

Mathematical Simulation of Acid Concentration Effects during Acid Nitric Leaching of Cobalt from a Mixed Cobalt-Copper Oxide

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Abstract—Cobalt was acid nitric leached from a mixed cobalt-copper oxide with variable acid concentration. Resulting experimental data were used to analyze effects of increase in acid concentration, based on a shrinking core model of the process. The mathematical simulation demonstrated that the time rate of the dissolution mechanism is an increasing function of acid concentration. It was also shown that the magnitude of the acid concentration effect is time dependent and the increase in acid concentration is more effective at earlier stage of the dissolution than at later stage. The remaining process parameters are comprehensively affected by acid concentration and their interaction is synergetic.

Keywords—Acid effect, Cobalt, Cobalt-copper oxide, Leaching, Simulation

I. INTRODUCTION

LEACHING process is one of the most frequently employed techniques in extractive metallurgy for the recovery of value using aqueous solutions. Low energy consumption, reduced environmental pollution, and the ability to treat low grade ores are amongst attracting features which motivate its application in hydrometallurgical routes. Over the past few decades, numerous pieces of work were conducted on the dissolution of minerals aiming at understanding, controlling and optimizing effects of process parameters on the extraction yield [1]-[16]. Attempts to deduce quantitative relations between the process parameters and extraction yield are reported [1]-[16]. These kinds of relations are useful for the development of optimization procedures and the design of control loops in industrial processes. The understanding of the process behaviour and its supervision through process control technics are essential for optimal economic performance of the plant.

Besides the above, cobalt is considered as a strategic material of modern industry; its global demand has steadily increased over decades and its application extends over a variety of fields including rechargeable batteries, superalloys used in turbines and turbo reactors, pigment, colour agent, corrosion resistant alloys, catalyst and magnetite. Cobalt is obtained mostly as a by-product of other metals such as copper and nickel. Recently it has been recognized that the African copper belt deposit of mixed copper-cobalt oxide is set to

become a major source of cobalt at global level [16] and driven by increasing environmental pressure, extraction route will preferentially head toward hydrometallurgical methods such as roast-leach-electrowin (RLE) and direct whole leach (WOL)[17].

Whereas modelling is useful for a better understanding and optimization of the process, no reported work have been found on the modelling of process parameter effects during the dissolution of cobalt from mixed copper-cobalt oxide. The present paper reports on a mathematical simulation of effects of acid concentration during acid nitric leaching of cobalt from a mixed copper-cobalt oxide. The simulation was based on a shrinking core model [18], [19] of the process. The metal was acid leached at a reference acid concentration. Then, based on the shrinking core mechanism [18], [19], a mathematical model was determined by fitting of experimental data. The acid concentration was subsequently varied, then the resulting experimental data was introduced in the model and effects of the variation in acid concentration were mathematically analysed based on the model.

II. EXPERIMENTAL

Experimental data were obtained from previous experiments where cobalt was nitric acid leached from the mixed cobalt-copper oxide originated from central Africa. The leaching was conducted in a 500 ml glass beaker at solid to liquid ratio of 23.6. The solid particles size was set at 80% less than 75 μm . The temperature was kept constant at 25°C and stirring speed at 300 rpm [20]. The reference acid concentration was 0.6M. Then all the remaining parameters being the same, the metal was also leached at two other acid concentrations 1.2 M and 2 M. Resulting experimental data are presented in Figure 1.

Experimental data obtained at the reference concentration were tested according the shrinking core model (SCM) of solid-fluid heterogeneous reaction [17, 18]. The model is expressed as an equation where the first member is a function of the extraction yield and the second member a function of time and process parameters. The first member of the equation is denoted $f(x)$ and the second member $t^a \times g(u_i)$. Extraction yield, time and process parameters are respectively

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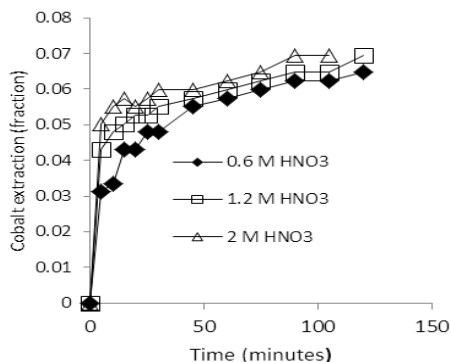


