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# MODELING OF

# THE LEACHING OF OXIDE COPPER ORES

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BUREAU OF MINES

by

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16. Abstract (Limit: 200 words)


A model for the leaching of oxide ores is developed and correlated with laboratory tests for percolation leaching of copper oxide ore. Using the model, recovery of metal values and lixiviant concentration of the effluent solution at any time may be evaluated. For the copper oxide ore a simplified version of the model is examined for the leaching mechanism consisting of: 1) a surface flush reaction with the highest rate of lixiviant consumption; 2) penetration of lixiviant to react with copper minerals and gangue constituents; and, 3) slow lixiviant consumption, mostly by residual gangue materials. The simplified model is able to explain reasonably the leaching behavior of copper oxide ore by introducing a concept of effective initial size to correct for packing in a bed of fine particles.


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The results presented in this report include and extend many of the concepts developed by William Averill (Ref. 15) relative to the leaching of copper from low grade copper ores.

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MODELING OF THE LEACHING OF OXIDE COPPER ORES

by

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SUMMARY

The object of the work presented in this report was to refine the maximum gradient model with phenomenological concepts drawn reasonably from the experimental data for the leaching of copper oxide ores. A mathematical formulation was derived from a consideration of material balance and simplified for copper oxide leaching on the basis of physical and chemical concepts. The leaching behavior of the copper oxide ores was analyzed according to a semi-empirical model in this study. Intrinsic kinetic parameters determined from batch leach tests have been successfully extended to predict results for flow systems simulating conditions expected in dump leaching and solution mining applications.

## INTRODUCTION

In recent years interest in hydrometallurgy, particularly in the case of in-situ leaching and solution mining has remained at a high level (1, 2). There are several studies published on the development of scale-up principles. D'Andrea and Runke (3) described research on in-situ copper leaching at the Emerald Isle Mine whose dominant copper mineral is chrysocolla. The program was directed to develop in-situ leaching methods for 200,000 tons of ore exposed in a pit bottom and also 1,500,000 tons of ore under 200 feet of overburden adjacent to the pit. Ito (4) described the problems involved in the application of an in-place leaching technique in Japan. Ranchers Exploration published results for the in-situ copper leaching at Old Reliable (5) (4,000,000 tons of mixed oxide-sulfide ore) and Big Mike Mine (6) (475,000 tons of mixed ore). In each case, the effort was similar in nature, a full scale experimental trial. Lewis et al. (7) have made an economic analysis of the in-situ extraction of copper, gold and uranium. The extraction technology and economics for these metals have much in common.

Modeling is a mathematical tool that attempts to explain all phenomena in terms of the associated physics and chemistry. Modeling from first principles alone is certainly a worthy goal for the long term but is not totally realistic at the present time because of the complexity of solution mining systems and the lack of fundamental data. Attempts to relate laboratory results to field conditions has met with some degree of success. Grimes (8) developed a penetration model to predict uranium extraction rates in underground bacterial leaching of an as blasted ore. The model is based upon the hypothesis that extraction is directly proportional to the volume of a piece of ore that is penetrated by the leaching agent, and that each piece of ore, regardless of size, has been penetrated radially from external surface to the same depth at a given leaching time. The modeling of leach dumps and in-situ systems of low grade copper sulfides has received much attention. A physicochemical model based upon the continuity equation for oxygen in spherical coordinates was developed by Bartlett (9) and examined for leaching of copper sulfide ores. A reaction zone model introduced by Braun et al. (10) has been successfully applied to primary copper sulfide ores and more recently to secondary copper sulfides (11). The same type of model was applied to a kinetic study of the acid leaching of chrysocolla (12). A modified steady-state approximation of the continuity equation has been applied by Madsen and Wadsworth (13) to the leaching of enriched copper sulfide ores.

The modeling of the leaching of copper oxide ores has not received as much attention as sulfide leaching. The acid leaching of copper oxide ores generates a vertical acid concentration gradient in the ore heap, which is not generally observed in sulfide deposits. Shafer et al. (14) have verified Roman's model (15) and were able to predict the leaching behavior for a relatively large scale column test on coarse ore. However, the model has limitations with respect to acid consumption predictions. More recently a diffusion model was incorporated with a maximum gradient, plug flow model (16) to estimate acid consumption and its subsequent influence on leaching kinetics.

The object of this work is to refine the maximum gradient model with phenomenological concepts drawn reasonably from the experimental data. A mathematical formulation is derived from a consideration of the material balance and simplified for copper oxide leaching on the basis of phenomenological concepts. The leaching behavior of the copper oxide ores is analyzed according to the semi-empirical model employed in this study. The application of the maximum gradient model is confined to laboratory results only in this study. Hopefully the analysis provides an adequate basis for extension to field in-situ conditions.

## EXPERIMENTAL

The copper oxide ore used in this study was supplied by Occidental Minerals Corporation from their Cerrillos property near Santa Fe, New Mexico, and was in the form of broken core samples consisting of chunks averaging four inches in diameter. A mineralogical report indicated that the sample contained predominantly neotocite (Fe, Mn, Cu) $SiO_3$ as blebs and specks on fracture surfaces, and brochantite $CuSO_4.3Cu(OH)_2$ was present in lesser amounts as crystals and masses on fracture surfaces, along with traces of finely disseminated copper pitch. The presence of copper in a predominantly manganese-iron precipitate was noted using emission spectroscopy. Table I summarizes the results of porosity tests and assays (16).

