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Modelling of multicomponent reactive transport in finite columns — Application to gold recovery using iodide ligands

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Abstract

Existing semi-analytical solutions to the problem of reactive transport in porous media are either restricted to single aqueous species, to decoupled processes or to infinite/semi-infinite domains. Our approach addresses the problem of multicomponent reactive transport in finite columns, where coupling feedbacks emanating from the non-equilibrium thermodynamics of chemical species are taken into account. The main purpose of this research work is to investigate the in-situ leaching of precious metals – a technique that is expected to be relevant to the Earth's regolith consisting of fragmented and/or weathered rocks where permeability is sufficiently high for reactive transport. Producing precious metals from such areas may be beneficial especially when the grade is too low for conventional mining techniques to be applicable.

The proposed solution method is validated experimentally using existing tests of column leaching using iodine-based lixiviants. The obtained results show good agreement with the experimental data. In addition, the results indicate that the rate of effluent gold concentration increases until its maximum when the flow velocity, concentration of iodine lixiviants, or specific surface increase. After the peak, the behaviour is more complex and the obtained results allow to optimise the amount of recovered gold.

Keywords: Thermodynamics; In-situ leaching; Reactive transport; Lixiviants;

Components.

1. Introduction

Decreasing grades of mineral deposits have resulted in tremendously increasing volumes of fragmented, mined and processed rock masses to meet the global demand on precious metals. Immense surface and underground mining projects have been made possible because of modern highly sophisticated mining and processing machinery. The average gold grade of currently producing mines is of about 1 g/t and the average grade of undeveloped deposits is of about 0.7 g/t (Martens et al., 2018). Current deposits (producing and undeveloped) hold approximatively 85500 t of gold, 28 % of which cannot be extracted economically with conventional techniques (Sebag, 2012). Given today's gold price (\$1290 per tonne), the value of gold left in place is approximately \$1 trillion.

The abundance of low-cost energy and water supply contributed significantly to the success of conventional surface and underground mining. However, maintaining the current level of energy and water costs and availabilities is questionable. The fluctuation of commodity prices is exerting additional pressures on conventional mining approaches. The impact of large-scale visibility, environmental footprints, and waste disposal facilities on local communities is sparking unprecedented numbers of jurisdictions. These constraints and others that are omitted in this paper can compromise the future of conventional mining technologies, prompt deep changes and motivate the introduction of more competitive approaches. Dissolution and subsequent recovery of valuable minerals from subsurface deposits known as in-situ leaching (ISL) is receiving renewed attention as an appealing alternative that requires lower investment and consumes less energy compared to conventional mining technologies. The principle of ISL is illustrated in Figure 1; reactive fluids are injected within an orebody and collected as a pregnant solution that is then processed to extract the valuable minerals. According to the World Nuclear Association, the amount of uranium produced

by ISL has increased steadily and reached 48 % of the global supply in 2017 with recoveries that can reach up to 90 %. ISL of precious metals is not commercially operational yet due to the lack of environmentally friendly lixivants.

Figure 1: Principle of in-situ leaching

Commonly available lixivants capable to unlock precious metals from pristine rock masses are highly toxic and/or extremely harmful to adjacent ecosystems. For example, cyanide is among the robust and cost-effective lixivants of precious metals, but it is reluctantly accepted by mining stakeholders because of its toxicity and carbon emission (Chamberlain and Pojar, 1984). Less hazardous substitutes such as thiourea (Yannopoulos, 1991), thiosulfate-copper-ammonia systems (Aylmore and Muir, 2001; Feng and van Deventer, 2010) and halides (Angelidis et al., 1993; Davis et al., 1993; Qi and Hiskey, 1991) have been tested on natural geomaterials (Johns and Parr, 2010). In particular, iodine-iodide ($I_2 - I^-$) systems that are of lower toxicity are being investigated as potential alternatives (Roberts et al., 2010, 2009). Recent research work revealed new processes that can dissolve precious metals (e.g. gold and silver) using benign reagents (Eksteen and Oraby, 2015; Oraby and Eksteen, 2015); in the presence of oxidant(s) such as cupric ions, oxygen and hydrogen peroxide, glycine dissolves precious metals at various levels of pH and temperature. Alkaline glycine systems proved to be conducive to gold leaching because they are non-toxic, selective over non-sulphide gangue, recyclable, biodegradable, producible on-site, and relatively cheap. The new discovery has

the potential to revolutionise the mining industry provided that the reactive transport of pregnant solutions in thermo-poro-materials are investigated further. To become fully operational, ISL mining of precious metals has to overcome other major hurdles that include the heterogeneous character of natural geomaterials, the poor infiltration of lixiviants, the mechanical deformations of host rocks, and the energy/matter exchanges.

In the current paper, we propose a reactive transport model that predicts the behaviour of the system $\text{Au} - \text{I}_2$ under different conditions. The proposed research aligns with a series of contributions on the thermal-hydraulic-mechanical-chemical coupling within the principles of non-equilibrium thermodynamics (Poulet et al., 2010, 2012; Karrech et al., 2012; Karrech, 2013; Karrech et al., 2015) and gold mineralisation (Zhang et al., 2012, 2013).

Modelling reactive transport requires sets of balance and reaction equations. When the problem is neither isochoric nor isothermal, the conservation of mass is combined with additional balance quantities that describe the exchange of heat, momenta and entropy (Karrech, 2013). Conceptual models that underpin the reactive transport equations include the advection-dispersion, dual-domain mass transfer, fractal and fractional derivative approaches, and random walk transport. The current paper belongs to the first category. Transported species undergo fast or slow reactions, which can be homogenous (in one phase) or heterogenous (inter-phases) as classified by Rubin (1983). When the reactions are sufficiently fast (e.g. most homogeneous aqueous species), they are considered in equilibrium. However, the kinetic behaviour becomes pertinent when the reactions are heterogeneous (e.g. minerals reacting with aqueous species). To solve complex reactive transport problems, the common practice is to use the concept of components. This technique reduces the number of transport equations and decouples some of them through simple Gauss-Jordan elimination (Steefel and MacQuarrie, 1996; Saaltink et al., 1998). More recently, Molins et al. (2004) introduced a systematic method that derives the expressions of chemical components while maximising the number of equations that contain neither feedbacks (source/sink) nor

heterogeneities (effects of minerals). In computer codes, this technique can be combined with sequential iteration or direct substitution approaches (known as SIA and DSA) to solve coupled transport equations (e.g. Parkhurst (1995); Xu and Pruess (2001)). In the current paper, SIA and DSA are not relevant because we propose a semi-analytical technique where the solutions are explicit.