Fig. 1 Cobalt dissolution in function of time at three different acid concentrations

TABLE I
TEST OF EXPERIMENTAL DATA AGAINST SHRINKING CORE MODEL

Model mechanism	$f(x)$	R^2 Coefficient of linear correlation between $f(x)$ and $t^{1/2}$
SCM, kinetics controlled by diffusion through the solid ash layer (spherical particle)	$1 - \frac{2}{3}(1-x)^{3/2} + \frac{1}{3}(1-x)^{3/2}$	0.978
Kinetics controlled by diffusion through the solid ash layer (flat plate grain)	x^2	0.978
Mixed kinetics determining steps (diffusion through solid layer and mass transfer through liquid film)	$\frac{1}{3} \ln(1-x) - \left[1 - (1-x)^{1/3} \right]$	0.980

denoted x , t and u_i . The model is verified generally by testing the linear correlation between $f(x)$ and t^a while $g(u_i)$ is kept constant [1]-[16]. The above experimental data represented in Figure 1 were found to fit a kinetics model determined by diffusion through solid ash layer and/or mass transfer through the liquid film, table I. Therefore the process was represented by the following mathematical model

$$\frac{1}{3} \ln(1-x) - \left[1 - (1-x)^{1/3} \right] = kC^b t^{1/2} \quad (1)$$

In equation (1) x , C and t respectively represent the dissolved fraction of metal, the acid concentration and the leaching duration. Factor k provides the measure of the comprehensive effect of the remaining process parameters. Exponent b is a positive or negative real number.

III. ACID CONCENTRATION EFFECTS

A. Effect on time exponent

Experimental data obtained at 1.2 M and 2 M acid concentration were also introduced in the model to investigate effects of increase in acid concentration. Table II shows that the coefficient of linear correlation decreased with increasing acid concentration. This suggested a change in the process mechanism.

TABLE II
EFFECT OF ACID CONCENTRATION ON THE PROCESS MECHANISM

Model mechanism	$f(x)$	R^2 Coefficient of linear correlation between $f(x)$ and $t^{1/2}$
		0.6 M 1.2 M 2 M
Mixed kinetics determining steps (diffusion through solid layer and mass transfer through liquid film)	$\frac{1}{3} \ln(1-x) - \left[1 - (1-x)^{1/3} \right]$	0.980 0.842 0.663

The increase in acid concentration was expected to speed up the process. As a result the mechanism ought to obey a higher time rate, subsequently the time exponent in the model to decrease. To better view and interpret this effect the time exponent was varied in diminution. Then the coefficient of correlation, the acid concentration and the time exponent were graphically represented as shown in Figure 2

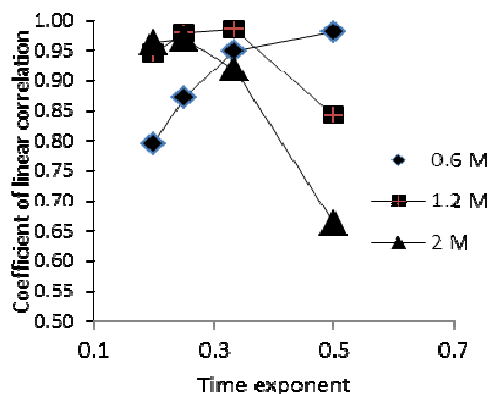


Fig. 2 Change in time exponent as a function of acid concentration

Figure 2 shows the variation of the coefficient of correlation R^2 in function of time exponent for each acid concentration. As the best fit corresponds to the highest R^2 on the curve, by comparing the three concentration curves it can be seen that the best fit shifts from the highest to the lowest time exponent when the acid concentration increases. This demonstrates that the increase in acid concentration affects the whole process mechanism by increasing the time rate of the mechanism. Subsequently the mathematical expression of the model evolves with the increase in acid concentration through time exponent as shown in equation (2) and table III

$$\frac{1}{3} \ln(1-x) - \left[1 - (1-x)^{\frac{1}{3}} \right] = kC^b t^a \quad (2)$$