TABLE A. Density, Porosity and Grade of Ore

| size interval (mm) | density ($gm/cm^3$) | porosity (1%) | Cu grade (wt %) | Fe grade (wt %) |
|---|---|---|---|---|
| 26.9 x 13.5 | 2.4 | 3 | 0.382 | 0.88 |
| 13.5 x 4.76 | 2.4 | 3 | 0.365 | 0.94 |
| 4.76 x 3.36 | 2.4 | 3 | 0.401 | 0.97 |
| 3.36 x 2.36 | 2.4 | 3 | 0.377 | 0.84 |
| 2.36 x 1.70 | 2.4 | 3 | 0.416 | 0.86 |

The material was crushed and screened into the size fractions used and referred to in each of the experiments. The experiments were carried out with mono-sized material in small diameter columns. Glass tubes, 4.1 cm diameter by 45 cm long and PVC tubes, 5.5 cm diameter by 122 cm long were used for the percolation leach experiments. Figure 1 illustrates the systems used in these leaching tests. Reagent grade sulfuric acid was used to make a solution of desired acidity. The solution in a reservoir was pumped into a constant head tank, which was used to guarantee a constant flow rate. The solution was distributed at the tops of the

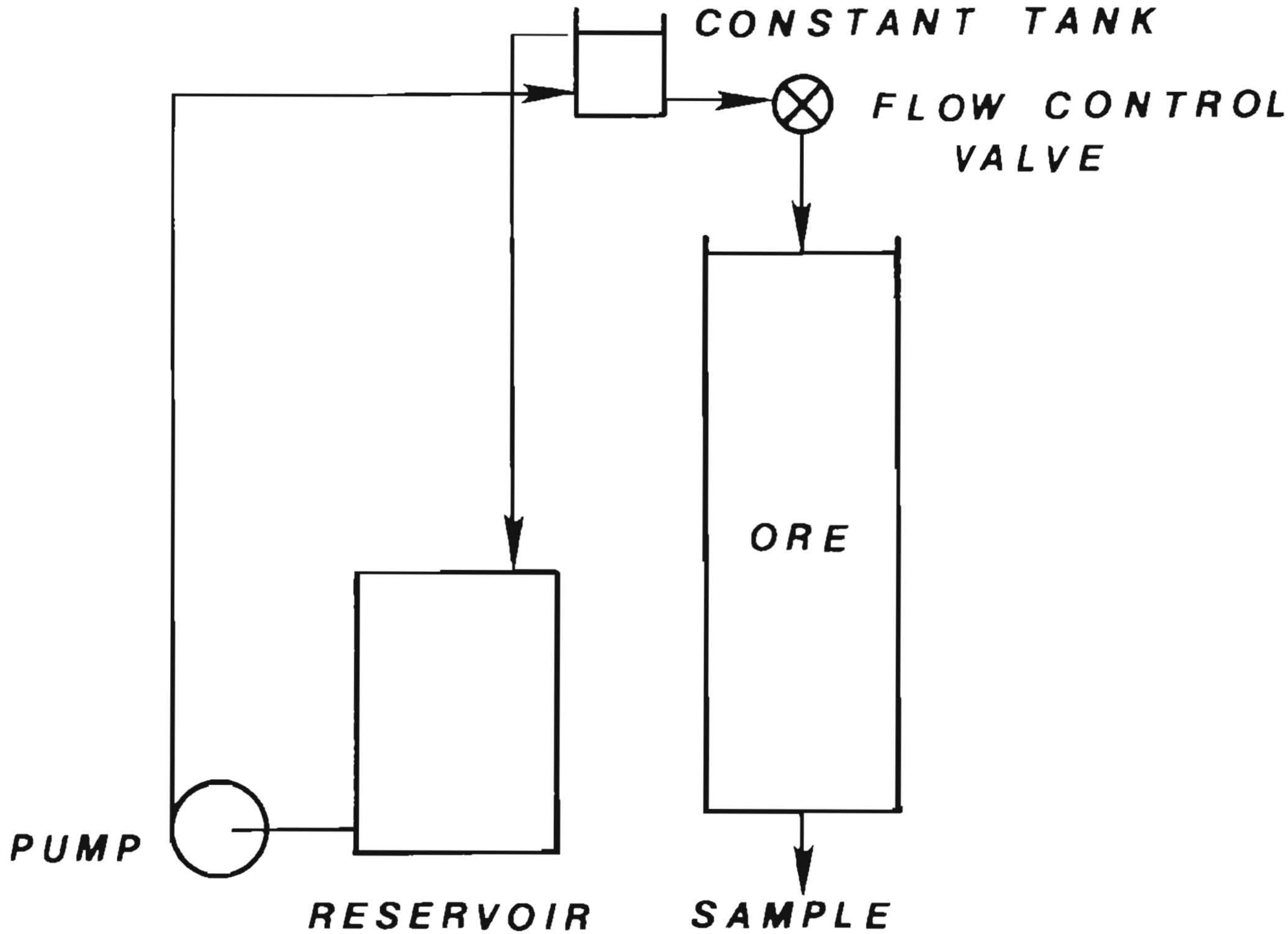


Figure 1. Schematic representation of the apparatus used in this study.

columns with a glass wool pad. The volume of the solution collected at the bottom of the column was measured, sampled and assayed for various time intervals. At the conclusion of each experiment the ore was drained and a sample taken for total copper. A Perkin-Elmer model 305 atomic absorption spectrophotometer was used for analysis.

Batch tests were carried out using a 0.5 ℓ round bottom flask provided with stirrer and fritted glass sampler. Approximately 25 g of ore were added to 0.3 ℓ of solution. Agitation was not sufficient to suspend the course particles but was that needed to pump the solution freely through the bed of coarse particles resting on the flask bottom. Results indicated the agitation was sufficient to eliminate interparticle diffusion as rate limiting thus providing particle reaction kinetics for subsequent use in the general model. Solution samples of 10 $cm^3$ were removed at regular intervals for solution analysis.

## MATHEMATICAL FORMULATION

A general model based upon the equation of continuity for mass transport, incorporating intrinsic kinetic parameters, was developed. For a cylindrical column of cross sectional area A and of lenght L, assuming plug flow, the lixiviant balance consideration yields

$$\frac{\partial c(x,t)}{\partial t} + \frac{\upsilon}{\varepsilon}\frac{\partial c(x,t)}{\partial x} = \dot{R}$$

$$c(0,t)_r = \text{feed concentration}, \quad c(x,0) = 0 \qquad (1)$$

where $\upsilon$ and $\varepsilon$ are solution velocity and fractional void space respectively, $\dot{R}$ is net rate of generation of lixiviant per volume of liquid, and x is the distance measured from the top of the column. Assuming spherical ore particles, the rate of diffusion of lixiviant within an ore particle at position r may be given by

$$n = -D\,\frac{4\pi r^2}{\phi}\,\frac{\partial c(x,r,t)}{\partial r} \qquad (2)$$

where $\phi$ is the geometry factor and D is the diffusivity of the lixiviant through the pore space of the particle, which may be allowed to vary. From consideration of the lixiviant balance in spherical coordinates the lixiviant concentration profile c(x,r,t) in an ore particle may be expected to satisfy the equations

$$\frac{\partial c(x,r,t)}{\partial t} = (\dot{r}) + \frac{1}{\varepsilon_p r^2}\,\frac{\partial}{\partial r}\,r^2 D\,\frac{\partial c(x,r,t)}{\partial r}$$

$$c(x,r_o,t) = c(x,t), \quad c(x,r,0) = 0, \quad \left.\frac{\partial c(x,r,t)}{\partial r}\right|_{r=o} = 0 \qquad (3)$$

where $\varepsilon_p$ is the porosity of the ore particle and $(\dot{r})$ is the net rate of generation of the lixiviant per volume of liquid in the ore particle.

