mass transfer controlled and will therefore be a function of the gold concentration in solution. When fresh activated carbon is introduced in sufficient quantities, the rate of gold adsorption on the activated carbon should more than match that at which it is released from the preg-robbers. Under such conditions the gold in solution would be kept at relatively low levels and kinetics of desorption from the preg-robbers favoured while adsorption on the virgin activated carbon should still be possible due its low gold concentration. It is for this reason, that the gold loading on the activated carbon should be limited to prevent conditions that could favour desorption from the activated carbon in the HiTeCC process. For ores with a very low preg-robbing gold loading this will prove most difficult as the lower the loading on the preg-robbing, the lower the loading on the activated carbon must be to allow for preferential adsorption onto the activated carbon.

A direct comparison of the gold loading of the preg-robbing and that of the activated carbon is however flawed. Preg-robbing capacities are defined as a gold loading per mass of ore. Considering that the carbon within the ore is the sole adsorbent, a more accurate comparative measure would be to calculate the gold loading based on its carbon content. For a sample of Ore 1 with a carbon content of 3.8 % at a preg-robbing gold loading of 6.9 g/t, the preg-robbing carbon gold loading would be 181.6 g/t carbon. Table 13 summarises the results of the HiTeCC tests conducted at different activated carbon concentrations and gold loadings. When comparing the relative carbon gold loadings, it becomes apparent that both carbon sources contribute to the overall gold balance. The eluted carbon with its relatively higher gold loading, compared with the preg-robbing, lost gold to the preg-robbing, with the regenerated carbon capable of adsorbing some gold. The activated carbon concentration compounds the effect of the activated carbon gold loading, with higher concentrations leading to increased desorption or adsorption based on the gold loading of the activated carbon compared with the preg-robbing carbon gold loading.

Table 13 Metso Outotec HiTeCC alternate activated carbon gold loading test comparing the effects of using regenerated and eluted activated carbon as adsorption medium during the HiTeCC process.

Carbon tested	Hot phase carbon concentration (g/L)	Initial activated carbon gold loading (g/t)	Gold recovery from preg-robber (%)
<i>Regenerated activated carbon</i>	30	45.0	39.1
	40	45.0	46.4
<i>Eluted activated carbon</i>	30	224.0	-20.3
	40	224.0	-42.0

Standard conditions: 30 g/L NaOH, Ore 1 ore gold loading: 6.9 g/t

When comparing the gold recovery for the HiTeCC tests (Table 14) it becomes evident that the single addition of carbon was far more effective in recovering gold from the preg-robber. This can be explained by the effect that temperature has on the process. During the desorption phase, the preg-robber and activated carbon are exposed to high temperatures. For both, desorption will be favoured therefore lower gold loadings can be expected. During the double addition of activated carbon, the carbon was removed prior to cooling the pulp, thereby limiting the amount of gold that could adsorb.

The single addition experiment allowed adsorption to occur onto the activated carbon at low temperature leading to higher gold recoveries. The duration of the desorption phase within the times explored did not play a role in the gold recovered.

Table 14 Metso Outotec HiTeCC batch test results as performed on samples of Ore 1 and 3 at a temperature of 70 °C.

Experiment	1st addition concentration (g/L)	2nd addition concentration (g/L)	Desorption phase duration (min)	Gold recovered (%)
<i>HiTeCC Test – 2</i>	30	20	800	33.45
<i>HiTeCC Test – 3</i>	30	20	800	27.48
<i>HiTeCC Test – 4</i>	30	20	400	29.17
<i>HiTeCC Test – 5</i>	30	20	400	31.93
<i>HiTeCC Test – 6</i>	20	–	400	63.76
<i>HiTeCC Test – 7</i>	30	–	400	65.60

Introduction of activated carbon led to an increased rate of desorption over all experiments as indicated in Figure 8 and Figure 9. The introduction of a competitive adsorbent leads to higher desorption rates from the preg-robbing, as the mass transfer is driven by the gold concentration gradient between the solution and particle surface. When increasing the activated carbon concentration, the rate further increased, as the gold in solution would be lower due to adsorption on the activated carbon. This effect can be explained in terms of a gold balance of the process. Both the gold on the activated carbon and preg-robbing contribute to the overall process, with the rates of both desorption and adsorption decreasing with time as the least and most favoured sites, respectively, on the preg-robbings and activated carbon move closer to equilibrium. The steady-state concentration of gold in solution would be difficult, if not impossible, to predict considering the many variables involved. However, conditions for gold recovery from preg-robbings should be most favourable with the addition of high concentrations of high activity virgin activated carbon.

The HiTeCC tests show how the mass transfer of desorption from the preg-robbing in most instances exceeds that of adsorption onto the activated carbon. The high desorption and adsorption rates of gold on preg-robbings, seen during the desorption tests as well, are probably due to the small particle size of the preg-robbings.

3.5 Ore dependence of isotherm and sorption capacity

Metso Outotec performed PRI tests as prescribed by the Barrick Gold Mines Incorporate test with residence times ranging from 6 to 30 hours on samples of Ore 1, 2 and 3. The PRI test results illustrate the highly variable nature of preg-robbings. A comparison of the preg-robbing indices (Table 15) of the different ores shows a direct correlation to the specific ore, confirming the assumption that different preg-robbing ores will have variable preg-robbing properties. Within the same ore, however, there also exists a large range of PRI values, which further emphasises the need to account for this when treating preg-robbing ores.

When a linear version of equation 4 is fit to the PRI test data, by applying a least sum of squares fit, with only the isotherm constant as a variable. The resulting isotherm constants could be determined. The result of the model fit is shown in Figure 15, linear isotherms were determined for the different PRI test data sets; here it is again assumed that a linear isotherm is valid due to the low gold loading of the preg-robbings. Comparing the isotherm constants from the model fit to the PRI indices of the various ore samples shows a direct near linear relationship (Figure 16). The results of PRI Test – 4 did not converge due to the highly variable data points within the first 50 minutes of the test and was therefore omitted.

This should be expected as the PRI test is a quasi-equilibrium test that relates the amount of gold adsorbed onto the ore within a specific time. Gold adsorption only reaches equilibrium after weeks, but the majority of gold is adsorbed in the early stages of the process. If sufficient bottle roll tests are performed for a preg-robber, a database of PRI vs. isotherm constants can be derived, which would enable prediction of the isotherm through an easy test like the PRI test. The same relationship does not hold for the mass transfer coefficient (Figure 17), but the PRI test data can easily be used to fit equation 4 to determine this experimentally.

Table 15 Metso Outotec PRI test results for different ore samples.

Test	Ore	Preg-robbing index (%)
<i>PRI – Test 1</i>	Ore 1	46.95
<i>PRI – Test 2</i>	Ore 1	66.90
<i>PRI – Test 3</i>	Ore 2	98.15
<i>PRI – Test 4</i>	Ore 2	99.70
<i>PRI – Test 5</i>	Ore 3	84.80
<i>PRI – Test 6</i>	Ore 3	64.45

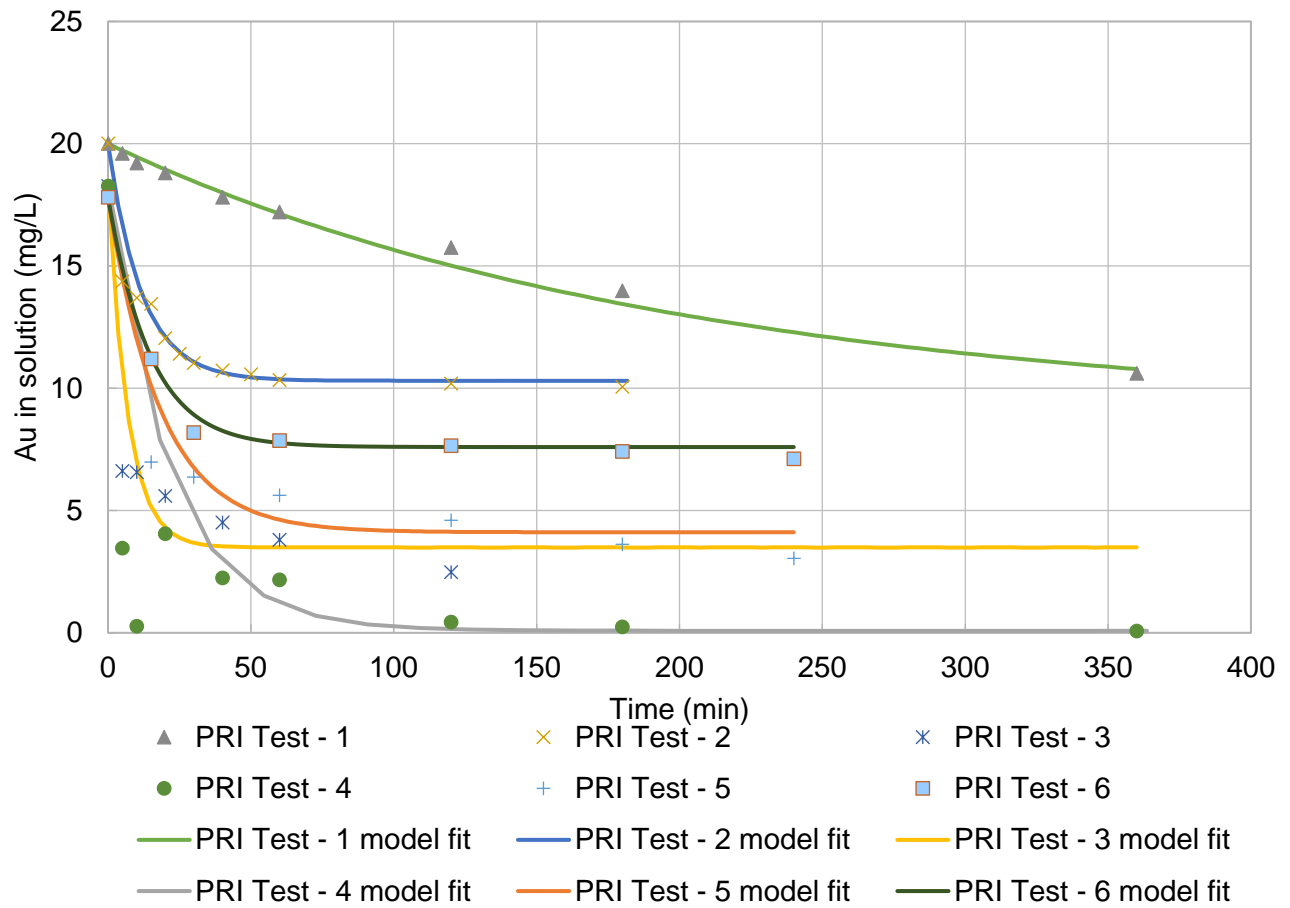


Figure 15 Adsorption model fit of Metso Outotec PRI test results for samples of Ores 1, 2 and 3.

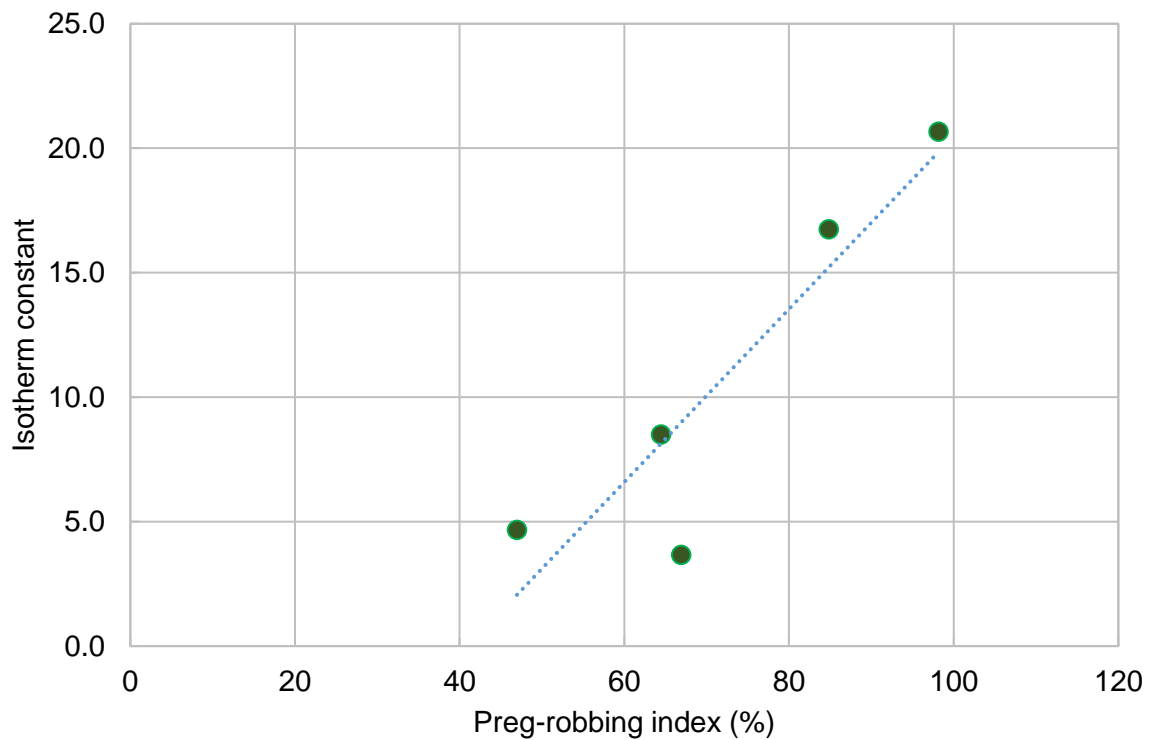


Figure 16 Linear isotherm constant as a function of the PRI.

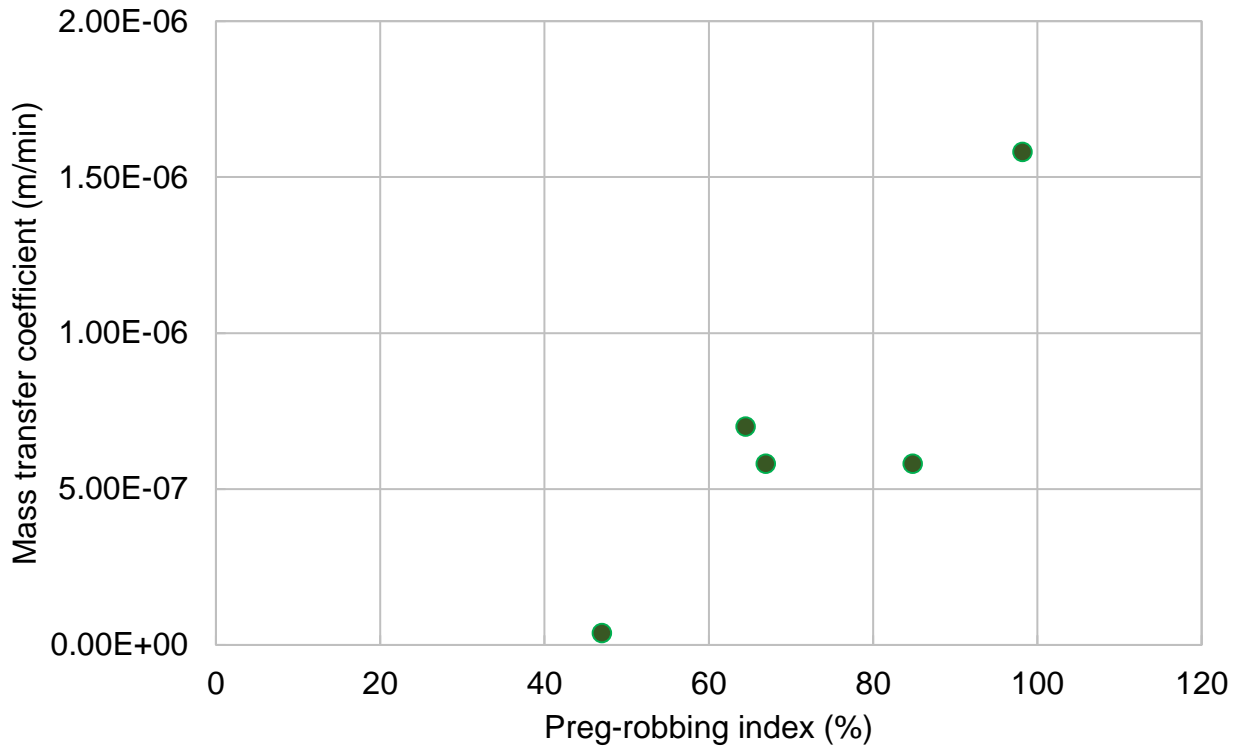


Figure 17 Mass transfer coefficient results of PRI test data fit as a function of preg-robbing index.