Analytical and/or semi-analytical techniques are usually considered advantageous over numerical methods, because their explicit expressions reflect the importance of each physical parameter. They are also useful to establish engineering standards and to quality-assure numerical methods. The relatively recent analytical solutions that have been proposed include the work of Sun et al. (1999); Clement (2001); Quezada et al. (2004) who used similarity transformation to decouple the system of reactive transport equation and Laplace transform to estimate the variation of concentrations with respect to time and space. However, their approaches do not take into account the concept of components; thereby, limiting their application to linear systems with first order reactions. You and Zhan (2013) proposed an analytical solution to the problem of transport in a finite column. Their approach uses distance-dependent dispersivities, but it is limited to a single chemical species. Based on the work of Molins et al. (2004), Sanchez-Vila et al. (2010) developed an exact analytical solution for the reactive transport of about five species using the concept of multi-components. Their formulation included kinetic and equilibrium reactions within a one-dimensional saturated column.

In this paper, we propose a comprehensive approach that uses the concept of multi-components as described by Sanchez-Vila et al. (2010) to formulate the problem. However, our system includes more chemical species and more complex coupling because the kinetic rates and the equilibrium expressions are non-linear multi-variable functions. Moreover, our approach uses the finite column results of You and Zhan (2013) and Laplace transformation (Wang and Zhan, 2015) instead of pure numerical methods. We then use the new solu-

tion strategy to investigate the leaching process of native gold using iodide ligands. The experimental data of Roberts et al. (2010) are used to validate our model. Confident that the experimental and semi-analytical results are in agreement, we study the effects of flow velocity, concentration of lixiviants, and grain size distribution on gold recovery.

2. Reactive transport model

2.1. Conservation of mass

Consider a heterogeneous system of n_s species undergoing n_r chemical reactions. The system is treated as a continuum domain. As shown by Karrech (2013), the conservation of mass of a given species i , within a control domain Ω can be written:

$$\int \left\{ \frac{d}{dt} \rho_i + \nabla \cdot (\rho_i \mathbf{v}_i) + \sum_{r=1}^{n_r} m_{i@r} \right\} dV = 0 \quad (1)$$

where ρ_i [kg m⁻³] is the apparent density that represents the mass of the species i per unit of total volume, $\mathbf{v}_i$ [m s⁻¹] is the velocity of i with respect to a stationary frame, and $m_{i@r}$ [kg m⁻³ s⁻¹] is the mass production rate of i through the reaction r . As suggested by Coussy (2004), the porous medium is composed of bounded solid grains that represent the skeleton and connected pore spaces that are occupied by a fluid. The fluid particles flow within the porous space such that their trajectories remain continuous, which allows to decompose the volume integrals into solid and fluid phases. Similarly, Karrech (2013) extended this approach to reactive transport by assuming that each fluid particle flows along a path that entirely belongs to the connected pore spaces. Therefore, each species streamlines trajectories that belong to a continuum within the porous space such that we cast the control volume to the solid and fluid phases referred to by the subscripts s and f , respectively, and use the substantial derivative defined by $\frac{d^s(\cdot)}{dt} = \frac{\partial(\cdot)}{\partial t} + \mathbf{v}_0 \cdot \nabla(\cdot)$ to

rewrite the conservation equation (1) in the forms:

$$\int_f \left\{ \frac{d^s i}{dt} + \rho_i \mathbf{v}_0 + \rho_i (\mathbf{v}_f - \mathbf{v}_0) + \rho_i (\mathbf{v}_i - \mathbf{v}_f) \right\} dV_f = \sum_{r=1}^{n_r} \int_f m_{i@r} dV_f, \text{ and} \\ \int_s \left\{ \frac{d^s i}{dt} + \rho_i \mathbf{v}_0 \right\} dV_s = \sum_{r=1}^{n_r} \int_s m_{i@r} dV_s \quad (2)$$

where $\mathbf{v}_0$ is the velocity of the solid skeleton. The apparent density ρ_i can be expressed in terms of porosity, ϕ , molar concentration, c_i [mol m⁻³] and molar mass $\mathcal{M}_i$ [kg mol⁻¹] as $\rho_i = \phi c_i \mathcal{M}_i$ in the fluid control volume and as $\rho_i = (1 - \phi) c_i \mathcal{M}_i$ in the solid phase, provided that the porous medium is fully saturated. However, equation (2) can be generalised to the context of multi-phase flow. To describe the species transport in the context of saturated porous media, equations (2) can be rewritten as

$$\int_f \left\{ \frac{d^s c_i}{dt} + c_i \mathbf{v}_0 + (c_i \mathbf{V}_f) + \mathbf{J}_i \right\} dV_f = \sum_{r=1}^{n_r} \int_f n_{i@r} dV_f, \text{ and} \\ \int_s \left\{ \frac{d^s (1 - \phi) c_i}{dt} + (1 - \phi) c_i \mathbf{v}_0 \right\} dV_s = \sum_{r=1}^{n_r} \int_s n_{i@r} dV_s \quad (3)$$

where $\mathbf{V}_f = (\mathbf{v}_f - \mathbf{v}_0)$ describes the seepage velocity, $\mathbf{J}_i = -c_i (\mathbf{v}_i - \mathbf{v}_f)$ is the chemical dispersion flux, $\mathbf{v}_f$ is the velocity of the fluid particles, and $n_{i@r}$ [mol m⁻³ s⁻¹] is the molar production rate of i through the reaction r since $\mathcal{M}_i n_{i@r} = m_{i@r}$. We consider that the chemical dispersion flux within the fluid mixture can be expressed as $\mathbf{J}_i = -\mathbf{D} \nabla c_i$, where $\mathbf{D}$ [m² s⁻¹] is the second order dispersion tensor. In addition, we neglect the deformation of the skeleton and assume that the fluid phase is incompressible. Therefore, by applying the localisation theorem we obtain

$$\frac{dc_i}{dt} + \mathbf{V}_f \cdot \nabla c_i - \nabla \cdot (\mathbf{D} \nabla c_i) = \sum_{r=1}^{n_r} n_{i@r} = \sum_{r=1}^{n_r} \nu_{ir} r \\ \frac{(1 - \phi) dc_i}{dt} = \sum_{r=1}^{n_r} n_{i@r} = \sum_{r=1}^{n_r} \nu_{ir} r \quad (4)$$

where ν_{ir} is the stoichiometric coefficient of the species i in the reaction r , and r_r [mol m⁻³ s⁻¹] is the corresponding rate of reaction. The reaction speed depends on several mechanisms that are difficult to describe analytically under various conditions of temperature, pressure, and composition. Experimental approaches are usually used to identify empirical rates of reactions. In this study, we assume that the rate of each heterogeneous reaction is governed by a specific mineral or phase:

