Predictive Models of Leaching Processes: A Critical Review

Nhlanhla Othusitse, and Edison Muzenda

***Abstract*—**This paper critically reviews models employed in various leaching processes. The aim of this work is to study various leaching models for the development of a model that can predict both recovery and reagent consumption using available mineralogical data. The envisaged model will be used as a tool for predicting hydrometallurgical routes from mineralogical data. The development of a hydrometallurgical process is a vital step in designing a mineral processing plant. Modelling can provide reliable data for preliminary feasibility studies and this simplifies the decision making process. Under the current economic climate which is characterized by falling metal prizes, reduction of production costs and improving efficiency may increase the profitability of mineral processing businesses. The development and success of the proposed model will add value to the copper extraction and beneficiation value chain.

***Keywords*—**Hydrometallurgical process, modelling, reagent consumption, solubility.

I. Introduction

MODELLING has been used in various leaching operations to gain understanding of the process and subsequently help in decision making. Several models were employed over the years for leaching of various minerals, gold attracting the most attention probably because of its high economic value relative to other metals (e.g., copper, manganese and zinc). These models include; shrinking core models (SCM), kinetic models, reaction models, thermodynamic models, empirical and semi-empirical models, variable activation energy models, geochemical models and thermodynamic models. The shrinking core models; shrinking core –shrinking particle, shrinking core –constant particle size and shrinking particle, are some of the earliest models developed to describe heterogeneous non-catalytic reaction kinetics [1]. Between 1960s and 1980s most researchers focused on these models but some of the models aspects were not tested in the hydrometallurgical field [2]. However in the past two decades these models gained popularity in hydrometallurgy, finding application in gold cyanidation, zinc dissolution, manganese, uranium and copper leaching. Reference [3] incorporated the shrinking particle model into a mathematical model to develop a rate expression which describes the leaching of gold ores. An improved shrinking core model with variable activation energy was developed for kinetic modelling of manganese ore leaching [4]. Reference [5] adopted the shrinking core model to develop a mathematical model for zinc ore leaching. Recent applications of the shrinking core model are reported by [6] and [7] who investigated the effects of particle size distribution in leaching reactors and in predicting the leaching behaviour of high carbonate uranium ores. A lumped pseudo homogenous kinetic model was applied by [8] to fit gold concentration as a function of time using least square method. Another application of kinetic modelling was derived in gold ore leaching by [9] to predict cyanide conversion as a function of time, its concentration and temperature. Furthermore an empirical model was derived to predict gold recovery from coarse particles. Another empirical model was used to calculate cyanide consumption in gold ore leaching [10]. A semi empirical model was employed for describing the behaviour of conventional and electrochemical bioleaching of copper sulphide concentrates [11]. A geochemical modelling code was used to measure malachite solubility in ammonia, ammonium chloride and their mixed solutions [12]. A thermodynamic model was derived by [13] for the solubility of malachite in a mixed solution of ammonia, ammonium chloride and ethylenediamine. Although various models have been proposed for different leaching applications, none uses mineralogical data to predict the most probable hydrometallurgical process route.

The purpose of this paper is to review and evaluate the available leaching models, their applicability to leaching of copper ores, with the aim of developing a model that can be used to predict copper solubility and the reagent consumption during leaching. The developed model will be used a tool for hydrometallurgical process route selection. Similar studies include those of [10] whose model gives account of the effects of gold surface exposure, cyanide and oxygen concentrations on leaching performance. Furthermore, it estimates the cyanide consumption by an empirical model. Similarly geochemical modelling was used by [12] to predict solubility of malachite, using synthetic mineral hence other parameters influencing the solubility of copper could not be accounted for.

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II. Models

In this section existing models in hydrometallurgy are critically evaluated.

Leaching and kinetic models are not discussed as independent models because of their application as sub-models in most of the studies reviewed.

A. Shrinking Core Models (SCM)

In heterogeneous liquid-solid reactions there are a number ways in which reactions occur at the particle surface. The particle may react with the liquid reactant giving soluble product(s), where the particle shrinks until it disappears as the reaction progresses, Fig. 1 (a). The solid may also react to produce an insoluble product whereby the reacting core shrinks while the particle does not change in size, Fig. 1 (b). The last scenario is where the solid reacts and a gelatinous layer forms around the surface of the particle while the unreacted core shrinks, Fig. 1 (c).