To define a parameter through which the preg-robbing capacity of a specific sample could be determined, a set of samples of Ore 3 was analysed for carbon and gold content. When comparing the preg-robbing gold loading (gold loading per ton of preg-robbing carbon) to the carbon content of different samples of the ore, no relationship is evident (Figure 18).

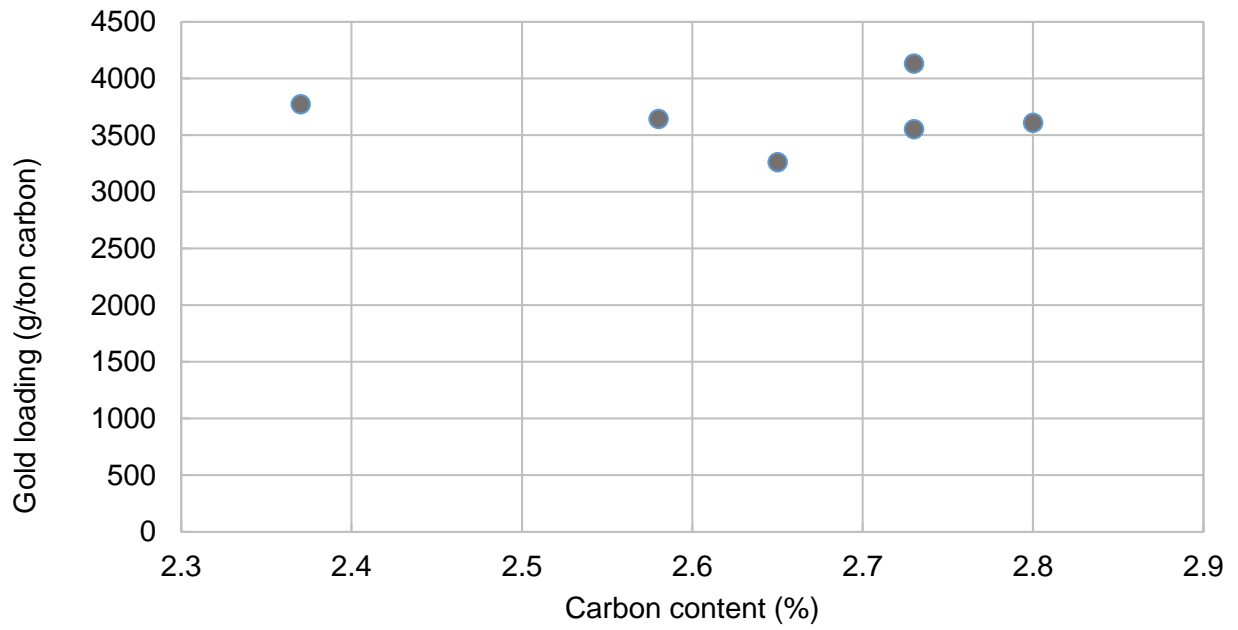


Figure 18 Ore 3 preg-robbing gold loading and carbon content of different ore samples.

4 PROCESS MODELLING

The aim of the present work was to develop a model of the HiTeCC process to support decisions on the applicability of the HiTeCC process to recover further gold from biooxidised and CIL processed preg-robbing ores, as well as for the optimization and improved design of such plants.

This section is devoted to the development and testing of a HiTeCC process model that can be used to design and optimize current and future operations. The most important factors considered when developing the HiTeCC model were the relative adsorption and desorption rates and dynamic balance that exists between the adsorbed gold on both the activated carbon, preg-robbler and in solution. Batch laboratory scale and plant models were developed. All models were tested using existing experimental and plant data. The models developed were evaluated against their ability to predict overall gold desorption and accurate kinetic behaviour.

The characteristic ore isotherms for Ore 1 and Ore 3 were determined using experimental work completed by Metso Outotec and bottle roll test work, respectively.

Batch and plant models were coded in the GNU Octave v 5.1.1 programming package. For integration the ODE45 (Runga Kutta 4th order) function was used. An automated solver was coded for curve fitting, using initial values determined using the equilibrium conditions of the experimental data provided. The batch model coding is included in Appendix A and the plant model coding is included in Appendix B.

The plant model was developed assuming a chosen overall recovery. The inter-stage gold values of the preg-robbler and activated carbon were then calculated using a gold mass balance.

4.1 Batch models

Two approaches are required when defining process parameters: the first is to model a process at laboratory scale, allowing for the determination of the required kinetic and equilibrium parameters. This is then incorporated into a model that can be used to predict possible process design parameters. A similar approach has been followed here.

As all the available gold for recovery is adsorbed onto the preg-robbing material, a balance between the preg-robbled gold and recovered gold on the activated carbon exists, with gold in solution being a function of the relative distribution between the two adsorbents.

The adsorption of gold from low aqueous concentrations of aurocyanide on activated carbon is, as mentioned in paragraph 1.3 typically mass transfer controlled. The adsorption–desorption itself is assumed to happen instantaneously compared to the rate of mass transfer to and from the interface. The relative mass transfer rates and how this, as well as the overall equilibrium, is affected by the HiTeCC parameters, will determine the overall recovery.

The adsorption of gold onto activated carbon has been extensively studied. Gold adsorption initially occurs at the surface of carbon particles, and the adsorbed species then diffuse across the surface and into the pores of the particles over time. As the surface becomes loaded, the overall adsorption slows as the slower internal diffusion becomes rate determining. This phase of “swift” adsorption occurs for carbon loadings up to 3000 g/t (Pleysier *et al.*, 2008) and at such loadings the adsorption reaction has the highest heats of adsorption, making desorption difficult.

Most preg–robbing ores have loading capacities ranging from 0.5 – 500 g/t (Avraamides *et al.*, 2009), which if normalized to a preg–robbing carbon gold loading, equates to loadings in excess of 3000 g/t. To simplify the modelling approach some practical assumptions were required.

Due to the small particle size it is assumed that no internal mass transfer mechanisms play a role in the process, leaving only film diffusion as the rate limiting step. Other assumptions were made when compiling the preg–robbing mass transfer adsorption equation for a batch reactor including that:

- 1) All particles are spherical.
- 2) Carbonaceous materials are the only participating adsorbents.
- 3) Particles can be assumed to have a uniform particle size and density.
- 4) Carbon particles within the slurry are fully liberated.

During the HiTeCC process, virgin activated carbon is introduced into the circuit. The rate of adsorption of gold onto activated carbon in CIL and CIP processes is typically limited by film diffusion due to the relatively short residence times of these circuits. For HiTeCC the same principle applies, and equation 7 can be used to define the sorption onto activated carbon as well, in the following form.

$$\frac{dc_b}{dt} = \frac{-k_a \cdot (C_b - (Q/B)^{\frac{1}{N}})}{P.D.V} \quad (8)$$

where:

C_b : The solution gold concentration the bulk solution

k_a : Kinetic mass transfer coefficient for activated carbon

Q : Carbon gold loading of activated carbon

- B : Freundlich pre-exponential constant for activated carbon
 N : Freundlich exponential constant for activated carbon
 P : Density of activated carbon
 D : Diameter of the activated carbon particle
 V : Volume of the reactor

By combining equations 7 and 8, the total mass balance then becomes:

$$\frac{dCb}{dt} = \frac{kc.(Cb-(q/\beta)^{\frac{1}{N}})}{\rho.d.V} - \frac{ka.(Cb-(Q/B)^{\frac{1}{N}})}{P.D.V} \quad (9)$$

which, assuming uniform density of carbon and equilibrium, simplifies to equation 10.

$$\frac{kc.(Cb-(q/\beta)^{\frac{1}{N}})}{d} = \frac{ka.(Cb-(Q/B)^{\frac{1}{N}})}{D} \quad (10)$$

Also note that the overall gold balance requires that the total gold within the system is divided between the gold in solution, gold on the activated carbon and the gold on the preg-rober.

The equilibrium concentrations at a specific temperature on both the preg-rober and activated carbon can be determined by assuming that fully reversibly adsorbed gold is present on both preg-rober and activated carbon. At low gold loadings the Freundlich isotherm can be approximated to be linear and equation 10 may be simplified to:

$$\frac{-kc.(Cb-q/\beta)}{d} = \frac{-ka.(Cb-Q/B)}{D} \quad (11)$$

This set of equations provides a simple mathematical representation of the batch HiTeCC system through which the process can be modelled. A similar approach was taken by Rees and Van Deventer (2001) when modelling a CIL system with a preg-rober present.

In the present work, the preg-robbing adsorption was modelled to predict possible gold recovery using the HiTeCC process. In addition, a comparison was also made between the adsorption and desorption response curves modelled for a specific ore, which could prove valuable in predicting preg-rober behaviour in both CIL/CIP and HiTeCC processes.

The batch models were calibrated and tested using existing experimental data. Preg-robbing isotherm and kinetic response curves were used to determine the level of preg-robbing behaviour

exhibited by a specific ore. In this case, the preg-robber batch adsorption was described by equation 7 whereas equation 9 was used to model the HiTeCC batch process.

4.2 Desorption model validation

To validate the applicability of the desorption isotherm, a comparison was done between the output from the dynamic batch desorption model, using an experimentally determined isotherm and kinetic constants, and an experimentally determined desorption profile.

Two approaches to determining preg-robber isotherms were used as part of this work. The first was to use desorption test data on Ore 1 to fit the desorption model to experimental data. Secondly, bottle roll test work on Ore 3 was performed to specifically determine isotherms by curve fitting the Freundlich isotherm to the resulting isotherm data, as discussed in Section 3. The resulting isotherms (included in Figure 19) were used to calculate a heat of adsorption and to simulate the response of Ore 3. The two approaches were necessary as a sample of Ore 1 was not available. This also proved to be a useful comparison of the effectiveness of using derived isotherms versus experimentally determined isotherms.

Experimental and plant work performed by Metso Outotec on Ore 3 under HiTeCC conditions dictated the conditions for the bottle-roll tests on Ore 3. Using the results from the bottle roll test work a heat of adsorption of ~24 kJ/mol was calculated for Ore 3. This is much lower than calculated for Ore 1, which may be explained in terms of the expected higher heats of adsorption of the initial adsorption at more favourable adsorption sites or steric hindrance increasing with loading.

The Metso Outotec desorption tests for Ore 3 were performed at 80 °C with a NaOH addition of 30 g/L; the corresponding experimentally determined isotherm is given by equation 12:

$$q = 12.9.(C_s)^{0.52} \quad (12)$$

where:

q : Gold loading of preg-robber

C_s : Gold solution concentration at the carbon surface

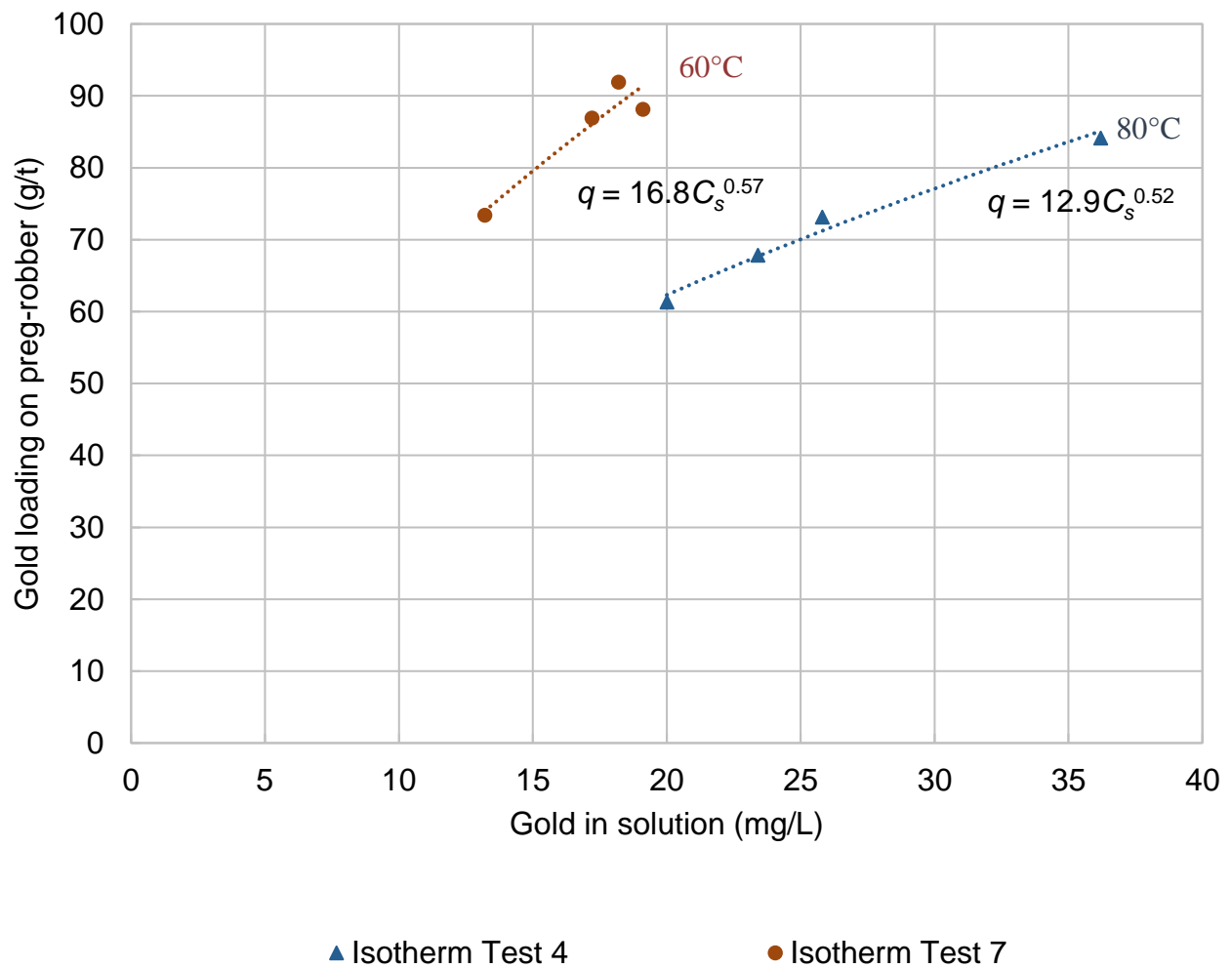


Figure 19 Experimentally determined isotherms for Ore 3 at a NaOH concentration of 30 g/L.

Using the isotherm and the desorption test data, a mass transfer coefficient for Ore 3 could be determined by fitting the desorption model derived in equation 5 to the desorption test data. An accurate fit of the data would imply that the experimentally determined isotherm was accurate in predicting the equilibrium of the desorption test. The results of the fit are illustrated in Figure 20. The mass transfer coefficient of the desorption experiment was found to be 0.31×10^{-6} m/min. The bottle roll test results showed that the isotherms at low concentration could be approximated by a linear isotherm, as also found by other researchers (Bailey, 1987; de Andrade Lima, 2007).