The term $\dot{R}$ may be related to $n$ by

$$\dot{R} = nd \quad + \quad \text{(other terms)} \tag{4}$$

where d is number density of the ore particles of radius $r_0$ in the column and (other terms) include net lixiviant generation outside or at the surface of the ore particles; for instance, the effect of salt precipitation and/or dissolution if any. For a narrow ith size fraction in a broad particle size distribution, equations (3) for $c(x,r_i,t)$ with $c(x,r_{io},t) = c(x,t)$ are coupled with equation (1) through $\dot{R} = \Sigma_i n_i d$ + (other terms). In principle, the concentration profile within the column and ore particles may be obtained. In the case of copper oxide leaching, the lixiviant is hydrogen ion. Copper recovery can then be calculated from the knowledge of the stoichiometry; i.e. moles of copper releated for each mole of hydrogen ion consumed.

A shrinking core model was applied in this analysis to examine the validity of the general formulation applied to copper oxide leaching. Essentially the model involves quasi-steady state diffusion of the lixiviant through the previously reacted portion of the ore particles, followed by chemical reaction at the surface of the unreacted core. Mathematically this model may be identified with the reaction zone model proposed by Braun et. al. (10). Since small size fractions of ore have been used for this study the surface reaction term may not be negligible compared to the diffusion component. Models involving diffusion only have been used by several investigators (14,16) to explain the leaching behavior of oxide ores in columns.

Assuming quasi steady state, equation (2) may be integrated with respect to distance only, to yield $(c(x,t)=c(x,r_{io},t))$

$$n_i = -\frac{4\pi r_{oi} r_i}{\phi_i (r_{oi} - r_i)} \; D_e \; (c(x,t) - c(x,r_i,t)) \tag{5}$$

where $D_e$ is effective diffusivity of the lixiviant through the reacted shell of the particle. The effective diffusivity is related to the porosity of the reacted portion of solid and the tortuosity, $\tau$, by the equation $D_e = D\epsilon_p/\tau$.

If the chemical reaction at the surface at radius $r_i$ is assumed to be first order, $n_i$ may be expressed as

$$n_i = - \frac{4\pi r_i^2}{\phi_i} kc(x,r_i,t) \qquad (6)$$

where k is the reaction rate constant. Eliminating $c(x,r_i,t)$ from (5) gives

$$n_i = - \frac{4\pi r_{oi}^2}{\phi_i} \frac{c(x,t)}{\frac{r_{oi}}{D_e}\frac{r_{oi}-r_i}{r_i} + \frac{r_{oi}^2}{k\ r_i^2}} \qquad (7)$$

The number of moles of copper in an ore particle or radius $r_i$ is

$$\left(\frac{4\pi}{3} r_i^3\right) \times (\text{ore density}, \rho_i) \times (\text{Cu grade})$$

The rate of reaction may then be expressed for a given particle as

$$\frac{d}{dt}\left(\frac{4\pi}{3} r_i^3 \rho_i \alpha_i\right) = n_i \qquad (8)$$

where $\sigma$ = (Cu grade) x (stoichiometry factor). It is useful to express the rate in terms of fraction reacted, $\alpha_i(x,t)$. For a given particle of initial radius $r_{io}$

$$\alpha_i(x,t) = 1 - \frac{r_i^3(x,t)}{r_{oi}^3} \qquad (9)$$

Substituting $\alpha_i(x,t)$ for $r_i$ in equation (8) gives the rate equation

$$\frac{d\alpha_i(x,t)}{dt} = \frac{3}{\rho_i \sigma_i r_{oi}} \frac{c(x,t)}{\frac{r_{oi}}{D_e}\left((1-\alpha_i(x,t)^{-1/3}-1\right) + \frac{1}{k}\left(i-\alpha_i(x,t)\right)^{-2/3}} \qquad (10)$$

where $\sigma_i$ includes the geometry factor. Equation (10) is coupled with equation (1) through equation (4) to give $\alpha_i(x,t)$ and $c(x,t)$. Since equation (10) is derived from the shrinking core model (or the reaction zone model) there must be no lixiviant consumption in the reacted portion of the ore particle. In the study of copper oxide leaching, the consumption of acid is too high to be explained by copper release alone, particularly in the later stages of leaching. An independent term due to gangue materials has, therefore, to be taken into account for $\dot{R}$, the net rate of generation of acid in the column. In this investigation $\dot{R}$ is represented by three different constants corresponding to the three stages of leaching, which will be described in the following section. Equation (1) may then be written as

$$\frac{\partial c(x,t)}{\partial t} + \frac{\upsilon}{\varepsilon}\frac{\partial c(x,t)}{\partial x} = -\left(\sum_i \frac{B_{i\ell}}{r_{oi}}\right)c(x,t)$$

$$B_{i\ell} = \begin{cases} B_{i1} & 0 \le t < t_1 \\ B_{i2} & t_i \le t < t_2 \\ B_{i3} & t_2 \le t \end{cases} \tag{11}$$

In general $t_1$ and $t_2$ depend upon the sizes i. For a multi-particle sized ore $B_{i\ell}$ includes the weight fraction $w_i$ of the size i. Total fraction reacted $\alpha(x,t)$ at x is given by

$$\alpha(x,t) = \sum_i w_i \alpha_i(x,t) \tag{12}$$

The fraction reacted for the entire column $\alpha_T(t)$ is given by

$$\alpha_T(t) = \frac{1}{L}\int_0^L \alpha(x,t)\ dx. \tag{13}$$

## RESULTS AND DISCUSSION

The overall behavior of copper oxide leaching is revealed in Figures 2 and 3. As seen in Figure 2 the effluent hydrogen ion concentration reaches a certain fraction of the feed concentration in several days of leaching and varies slowly afterward. The acid is consumed continuously even after leaching most of the copper. Figure 3 is a plot of copper recovery represented by fraction reacted of an ore particle versus a "normalized" hydrogen ion consumption. Normalized is defined as the cumulative amount of hydrogen ion consumed divided by the total original amount of copper in the column. As seen in Figure 3, within experimental error, a linear relationship between copper recovery and acid consumption can be stated as a characteristic of leaching behavior. The deviation from linearity may be ascribed mostly to the gangue materials consuming acid independently from copper minerals. Coarser materials may be expected to consume more acid for the same degree of copper recovery. From the linear relationship the stoichiometry factor of 3.9 on a mole basis is indicated.