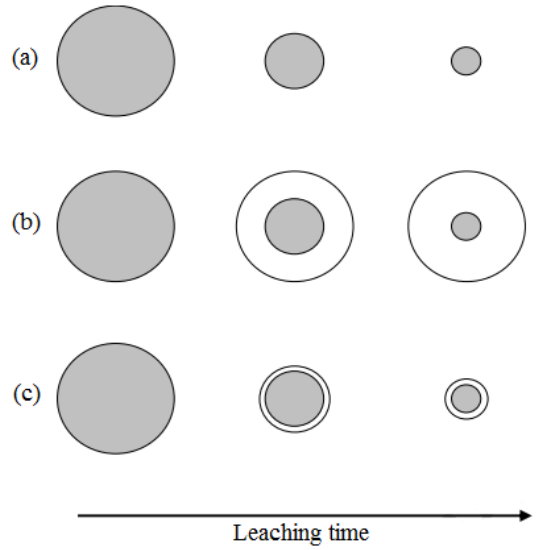

Fig. 1 illustrates various mechanisms of leaching (a) Shrinking particle, (b) shrinking core-unchanging particle and (c) shrinking core-shrinking particle [5].

These are the most popular models in hydrometallurgy since many leaching processes conform to kinetic models for heterogeneous solid-liquid reactions which are best described by these models [14].

References [1] and [14] stated that for chemically controlled reaction (1) is used.

$$kt = 1-(1-x)^{1/3} \tag{1}$$

In (1), x is the is the fractional conversion given by $x = C/C_o$ and k is the apparent rate constant calculated as in (2);

$$k = \frac{k_s C_A}{R_o \rho} \tag{2}$$

In (2), k_s is the rate constant of the reaction, ρ is the density of the mineral, R_o is the radius of the unreacted particle and C_A is the reactive concentration in the solution.

Conversely if the kinetics described by the model is diffusion controlled then (3) is used.

$$kt = 1-\frac{2}{3}x-(1-x)^{2/3} \tag{3}$$

Here k is calculated as;

$$k = \frac{DC_A}{R_o^2 \rho} \tag{4}$$

D is the diffusion coefficient of the mineral species.

A variant of the SCM is reported in [14]. This is a stochastic model for control by chemical reactions on the non-reacting particle surface. It considers the heterogeneity of solid minerals by introducing a stochastic distribution for the rate constant (k_s) such that the shrinking core model is a function of the change of conversion with time as shown in (5)

$$k_s(x) = 2k_o(1-x). \tag{5}$$

In (5) $k_s = k_{max}/2$

B. Variable Activation Energy Model for Leaching Kinetics

This is characterized by grouping or lumping together rate limiting factors to a single parameter. It was first applied by [15] who postulated that the limiting factors could be lumped into a single reaction resistance expressed as an activation energy barrier. This was a compromise, because describing the leaching behavior of low grade ore, basic classical kinetics are too limited and rigorous characterization of all the physico-chemical effects would be overwhelmingly difficult. This model considers the variability of mineral reactivity and diffusional resistance.

In principle, reaction occurs such that the highly reactive or available particles react first leaving behind the more refractory ones and inert material. Linear dependence of the activation energy on the residual metal concentration $[C_M]$ is assumed therefore a decrease in metal concentration results in increased activation energy, E, which is expressed as in (6).

$$E = E_o\{1-\alpha[C_M]\} \tag{6}$$

In (6), E_o is the activation energy when $[C_M] \rightarrow 0$ and α is a constant.

Substituting (1) into the Arrhenius equation gives (7)

$$\begin{aligned} k &= A\exp(-E/RT) \\ &= A\exp(-E_o\{1-\alpha[C_M]\}/RT) \end{aligned} \tag{7}$$

In (7), A= Arrhenius constant and R= ideal gas constant.