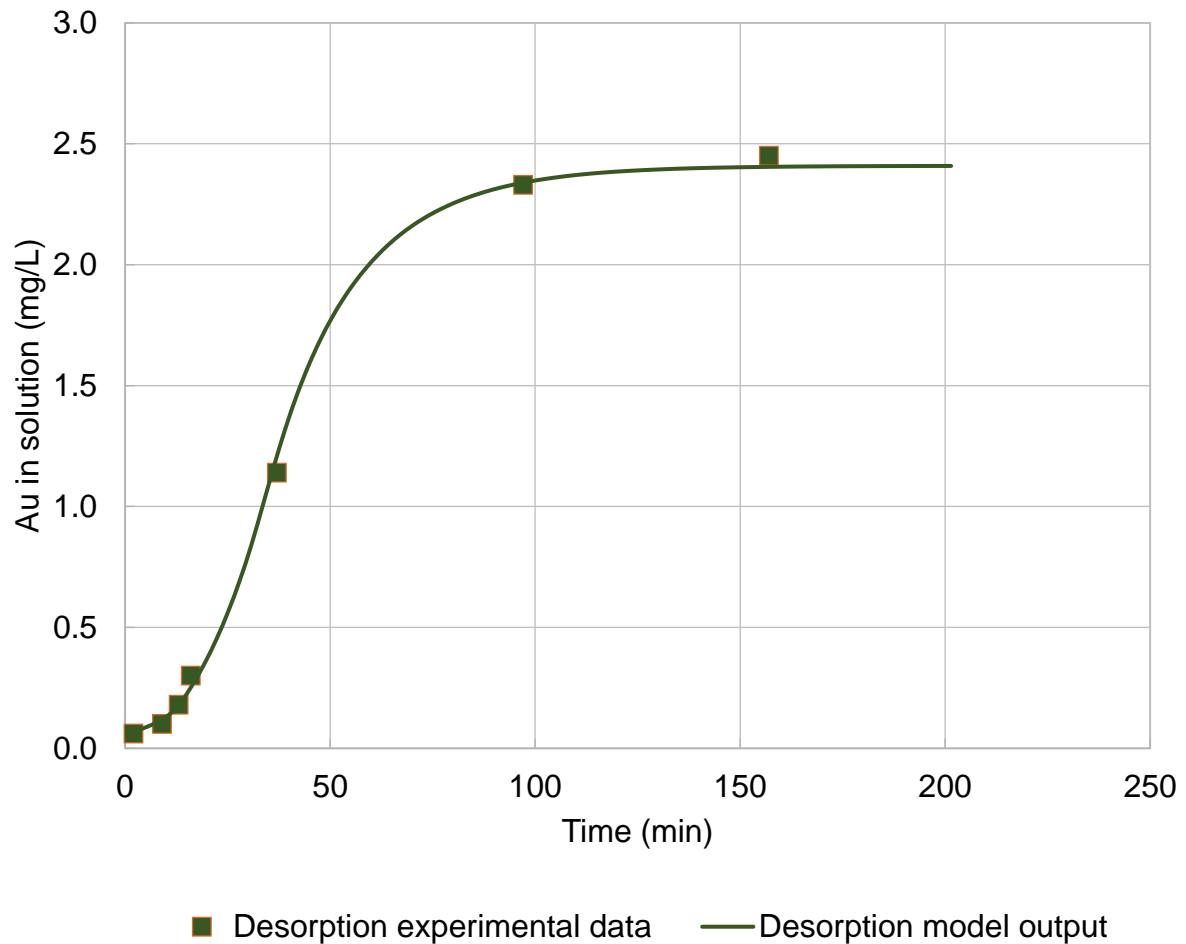


Figure 20 Metso Outotec desorption test results compared to the Ore 3 desorption model simulation result.

The experimentally determined isotherm adequately predicted the equilibrium achieved in the desorption experiment. To compare its repeatability, the isotherm was used to predict the response of the PRI tests performed on Ore 3, PRI-Test 5 and 6. PRI-Test 6 was performed at a temperature of 30 °C, the mass transfer coefficient determined for this experiment was 0.51×10^{-7} m/min. The model output and original experimental data are shown in Figure 21.

To assess the repeatability, the second PRI test (PRI-test 5) was simulated using the kinetic mass transfer coefficient determined for PRI-test 6. The result of this simulation, shown in Figure 22, indicated that the model predicted the overall desorption concentration satisfactorily but poorly simulated the kinetic response.

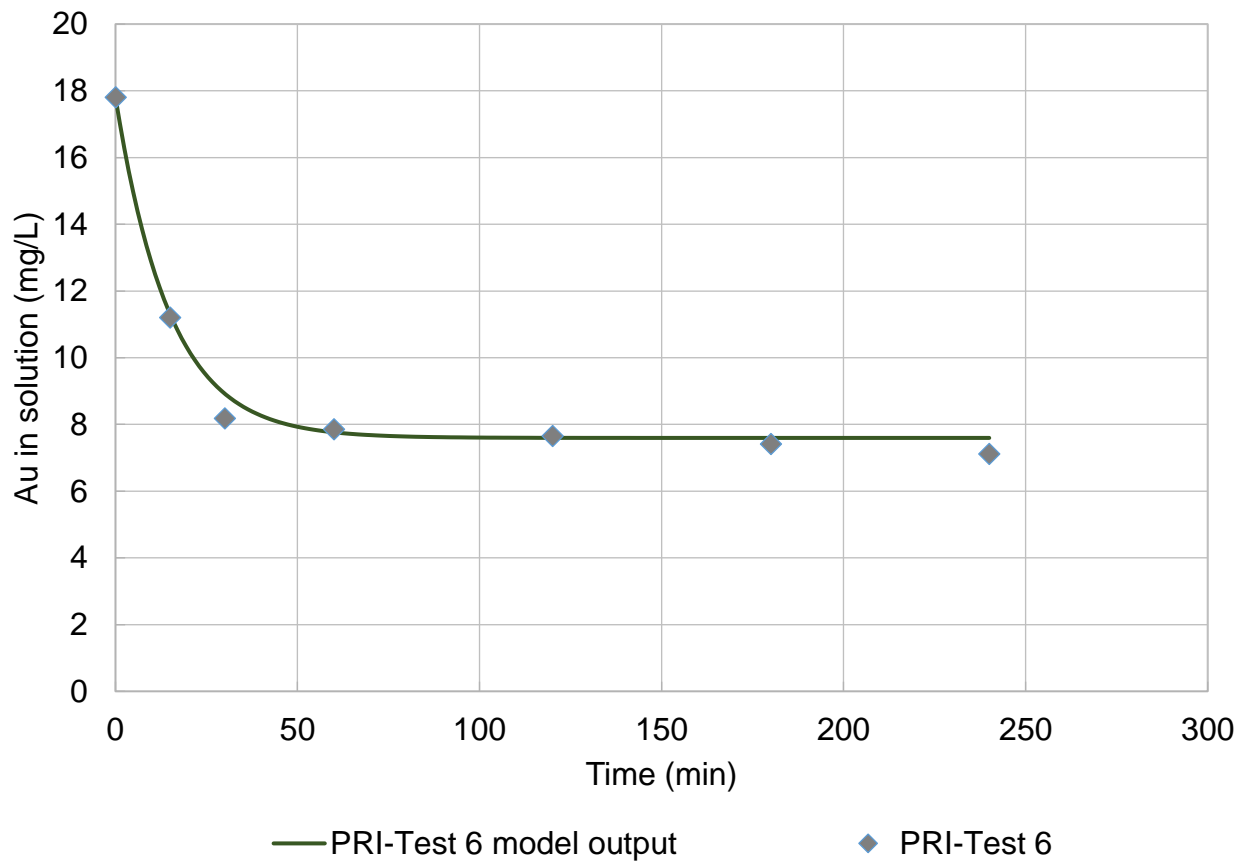


Figure 21 Metso Outotec PRI-Test 6 test and simulation results.

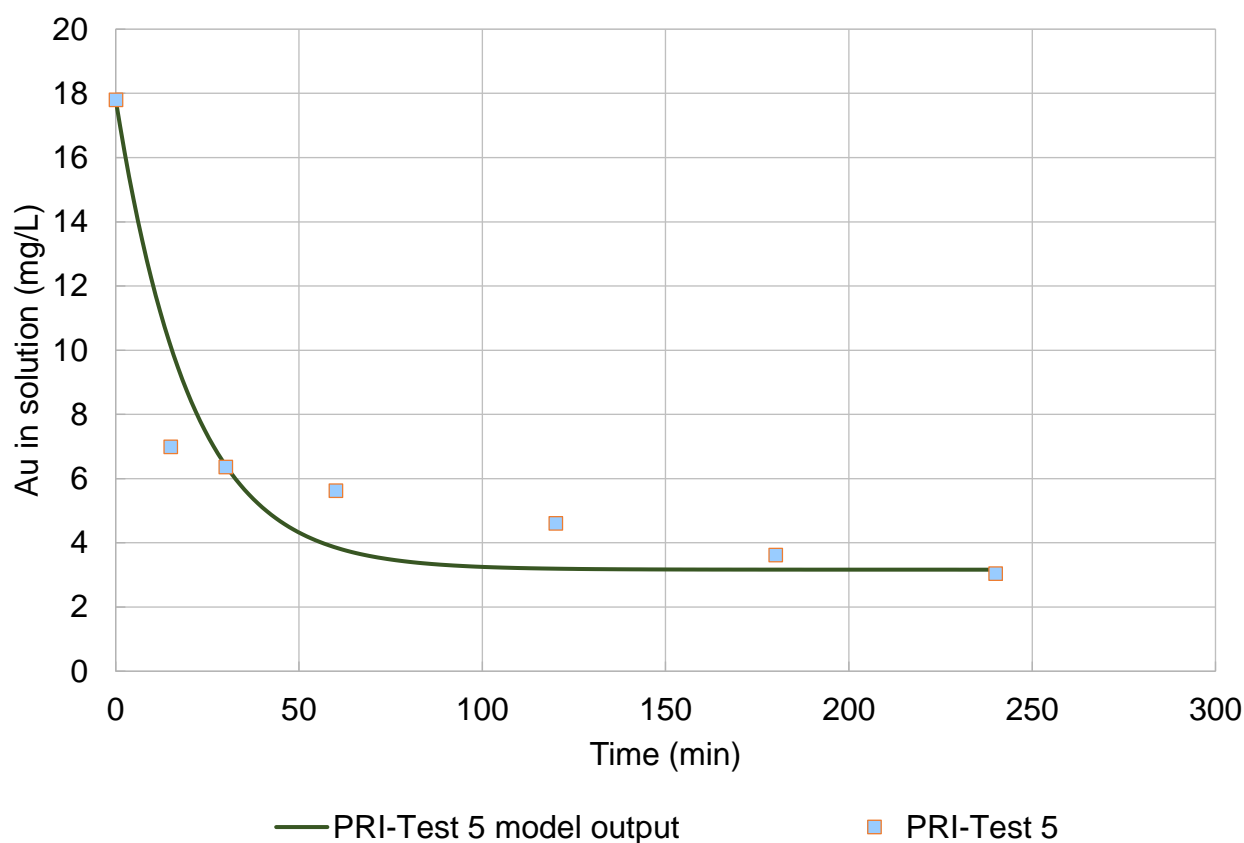


Figure 22 Metso Outotec PRI-Test 5 test and simulation results.

The desorption model was further tested by determining isotherms and mass transfer coefficients for the desorption experiments conducted on Ore 1. The desorption model and a linear isotherm were fitted to the experimental data, with the resulting isotherm constants summarized in Table 16. These constants were used with the Gibbs–Helmholtz equation to calculate the heat of desorption. Given these parameters, the desorption experiments were simulated and compared with the original experimental data, as shown in Figure 23.

Table 16 Curve fit results of the Metso Outotec desorption experiments performed on Ore 1.

Test	β	Temperature (°C)	k_c (m/min)
<i>Desorption Test 1</i>	15.0	50	2.37×10^{-7}
<i>Desorption Test 2</i>	7.4	60	2.50×10^{-7}
<i>Desorption Test 3</i>	3.1	70	1.00×10^{-7}
<i>Desorption Test 5</i>	4.1	70	1.00×10^{-7}

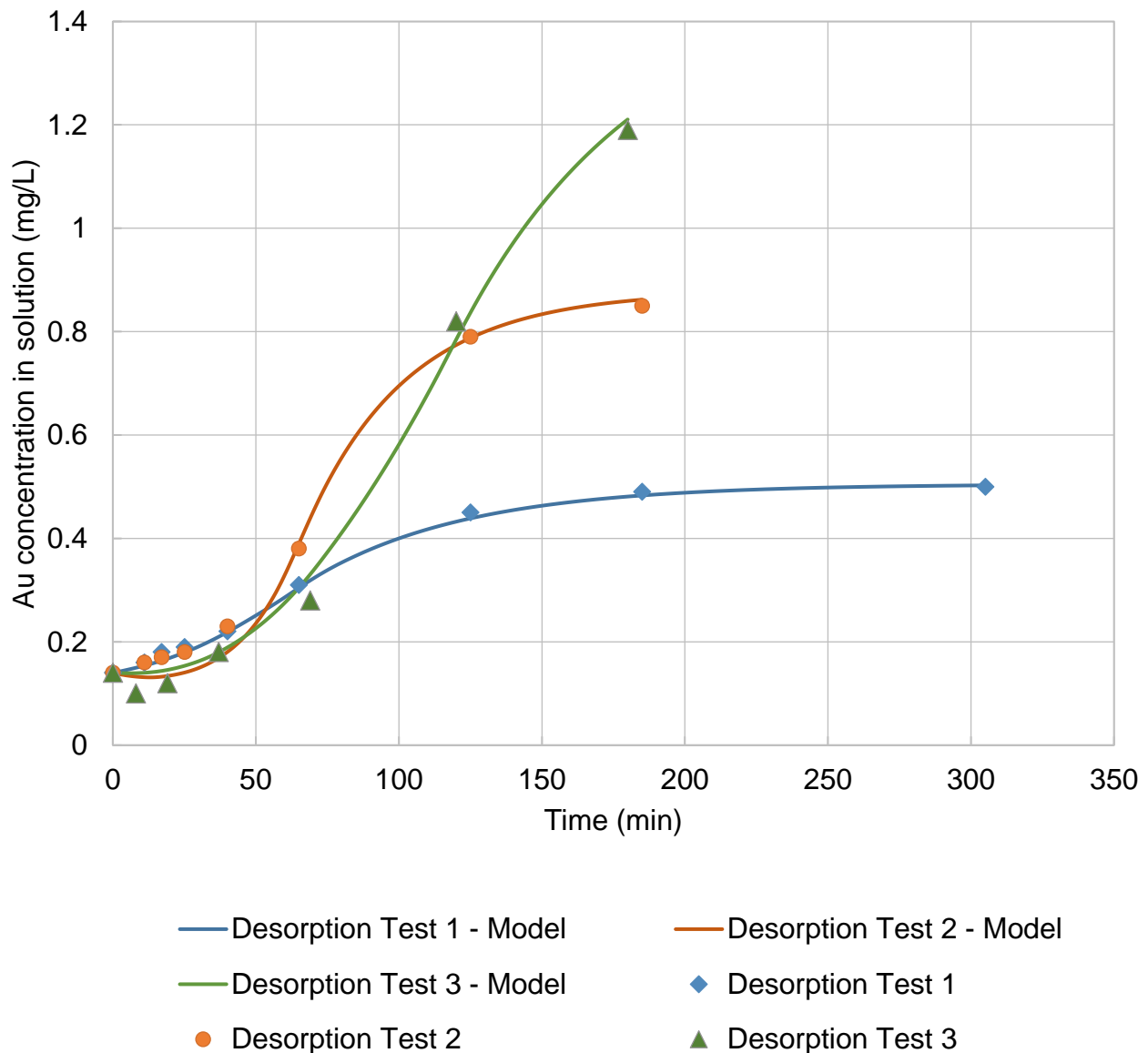


Figure 23 Metso Outotec desorption test and simulation results.

From the model fit data of both desorption and adsorption (PRI) experiments, it is clear that the model effectively predicts the behaviour of the ore if enough experimental data are used to determine a range of kinetic responses. Furthermore, the isotherm determined for desorption can be used to predict the adsorption behaviour for an ore, with only the kinetic response to be separately quantified using experimental data. This has been shown by Van Deventer and Van der Merwe (1994) for activated carbon but has been now been confirmed for preg-robbers.

The use of isotherms to predict the behaviour of a preg-robber has been shown to be effective and the application of the desorption model was effective at modelling both adsorption and desorption processes.

4.3 HiTeCC batch model validation

The HiTeCC batch model comprises modelling the parallel adsorption–desorption to and from the activated carbon and preg–robber, respectively. Multiple HiTeCC batch experiments were conducted on Ores 1 and 3. The isotherm, heat of adsorption and kinetic mass transfer constants determined for Ore 1 were then used to predict the behaviour of Ore 1 in batch HiTeCC experiments; this process was repeated for Ore 3.