In order to investigate ore particle kinetics for the leaching, batch tests were conducted for different initial acid concentrations. The acidity was allowed to vary in the process of leaching. The study of the batch tests suggested the following mechanism of the leaching behavior; (i) flushing of the ore surfaces with the highest rate of acid consumption, (ii) penetration of acid to react with copper mineral and gangue constituents, (iii) slow acid consumption mostly by gangue materials. Figure 4 shows the results of the batch tests. Solid lines are calculated on the basis of the leaching mechanism described above. The effective diffusivity of $1.19 \times 10^{-7}$ $cm^2/sec$ and the surface reaction rate constant of $1.11 \times 10^{4}$ cm/sec were determined. As seen in Figure 5 the logarithm of normalized hydrogen ion concentration (pH - initial pH) can be represented by two different slopes within the period of time considered. The normalized effluent hydrogen ion concentration for slow systems are shown in Figures 2, 6, 7, and 8. The concentrations can also be represented by

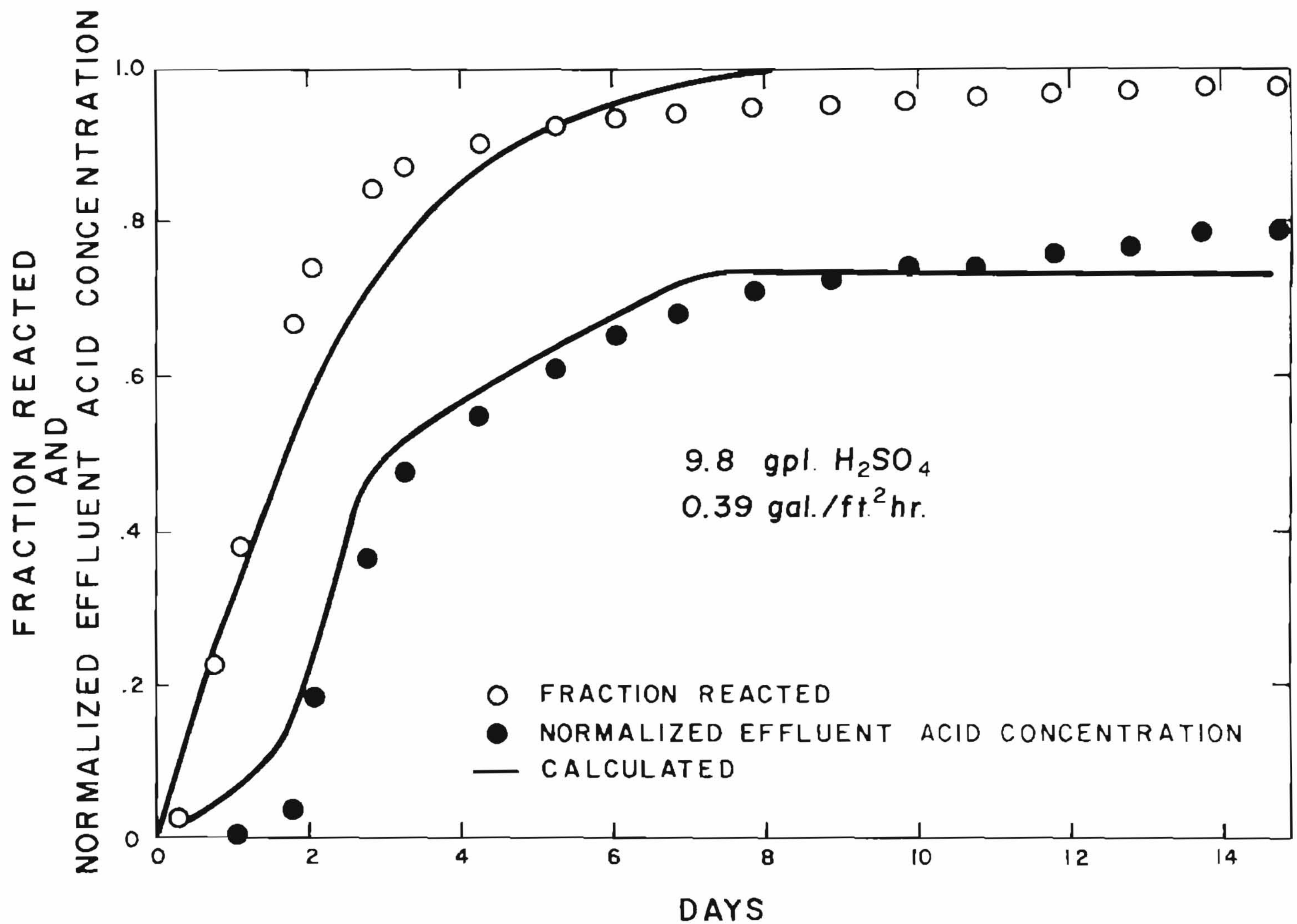


Figure 2. The copper recovery and normalized effluent acid concentration data for 2.36 x 1.70 mm ore.