TABLE III
EFFECT OF ACID CONCENTRATION ON TIME EXPONENT

Acid concentration	a
0.6 M	1/2
1.2 M	1/3
2 M	1/5

B. The magnitude of the effect of acid concentration

The magnitude of acid concentration effects is measured by the exponent b in equation (1). The exponent b was subsequently analysed based on equation (1) when the acid concentration varies at constant time. Only three level of concentration was made available from the experimental database. Then based on equation (1), all other process parameters being constants, $\ln[f(x)]$ was plotted against $\ln(C)$ to determine the exponent of the acid concentration. The later was graphically determined as the slope of the obtained experimental curve. With only three available experimental points, the graphical determination was not statistically viable. However, using several constant value of time, good enough number of plots was generated to provide a

statistical trend of the slope in function of time. Obtained values of the acid concentration exponent are shown in function of time in Figure 3.

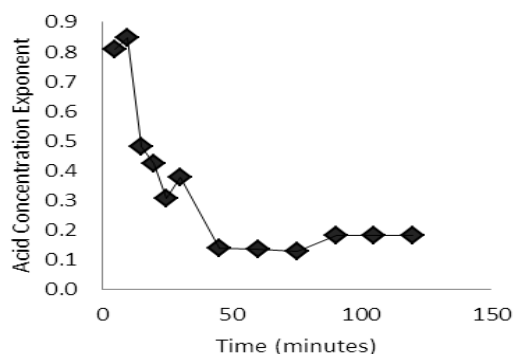


Fig. 3 Variation of the exponent of acid concentration during leaching

The plot clearly shows the decreasing trend of acid concentration exponent with increasing leaching time. It also reveals two different kinetics steps, the first one up to about thirty minutes where the decrease is fast and the second one where the decrease is almost totally dumped. To understand this it was resorted to the fact that the process kinetics is determined by the diffusion through the ash layer. Hence as the leaching time increases, the product layer increases in size and in density. As a consequence the resistance to diffusion increases, then the magnitude of the effect of increase in acid concentration is subsequently dumped.

Obtained results imply that the acid concentration exponent is a decreasing function of time and the decreasing trend ought to be logarithmic or exponential in order to be consistent with the type of mechanism described in the previous paragraph. The variation function was numerically determined by mathematical regression as shown in Figure 4 and equation (3)

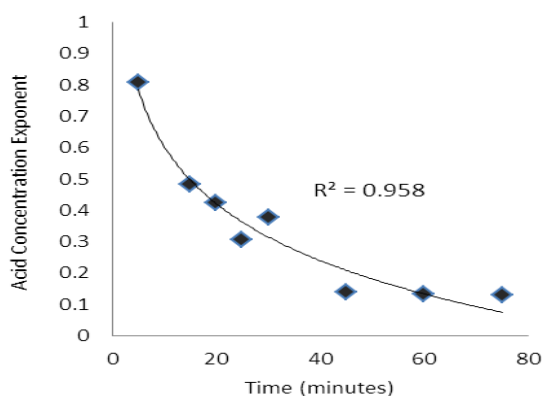


Fig. 4 Acid concentration exponent in function of time

$$b(t) = -0.262 \ln(t) + 1.207 \quad (3)$$

C. Effect on the remaining process parameters

All the remaining process parameters being constant, consequently the coefficient k in equation (2) should remain constant. Its value was determined from the plot of $\ln[f(x)]$ against $\ln(C)$. According to equation (2), $\ln(kt^a)$ is equal to the intercept of the plot on $\ln[f(x)]$ axe. As the time exponent varies with the acid concentration, its value was averaged between the three concentrations for a first estimation of the coefficient k . The latter was then computed for each time and results are shown in table IV.