For computational convenience the equation was summarized as in (8);

$$k = \exp\left\{\frac{b_1[C_M]-b_2}{T}+b_3\right\} \tag{8}$$

In (8), $b_1 = \frac{E_o\alpha}{R}, b_2 = \frac{E_o}{R}, b_3 = \log_e A$

The model was applied to describe leaching of base metal (copper) and the rate equation was given as in (9)

$$-\frac{d[C_{Cu}]}{dt} = k[C_{Cu}]p_{HCl} \tag{9}$$

In (9), p_{HCl} =partial pressure of hydrogen chloride and $[C_{Cu}]$ = residual copper concentration.

Another application was in precious metals, cyanidation of gold ore. Here the rate equation was as in (10)

$$-\frac{d[Cu]}{dt} = k([C_{Au}] - [C^*_{Au}]) \quad (10)$$

In (10), $[C^*_{Au}]$ = concentration of completely refractory gold.

In both examples, the proposed model showed good agreement with experimental data.

Improvements to this model were later reported by [16] and [17]. A second order kinetic equation suggested by [16] was useful in describing gold cyanidation kinetics. The proposed kinetic equation is shown in (11).

$$-r_{Au} = k([Au]_s - [Au]_{s,\infty})^2 \quad (11)$$

In (11), k= overall rate constant and $[Au]_s$= gold concentration.

First order kinetics was proposed by [17] as in (1) but assuming the overall rate factor, k, to be constant. A lumped kinetic model was later investigated by [8] to produce kinetic models for gold ore cyanidation and cyanide consumption.

Although the proposed models function well for some cases, they are limited because they do not take into account the reagent concentration nor particle size effects [18]. It is also important to note that the variable activation energy concept only covers changes in the reactivity and rate -limiting mechanism. Aspects of concentration (which fall under mass effects) are not taken into account by this model.

The most recent application of the variable activation energy model is presented in [19] where a description of the acid dissolution of manganese was proposed using a mathematical model based on the shrinking core model. This SCM accounted only for the overall stoichiometry of dissolution while the presence of an intricate network of degradation reactions of carbohydrates and the reliance of reaction rate on conversion were accounted for by variable activation energy approach. The modified equation is expressed as in (12).

$$\frac{dX}{dt} = \left(\frac{C}{R_p}\right)\exp\left[-\left(\frac{E_A}{R}\left(\frac{1}{T}-\frac{1}{T'}\right)+\frac{b_1 X^{b2}}{RT}\right)\right] \times (C_{AO} - C_{AS}X)^{na}(C_{LO} - C_{LS}X)^{nl}(1-X)^{2/3} \quad (12)$$

In (12), X is manganese extraction (0<X<1), C= constant, R_p= particle size (μm), E_A= activation energy, T'= reference temperature (K), R= ideal gas constant, b_1 and b_2 = parameters relating to the activation energy, C_{A0} and C_{L0}= initial acid concentration and initial lactose concentration in the selected test respectively, na and nl = reaction order with respect to acid and lactose respectively, C_{AS} and C_{LS} =stoichiometric sulphuric acid and glucose requirement respectively.

Although the model gives good description of the leaching of a particular size of manganese dioxide leaching, it does not account for the precise effect of particle size on the dissolution of manganese [4].

C. Empirical and Semi-Empirical Models

In [9] an empirical model was applied in evaluating kinetic and diffusion phenomena in cyanide leaching of crushed run-off-mine gold ores. Two models, a kinetic model and a reaction model for particle size, proved inadequate hence a subsequent empirical model based on the first two was derived. The equation for the kinetic model is as in (13)

$$G_o = \frac{dX'}{dt} = G_o\frac{(1-X')^{\varphi}}{\omega} \quad (13)$$

In (13), $X' = \frac{X}{X_{\max}}$, X = the gold extraction, X_{max} = maximum gold extraction, t = time (s), φ = topological exponent, G_0 = initial gold grade (kmol Au/kg ore) and ω = reaction time scale. The final empirical modelling equation is as in (14).

$$\left(\frac{dX'}{dt}\right)^i = k'\exp\left[\frac{-E}{RT}\right]C^n_{NaCN}C^{0.50}_{O_2}(1-X'^{(i)})^{\varphi} \quad (14)$$

The results of this model do not agree with literature that diffusion is the rate-controlling step in gold heap leaching, rather it suggests that dissolution from crushed run-off-mine particles is the controlling step in large columns and well mixed tanks.