The HiTeCC batch experiments were carried out by heating preg–robber slurries from Ore 1 and Ore 3 in the presence of activated carbon. The addition time, and concentration of activated carbon were varied, and the resulting gold concentration in solution profile measured. The results of these experiments are shown in Figure 24 and Figure 25.

The HiTeCC model requires the use of an activated carbon isotherm and kinetic constant. As these were not available, they had to be determined by fitting the HiTeCC batch model to experimental data. Using the isotherm determined for Ore 1 during the desorption experiments, HiTeCC – Test 6 data were used to determine constants for the activated carbon used during these experiments. The resulting activated carbon isotherm and kinetic constant were used in combination with the HiTeCC batch model to simulate other HiTeCC experiments. The activated carbon isotherm and kinetic constants are given in Table 17.

Table 17 HiTeCC batch model parameters calculated from experimentally fitted data determined at 70 °C.

<i>Adsorbent</i>	<i>B</i> <i>(m³/t)</i>	<i>k_c</i> <i>(m/min)</i>
<i>Preg-Robber, Ore 1</i>	0.00761	6.9×10 ⁻⁴
<i>Activated carbon</i>	1.668	1.7×10 ⁻⁵

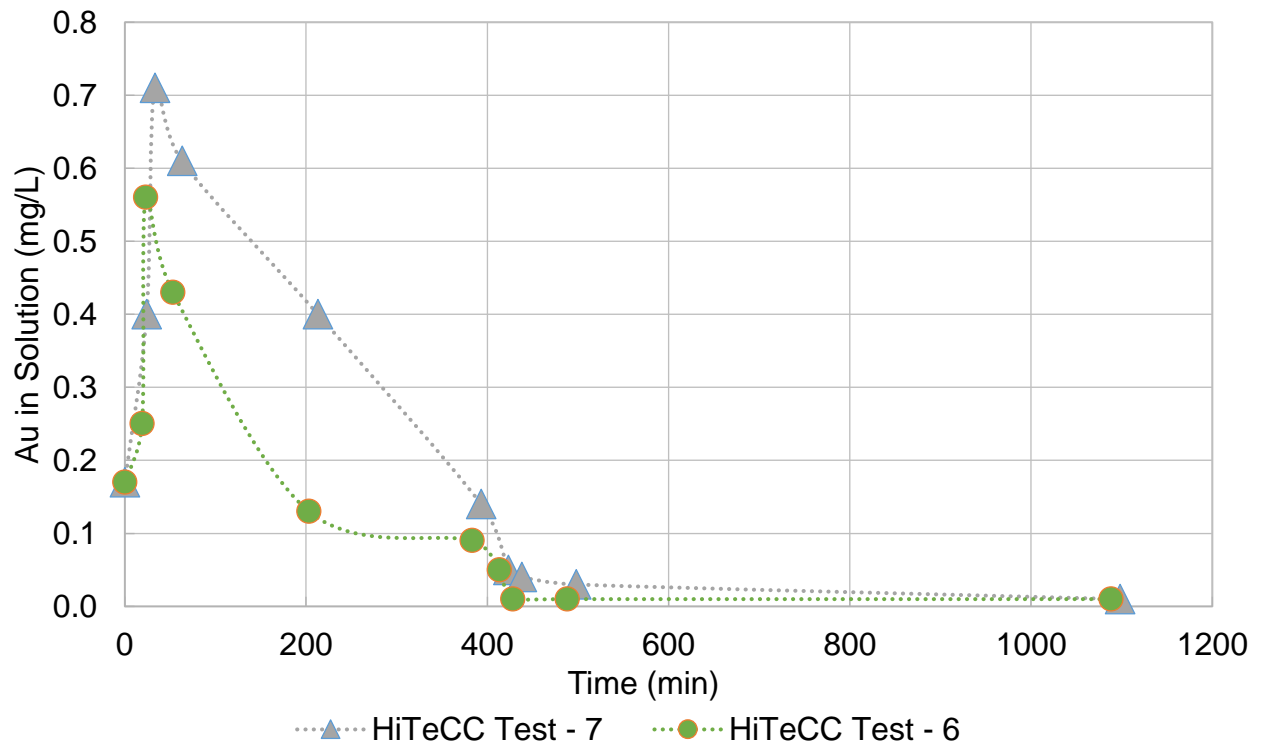


Figure 24 Metso Outotec single carbon addition HiTeCC batch test results.

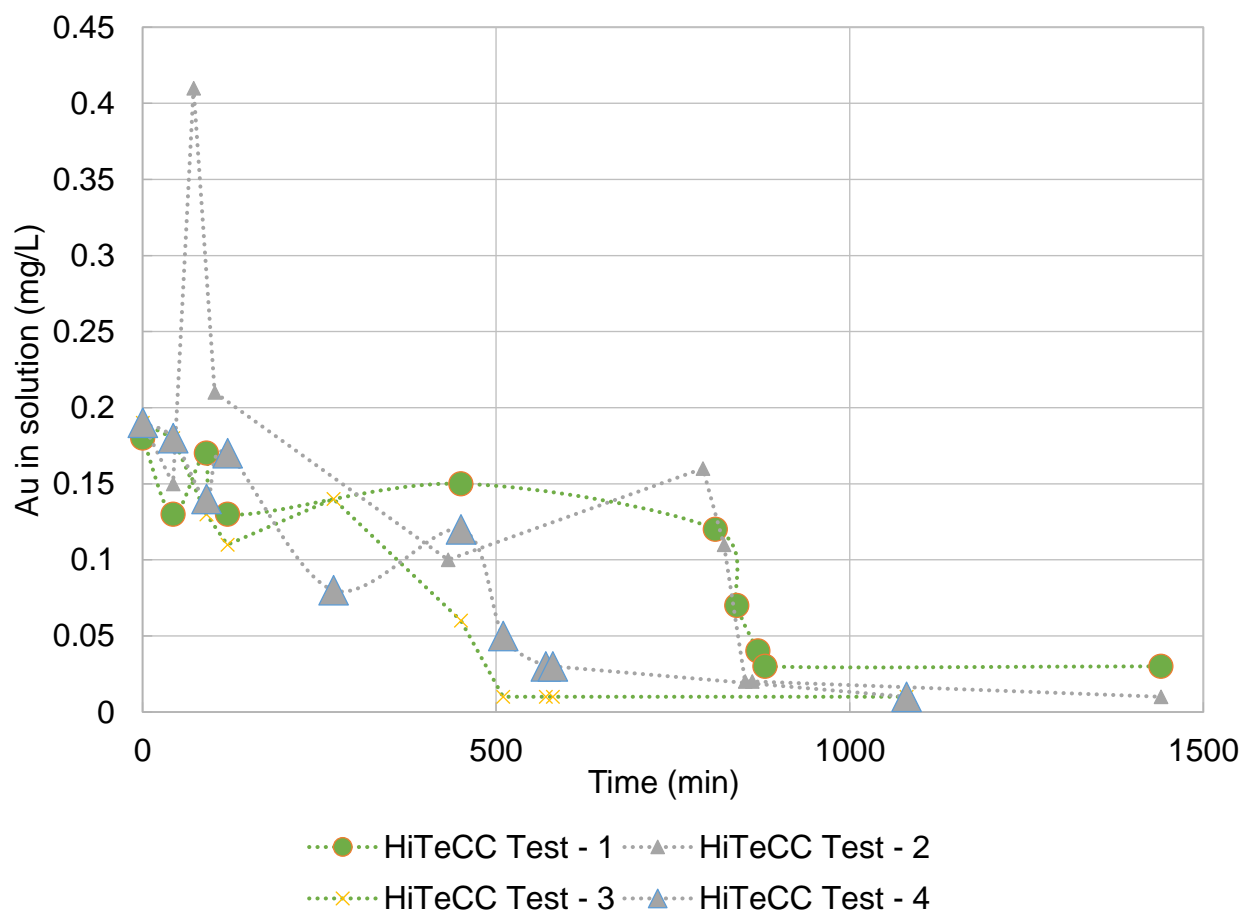


Figure 25 Metso Outotec double carbon addition HiTeCC batch experiments.

HiTeCC tests 6 and 8 were simulated using the respective isotherms for Ore 1 and 3. In each instance it was assumed that the same activated carbon was used as adsorbent. The results of the model simulations are shown in Figure 26 and Figure 27 respectively.

Using the experimentally determined HiTeCC batch model parameters, the HiTeCC batch experiment results were successfully simulated. The simulation was more accurate for Ore 3, for which the isotherm was determined experimentally as opposed to the data-fitted isotherm used for Ore 1. This is to be expected, as the conditions for determining the isotherm for Ore 3 were matched to the conditions of the HiTeCC test. This further highlights the importance of determining accurate isotherms for the preg-robber being treated.

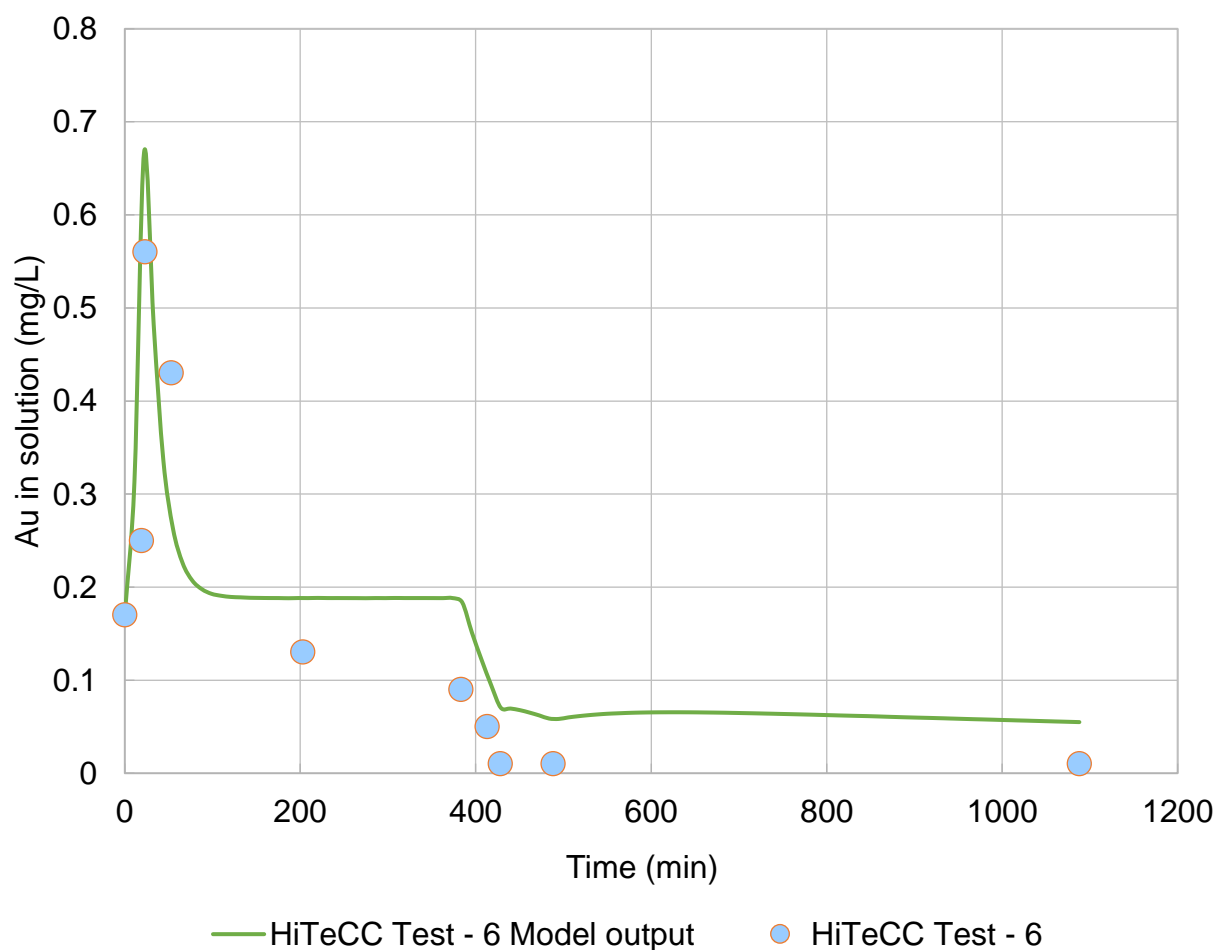


Figure 26 Metso Outotec HiTeCC batch test single carbon addition simulation results – Ore 1.

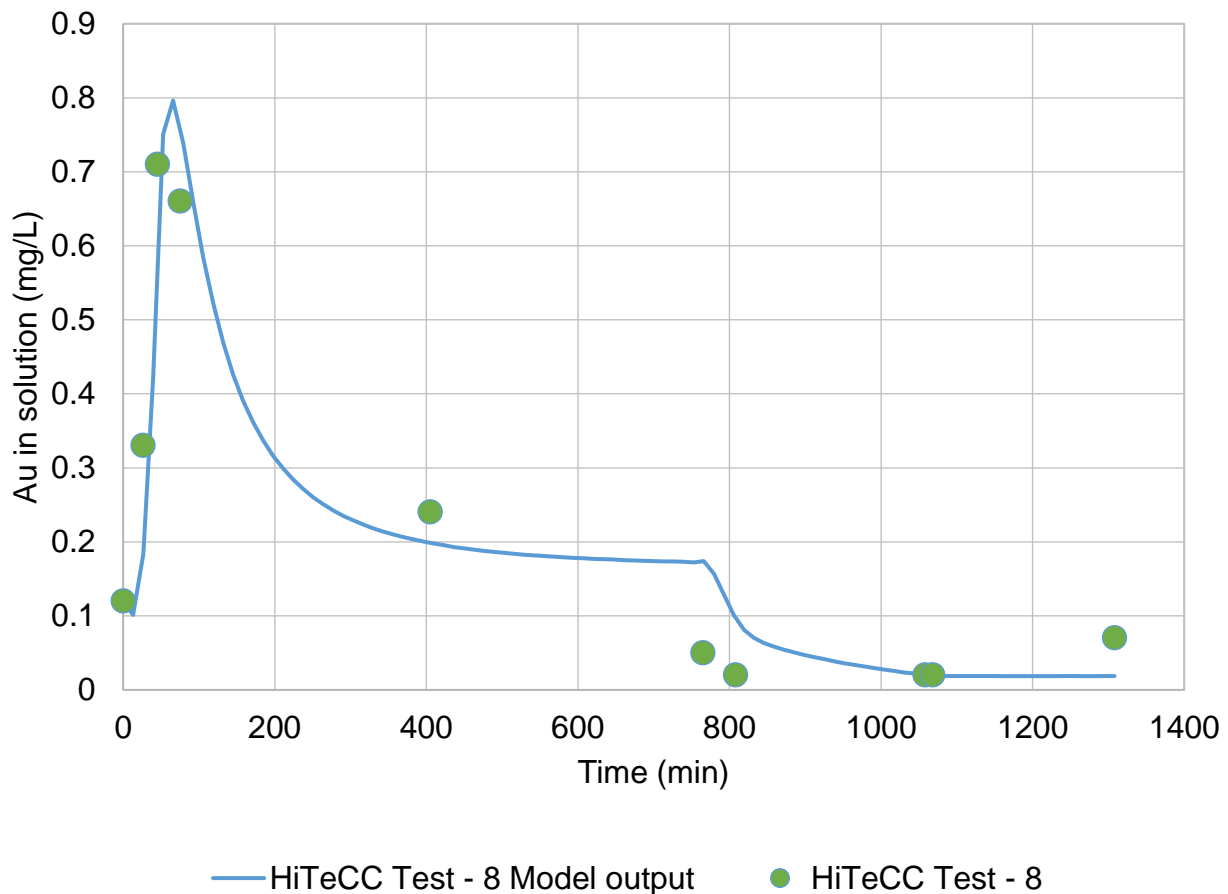


Figure 27 Metso Outotec HiTeCC batch test single carbon addition simulation results – Ore 3.

4.4 Plant models

Having shown the accuracy of the film diffusion model at predicting preg-robbing behaviour the logical next step was to extend this to plant scale. The HiTeCC process flow is similar to standard CIL processes as it is performed in a series of CSTRs with activated carbon flow counter current to the slurry flow.