$$r_r = r_r(c_1 \dots c_{n_s}) \left(\frac{c_r}{c_{0r}} \right)^\alpha \quad (5)$$

where r_r [mol m⁻² s⁻¹] is the rate of reaction per unit surface of some solid species r , $\frac{A_0}{V}$ is the specific surface, A_0 [m²] is the surface area of the solute exposed to chemical etching, V [m³] is the volume of the solvent which is either a fluid in ϕ_f or a solid in ϕ_s , c_{0i} (resp. c_i) is the initial (resp. current) amount of the species associated with the reaction r , and α is a shape parameter that coincides with 2/3 in the cases of spheres and cubes and that we consider equal to unity in the current study. It should be pointed out that in the case of sequential reactions, the sum $\sum_{r=1}^{n_r} \nu_{i@r}$ reduces to $\nu_{i@r}$. Since the purpose of this paper is to introduce a general approach, the reactions are not necessarily sequential. When the reactions between the species are rapid compared to the diffusion and advective processes, it is adequate to describe them using equilibrium thermodynamic approaches. The relatively slower ones (e.g. dissolution, precipitation, redox) require kinetic formulations. The thermodynamic and kinetic formulations provide relationships between the species activities. The laws of mass action or equilibrium constants can be used to relate these activities algebraically.

2.2. Decoupling of the reactive transport equations

This subsection discusses the decoupling of the reactive transport equations, which is a precondition for the subsequent semi-analytical solution. As mentioned in the previous

subsection, the mixture includes n_s species that undergo n_k kinetic reactions and n_e equilibrium reactions. As explained by Saaltink et al. (1998) and Molins et al. (2004), the chemical species in a given mixture can be either primary (building blocks of the system) and secondary (depend on the primary species through the laws of mass exchange). The system of coupled transport (4) is first rearranged such that the first $n_s - n_k - n_e$ rows describe the equilibrium primary species, the following n_k rows describe the species undergoing kinetic reactions and the last n_e rows correspond to the number of equilibrium reactions (n_e is also the number of secondary species). Since equilibrium reactions entail dependencies between the species, it is convenient to define the number of components as $n_c = n_s - n_e$. Every component can be represented as the combination of one or several species. The system can be represented compactly by using matrix notation as follows:

$$\mathbf{c} + \mathcal{L}\mathbf{c} = \mathbf{S}_e^t \boldsymbol{\xi}_e + \mathbf{S}_k^t \boldsymbol{\xi}_k \quad (6)$$

where $\mathbf{c}$ is the concentration vector, $\mathcal{L}$ is a linear operator that describes the transport in the fluid mixture; it equals $\text{diag}(\mathbf{V}_f \cdot) - (\mathbf{D} \cdot)$ in the case of aqueous species and vanishes to zero otherwise, $\boldsymbol{\xi}_e = \mathbf{R}_{(n_c \ n_e)}^{-1} \boldsymbol{\xi}_{(n_c)}$ and $\boldsymbol{\xi}_k = \mathbf{R}_{(n_k \ n_k)}^{-1} \boldsymbol{\xi}_{(n_k)}$, where $\mathbf{R}$ is a diagonal matrix that contains 1 when the species belongs to the fluid phase and $(1 - \cdot)$ in the opposite case. The matrices $\mathbf{S}_e$ and $\mathbf{S}_k$ are stoichiometric blocks corresponding to the species in equilibrium and kinetic reactions, respectively. The two blocks can be expressed by concatenation as $\mathbf{S}_e = [\boldsymbol{\nu}_{(n_e \ n_c)} \ -\mathbf{I}_{(n_e \ n_e)}]$ and $\mathbf{S}_k = [\boldsymbol{\nu}_{(n_k \ (n_c - n_k))} \ -\mathbf{I}_{(n_k \ n_k)} \ \mathbf{0}_{(n_k \ n_e)}]$, where $\mathbf{I}$ and $\boldsymbol{\nu}$ are respectively the identity and stoichiometric matrices. The overall stoichiometric matrix can be written as

$$\mathbf{S} = \begin{bmatrix} \mathbf{S}_e \\ \mathbf{S}_k \end{bmatrix} \quad (7)$$

Solving equation (6) is a difficult task because the system is fully coupled and involves non-linear feedbacks, which explains the formidable scarcity of analytical solutions to complex reactive transport problems. Among the noticeable solution strategies, it is worthwhile mentioning the work of Sun et al. (1999); Clement (2001) who used similarity transformation to decouple the system and used Laplace transform to integrate it with respect to time. However, their technique works only when $\mathbf{R}$ is a diagonal scalar matrix (the diagonal terms are all equal). Quezada et al. (2004) addressed this limitation by considering various retardation factors. The solution methods proposed by Quezada et al. (2004), Sun et al. (1999), and Clement (2001) are limited to first-order kinetic interactions and infinite or semi-infinite integration domains. Alternatively, Gauss-Jordan elimination can be used to decouple the system of equations (6) as suggested by Saaltink et al. (1998) and Steefel and MacQuarrie (1996). A full rank matrix $\mathbf{U}_c$ that is orthogonal to $\mathbf{S}_e$ can be used to reduce the number of differential equations and to eliminate the source term $\mathbf{S}_e^t \boldsymbol{\xi}_e$ since $\mathbf{U}_c \mathbf{S}_e^t = \mathbf{0}$. The matrix $\mathbf{U}_c$ that can be selected of size $n_e - n_s$ is not unique. A convenient form that works well when all species are mobile is

$$\mathbf{U}_r = \left(\begin{array}{c|c} \mathbf{I}_{(n_e-n_k) \times (n_e-n_k)} & \boldsymbol{\nu}_{n_k \times (n_e-n_k)} \\ \hline \mathbf{0}_{(n_e-n_k) \times n_k} & \mathbf{I}_{n_k \times n_k} \end{array} \right) \left(\begin{array}{c|c} \mathbf{I}_{(n_e-n_k) \times (n_e-n_k)} & \boldsymbol{\nu}_{n_k \times (n_e-n_k)}^t \\ \hline \mathbf{0}_{(n_e-n_k) \times n_k} & \mathbf{I}_{n_k \times n_k} \end{array} \right) \quad (8)$$

When the species are not all mobile, one or more algebraic kernels can be used as multipliers to decouple the system of PDEs. Consider the kernel $\boldsymbol{\kappa}$, such that $\mathbf{U} = \boldsymbol{\kappa} \mathbf{U}_r$ and multiply the system (6) by $\mathbf{U}$, leads to

$$\mathbf{u} + \mathcal{L}\mathbf{u} = \mathbf{U} \mathbf{S}_k^t \boldsymbol{\xi}_k \quad (9)$$

where the chemical components are expressed as

$$\mathbf{u} = \mathbf{U} \mathbf{c} \quad (10)$$

Note that the operator $\mathcal{L}$ is commutative with any matrix of the same order because it is diagonal.