In [10] a leaching model was developed to consider the concentration of cyanide and oxygen in gold ore leaching. An empirical model was then used to estimate cyanide consumption. The dissolution model was based on electrochemical and diffusion mechanisms [20]. By using an existing model and Fick's law of diffusion, the oxygen and cyanide molar diffusion rates (ϕ) were represented as in (15) and (16) respectively.

$$\phi_{O_2} = \frac{D_{O_2}A_c[O_2]}{\sigma_o} \quad (15)$$

$$\phi_{CN} = \frac{D_{CN}A_A[O_2]}{\sigma_o} \quad (16)$$

In (15) and (16) A_A and A_C =surface areas of anodic and cathodic reaction respectively, $[O_2]$ = oxygen concentration, D_{CN} and D_{O_2} = diffusivities of cyanide and oxygen in the pulp phase, and σ_o= thickness of the boundary layer, which is considered as dependent on impeller rotation speed. The calibrated model was able to present a description of the gold ore leaching behaviour depending on particle size distribution.

Although it is a challenge to develop rigorous cyanide consumption models, an improved pseudo-homogenous model was proposed by [8]. It was adopted to account for; cyanide concentration, ore particle size, copper $[Cu]$ and sulphur $[S]$ concentrations in the ore. Thus the cyanide consumption ($\omega_{CN}(d_p)$) per unit time and mass of liquid for ore particle size d_p is expressed as in (17)

$$\omega_{CN}(d_p) = k'_{c1}[CN]^{\alpha 1}[Cu]^{\beta 1} + k'_{c2}[CN]^{\alpha 2}[S]^{\beta 2} + \frac{k_d[CN]}{\sigma_o d_p^{\theta_3}} \quad (17)$$

In (17), k'_{c1} = kinetic rate constant associated to copper-bearing minerals and $[Cu]$= Cyanide concentration in solution,

θ_3, $\alpha 1$, $\alpha 2$, $\beta 1$, $\beta 2$= coefficients to be estimated from experimental data k_d= kinetic rate constant associated with cyanide diffusion and k'_{c2}= kinetic rate constant associated with sulphur –bearing minerals.

This model was used as a preliminary study towards understanding of the effectiveness of various cyanidation flowsheets for the purpose of minimizing cyanide consumption while maximising gold dissolution.

Reference [11] developed a mechanistic model that simulates the conventional and electrochemical bioleaching of copper sulphide concentrates in stirred tank reactors. In the progression of conventional and electrochemical bioleaching of copper concentrates, a semi-empirical model was derived to predict the following; copper recovery, conversion of various sulphide minerals, variation of oxidation reduction potentials (ORP) and pH. The model was developed by integrating the combined rate equations for individual minerals. This model accounts for effects of t ORP and pH; mineralogical composition of feed, presence of iron and sulphur oxidising micro-organisms, initial pH of solution, jarosite precipitation and initial concentration of ferric and ferrous iron on copper recovery, The model results were precise and accurate and comparable to experimental data. This serves as a validation of the model in predicting the performance of electro-bioleach reactor.

D. Geochemical Modelling

Geochemical speciation codes and thermodynamic modelling were used to calculate the solubility of malachite as well as to understand the behaviour of the system in the presence of ammonia, ammonium chloride and their mixed solution [12]. The Gibbs free energy minimisation program (GEMS-PSI) was used to determine the presence, amount and composition of different phases found in the system. GEMS is a versatile geochemical modelling code that can calculate equilibrium phase assemblage and speciation in a complex system from its overall bulk elemental composition. Activity coefficients of aqueous species γ_i with individual ion-size parameters α°_{γ} and a common third parameter b_{γ} were given as in (18).

$$\log \gamma_i = \frac{-A_{\gamma} Z_j^2 \sqrt{I}}{1 + B_{\gamma} \alpha_{\gamma}^{o} \sqrt{I}} + b_{\gamma} I \tag{18}$$

In (18), Z_j denotes the charge of species j, I is the effective molal ionic strength, b_{γ}=0.064 at 25 °C, and A_{γ} and B_{γ} are P and T-dependent coefficients.