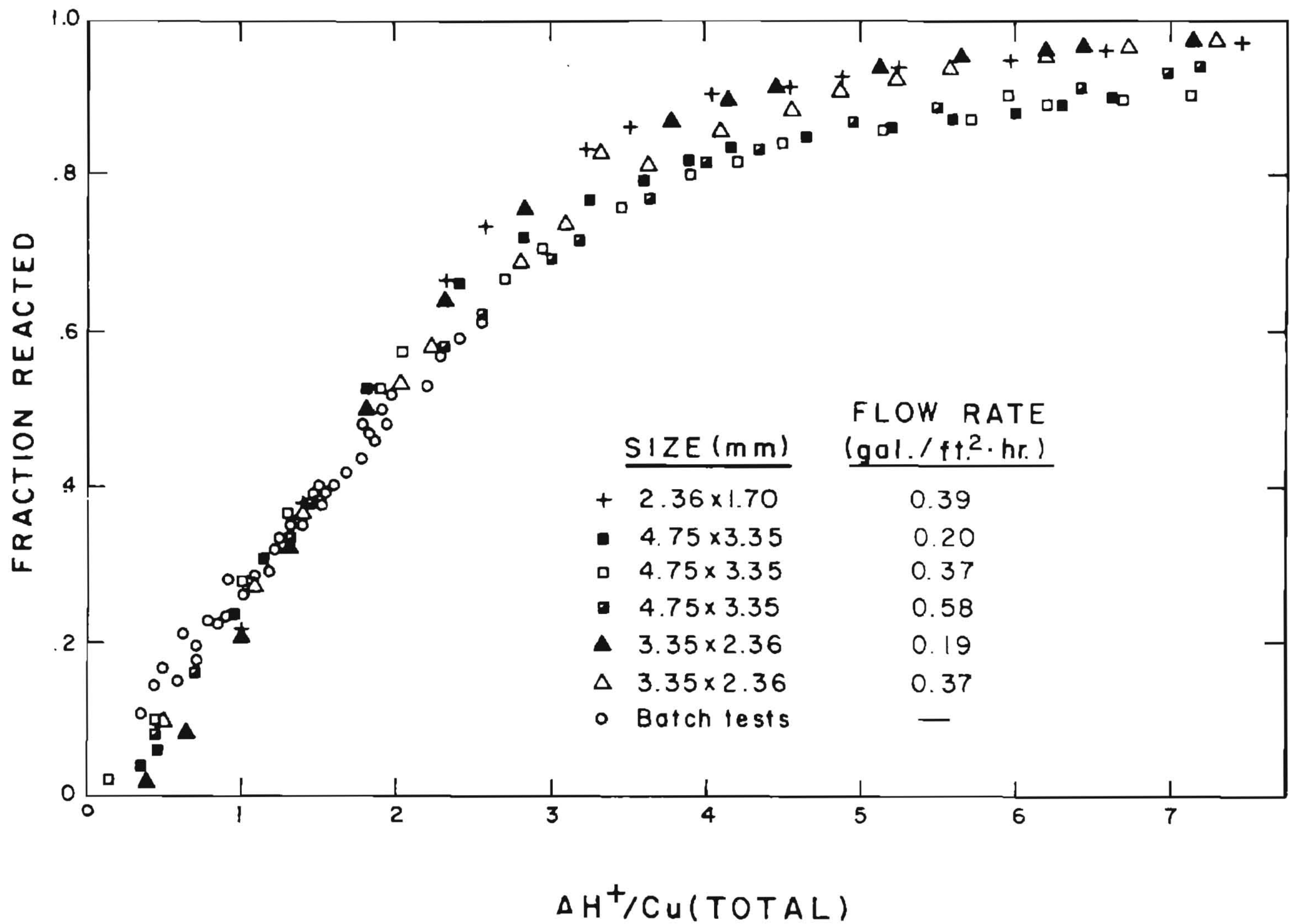


Figure 3. Copper recovery versus normalized acid consumption, cumulative acid consumption divided by total original copper in the column.

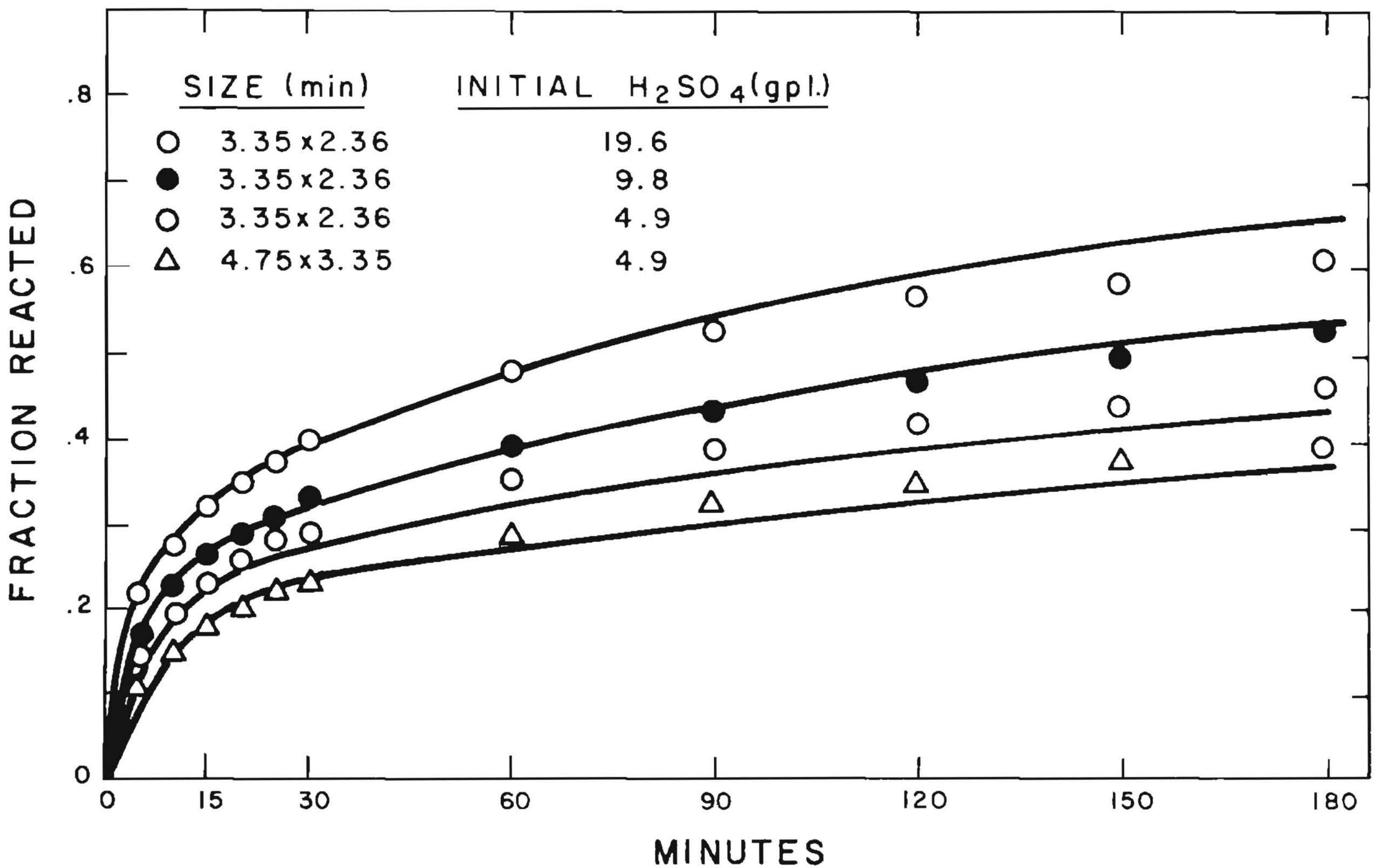


Figure 4. Batch test data. Solid lines represent calculated curves according to the model.