Figure 28 shows an overview of a single stage of the HiTeCC process that was used as a basis for the plant model derivation. The process consists of two different stages, each consisting of multiple reactors that were assumed to be at steady state. The first desorption step was performed at elevated temperature while the second adsorption step was done at ambient temperature.

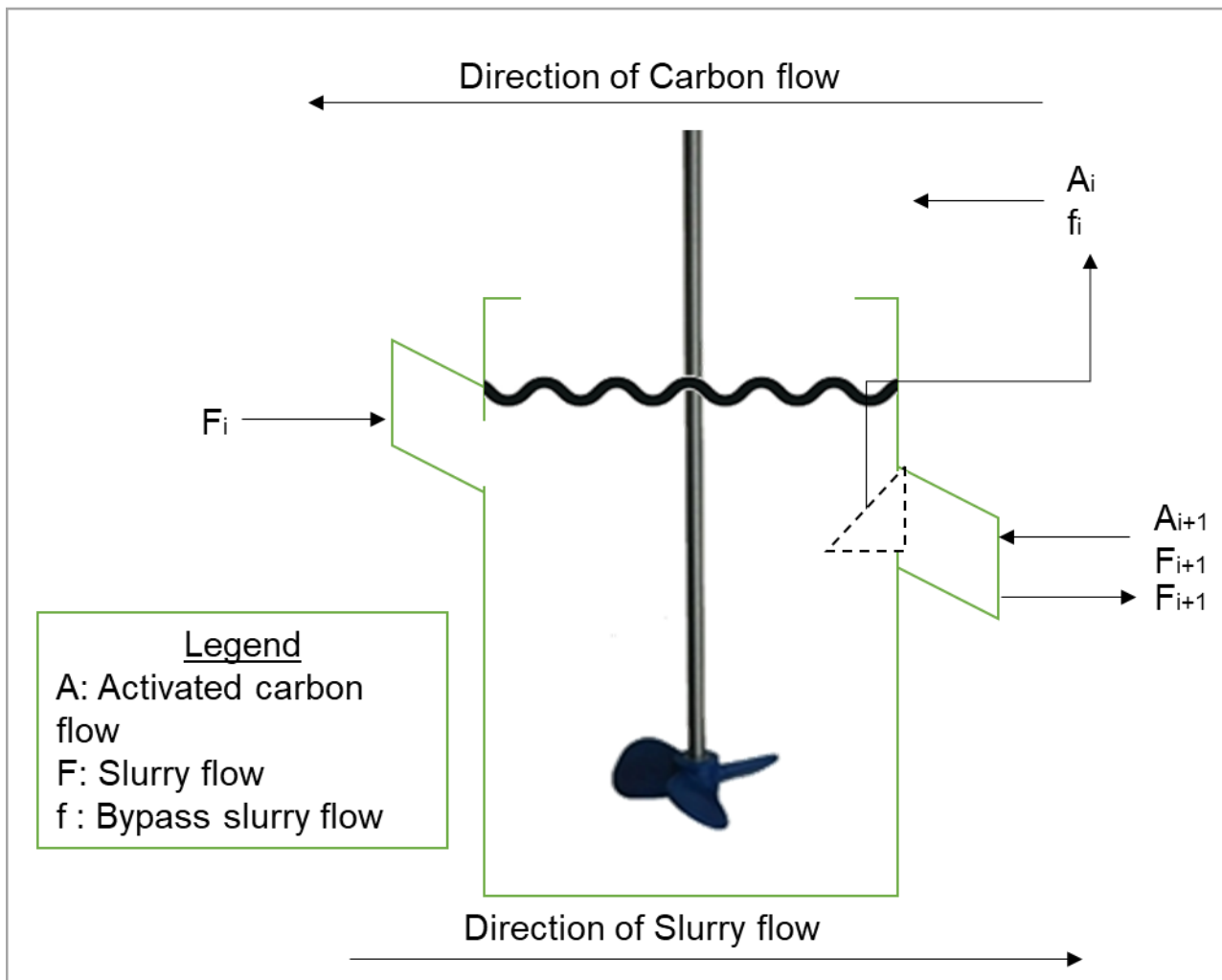


Figure 28 HiTeCC CSTR single unit diagram, with mass balance annotation

The overall mass balance over one unit cell of the HiTeCC process includes the flow of slurry and activated carbon into and out of the cell. Gold transfer between the preg-rober and activated carbon is then modelled as sorption processes with the overall gold balance being a function of the gold loading on both adsorbents, temperature and the caustic concentration. The sorption was modelled using the film diffusion model.

As with the batch experiments, the mass transfer is assumed to be rate limiting, i.e. the adsorption reaction itself is assumed to be significantly faster than the mass transfer processes. Equation 13 gives a generalized form for the adsorption/ desorption rate from either the activated carbon or preg-rober.

$$r = k_c.(C_b - C_s)/d, \quad (13)$$

where:

r : Rate of gold adsorption on a single particle

- k_c : Kinetic mass transfer coefficient
 C_b : Bulk gold solution concentration
 C_s : Gold solution concentration at the carbon surface
 d : Particle diameter

Here we defined the rate of mass transfer to and from the preg-robber and activated carbon as r_p and r_{ac} , respectively.

The following steady state mass balances hold for the process.

The overall material balance consisting of the activated carbon, slurry and bypass slurry flow:

$$F_i + A_i + f_i = F_{i+1} + A_{i+1} + f_{i+1}, \quad (14)$$

The unit gold mass balance:

$$S_i.Cb_i + x.F_i.q_{orei} + q_{aci}.A_i + x.f_i.q_{orei} + S_i.Cb_i = S_{i+1}.Cb_{i+1} + x.F_{i+1}.q_{orei+1} + q_{aci+1}.A_{i+1} + x.f_{i+1}.q_{orei+1} + S_{i+1}.Cb_{i+1}, \quad (15)$$

where:

- C_{bi} : Bulk gold solution concentration previous reactor
 C_{bi+1} : Bulk gold solution concentration current reactor
 q_{orei} : Gold loading preg-robber previous reactor
 q_{orei+1} : Gold loading preg-robber current reactor
 q_{aci} : Gold loading activated carbon previous reactor
 q_{aci+1} : Gold loading activated carbon current reactor
 F_i : Slurry inlet flow
 F_{i+1} : Slurry outlet flow
 f_i : Bypass Inlet flow
 f_{i+1} : Bypass Outlet flow
 S_i : Solution inlet flow
 S_{i+1} : Solution outlet flow
 s_i : Bypass solution inlet flow
 s_{i+1} : Bypass solution outlet flow
 A_i : Activated carbon inlet flow
 A_{i+1} : Activated carbon outlet flow
 x : Mass fraction ore in slurry

It was assumed that the slurry, activated carbon and bypass slurry mass flows remained constant over the process, therefore: $F_i = F_{i+1}$, $S_i = S_{i+1}$, $A_i = A_{i+1}$, $f_i = f_{i+1}$.

$$S_i.C_{bi} + x.F_i.q_{orei} + q_{aci+1}.A_i + x.f_i.q_{orei+1} + s_i.C_{bi} = S_i.C_{bi+1} + x.F_i.q_{orei+1} + q_{aci}.A_i + x.f_i.q_{orei} + s_i.C_{bi+1} \quad (16)$$

$$q_{aci+1}.A_i - q_{aci}.A_i = S_i.C_{bi+1} - S_i.C_{bi} + x.F_i.q_{orei+1} - x.F_i.q_{orei} + x.f_i.q_{orei} + x.f_i.q_{orei+1} + s_i.C_{bi+1} - s_i.C_{bi} \quad (17)$$

$$A_i.\Delta q_{ac} = (S_i + s_i).\Delta C_b + (F_i + f_i).x.\Delta q_{ore} \quad (18)$$

The changes in the carbon, preg-robber and solution concentrations are based on the relative sorption rates, which are given as follows:

$$\Delta q_{ac} = V \times r_{ac} / M_{AC} \quad (19)$$

$$\Delta q_{ore} = V \times r_p / M_{ore} \quad (20)$$

$$\Delta C_b = V \times (r_p - r_{ac}) / S \quad (21)$$

where:

r_{ac} : Rate of activated carbon sorption

r_p : Rate of preg-robber sorption

M_{ore} : Preg-robber mass flow

M_{AC} : Activated mass flow

S : Solution flow

V : Reactor volume

The simultaneous solution of equations 13 – 21 allowed for a stage-by-stage evaluation of the HiTeCC process and enabled optimization of various parameters.

The particle size, and transfer rate of the activated carbon were assumed to remain the same throughout the process with no material losses. The preg-robber particle size used as part of the batch test work was used for the plant model, as the rate is highly sensitive to particle size.

4.5 HiTeCC Plant model validation

The plant model was validated using existing plant data for the operations treating Ore 1 and 3. A simulation using isotherms and mass transfer coefficients determined for Ore 1, Ore 3 and the activated carbon as part of the HiTeCC batch experiments was performed. For both simulations, the relevant isotherm, operating temperature and plant mass flows were dictated by current plant conditions.

The operating conditions of the respective plants are listed in Table 18. The processes operate with a hot stage temperature of 70 °C and a cold stage temperature of 30 °C. For modelling purposes, it was assumed that the initial temperature was 75 °C and that the cold stage temperature 40 °C with a 10 °C temperature drop between successive HiTeCC reactors. The isotherm and kinetic parameters used for the simulation are summarised in Table 19. The kinetic parameters determined during the desorption and HiTeCC tests were adjusted to m/h units from the original m/min. HiTeCC plant data for the operations treating both ores were obtained from Metso Outotec. The gold loadings on both the ore and activated carbon, and solution concentration of each stage were recorded.

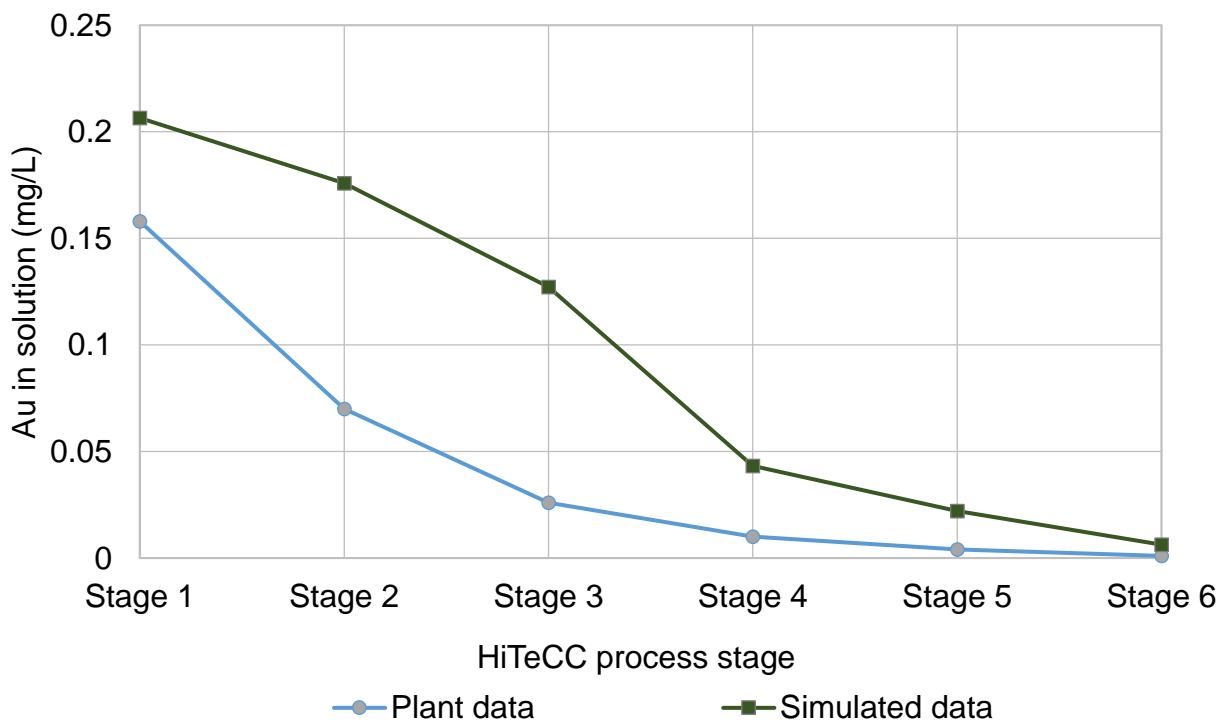
The operations were simulated using the HiTeCC plant model. The gold loading of the preg-robber and activated carbon and solution gold concentration were simulated and compared with plant data. The results are shown in Figure 29, Figure 30, Figure 31, Figure 32, Figure 33 and Figure 34. The HiTeCC stages referred to in all figures refer to individual HiTeCC reactors, stages 1 – 3 are desorption (hot) stages and stages 4 – 6 are adsorption (cold) stages.

Table 18 HiTeCC plant operational parameters.

<i>Property</i>	<i>Unit</i>	<i>Ore 1</i>	<i>Ore 3</i>
<i>Feed rate</i>	t/d	580	211
<i>Solids density</i>	kg/L	2.8	2.8
<i>Slurry density</i>	kg/L	1.26	1.26
<i>Slurry flow rate</i>	L/h	79 530	28 730
<i>HiTeCC head grade</i>	g/t	8	21
<i>HiTeCC tail grade</i>	g/t	5	16
<i>Number of stages per phase</i>		3	3
<i>Reactor volume</i>	L	159 060	75 000
<i>Au loading on Fresh activated carbon</i>	g/t	150	150
<i>Activated carbon particle size</i>	mm	1.5	1.5
<i>Activated carbon loading</i>	g/L	20	20
<i>Total carbon inventory</i>	kg	19 087	9000

Table 19 Ore 1 and 3 HiTeCC model isotherm constants and kinetic constants.

<i>Model constant</i>	<i>Ore 3 isotherm and kinetic parameters</i>	<i>Ore 1 isotherm and kinetic parameters</i>	<i>Activated carbon isotherm and kinetic parameters</i>
B_o	0.0045	6×10^{-7}	0.22
n	0.5252	1	1
k_c (m/h)	0.0009	0.0014	0.0010
ΔH (kJ/kmol)	-23 300	-46 794	-26 333

**Figure 29** HiTeCC simulation results of the gold concentration in solution of a HiTeCC process treating Ore 1, using experimentally determined isotherm and kinetic parameters.

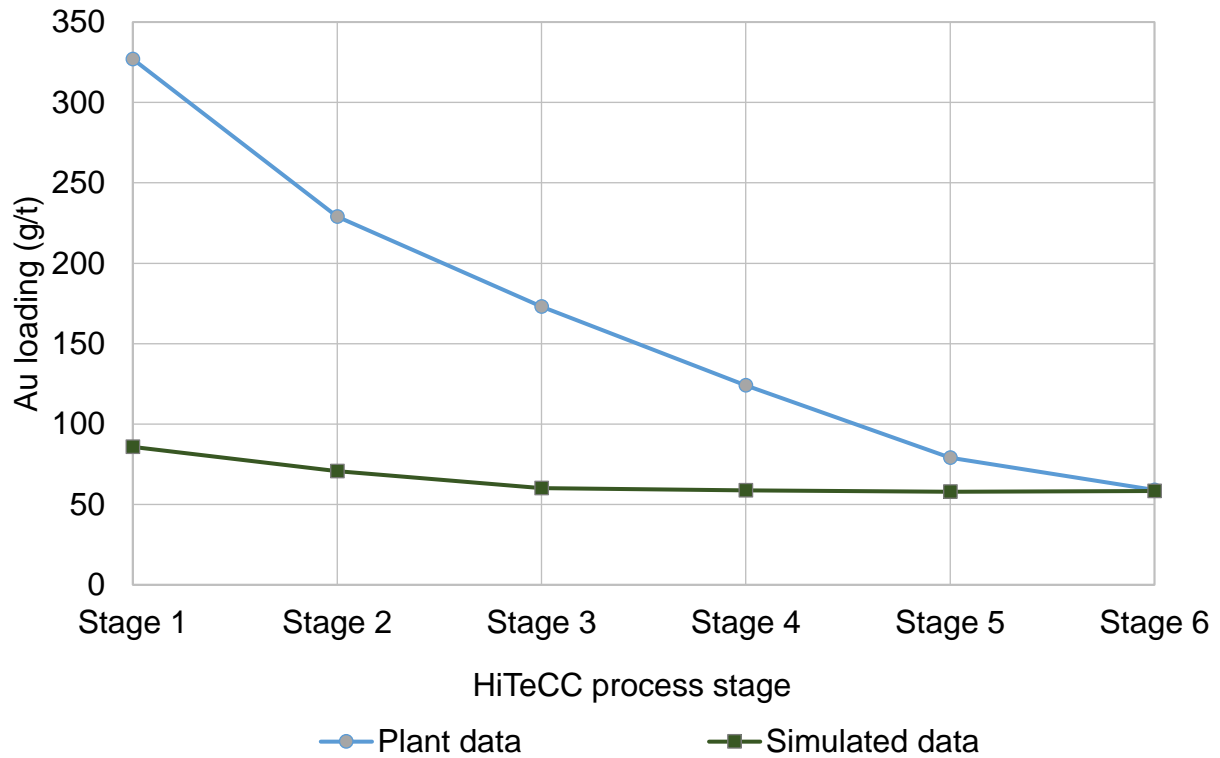


Figure 30 HiTeCC simulation results of the activated carbon gold loading of a HiTeCC process treating Ore 1, using experimentally determined isotherm and kinetic parameters.