Modelling results match well to experimental data and it was found that higher rates of copper recovery from ammonia leaching of malachite can be realised by choosing optimum operation conditions where CuO(s) and $Cu(OH)_{1.5}Cl_{0.5}$(s) solid formations can be evaded.

E. Thermodynamic Modelling

Reference [13] used a thermodynamic model to calculate solubility of malachite $Cu_2(OH)_2CO_3$ in the ammonia-ammonium chloride-ethylenediamine(En)-water system. Exponential computation method based on both mass balance and charge balance was used to make the calculation. The computation method was adopted from [21], [22] who proposed that concentration of ionic species in solution can be expressed as in (19).

$$[X] = \exp\left(a + bpH + c\varphi + e\ln[L_1] + f\ln[L_2]..\right) \tag{19}$$

In (19), *a,b,c,e and f* are coefficients; φ is the value of potential which is only needed when redox reactions exist; L_1, L_2, … are the free ions including free metal ion, free ligands and other free ions besides H^+ and OH.

The dissolution equation for malachite was given as in (20),

$$Cu_2(OH)_2CO_3 = 2Cu^{2+} + 2OH^- + CO_3 \qquad K_{sp} = 10^{-33.78} \tag{20}$$

$$[Cu^{2+}] = 10^{-33.78/2}[OH]^{-1} \cdot [CO_3^{2-}]^{-0.5} = 10^{-16.89} \times 10^{14.18}[H^+] \cdot [CO_3^{2-}]^{-0.5} \tag{21}$$

After determining the mass balance expressions, and the charge balance equation, the equation groups were solved using MATLAB. Verifying tests showed that the thermodynamic model is correct and reliable. This model is useful in the selection of a lixiviant with suitable concentration of ammonia, ammonium chloride and ethylenediamine.

III. General discussions

The shrinking core model has been useful in describing the kinetic characteristics of heterogeneous liquid-solid systems, but some challenges with describing the effects of particle size were reported in [8] and [4]. Evidence presented by [23] showed that leaching models that do not take variation of particle size into consideration are susceptible to flawed conclusions. Efforts to address the particle size challenge are shown in [19] and [7]. They employed mathematical techniques of regression analysis and Gates Gaudin Schumann density function. Despite the numerous studies describing metallurgical reactions in terms of the shrinking core models, these models are only manageable mathematically for concentrated reactants which possess the same composition and are of manageable shapes, for example spherical or square in shape. If these conditions are not met then complications in chemical reaction control will occur due to physical properties and mineralogical factors which can influence reaction rate [15]. However the models can be used to consider the polydispersity of solid particles using structure models expressed by population balances [24].

In variable activation energy models, [3] reported that by lumping together rate limiting effects, previous leaching models fail to account for processes occurring during particulate leaching, so they are relevant for homogenous kinetics, whereas leaching is a heterogeneous process where the surface area diminishes as reaction proceeds. Conversely, [15] illustrated that the variable activation energy concept accounts for highly nonlinear kinetics and effects of temperature on the reaction. The ability of this model to account for complex network of reactions [19], could be useful in handling the intricate network of reactions met in leaching copper ores.

Empirical and semi–empirical models perform well in evaluating kinetic characteristics and diffusion phenomena. They can be used to describe effects of concentration on

reactants so that values of recovery and consumption can be calculated. The ability of the models to combine solubilities of other mineral species to calculate overall recovery [11], could lend strength to the desired model. Nevertheless [25] reported that these models are however limited to the particular process they were applied in and within the bounds of the data collected.

The geochemical model proposed by [12] gave quantitative estimates of copper solubility by means of total dissolved copper contour plots. Thermodynamic modelling incorporated into this model can provide distribution of copper species at equilibrium as a function of the leaching agents. This model provides a good description of the chemical behaviour of different copper species in ammonia –ammonium solutions. Although recovery was calculated from this model, it is limited to systems where synthetic ore is used (e.g. [12]) or where the gangue is inert. Since this model does not account for possible reagent consumption due to interactions of gangue minerals with lixiviant, its application for the envisaged model would be constrained.