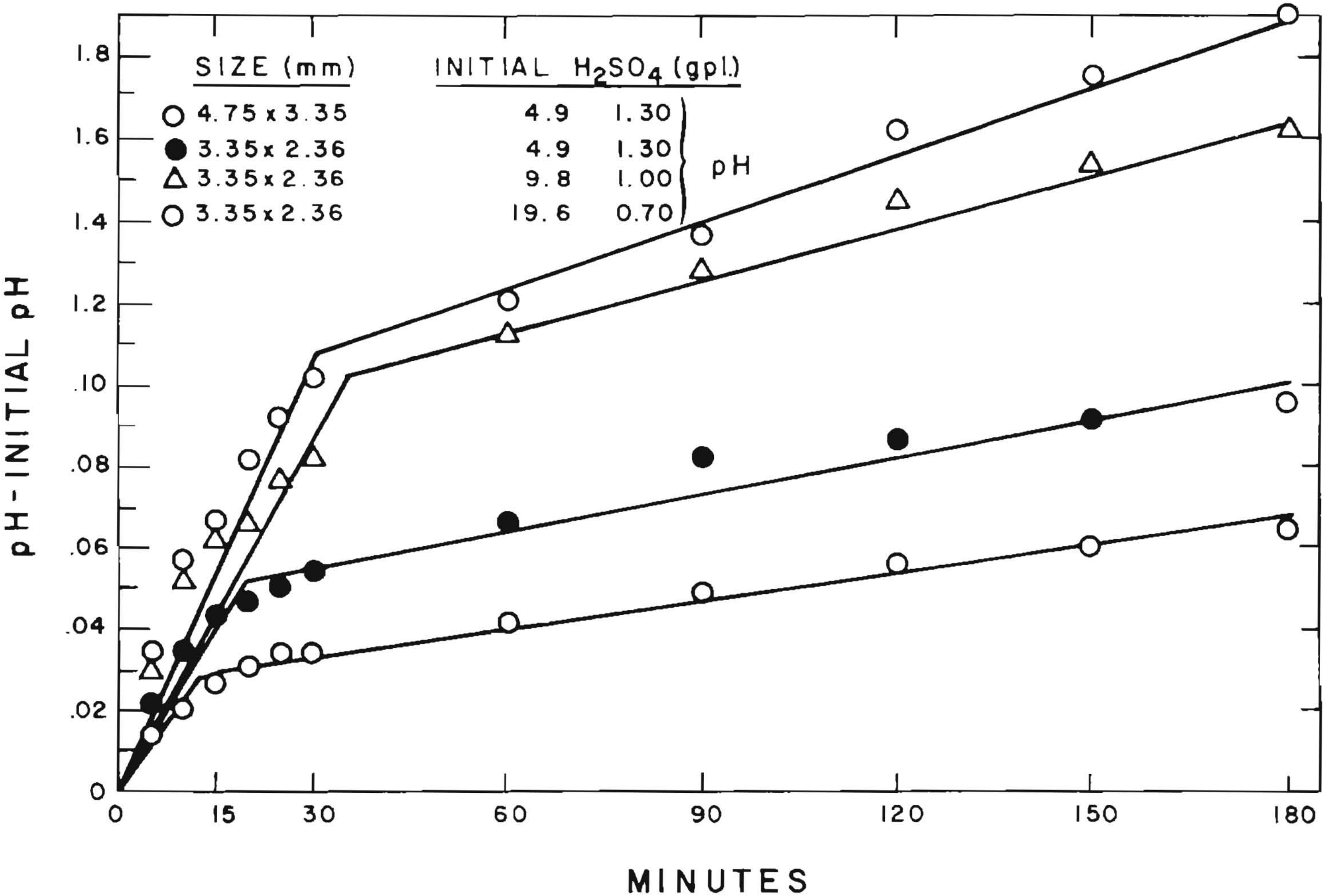


Figure 5. Batch test data. Solid lines are used for the calculation of copper recovery shown in Figure 3.