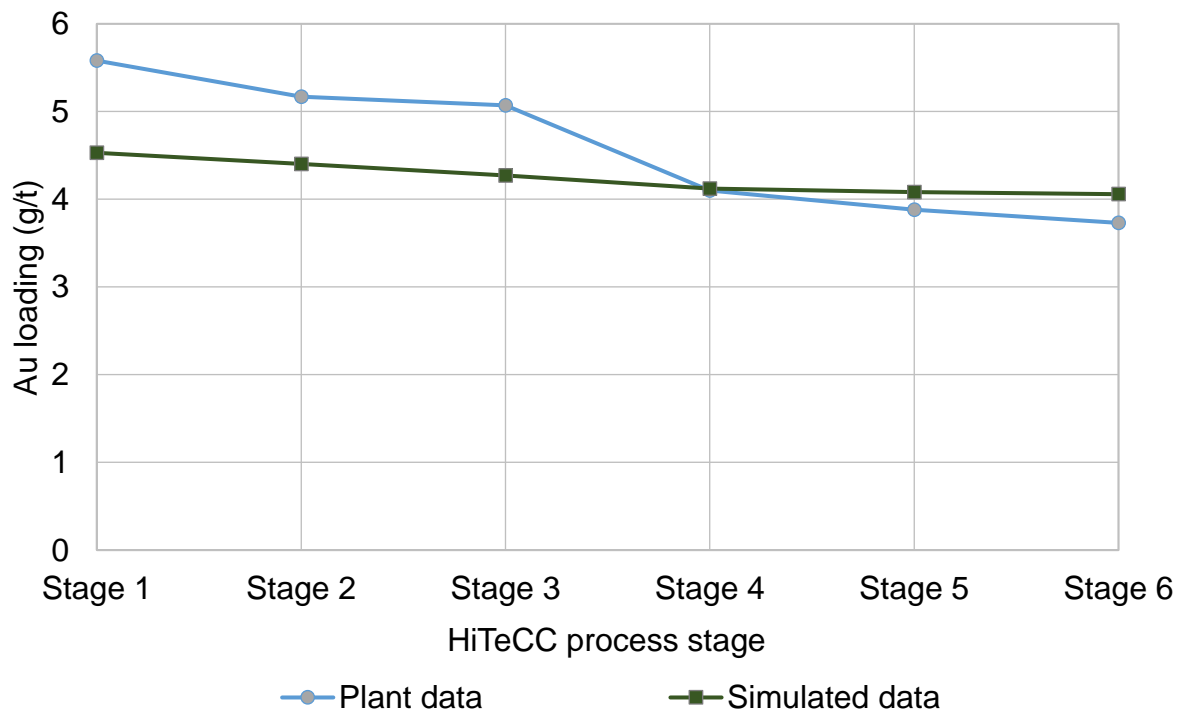


Figure 31 HiTeCC simulation results of the preg-rober gold loading of a HiTeCC process treating Ore 1, using experimentally determined isotherm and kinetic parameters.

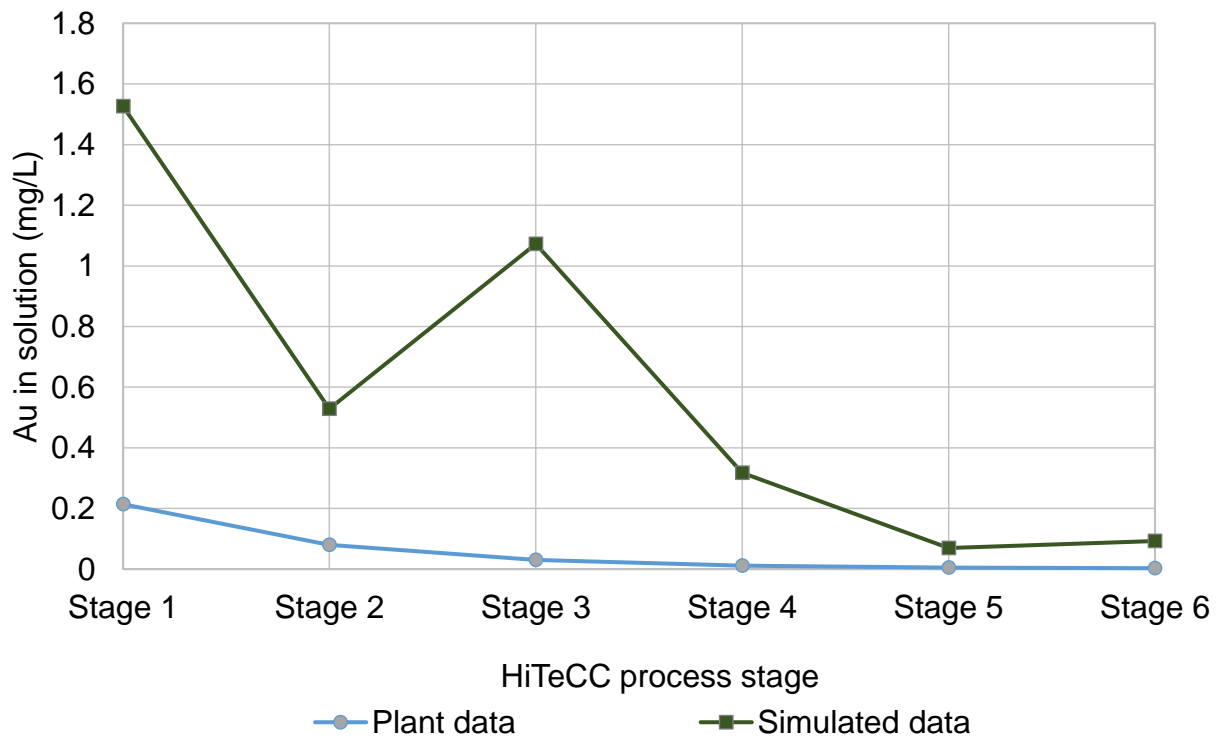


Figure 32 HiTeCC simulation results of the gold concentration in solution of a HiTeCC process treating Ore 3, using experimentally determined isotherm and kinetic parameters.

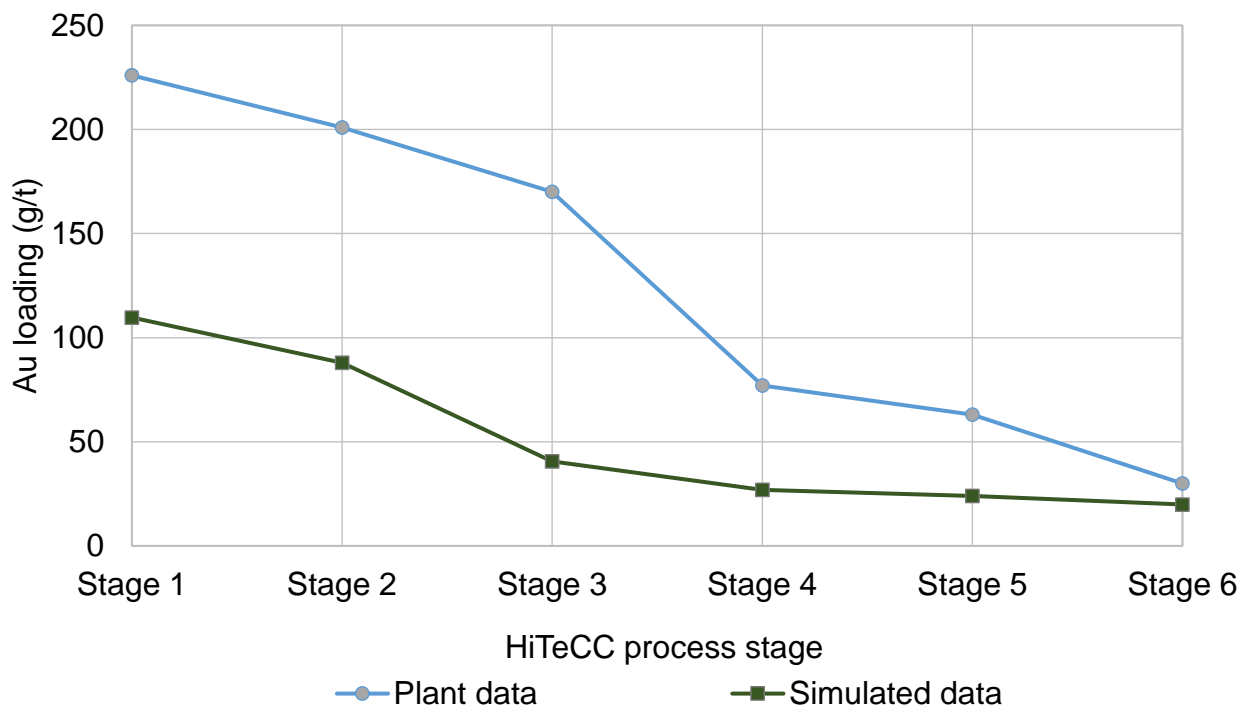


Figure 33 HiTeCC simulation results of the activated carbon gold loading of a HiTeCC process treating Ore 3, using experimentally determined isotherm and kinetic parameters.

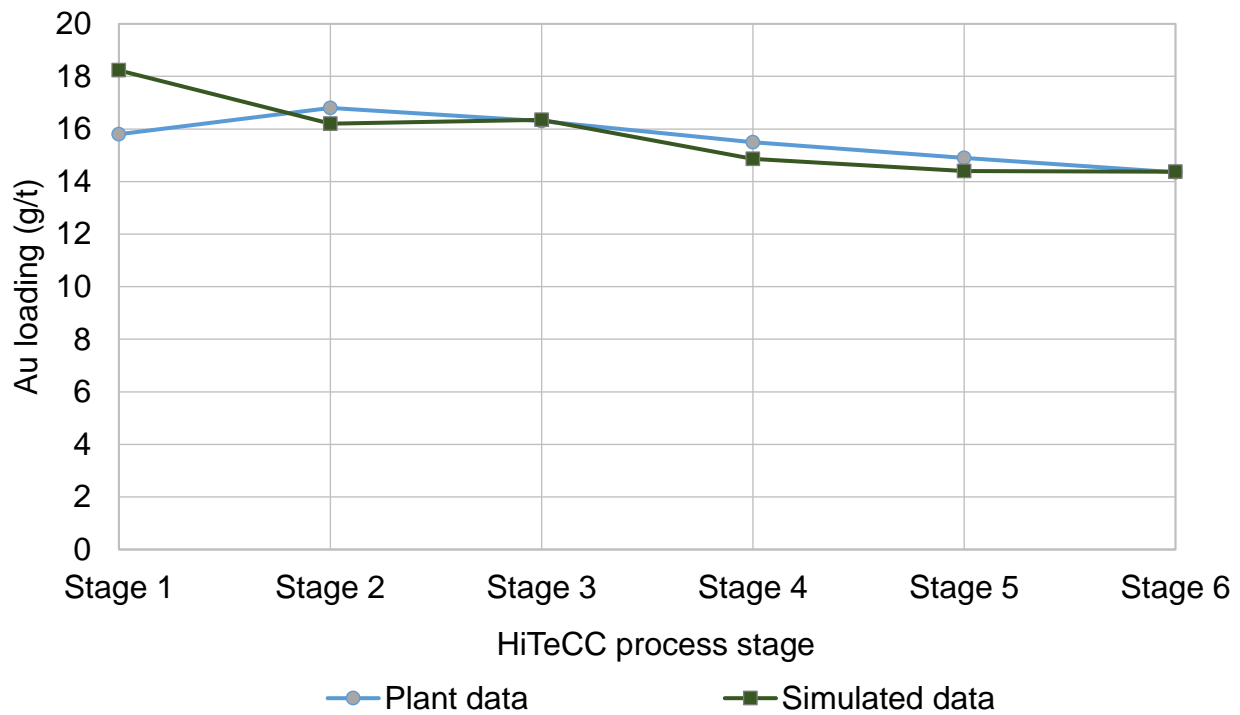


Figure 34 HiTeCC simulation results of the preg-robber gold loading of a HiTeCC process treating Ore 3, using experimentally determined isotherm and kinetic parameters.

Comparing the plant results with the simulation, it becomes clear that the model was able to accurately predict the desorption from the preg-robber but not adsorption onto the activated carbon with the balance of the gold reporting to solution. When running the simulation, activated carbon isotherms and kinetic mass transfer coefficients were used that had been determined experimentally as part of the HiTeCC development work. It can therefore be assumed that the activated carbon used on site behaved differently to that used during experimental work. In addition, averaged residence time and particle size were used as part of the model, where in fact a residence time and particle size distribution existed. It is likely then that model under accounted for the effect of having finer particles or activated carbon which were in contact with the slurry for longer periods of time. This impacted on the overall loading of the carbon which would explain the results seen from the simulation.

The importance of using virgin activated carbon has been demonstrated; what has also been shown is how the rate of desorption from the ore far exceeds adsorption onto the activated carbon. Optimization of the kinetic requirements of the activated carbon can therefore contribute significantly to the recovery of the process. Knowing the kinetic requirements of the activated carbon is, by default, an important factor in optimizing any HiTeCC process.

As a test of the model's ability to optimize a process parameter, the simulation was repeated, but the activated carbon mass transfer coefficient allowed to optimize. This simulation adjusted the kinetic

mass transfer coefficient with the limits of a realistic solution, i.e. a solution that produced real values within the constraints of the process. After optimization the simulation was repeated with the adjusted activated carbon mass transfer coefficient and delivered the results shown in Figure 35, Figure 36, Figure 38, Figure 35, Figure 39 and Figure 40.