Although the thermodynamic model proposed by [13] has a similar limitation as [12], it shows desirable properties. It significantly reduces the number of variables such that solving nonlinear equations on a computer becomes manageable.

The proposed model will consider aspects of; mineralogy, particle size effects, transport phenomena, liquid-solid interactions, chemistry of leaching systems and dissolution kinetics to make predictions of copper solubility and reagent consumption. The model results will be used to predict a process route from mineralogy data. From this review the shrinking core models would provide a good foundation for the model. Semi –empirical and thermodynamic modelling are also attractive for application in the main model. Variable activation energy models would not be applicable unless coupled with SCM. Geochemical modelling would be useful for describing the chemistry of leaching and the interaction of liquid-solid phases.

IV. Conclusion

This paper reviews various models used in leaching processes and their applicability to copper leaching for the purpose of predicting copper solubility and reagent consumption. From the models reviewed, shrinking core semi –empirical and thermodynamic models have desirable characteristics for the proposed model. The proposed model will be used in the development of a hydrometallurgical process route.

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References

[1] O. Levenspiel, Chemical Reaction Engineering, 2nd ed. New York: Wiley, 1972, pp. 361–373.

[2] Kn. C. Liddell, "Shrinking core models in hydrometallurgy: What students are not being told about the pseudo-steady approximation," Hydrometallurgy, vol. 79, no. 1–2, pp. 62–68, Sep. 2005.

[3] F. K. Crundwell and S. A. Godorr, "A mathematical model of the leaching of gold in cyanide solutions," vol. 44, pp. 147–162, 1997.

[4] F. Beolchini, M. P. Papini, L. Toro, M. Trifoni, and F. Vegliò, "Acid leaching of manganiferous ores by sucrose: Kinetic modelling and related statistical analysis," Miner. Eng., vol. 14, no. 2, pp. 175–184, Feb. 2001.
http://dx.doi.org/10.1016/S0892-6875(00)00173-4

[5] V. Safari, G. Arzpeyma, F. Rashchi, and N. Mostoufi, "A shrinking particle—shrinking core model for leaching of a zinc ore containing silica," Int. J. Miner. Process., vol. 93, no. 1, pp. 79–83, Sep. 2009.
http://dx.doi.org/10.1016/j.minpro.2009.06.003

[6] F. K. Crundwell, N. du Preez, and J. M. Lloyd, "Dynamics of particle-size distributions in continuous leaching reactors and autoclaves," Hydrometallurgy, vol. 133, pp. 44–50, Feb. 2013
http://dx.doi.org/10.1016/j.hydromet.2012.11.016

[7] A. R. Kacham and a. K. Suri, "Application of a topochemical reaction model to predict leaching behavior of high carbonate uranium ores in alkaline solutions: An experimental case study," Hydrometallurgy, vol. 141, pp. 67–75, Jan. 2014.
http://dx.doi.org/10.1016/j.hydromet.2013.10.005

[8] L. R. P. de Andrade Lima and D. Hodouin, "A lumped kinetic model for gold ore cyanidation," Hydrometallurgy, vol. 79, no. 3–4, pp. 121–137, Oct. 2005.
http://dx.doi.org/10.1016/j.hydromet.2005.06.001

[9] S. C. Bouffard and D. G. Dixon, "Evaluation of kinetic and diffusion phenomena in cyanide leaching of crushed and run-of-mine gold ores," Hydrometallurgy, vol. 86, pp. 63–71, 2007.
http://dx.doi.org/10.1016/j.hydromet.2006.11.004

[10] S. Bellec, D. Hodouin, and C. Bazin, "Modelling and simulation of gold ore leaching," in World Gold Conference 2009, 2009, pp. 51–60.