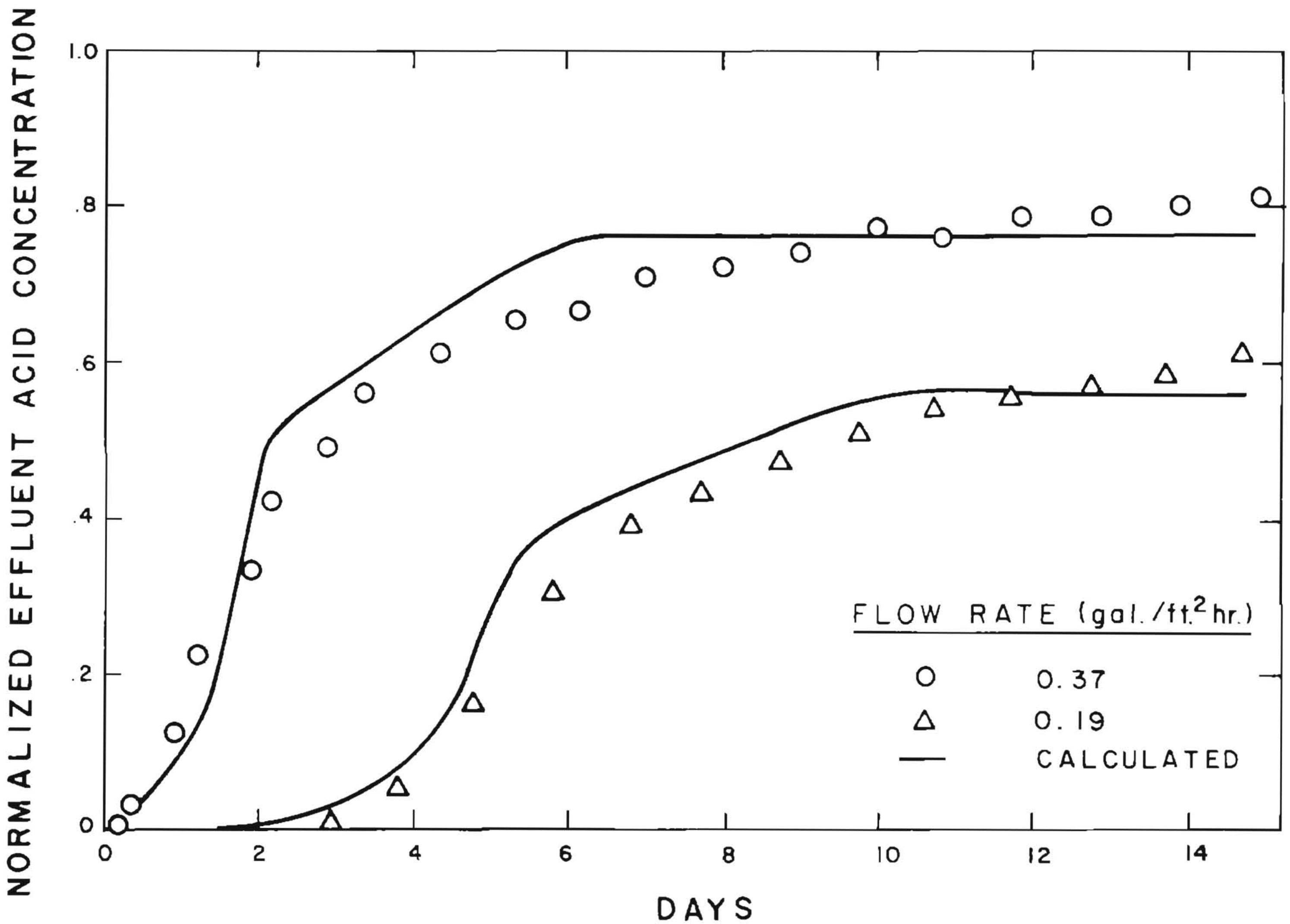


Figure 6. The normalized hydrogen ion concentration of effluent solution for 3.36 x 2.36 mm ore. Feed acid was 9.8 gpl $H_2SO_4$.

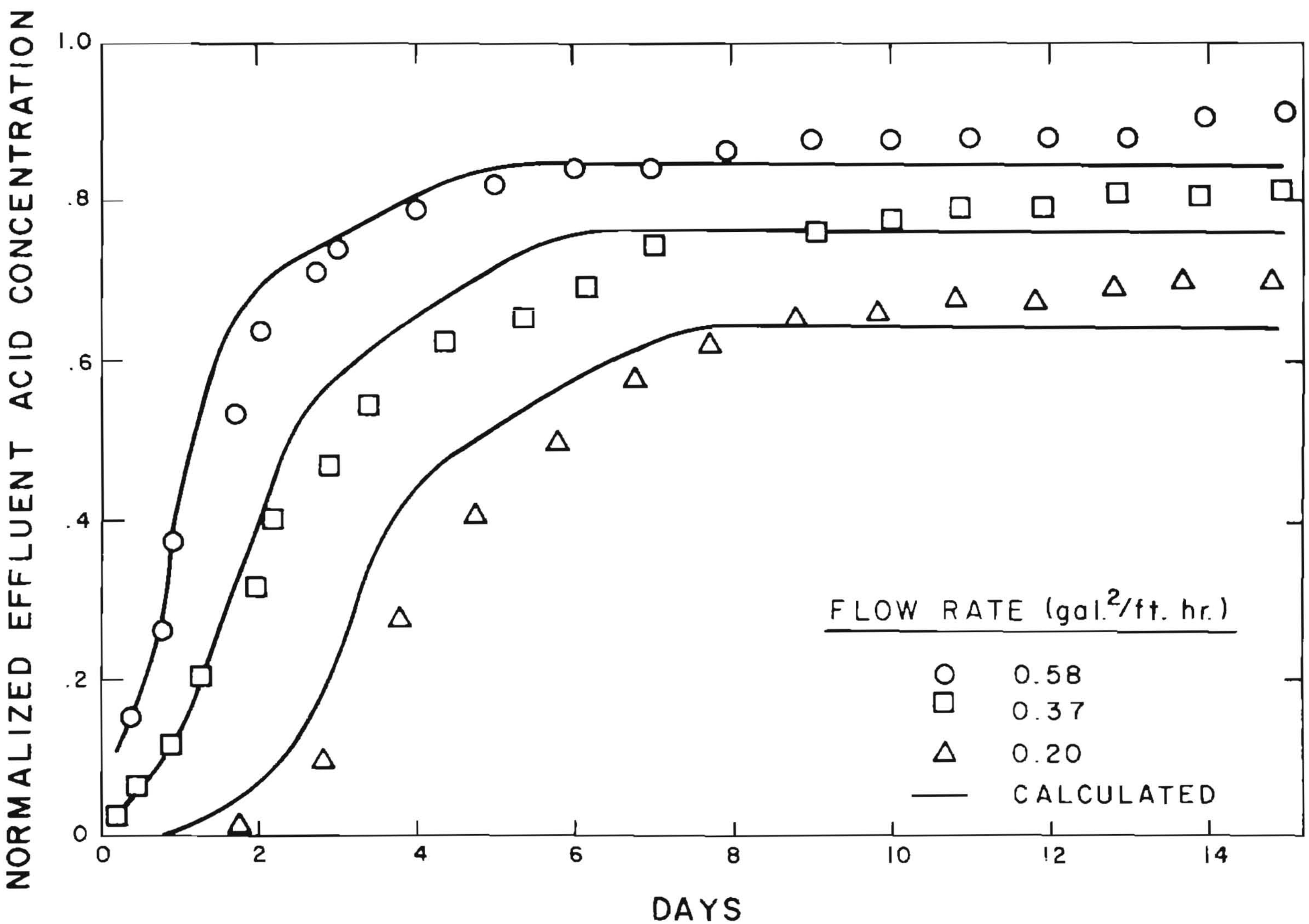


Figure 7. The normalized hydrogen ion concentration of effluent solution for 4.76 x 3.36 mm ore. Feed acid was 9.8 gpl $H_2SO_4$.