TABLE IV
EXPERIMENTAL VALUES OF COEFFICIENT k IN FUNCTION OF TIME

Time (minute)	$k \times 10^5$
5	5.0
10	4.7
15	5.4
20	5.0
25	5.2
30	5.1
45	5.2
60	5.1
75	5.1
90	5.3
105	-
120	5.3
AVG	5.1
Std	0.2

The first estimate of k was then used in equation (2) and empirically adjusted to fit each time exponent. This means, the value of k was modified until to obtain an acceptable equality between $f(x)$ and $t^a \times g(u_i)$ as requested by the model in equation (2). The function $f(x)$ was computed for each concentration, using experimental values of metal extraction. The second member of the equation (2) was also computed for each concentration, using experimental values of time. Then if coefficient k is correct, values of the two members of equation (2) obtained from experimental data should be equals. The graphical comparison is shown in Figures 5 to 7 and obtained values of coefficient k are shown for each concentration in table V

TABLE V
FACTOR k IN FUNCTION OF ACID CONCENTRATION

Acid concentration	k
0.6 M	2.6×10^{-5}
1.2 M	5.1×10^{-5}
2 M	8.0×10^{-5}

From table V, it could be noticed that the factor k increases with increasing acid concentration

IV. DISCUSSION AND CONCLUSION

Experimental data pertaining to the nitric acid dissolution of cobalt from a mixed cobalt-copper oxide were analysed based on the shrinking core mechanism with a kinetics determined by the diffusion through the ash layer and the fluid film. The analysis consisted in a mathematical simulation of acid concentration effects.

Increase in acid concentration introduced significant modifications of the leaching process as expressed by equations (2) and (3), and tables III and V.

It was observed that increase in acid concentration speeds up the whole process. This was shown by the subsequent decrease in time exponent in the equation of the model, denoting a higher time rate of the whole process. So the time exponent in the model is a decreasing function of the acid concentration and the mathematical expression of the model evolves with the acid concentration.

The analysis also revealed that the process mechanism affects the acid concentration effect. Due to increased resistance to diffusion resulting from the increase in size and density of the ash layer, it was shown that the magnitude of the concentration effect is time dependant. It decreases with increased leaching time. So the increase in acid concentration is more effective at earlier stage of the leaching than at later stage. The above could also provide explanation to the quick initial dissolution followed by a slow kinetics generally observed during metal leaching.

The analysis demonstrated also that the acid concentration interacts effectively with the remaining process parameters as shown through the variation of the factor k that represents effects of the remaining process parameters in equation (2). The increasing trend of k when the acid concentration increases shows that the interaction is synergetic.

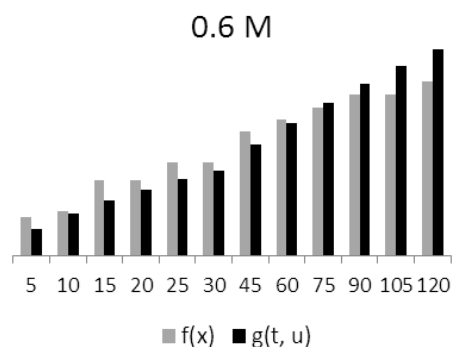


Fig. 5 Model fitting at 0.6 M

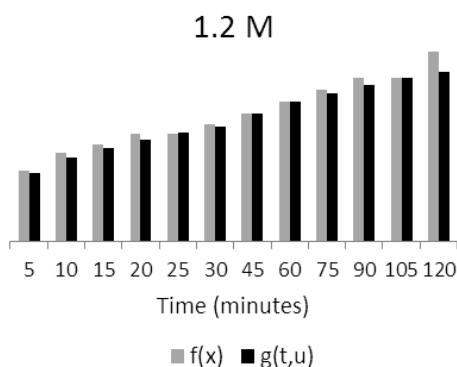


Fig. 6 Model fitting at 1.2 M

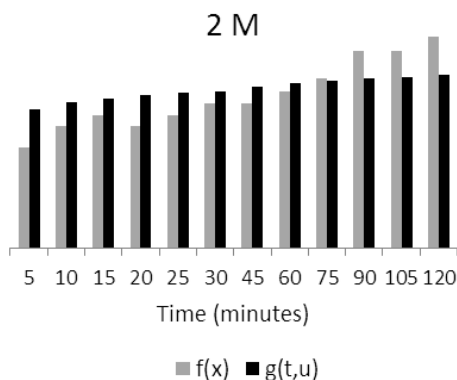


Fig. 7 Model fitting at 2 M

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