[11] A. Ahmadi, M. Ranjbar, M. Schaffie, and J. Petersen, "Kinetic modeling of bioleaching of copper sulfide concentrates in conventional and electrochemically controlled systems," Hydrometallurgy, vol. 127–128, pp. 16–23, Oct. 2012.
http://dx.doi.org/10.1016/j.hydromet.2012.06.010

[12] X. Wang, Q. Chen, H. Hu, Z. Yin, and Z. Xiao, "Solubility prediction of malachite in aqueous ammoniacal ammonium chloride solutions at 25 ° C," Hydrometallurgy, vol. 99, no. 3–4, pp. 231–237, 2009.
http://dx.doi.org/10.1016/j.hydromet.2009.08.011

[13] W. Liu, M. T. Tang, C. B. Tang, J. He, S. H. Yang, and J. G. Yang, "Thermodynamics of solubility of Cu2(OH)2CO3 in ammonia-ammonium chloride-ethylenediamine(En)-water system," Trans. Nonferrous Met. Soc. China (English Ed., vol. 20, no. 2, pp. 336–343, 2010.

[14] F. R. Carrillo-Pedroza, M. J. Soria-Aguilar, E. Salinas-Rodríguez, A. Martínez-Luevanos, T. E. Pecina-Treviño, and A. Dávalos-Sánchez, "Oxidative Hydrometallurgy of Sulphide Minerals," in Recent Researches in Metallurgical Engineering - From Extraction to Forming, M. Nusheh, Ed. InTech, 2012.

[15] M. I. Brittan, "Variable activation energy model for leaching kinetics," Int. J. Miner. Process., vol. 2, pp. 321–331, 1975.
http://dx.doi.org/10.1016/0301-7516(75)90026-5

[16] M. J. Nicol, C. A. Fleming, and G. Cromberge, "Absorption of gold cyanide onto activated carbon. II. Application of the kinetic model to multistage absorption circuits.," Journal of The South African Institute of Mining and Metallurgy, vol. 84, no. 3. pp. 70–78, 1984.

[17] J. McLaughlin and G. E. Agar, "Development and application of a first order rate equation for modelling the dissolution of gold in cyanide solution," Miner. Eng., vol. 4, no. 12, pp. 1305–1314, Jan. 1991.
http://dx.doi.org/10.1016/0892-6875(91)90174-T

[18] L. R. P. D. A. Lima and D. Hodouin, "A lumped kinetic model for gold ore cyanidation," vol. 79, pp. 121–137, 2005.

[19] F. Vegliò, M. Trifoni, F. Pagnanelli, and L. Toro, "Shrinking core model with variable activation energy: a kinetic model of manganiferous ore leaching with sulphuric acid and lactose," Hydrometallurgy, vol. 60, no. 2, pp. 167–179, Apr. 2001.
http://dx.doi.org/10.1016/S0304-386X(00)00197-3

[20] F. Habashi, "Kinetics and mechanisms of gold and silver dissolution in cyanide solution," Bulletin of the Berau of Mines and Geology, 1967.

[21] M. Tang and T. Zhao, "Thermodynamic study on the basic and negative potential fields of the systems of Sb-S-H//2O and Sb-Na-S-H//2O.," Zhongnan Kuangye Xueyuan xuebao, vol. 18, no. 1, pp. 35–43, 1988.

[22] S.-H. Yang and M.-T. Tang, "Thermodynamics of Zn(II)-NH3-NH4Cl-H2O system," Trans. Nonferrous Met. Soc. China (English Ed., vol. 10, no. 6, pp. 830–833, 2000.

[23] J. Suni, H. Henein, G. W. Warren, and D. Reddy, "Modelling the leaching kinetics of a sphalerite concentrate size distribution in ferric chloride solution," Hydrometallurgy, vol. 22, no. 1–2, pp. 25–38, Jun. 1989.
http://dx.doi.org/10.1016/0304-386X(89)90039-X
[24] A. Velardo, M. Giona, A. Adrover, F. Pagnanelli, and L. Toro, "Two-layer shrinking-core model: parameter estimation for the reaction order in leaching processes," Chem. Eng. J., vol. 90, no. 3, pp. 231–240, Dec. 2002.
http://dx.doi.org/10.1016/S1385-8947(02)00038-4
[25] B. A. Wills, Will's Mineral Processing Technology, 7th ed. New York: John Wiley & Sons, Ltd, 2006.