2.3. Solutions of the decoupled transport equations

Molins et al. (2004) proposed four different kernels depending on the mode of reactive transport, in which cases the resulting number of differential equations does not necessarily coincide with the number of components n_c . Molin's technique can be useful for in-situ leaching as the species are not necessarily all mobile. We adopt the kernel that does not involve fixed activity species undergoing equilibrium reactions. Hence, the system (9) is the decoupled version of the reactive transport problem. In a one-dimensional domain, each term consists of a PDE of the form:

$$\frac{u_i}{t} + \mathcal{V}_f \frac{u_i}{x} - D \frac{\partial^2 u_i}{x^2} = k_i u_i \quad (11)$$

where $\mathcal{V}_f$ is the one-dimensional component of $\mathbf{V}_f$ and k_i is a piecewise function of time and space that is expressed based¹ on equations (5) and (9). The piecewise function is necessary in the proposed semi-analytical approach because the Laplace inversion is performed numerically and the feedback k_i needs to be updated after every time increment. The boundary conditions that affect the reactive transport in a finite column have been discussed by You and Zhan (2013). To summarise them, we consider inlet boundary conditions of the form

$$c_i(0, t) = c_i^0(t) \text{ or } \left[\mathcal{V}_f c_i - D \frac{\partial c_i}{\partial x} \right]_{x=0} = \mathcal{V}_f c_i^0(t) \quad (12)$$

¹The source term in equation (11) is the i^{th} member of the vector $\mathbf{US}_k^t \boldsymbol{\xi}_k$ as can be seen in equation (9). Since the members of $\mathbf{US}_k^t$ are constants, the source term is proportional to the rate $\dot{c}_i$ that is expressed in equation (5). Since the shape exponent is taken unity, the source term is of the form $k_i u_i$.

where the origin of the x-axis is at the position of the inlet. The conservation of mass at the end of the column can be expressed as

$$\left[\mathcal{V}_f c_i - D \frac{c_i}{x} \right]_{x=L} = \mathcal{V}_f c_i^e(t) \quad (13)$$

where $c_i^e(t)$ is the concentration at the exit point of the column that corresponds to $x = L$. To avoid extreme values of concentration within the transport domain, the supplementary condition $c_i(L, t) = c_i^e(t)$ is imposed, which results in the Danckwerts boundary condition

$$\frac{c_i}{x} \Big|_{x=L} = 0 \quad (14)$$

The boundary conditions (12-14) can be transformed using equation (10) to obtain

$$u_i(0, t) = u_i^0(t) \text{ or } \left[\mathcal{V}_f u_i - D \frac{u_i}{x} \right]_{x=0} = \mathcal{V}_f u_i^0(t) \quad (15)$$

$$\frac{u_i}{x} \Big|_{x=L} = 0$$

2.4. PDE solution using Laplace transform

To solve the PDE (11) along with the boundary conditions (15), we use the following dimensionless parameters for mathematical convenience:

$$\xi = \frac{u_i}{u_{ak}}, \quad \eta = \frac{u_i^0}{u_{ak}}, \quad \zeta = \frac{x}{L}, \quad \tau = \frac{t \mathcal{V}_f}{L}, \quad \mathcal{D} = \frac{D}{\mathcal{V}_f L} \text{ and } \theta_i = \frac{L k_i}{\mathcal{V}_f} \quad (16)$$

where $\mathbf{u}_{ak}$ [mol m⁻³] is an arbitrary constant value for concentration. Substituting the dimensionless quantities (16) into equations (11) leads to the following dimensionless problem

$$\begin{aligned} -\frac{i}{\xi} + \frac{i}{\xi} - \mathcal{D} \frac{d^2 i}{d\xi^2} &= -i_i \\ i(0) &= i_i^0 \quad \text{or} \quad \left[i - \mathcal{D} \frac{di}{d\xi} \right]_{\xi=0} = i_i^0 \\ \frac{di}{d\xi} &= 0 \end{aligned} \quad (17)$$

Applying Laplace transform to the system (17), we obtain

$$\begin{aligned} \mathcal{D} \frac{d^2 \bar{i}}{d\xi^2} - \frac{\bar{i}}{\xi} + (\bar{i} - s) \bar{i} &= -i_i(s) \\ \bar{i}(0) &= i_i^0(s) \\ \frac{d\bar{i}}{d\xi} &= 0 \end{aligned} \quad (18)$$

where s is the dimensionless Laplace variable and the over bar indicates the image by Laplace transform. The obtained differential equations are non-homogeneous with second members involving $-i_i(s)$. Since the initial concentrations are all uniform, the second members are constant with $i_i(s) = i_i(0) = i_i(0) = 0$. This means that the particular solution is $-i_i(s) = -i_i(0)/(s - i_i)$. However, the complementary (or homogeneous) solution is of the form

$$i = E \exp\left(\frac{1 - \sqrt{1 + 4\mathcal{D}(s - i_i)}}{2\mathcal{D}}\right) + F \exp\left(\frac{1 + \sqrt{1 + 4\mathcal{D}(s - i_i)}}{2\mathcal{D}}\right) \quad \text{where} \quad \sqrt{1 + 4\mathcal{D}(s - i_i)} \quad (19)$$

The boundary conditions of the differential equation (18) result in

$$E + F = i_i^0(s) = i_i(s) + i_i^0(s) \quad \text{and} \quad E \left(\frac{1 - \sqrt{1 + 4\mathcal{D}(s - i_i)}}{2\mathcal{D}}\right) \exp\left(\frac{1 - \sqrt{1 + 4\mathcal{D}(s - i_i)}}{2\mathcal{D}}\right) + F \left(\frac{1 + \sqrt{1 + 4\mathcal{D}(s - i_i)}}{2\mathcal{D}}\right) \exp\left(\frac{1 + \sqrt{1 + 4\mathcal{D}(s - i_i)}}{2\mathcal{D}}\right) = 0 \quad (20)$$

which means that the two constants are

$$E = \frac{{}_i^0(s) \exp\left(\frac{\chi}{D}\right)^{\frac{\chi+1}{\chi-1}}}{\exp\left(\frac{\chi}{D}\right)^{\frac{\chi+1}{\chi-1}} + 1} \text{ and } F = \frac{{}_i^0(s)}{\exp\left(\frac{\chi}{D}\right)^{\frac{\chi+1}{\chi-1}} + 1} \quad (21)$$

The inverse of Laplace transform has been obtained using the Zakian method which proved to work well in the case of transport equations (Wang and Zhan, 2015).