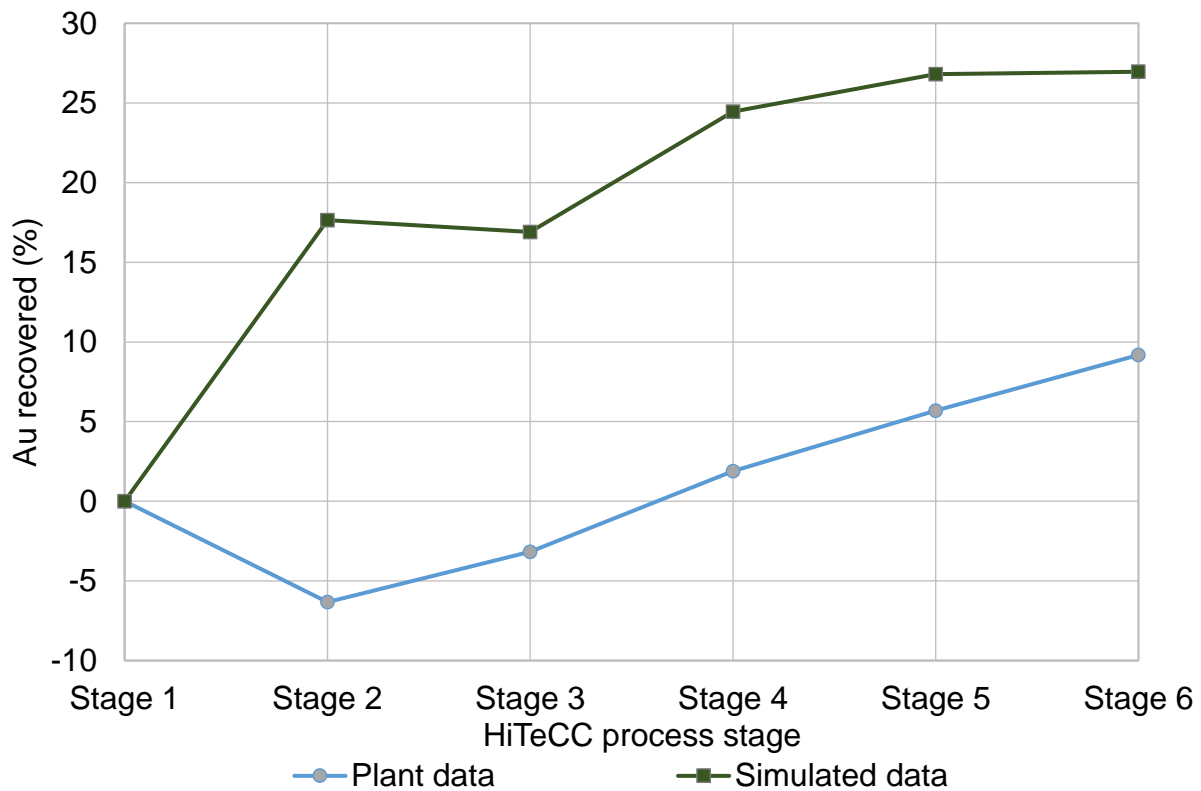


Figure 35 HiTeCC simulation results of the gold concentration in solution of a HiTeCC process treating Ore 1.

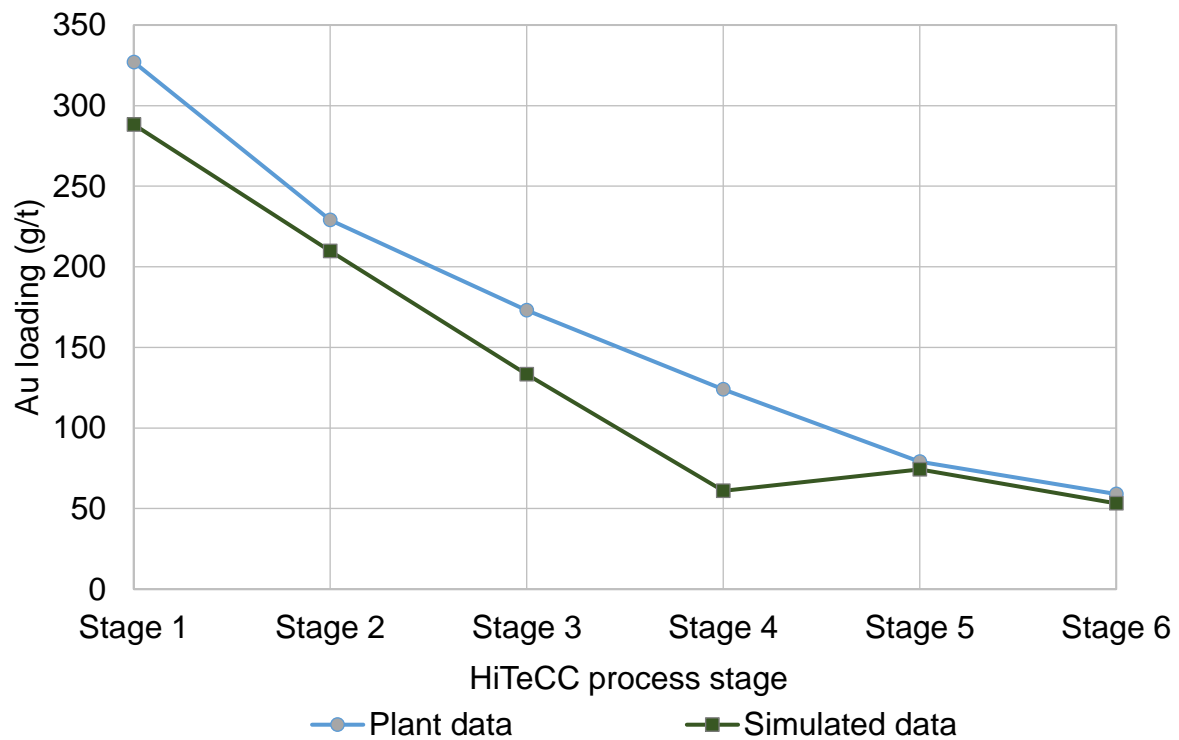


Figure 36 HiTeCC simulation results of the activated carbon gold loading of a HiTeCC process treating Ore 1.

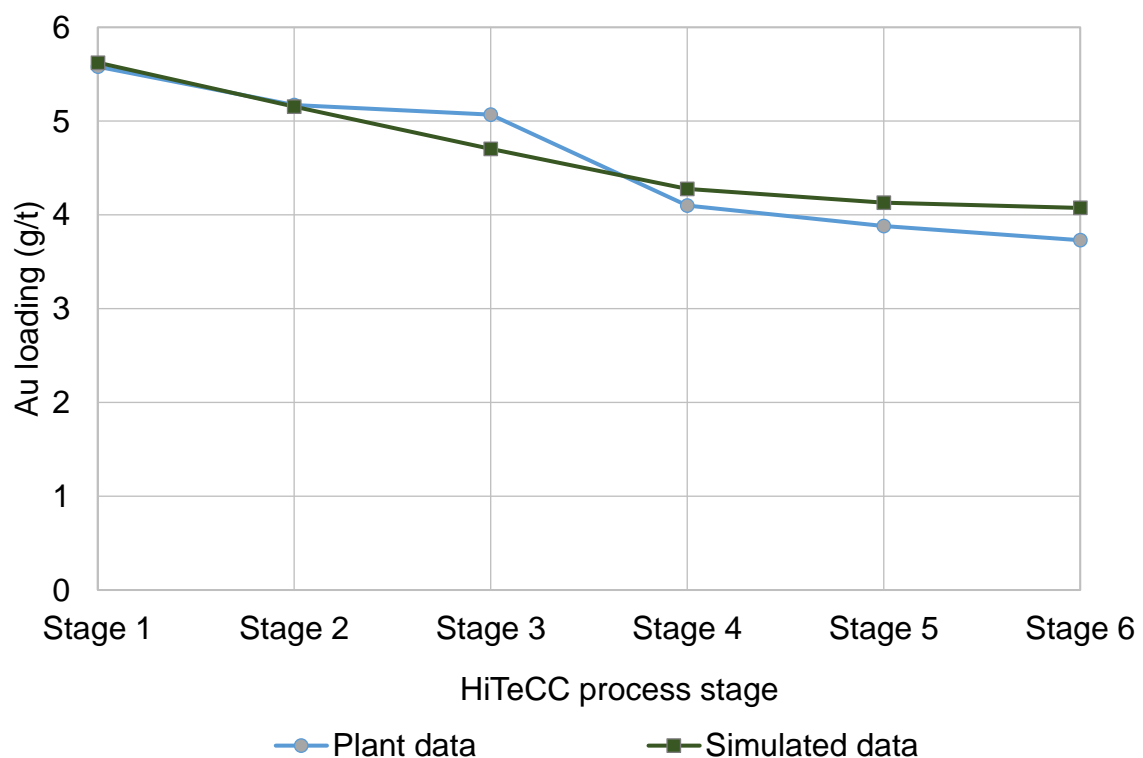


Figure 37 HiTeCC simulation results of the preg-robbing gold loading of a HiTeCC process treating Ore 1.

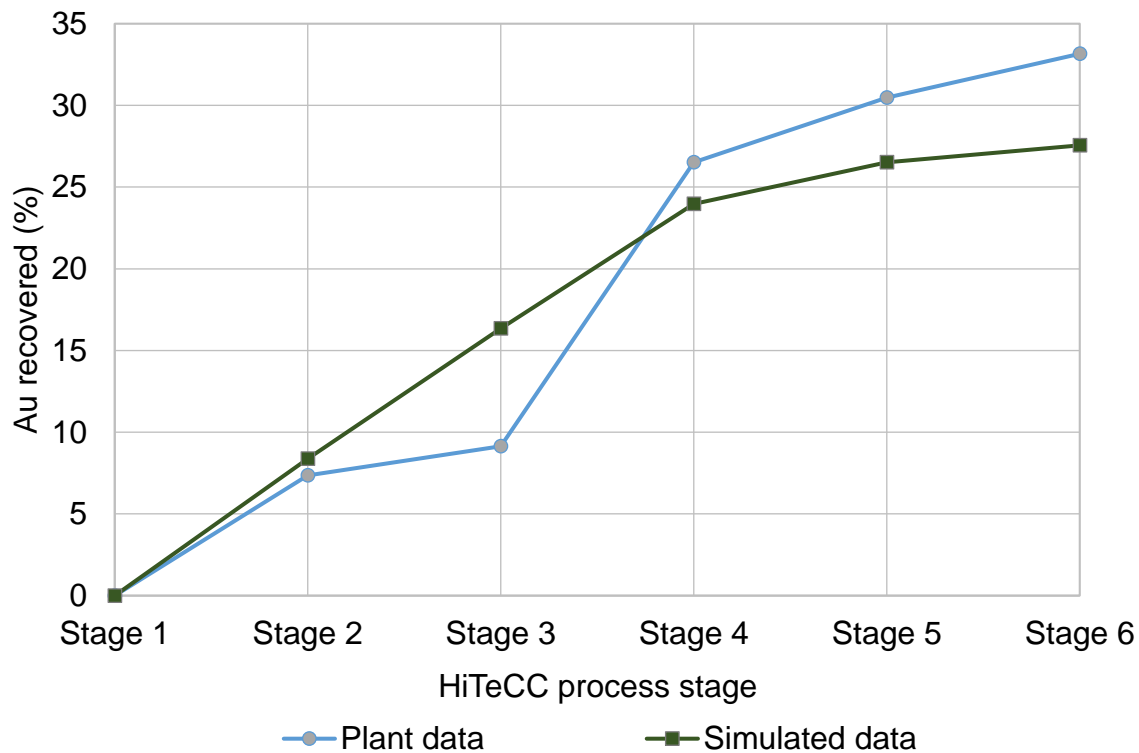


Figure 38 HiTeCC simulation results of the process recovery of a HiTeCC process treating Ore 3.

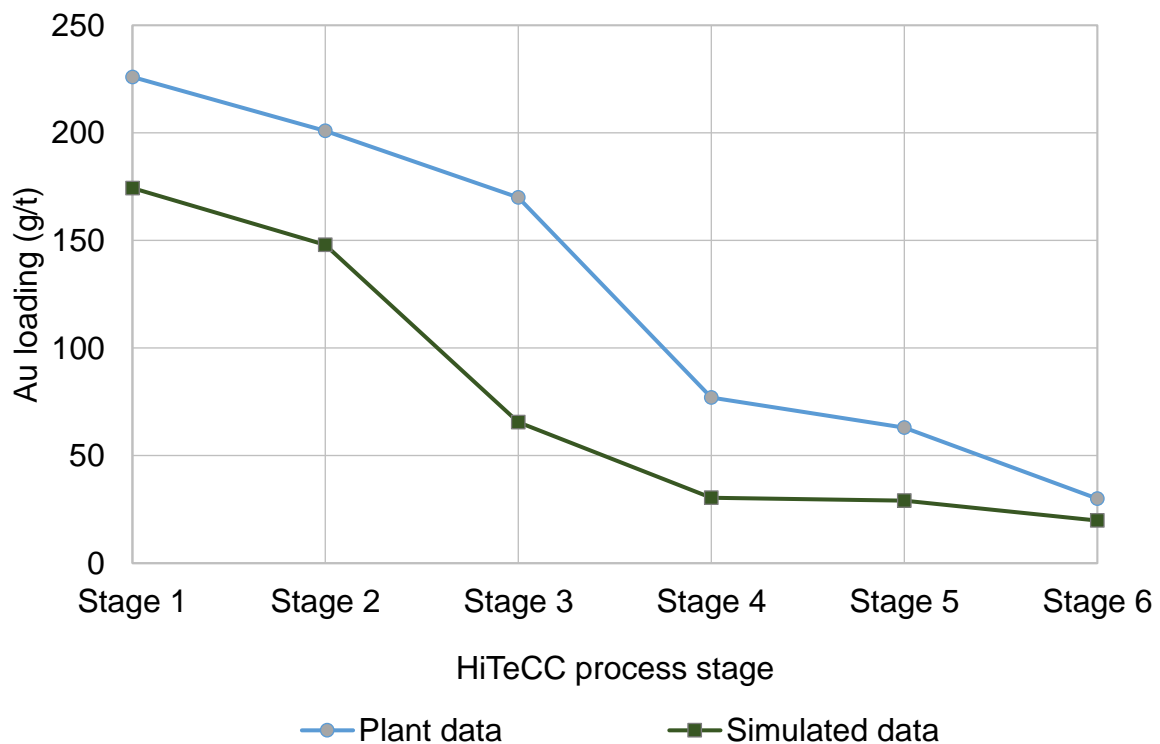


Figure 39 HiTeCC simulation results of the gold loading of the activated carbon of a HiTeCC process treating Ore 3.

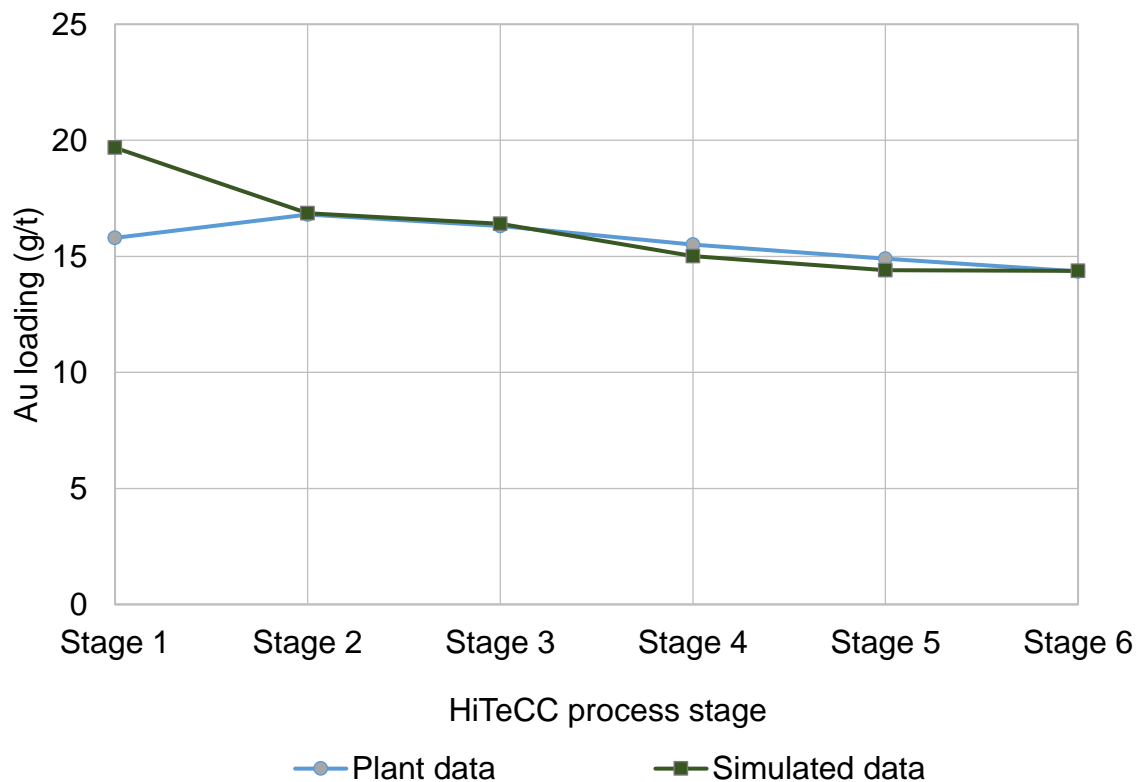


Figure 40 HiTeCC simulation results of the gold loading of the preg-robber of a HiTeCC process treating Ore 3.