2.5. Secondary species

As mentioned in the previous subsections, when a reaction is fast compared to the transport processes, equilibrium formulation is adequate. However, kinetic formulation becomes relevant otherwise. Combining equilibrium and non-equilibrium thermodynamic approaches to solve reactive transport problems is gaining momentum and attracting the attention of different researchers (Xu and Pruess, 2001; Steefel and MacQuarrie, 1996; Parkhurst, 1995; Molins et al., 2004; Sanchez-Vila et al., 2010; Karrech, 2013). In the case of equilibrium reaction at given temperature and pressure conditions, the relationship between activities and concentrations of reactants and products is determined using an equilibrium constant as follows:

$$K_r^{eq} = \prod_{i=1}^{n_r} ({}_i c_i)^{\nu_{ir}} \quad (22)$$

where ${}_i c_i$ is the activity coefficient, K_r^{eq} is the constant of chemical equilibrium, and n_r is the number of species involved in the reaction r . The constant of equilibrium can be calculated using the Gibbs free energy of reaction $\mathcal{G}_r = \sum_i \nu_{ir} G_i = -RT \ln K_r$, where G_i [Jmol⁻¹K⁻¹] is the Gibbs free energy of the species i . It is often necessary to first evaluate the ionic strength and use the models of Debye-Hückel, Güntelberg, or Davies to estimate the activity coefficients of the chemical species. In this study, the concentrations are small enough to assume that the coefficients remain close to unity. In the case of

kinetic reaction at a given temperature and pressure, the conservation of mass requires that

$$r = \frac{n_{i@r}}{i_r} = \frac{n_{j@r}}{j_r} \quad i, j = 1..n_r \quad (23)$$

where i and j are two species that contribute to the reaction r with their respective stoichiometric coefficients i_r and j_r .

3. Particularisation for the Au-I-H₂O system

3.1. Thermodynamic and kinetic conditions of gold recovery using iodine

In the absence of complexing ligands, the noble character of gold can be explained through a Pourbaix (pH-Eh) diagram that depicts the oxidation potential with respect to acidity and illustrates the thermodynamic stability of chemical species of the Au – H₂O system. As reported by Finkelstein and Hancock (1974) as well as Qi and Hiskey (1991), gold oxidation occurs only outside the domain of water stability, which explains the metal's corrosion resistance in water at ambient conditions. It can also be shown that temperature and pressure have little effect on the Au – H₂O system's stability, although when temperature increases, the region of HAuO₃²⁻ stability shifts to the acidic side and reaches a pH of about 10.5.

In the current study we focus on the Au – I – H₂O system. As shown in Figure 2, introducing iodide ligands to the system shifts the oxidation zone into the domain of water stability (coloured region). At high iodide concentrations ($[I^-] = 0.1 \text{ mol } \mathcal{L}^{-1}$), the gold can be oxidised in water provided that pH is lower than 13 and Eh is higher than about 0.5V. As concentration of iodide decreases, the stability zone shifts to the acidic side of the Pourbaix diagram. Note that the diagram also shows that acidic conditions are more favourable for the oxidation of gold using iodide ions.

According to Davis and Tran (1991), the reactions that govern the iodine-iodide system are listed in Table (1). The solubility of iodine ions in water is low, but it increases in the

Figure 2: Pourbaix diagrams of the Au – I – H₂O systems at ambient conditions using $[\text{AuI}_2^-] = [\text{AuI}_4^-] = [\text{HAuO}_3^{2-}] = 10^{-4}$ M. The diagram depicts the stabilities of water ($\text{---}\circ\text{---}$) and gold iodide complexes at different concentrations $[\text{I}^-] = 0.1$ (---), 10^{-2} ($\cdots$), and 10^{-3} M ($-\cdot-\cdot-$). The thermodynamic data are obtained from Kelly (1960) and Davis et al. (1993).

Table 1: Thermodynamic data of significant reactions (Angelidis and Kydros (1995), Davis and Tran (1991)). $ns = 8$, $ne = 3$, and $nc = ns - ne = 5$

Reaction	log K
(1) : $\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$	2.84
(2) : $\text{H}^+ + 2\text{I}^- + \text{HIO} \rightleftharpoons \text{I}_3^- + \text{H}_2\text{O}$	15.1
(3) : $\text{AuI}_4^- + \text{I}^- \rightleftharpoons \text{AuI}_2^- + \text{I}_3^-$	1.19
(4) : $\text{Au} + 0.5\text{I}_3^- + 0.5\text{I}^- \rightleftharpoons \text{AuI}_2^-$	-0.63

presence of iodide following the first reaction in the table. Other possible reactions were reported by Angelidis et al. (1993) in the forms

However, the reactions (24) are relevant only when $pH > 8$ and $pH < 2$, respectively. According to Angelidis et al. (1993), high concentration of gold—when the ratio $[\text{AuI}_2^-]/[\text{I}^-]$ reaches or exceeds 0.15—can also lead to the formation of gold iodide (AuI(s)) according to reaction

Practical applications involve lower concentration ratios $[\text{AuI}_2^-]/[\text{I}^-]$ than 0.15 and 2 pH 8, which means that we do not consider the three reactions (24-25) in the current study to simplify the problem. The rate of gold dissolution was obtained experimentally by Qi and Hiskey (1991) as:

$$r_{\text{Au}} = k_{\text{Au}} \exp\left(-\frac{E_a}{RT}\right) [\text{I}_3^-][\text{I}^-]^{0.5} \quad (26)$$

where $k_{\text{Au}} = 1.64 \times 10^{-3} \text{ mol}^{-0.5} \text{ L}^{1.5} \text{ m}^{-2} \text{ s}^{-1}$ is an empirical parameter $E_a = 34.4 \text{ kJ/mol}$ the activation energy, $R = 8.31446 \text{ Jmol}^{-1} \text{ K}^{-1}$ is the gas constant and $T = 298.15 \text{ K}$ is the temperature. The empirical expression (26) is valid in the range of pH 2-8. It assumes that the kinetic process is mainly controlled by diffusion of reactants through the boundaries to the surface of the gold particle. In addition, the experimental data show that the reaction is first order with respect to $[\text{I}_3^-]$ and half order with respect to $[\text{I}^-]$.

3.2. Identification of reactive components

Apart from water, the problem at hand involves 8 species that are governed by 3 equilibrium reactions in the range of pH 2–8. Therefore, five components can be considered to solve the problem of reactive transport. The stoichiometric matrix $\mathbf{S}$ defined by equation (27) can be arranged in columns that correspond to the primary species (H^+ , I^- , I_3^- , and AuI_2^-), kinetic immobile species (Au) and secondary aqueous species (I_2 , HIO , and AuI_4^-). The rows of $\mathbf{S}_e$ contain the secondary species whereas the unique row of $\mathbf{S}_k$ contains the kinetic immobile species Au . Using equation (7), it can be seen that the blocks $\mathbf{S}_e$ and $\mathbf{S}_k$

form the global stoichiometric matrix:

$$\mathbb{S} = \left(\begin{array}{c|cccccc|ccc} & \text{H}^+ & \text{I}^- & \text{I}_3^- & \text{AuI}_2^- & \text{Au} & \text{I}_2 & \text{HIO} & \text{AuI}_4^- \\ \hline \text{I}_2 & 0 & -1 & 1 & 0 & 0 & -1 & 0 & 0 \\ \text{HIO} & -1 & -2 & 1 & 0 & 0 & 0 & -1 & 0 \\ \text{AuI}_4^- & 0 & -1 & 1 & 1 & 0 & 0 & 0 & -1 \\ \hline \text{Au} & 0 & -0.5 & -0.5 & 1 & -1 & 0 & 0 & 0 \end{array} \right) \quad (27)$$

The matrix $\mathbf{U}_c$ can be obtained using the definition (8); the columns are labelled with all the species in accordance with the columns of $\mathbf{S}$ and the rows are labelled with the four equilibrium components $\sum \text{H}^+$, $\sum \text{I}^-$, $\sum \text{I}_3^-$, and $\sum \text{AuI}_2^-$ and the kinetic immobile species Au:

$$\mathbf{U}_c = \left(\begin{array}{c|cccccc|ccc} & \text{H}^+ & \text{I}^- & \text{I}_3^- & \text{AuI}_2^- & \text{Au} & \text{I}_2 & \text{HIO} & \text{AuI}_4^- \\ \hline \sum \text{H}^+ & 1. & 0. & 0. & 0. & 0. & 0. & -1. & 0. \\ \sum \text{I}^- & 0. & 1. & 0. & 0. & -0.5 & -1. & -2. & -1. \\ \sum \text{I}_3^- & 0. & 0. & 1. & 0. & -0.5 & 1. & 1. & 1. \\ \sum \text{AuI}_2^- & 0. & 0. & 0. & 1. & 1. & 0. & 0. & 1. \\ \hline \text{Au} & 0. & 0. & 0. & 0. & 1. & 0. & 0. & 0. \end{array} \right)$$

The kinetic reaction (fourth equation in Table 1) involves iodide (I^-), triiodide (I_3^-), and Diiodoaurate AuI_2^- . The combination obtained by Gauss-Jordan elimination results in a new primary conservative² component, $\sum \text{AuI}_2^-$. Adopting the classification of Molins et al. (2004), $\mathbf{U}_c$ shows that the component $\sum \text{H}^+$ is mobile conservative, the component Au is immobile non-conservative, and I^- , I_3^- , and AuI_2^- are mixed conservative. This classification is important to work out the non-linear operator $\mathcal{L}$ that affects the partial differential equation of transport. Although it works well when the species are all mobile, $\mathbf{U}_c$ is in-

²Conservative components are those that remain unaltered by equilibrium or kinetic reactions.

sufficient to solve the problem of reactive transport in our case because it delivers mixed conservative components. To overcome this restriction, we use a modified version of Molins kernel matrix

$$\kappa = \begin{pmatrix} & \Sigma H^+ & \Sigma I^- & \Sigma I_3^- & \Sigma AuI_2^- & Au \\ \Sigma H^+ & 1. & 0. & 0. & 0. & 0. \\ \Sigma I^- & 0. & 1. & 0. & -0.5 & 0. \\ \Sigma I_3^- & 0. & 0. & 1. & -0.5 & 0. \\ \Sigma AuI_2^- & 0. & 0. & 0. & 1. & -1. \end{pmatrix}$$

that eliminates the immobile species from the expressions of chemical components and reduces the number of differential equations to be solved. In total, the new system of PDEs contains $n_k + n_e$ less equations than the original problem of reactive transport written in terms of species. The final matrix that we use as multiplier of the original system of PDEs is expressed as:

$$\mathbf{U} = \kappa \mathbf{U}_c = \begin{pmatrix} & H^+ & I^- & I_3^- & AuI_2^- & Au & I_2 & HIO & AuI_4^- \\ \Sigma H^+ & 1. & 0. & 0. & 0. & 0. & 0. & -1. & 0. \\ \Sigma I^- & 0. & 1. & 0. & 0.5 & 0. & -1. & -2. & -0.5 \\ \Sigma I_3^- & 0. & 0. & 1. & 0.5 & 0. & 1. & 1. & 1.5 \\ \Sigma AuI_2^- & 0. & 0. & 0. & 1. & 0. & 0. & 0. & 1. \end{pmatrix}$$

The column in $\mathbf{U}$ corresponding to the immobile kinetic species is zero indicating that the immobile Au does not contribute to the new expression of chemical components. In addition,

the source terms of the mass balance equation are

$$US_k^t = \begin{pmatrix} & \text{Au} \\ \hline \sum H^+ & 0. \\ \sum I^- & 0. \\ \sum I_3^- & 0. \\ \sum AuI_2^- & 1. \end{pmatrix}$$

which implies that the terms $\sum H^+$, $\sum I^-$ and $\sum I_3^-$ are all mobile conservative while $\sum AuI_2^-$ has a source term. The three first PDEs of the mobile conservative components are independent and can be solved using direct techniques. However, the source term of the last component depends on the concentrations $[I^-]$ and $[I_3^-]$, as required by equation (26). Since the concentrations $[I^-]$ and $[I_3^-]$ are both large compared to the concentrations $[AuI_2^-]$ and $[AuI_4^-]$, we assume that their variations are close to those of $\sum I^-$ and $\sum I_3^-$ when we calculate the rate of reaction.

3.3. The reactive transport of auriferous species

To validate the model, we consider the experimental data of Roberts et al. (2010) who conducted leaching tests on gold ore samples extracted from orogenic gold deposits. Gold orbodies in this category are formed within large structural deformation zones of the crust and uppermost mantle. Orogenic deposition is usually characterised by high permeability during the formation phase, which may be conserved to a large extent at the present day. Weathered regions within orogenic deposits can be good candidates for in-situ leaching as their micro-texture can include fractured zones of enhanced permeability. In addition, they have the advantage of containing minor sulphides such as pyrite, which offers better selectivity during reactive transport. The ore samples used by Roberts et al. (2010) were particulate materials such as drill chips. In particular, the sample that was leached using

iodine was obtained from Tunkillia in South Australia's Gawler Craton where prolonged periods of weathering resulted in saprolite layers underlain by more intact saprocks. The porosity of upper saprolite layers ranges from 20 to 30 % according to Roberts and co-workers. The average grain size and gold grade were about 150 μm and 1.48 g/t, respectively. Ore XRD characterisation indicated that the sample included quartz, albite, orthoclase and muscovite (minor traces) but no pyrite.