The model now more closely approximated the gold removal from the preg-robber, but the remainder of the gold balance between the solution and activated carbon did not compare well with the site data. This could in part be due to the incorrect isotherm used for the activated carbon, as the isotherm, was not specifically that of the carbon used on site.

The experimentally determined isotherm and mass transfer coefficient of Ore 3 proved to be more accurate than the modelled isotherm used for Ore 1. This is to be expected as the modelled isotherm determined from the desorption tests would include more experimental error compared with the isotherm bottle-roll test work completed on Ore 3. The Ore 1 isotherm was also assumed to be linear due to the low gold loading on the preg-robber, which at higher gold loadings can be expected to be less accurate. The results however show that reasonable process modelling can be achieved for preg-robbers within the HiTeCC process.

The model is highly sensitive to the kinetic and isotherm constants and it is important that the experimental data be as accurate as possible.

4.6 HITECC DESIGN PROCEDURE

Design of a HiTeCC operation requires prior knowledge of both the ore and activated carbon used within the circuit. As shown in previous sections, the isotherms determined for activated carbon and preg-robbers can be used to predict the behaviour of a HiTeCC circuit at batch and plant scale, given an appropriate estimate of the mass transfer coefficients of both sorbents.

The procedure for designing an operation should then be as follows:

Step 1: Determine the isotherms for both the activated carbon and preg-robbers.

Step 2: Determine the relative flow rates of the ore and activated carbon. This will be based on the site-specific tailings flow rate. When using Equation 16 to determine the overall gold balance, some early estimates can be made with regard to the carbon addition requirement as well as the overall efficiency of the process.

Equation 16 can be used for a stage mass balance but also quantifies the overall mass balance. It can be assumed, that q_{aci} , C_{bi+1} and C_{bi} are negligibly small, the slurry transferred with the activated carbon is assumed to be negligible as well (s_i and f_i), reducing equation 18 to:

$$A_i.(q_{aci+1}) = (F_i).X.(q_{orei+1} - q_{orei}) \quad (22)$$

To determine the required q_{orei+1} , the process designer should choose the required recovery, that would be financially viable. This will be dependent on capital expenditure as well as operating costs. This will inevitably be an iterative process where the costs of the design will be calculated for a specific recovery and then adjusted. Finally, the required gold loading on the activated carbon should be specified. This would allow for the calculation of the overall carbon transfer rate/mass flow. The solid fraction and mass flow rate of the slurry are specified by the upstream process. By substitution of equations 19, 20 and 21 into equation 18, the operating plane of the process can be determined. For simplification f_i and s_i are assumed to be negligible.

$$A_i.(r_{ac}/M_{AC}) + r_{ac} = r_p + F_i.X.(r_p/M_{ore}); \quad (23)$$

$$r_{ac}.(A_i/M_{AC} + 1) = r_p.(F_i.X/M_{ore} + 1); \quad (24)$$

$$\text{With } r_{ac} = k_{ac} \times (C_b - C_{sac})/d_{ac}, \text{ and } r_p = k_p \times (C_b - C_{sp})/d_p; \quad (25)$$

with both C_{sac} and C_{sp} given by the isotherms for the preg-robber and activated carbon. Initially C_b is assumed to be zero, which allows for the calculation of M_{ore} . Once this is calculated, the volume per unit can be approximated.

These values can be used as starting point within the programmed model to back calculate the actual values of the different gold concentrations. This will give a profile of the gold in the residue and on the activated carbon. Any of the process parameters can be adjusted to determine the recovery profile; this can be done iteratively in conjunction with costing calculations to determine an optimized operation overview.

5 SUMMARY AND CONCLUSIONS

The recovery of gold from preg-robbing ores is a recognised challenge with conventional approaches to limit the losses associated with adsorption of aurocyanide on preg-robbers occasionally inadequate. The work done here has shown that the adsorption of gold on preg-robbers is reversible and can be adequately simulated using approaches similar to those used for gold adsorption onto activated carbon.

The present work indicates that temperature and the quality of the virgin activated carbon are critical for the effective use of the HiTeCC process to recover gold from preg-robbing materials. The calculated heats of adsorption for the two ores evaluated were -20 kJ/kmol and -50 kJ/kmol.

The ionic strength of the solution also affects the process, with higher values favouring adsorption onto preg-robbers, i.e., lowering desorption, regardless of the cation introduced. The effect that different ionic components have on the stability of adsorption is congruent with the effects seen with activated carbon. Ion exchange at the adsorption interface was noted when different cations were introduced, with potassium displacing sodium in the aurocyanide complex to form a potassium aurocyanide, which, as expected, was not as strongly adsorbed on the carbonaceous material.

Experimental results have shown that the addition of sodium hydroxide to the process inhibited desorption. The use of sodium hydroxide at plant scale should be reconsidered, as this has a direct cost implication on the desorption phase. A significant saving in steam consumption is possible if operating the desorption circuit without the addition of sodium hydroxide; a saving of 54 % was estimated for a typical case considered. It should be noted that addition of sodium hydroxide could potentially benefit the adsorption phase of the process although this was not conclusively demonstrated.

Using preg-robbing indices, desorption and isotherm tests, sorption isotherms were determined for known preg-robbers. It was shown, that a relationship exists between the PRI value and the pre-exponential constant of the isotherm for the adsorption of aurocyanide on the preg-robbers. The experimentally determined isotherms were good indicators of both desorption and adsorption behaviour, further emphasising the reversibility of preg-robbing adsorption. The ability to derive a relationship between the PRI value and the sorption isotherm for a preg-robbler provides a simple tool with which the isotherms for an ore can be determined without the need for extensive bottle-roll test work. If sufficient data points are generated, the resulting relationship may be applied to calculate the isotherm constants for the same ore.

The film diffusion adsorption-desorption model developed for preg-robbers is sufficient to predict

their dynamic behaviour. The model could accurately predict the ore behaviour for both adsorption and desorption experiments. This proved beneficial when compiling the HiTeCC process model which proved effective in simulating the HiTeCC batch and plant processes. It provides a simple tool with which design specifications for HiTeCC operations can be tested, and existing operations optimized.

The activated carbon activity, and concentration and temperature were identified as the most crucial controlled parameters of the HiTeCC process. The activity, gold loading and the quantum of activated carbon used define the concentration of gold in solution, which defines the gold recovery possible from the preg-robber. The process activated carbon inventory should be managed to maintain an activated carbon gold loading significantly lower than that on the preg-robber.

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7 APPENDIX A – BATCH MODEL PROGRAMMING CODING

#Gold Desorption/Adsorption Simulation

clear all

#-----First Thermodynamic and Kinetic parameters-----#

#-Beta-, -n, -kc-, -Ea-, -Hb-#

preg=[4.61*10^-3,0.5252,5.1*10^-7,0,-23300];

#-Beta-, -n, -kc-, -Ea-, -Hb-#

AC=[20,1,0.000025772,0,-11000];

#-----Slurry properties-----#

c = 98.2;#g/t

Ore = 1;#kg

vol = 4;#l

loading = 3.9;#g/t

acloading = 88;#g/t

slurry = [c,Ore,vol,loading,acloading];

#-----Integration function-----#

function Ddt = myode(t,C,tyd,temp,preg,AC,slurry)

AcOn = 0;

```
Oreon = 1;
```

```
#-----Experimental parameters-----#
```

```
dc    = 75/1000000;#m
```

```
if t < 1500
```

```
ACConl = 60;#g/l
```

```
endif
```

```
if t >= 1500
```

```
ACConl = 60;#g/l
```

```
endif
```

```
MassAC1 = slurry(3)*ACConl/1000;#kg
```

```
dcAC    = 2/1000;#m
```

```
#-----Dynamic modelling equations-----#
```

```
T = interp1(tyd,temp,t);
```

```
B = @(T) preg(1)*exp(-preg(5)/(8.314*(T+273)));
```

```
Kc = @(T) preg(3)*exp(-preg(4)/(8.314*(T+273)));
```

```
BAC = @(T) AC(1)*exp(-AC(5)/(8.314*(T+273)));
```

```
KcAC = @(T) AC(3)*exp(-AC(4)/(8.314*(T+273)));
```

```
Cs = @(C) ((C(2))/B(T))^(1/preg(2));
```

```

CsAC = @(C) (C(3)/BAC(T))^(1/AC(2));

dqdt = Oreon*6*Kc(T)*((C(1)-Cs(C))*slurry(3))/(dc*slurry(2));

dACdt = AcOn*(6*KcAC(T)*(C(1)-CsAC(C))*slurry(3))/(dcAC*MassAC1);

dcbdt = (-Oreon*dqdt*slurry(2) - AcOn*dACdt*MassAC1)/slurry(3);

Ddt = [dcbdt,dqdt,dACdt];

endfunction

#-----Experimental data-----#

graf = [0 17.8 20

15 6.98 20

30 6.36 20

60 5.62 20

120 4.6 20

180 3.61 20

240 3.04 20];

#-----Used to determine the size of integration-----#

plek = size(graf);

plekhou = plek(1,1);

rang = linspace(graf(1,1),graf(plekhou,1));

#-----Carbon Loading trend -----#

```

```
koolstofgraf(1,1) = c;

for a = 1:plek-1

koolstofgraf(a+1,1) = koolstofgraf(a,1)+(graf(a,2)-graf(a+1,2))*slurry(3)/slurry(2);

endfor

#-----Temperature trend-----#

temp = graf(:,3);

tyd = graf(:,1);

#-----Initial value and Integration-----#

init = [graf(1,2),c,0];

opts = odeset('RelTol',1e-2, 'AbsTol',1e-4);

[t,ant] = ode45(@(t,C) myode(t,C,tyd,temp,preg,AC,slurry), rang, init);

grote = size(graf);

grote(1,1);

err = 0;

Total = 0;

normerr= 0;

for y = 1:grote(1,1)

Total = Total + (graf(y,2));

endfor
```

```

avg = Total/grote(1,1);
for j = 1:grote(1,1)

err = err + ((graf(j,2))-(interp1(t(:,1),ant(:,1),graf(j,1))))^2;

normerr = normerr + (graf(j,2)-avg)^2;

endfor

rsquared = 1 - ( err/normerr)

#-----Plotting-----#
subplot (3, 1, 1);

plot(rang,ant(:,1),'k-',graf(:,1),graf(:,2),'go');

legend("Simulation","Data");

xlabel("Time – min");

ylabel("Au Con – g/l in Solution");

subplot (3, 1, 2);

plot(rang,ant(:,2),'k-',graf(plek(1,1),1),slurry(4),'go');

xlabel("Time – min");

ylabel("Au Con – g/kg on Ore");

subplot (3, 1, 3);

plot(rang,ant(:,3),'k-',graf(plek(1,1),1),slurry(5),'go');

xlabel("Time – min");

ylabel("Au Con – g/kg on AC");

```

8 APPENDIX B – REACTOR MODEL PROGRAMMING CODING

```

#Reactorsimulation

clear

#-----Reactor Conditions-----#

Sflow  = 28730/60; #l/min Slurry flow

Solidsden = 2.8; #kg/l Solids density

Slurryden = 1.26; #kg/l Slurry density

Solidperc = (Solidsden*1-Solidsden*Slurryden)/(Slurryden*(1-Solidsden));# Calculated solids
percentage

Solutionflow = Sflow *(1- Solidperc);#l/min Solution flow

Rvol  = 75000/3; #l Reactor volume

Massflow = 211*1000/(60*24); #kg/min Solids mass flow

restime = 12*60/3; #min Activated carbon residence time

ACflow  = 20*Rvol/(1000*restime);#kg/min Activated carbon transfer rate

TargetRecovery = 0.15; # Target recovery

stages = 6; # Initial number of stages estimate

#-----Ore Kinetic and Thermodynamic constants-----#

#-Beta-, -n, -kc-, -Ea-, -Hb-# - Isotherm and kinetic data for Preg-robber

preg=[4.61*10^-3,0.5252,8.9*10^-9,0,-23300];

dc  = 75/1000000; #m d80 Particle Diameter

```

#-----Activated Carbon Thermodynamic constants-----#

#-Beta-, -n, -kc-, -Ea-, -Hb-# - Isotherm and kinetic data for Activated carbon

AC=[0.009575,0.487,0.00000772,0,-34852];

dcAC = 1.5/1000;#m d80 Particle Diameter

#-----Starting conditions-----#

#-----Stage 6---to ---Stage 1-----#

temps =[30,30,30,70,70,70,70]; # Temperature profile, profile is entered in reverse order

qin = 15.8;# g/t Initial Preg-Robber gold loading

Acin = 0; #g/t Initial AC gold loading

qtargt = qin*(1-TargetRecovery); #Final Preg-robbing loading based on recovery

qout = qtargt; # assignment of outlet preg-robbing loading

cout = 0;# g/l Outlet gold in solution concentration

B = preg(1)*exp(-preg(5)/(8.314*(temps(6)+273))) #Preg-robbing Isotherm Pre-exponential constant calculation

Kc = preg(3);#Assignment of preg-robbing mass transfer kinetic coefficient

BAC = AC(1)*exp(-AC(5)/(8.314*(temps(6)+273))) #Activated Carbon Isotherm Pre-exponential constant calculation

KcAC = AC(3);#Assignment of preg-robbing mass transfer kinetic coefficient

#-----Graph reset-----#

graf = zeros(10,3);

```
#-----Cascade reactor calculation work-----#
```

```
a = 1;
```

```
while (a < 7);# Set the limit of the number of reactor stages to include
```

```
T = temps(a);
```

```
#-----CSTR Mass balance equations-----#
```

```
B = preg(1)*exp(-preg(5)/(8.314*(T+273)));
```

```
Kc = preg(3);
```

```
BAC = AC(1)*exp(-AC(5)/(8.314*(T+273)));
```

```
KcAC = AC(3);
```

```
#-----CSTR mass balance calculations-----#
```

```
qc = @(c) -c(1) + qout - (Kc*(cout-(qout/B)^(1/preg(2))))*Rvol/dc);
```

```
cc = @(c) -c(2) + cout -((KcAC*(cout - (c(3)/BAC)^(1/AC(2))))*ACflow*Rvol/dcAC) +  
(Kc*(cout-(qout/B)^(1/preg(2))))*Massflow*Rvol/dc)/Solutionflow;
```

```
acc = @(c) -Acin + c(3) - KcAC*(cout - (c(3)/BAC)^(1/AC(2))) *Rvol/dcAC;
```

```
y = @(c) [qc(c);cc(c);acc(c)];
```

```
#-----Solver answer-----#
```

```
#-Pregrobber Au Loading, Au in solution, Activated carbon Au Loading
```

```
start = [0,0,0];# Initial guess for the outlet gold loadings
```

```
g = fsolve(y,start);# Solver command
```

```
#-----Plotting set up-----#

graf(a,1) = g(1);

graf(a,2) = g(2);

graf(a,3) = g(3);

qout  = g(1);

cout  = g(2);

Acin  = g(3);

a = a + 1;

endwhile

#-----Plot command lines-----#

NumberofStages = a-1

Reactors(1:a,1) = a:-1:1;

graf(1:6,1:3);

subplot(4,1,1);

plot(Reactors([2:a]),graf([1:a-1],1));

title("Preg-robber");

xlabel("Stage number");

ylabel("Au Conc g/t");

subplot(4,1,2);
```

```
plot(Reactors([2:a]),graf([1:a-1],2));
```

```
title("Bulk solution");
```

```
xlabel("Stage number");
```

```
ylabel("Au Conc PPM");
```

```
subplot(4,1,3);
```

```
plot(Reactors([2:a]),graf([1:a-1],3));
```

```
title("Activated Carbon");
```

```
xlabel("Stage number");
```

```
ylabel("Au Conc g/t");
```

```
subplot(4,1,4);
```

```
plot(Reactors([2:a]),temps(1:a-1));
```

```
title("Temperature Profile");
```

```
xlabel("Stage number");
```

```
ylabel("Temperature – °C");
```