The sample was placed in a column of diameter 5 cm and height 1 m, sealed to avoid any fluid leakage and flooded with the leach solution from the bottom. A porosity of 33 % is used for simulation in the current paper. A peristaltic pump was used to inject the solution with a flow rate of 50 mL day^{-1} . The initial injected solution comprises 8 mM I^- and 1 mM I_3^- . Roberts et al. (2010) observed that the concentrations were doubled after 34 days, but the recovery peaks indicate that injection flow rate was doubled as well. The effluent solution was collected and analysed to estimate its chemical content. The dispersivity coefficient is taken $D = \alpha v_f$, where $\alpha = 0.01 \text{ m}$ is the dispersivity coefficient, as suggested by Martens et al. (2012). The specific surface is considered $\mathcal{S} = 1960 \text{ m}^2 \mathcal{L}^{-1}$, which is justified by the nanometer size of gold particles (e.g. Lowell et al., 2004, Ch.1). Following Martens et al. (2012), we compare the concentrations of species in the effluent solution to our semi-analytical results except that we do not include pyrite as a gangue material in our list of species (in accordance to the XRD characterisation of Roberts et al. (2010)).

As can be seen in Figure 3, the proposed model predicts the experimental results with an acceptable accuracy. In particular, the results show that the breakthrough took place after 14 days of leaching. In addition, the model and the experimental data both show that the effluent gold concentration reached a maximum of 4.4 ppm after 40 days. Moreover, a peak duration of about 12 days has been obtained due to the increase of iodide and triiodide concentrations in the feed concentration.

Figure 3: Experimental ($\circ$) and semi-analytical (—) results illustrating the reactive transport of (a) triiodide and (b) gold with respect to time.

3.4. Deduction of species from components

The solubility of iodine is enhanced by the presence of iodide as mentioned in 3.1. However, several authors (Hough and Ficklen, 1934; Nowaczyk et al., 1993; Lin, 1981; Ling, 1997) indicated that iodine can be lost by volatilisation. Such loss of iodine to the environment can partially explain the reduction of triiodide concentration, when it is not consumed by gangue minerals. To model the volatilisation phenomenon, we consider the equilibrium equation $I_2^{aq} \Leftrightarrow I_2^g$, between aqueous and gaseous iodine, where the equilibrium constant can be calculated as $K_0 = \exp \frac{-G_r}{RT} = 30.207 \text{ kPaM}^{-1}$. This equilibrium constant can be used to calculate the partition coefficient of iodine between water and gas: $H_{I_2^g} = K_0^{-1} RT^{-n_g}$, where $n_g = 1$ is the moles of gas on the products side of the reaction. The partition coefficient $H_{I_2^g} = 82$ is defined as the concentration of iodine in water over the concentration of iodine in the gas phase. The equilibrium between aqueous iodine, iodide and triiodide is initially established through the first equation in the system (1). Using equation (22), the initial concentration of aqueous iodine is $[I_2^{aq}]_{t=0} = \frac{[I_3^-]_{t=0}}{K_1[I^-]_{t=0}} = 0.18 \text{ mM}$. The system that

governs the change of concentrations can be written as follows:

$$\begin{cases} [I_2^{aq}]_{t=0} - x - y = H_{I_2^g} y \\ [I_3^-]_{t=0} + x = K_1([I^-]_{t=0} - x)([I_2^{aq}]_{t=0} + x + y) \end{cases} \quad (28)$$

Solving the system (28) shows that the changes in concentrations is $x = 0.186$ M and $y = 2.22$ M, which are too small to explain the decrease of triiodine concentration to 0.8 mM during the first 38 days. To explain this phenomenon, we adopt the postulate of Martens et al. (2012) who used a generic exchange reductant D, which is present as D_2 in the solid phase and dissolves into a species D^+ through the following reaction

If we assume that the system contains no I_2^{aq} , initially, the following system of equations describes the subsequent change of concentrations:

$$\begin{cases} [I_3^-]_{t=0} + x - y = -K_1([I^-]_{t=0} - x + 3y)x \\ 4y^2([I^-]_{t=0} - x + 3y)^3 = K_D([I_3^-]_{t=0} + x - y) \end{cases} \quad (29)$$

Solving the system (29) results in the concentrations $[I^-] = 10$ mM and $[I_3^-] = 80$ M during the first testing phase (before doubling the feed concentrations) and $[I^-] = 19.5$ mM and $[I_3^-] = 0.795$ mM during the second testing phase. This value is close to the final triiodine concentration reported by Roberts et al. (2010), which is $[I_3^-] = 0.8$ mM.

The equilibrium of HIO is described by the second equation in the system (1). If equilibrium is satisfied, equation (22) shows that

$$K_2 = 10^{15.1} = \frac{[I_3^-]}{[H^+][I^-]^2[HIO]}$$

Given that the concentrations $[H^+]$, $[I_3^-]$, and $[I^-]$ are all finite, it can be deduced that $[HIO]$ is negligible because K_2 is very large. Similarly, the third equation in the system (1) describes the equilibrium between AuI_2^- and AuI_4^- constrained by the constant

$$K_3 = 10^{1.19} = \frac{[AuI_2^-][I_3^-]}{[AuI_4^-][I^-]}$$

which means that $[AuI_2^-]$ is at least 15 times higher than $[AuI_4^-]$. With these considerations in hand, the matrix $\mathbf{U}$ can be used to express the components in terms of chemical species:

$$\begin{aligned} u_{H^+} &= [H^+] - [HIO] = [H^+] - \frac{[I_3^-]}{K_2[H^+][I^-]^2}, \text{ with no source term} \\ u_{I^-} &= [I^-] + 0.5[AuI_2^-] - 0.5[AuI_4^-] - [I_2^{aq}] - 2[HIO] \\ &= [I^-] - [I_2^{aq}] + 0.5[AuI_2^-] \left(1 - \frac{[I_3^-]}{K_3[I^-]}\right) - \frac{2[I_3^-]}{K_2[H^+][I^-]^2}, \text{ with no source term} \\ u_{I_3^-} &= [I_3^-] + 0.5[AuI_2^-] + 1.5[AuI_4^-] + [I_2^{aq}] + [HIO] \\ &= [I_3^-] + [I_2^{aq}] + 0.5[AuI_2^-] \left(1 + 3\frac{[I_3^-]}{K_3[I^-]}\right) + \frac{[I_3^-]}{K_2[H^+][I^-]^2}, \text{ with no source term} \\ u_{AuI_2^-} &= [AuI_2^-] + [AuI_4^-] = [AuI_2^-] \left(1 + \frac{[I_3^-]}{K_3[I^-]}\right) \\ &\quad \text{with a source term equal in magnitude to the dissolution of solid gold} \end{aligned} \quad (30)$$

Once the components are obtained, Newton's method can be used to deduce the individual concentration of species. However, the problem at hand can be simplified given the large equilibrium constants and the expected small concentrations of some of the species as shown earlier. These simplifications show that

$$u_{H^+} = [H^+] \quad u_{I^-} = [I^-] - [I_2^{aq}] \quad u_{I_3^-} = [I_3^-] + [I_2^{aq}] \quad \text{and} \quad u_{AuI_2^-} = [AuI_2^-] \quad (31)$$

Based on these considerations, the space variation of triiodine concentration is depicted in Figure (4), at different dimensionless times, τ . It can be seen that before 34 days,

the magnitude of the concentration plateau is of about 0.08 mM in accordance with the results of equation (29). A similar behaviour can be noticed in terms of dissolved gold concentration, except that the magnitudes reduce with respect to time. This reduction is related to the reaction rate of gold which depends non-linearly on solid gold concentration. As time progresses, the reaction fronts advance towards the end of the column. After 34 days, the feed concentrations increase which results in a higher magnitude of triiodine concentration, 0.8 mM and a depletion of solid gold close to the origin (vicinity of $x = 0$). As the process continues, it can be seen that gold concentration reduces with respect to time.

Figure 4: Concentrations of triiodide (LHS) and dissolved gold (RHS) along the ore column, at different non-dimensional times.

3.5. Parametric study

The leaching process involves a number of parameters that are controllable and others that are intrinsic to the chemical species. Among the important parameters that can be varied to optimise the leaching process, it is worthwhile mentioning the grain size distribution, the flow rate, the concentration of iodide/triiodide and temperature. These parameters are varied around the base-case model corresponding to the feed concentrations ($[I^-] [I_3^-] = (16,8)$

mM, the flow rate of 50 mL day^{-1} . Figure 5 shows the variation of triiodide concentration with respect to time and space at different flow rates. In particular, Figure 5_a indicates that the reaction front thickness increases with respect to time as the flow rate increases as can be perceived through the curve slopes that vary when the flow rate increases. The figure also shows that the impact of transport triiodide concentration increases non-linearly with flow rate. Despite the constant increments of flow rate, the curves are not equidistant as shown in Figure 5_b.

Figure 5: Effects of flow velocity on the transport of triiodide

Figures 6 show the effect of flow velocity, concentration of iodine lixivants, or specific surface increase on the variation of concentration with respect to space and time. In particular, the figure indicates that these variables affect the reaction fronts. More importantly, the results indicate the rate of effluent gold concentration increases until its maximum (the slope of the curves).

Figures 6_a and 6_b illustrate the effects of flow velocity on the dissolution and subsequent transport of gold. In particular, the latter shows that the peak of gold concentration increases as the flow rate decreases. In addition, the figure shows that the intensity of recovered gold increases when the flow rate decreases (the integral of dissolved gold concentration with

respect to time increases). This may suggest that slower flows are more beneficial, but there is a compromise between the flow speed and the dollar cost of time. However, it is worthwhile noting that there is a significant cost to pumping at increased flows which normally require increased pressure. The cost of time is normally less of an issue in ISL operations, but it is a significant issue in stirred tank applications.

Similarly, Figures 6_c and 6_d depict the effect of specific surface (inversely proportional to grain size) on the recovery of gold. As can be seen, the more surface exposure, the faster recovery is achieved. Indeed, the peak of gold concentration increases as the specific surface increases. More importantly, it can be seen that intensity of recovered gold increases slightly as α varies from 500 to 1000 m²g⁻¹ and decreases afterwards. This means that if the leaching duration is predefined, an optimum grain size can be identified using the current approach.

Finally, we study the effect of feed lixiviant concentration as represented in Figures 6_e and 6_f. The former figure shows that the concentration of dissolved gold exhibits a plateau followed by a sharp decrease indicating the reaction front, except when the lixiviant concentration is extremely high. Counter-intuitively, this particular case exhibits a transported peak of concentration. This phenomenon is due to the increase of reaction rate with the iodide and triiodide concentrations. The latter figure shows that the peak of dissolved gold concentration increases as the lixiviant concentrations increase. This is aligned with the fact that the reaction rate increases with the concentration of lixiviants. More importantly, it can be seen that the intensity of recovered gold decreases as the lixiviant concentrations increase (at least in the considered range of concentrations, beyond which other precipitation phenomena may occur).

Figure 6: Effects of flow velocity, specific surface and initial lixiviant concentration on the recovery of gold

4. Conclusions

Despite the success of in-situ leaching in clean-producing uranium around the globe (48% of the current world production), the industry remained reluctant to adopt a similar process for precious metals because of the lack of a suitable lixiviant. The only robust substance that can unlock gold from geomaterials is cyanide, but its toxicity hindered its application in unconfined spaces. Recent research initiatives proved that iodine a less harmful substance can be an acceptable candidate to extract precious metals from pristine environments.

In the current paper, we developed a mathematical formulation that predicts the reactive transport of lixivants and gold complexes to shed more light on the in-situ process. The proposed approach is semi-analytical to ensure that the impacts of physical parameters affecting ISL are assessed thoroughly. The solution procedure uses the concept of components to avoid solving the PDE corresponding to a large number of species along with the respective equilibrium and kinetic equations that relate them. This technique proved to be efficient and time-saving in predicting the behaviour of gold-iodine systems. To validate the model, we compared its results to existing experimental data. The two approaches produced an acceptable agreement, which demonstrates the model's reliability as an ISL predictive method.

A parametric study was conducted to investigate the effect of controllable parameters on the ISL process. We mainly focused on flow velocity, grain size distribution, and lixiviant concentration. The results showed that the intensity of recovered gold increases when the flow rate decreases, as the lixiviant concentrations increase, and exhibits a bell-shaped behaviour with respect to specific surface within the range of variables that we studied. These results may suggest that the model can be used to optimise gold recovery using iodine ligands. For example, we proved that compromises between the flow speed, lixiviant concentrations, and grain size can be identified.

It must be noted that iodine is an expensive chemical. Although it is less hazardous than cyanide, iodine can affect human organs when inhaled or absorbed through the skin. Therefore caution must be taken when iodine is used especially during the solution preparation and injection. In a future work, we will explore more benign approaches, with chemicals that are more environmentally friendly.

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Highlights

The potential of In-Situ Leaching for the recovery of precious metals;

A novel semi-analytical solution to the problem of reactive transport to describe gold recovery;

Complex geochemistry decoupling using Gauss-Jordan elimination;