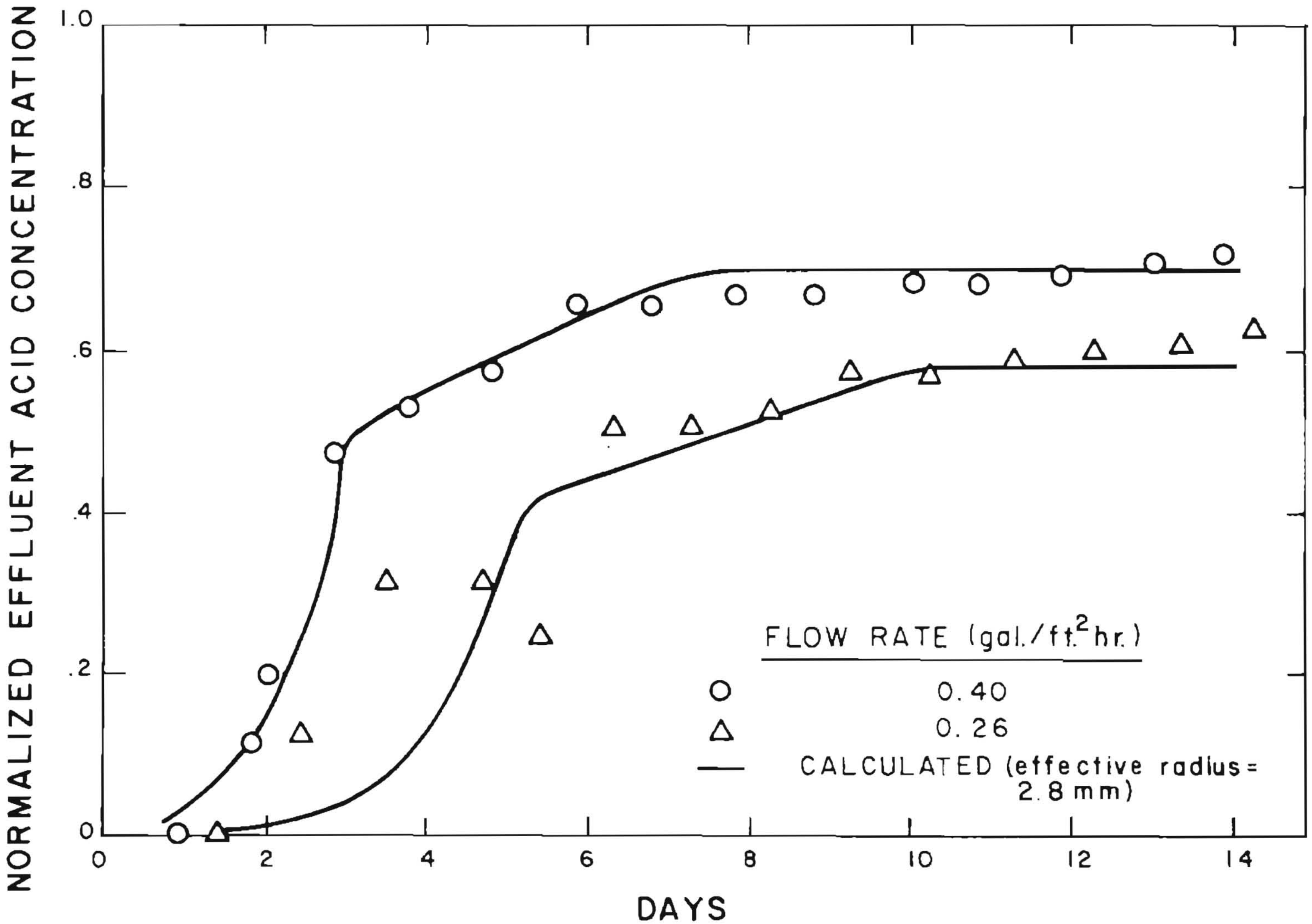


Figure 8. Inundated column leach data for two flow rates. Feed acid was 9.8 gpl $H_2SO_4$.

three lines, which may correspond to the three stages respectively. Because of the gangue constituents the first two constants may not precisely correspond to the first two stages respectively. There may be two types of gangue consuming acid. One can be treated independently from copper mineral. This is mainly responsible for acid consumption in later stages of leaching. The other is associated with the oxidized copper minerals. The behavior of the acid consumption, which may be described by the three stages, may be noted in Figure 3. In the batch tests the third stage was not reached, as is evident in the figure. Equation (11) was the result of introducing these three numbers.

The column is arbitrarily divided into increments. Since the same equations given in (10) and (11) hold for every increment, equation (11) is solved assuming an average concentration $\bar{c}_i(t)$ over the increment. The average concentration is then used to obtain average fraction reacted $\bar{\alpha}_i(t)$ over the increment from equation (10). Introducing the flushing stage the rate equation handled in this study is expressed as, for each increment

$$\frac{d\bar{\alpha}_i(t)}{ddt} = \frac{3k}{\rho_i \sigma_i r_{oi}} \bar{c}_i(t) \qquad \text{for flushing } (0 \leq \bar{\alpha}_i(t) \leq \bar{\alpha}_{oi}) \tag{14}$$

$$\frac{d\bar{\alpha}_i(t)}{ddt} = \frac{3}{\rho_i \sigma_i r_{oi}} \quad \frac{\bar{c}_i(t)}{\frac{r_{io}}{D_e}\left((1-\bar{\alpha}_i'(t))^{-1/3} - 1\right) + \frac{1}{k}(1-\bar{\alpha}_i'(t))^{-2/3}}$$

$$\bar{\alpha}_i(t) = \alpha_{oi} + (1-\alpha_{oi})\ \bar{\alpha}_i'(t) \qquad \text{after flushing } (\bar{\alpha}_i(t) > \alpha_{oi}) \tag{15}$$

Further details in the computation are described in Appendix A.

It is noted that there is large difference in the rate between the flow system and the batch system. This difference may be ascribed to the channeling of the lixiviant resulting in; (a) different effective surface area, and (b) different effective initial size of the ore due to clustering and by-pass. The solid lines in Figures 6 through 13 are calculated from equations (11), (14) and (15) with (a) and (b) taken into account. An $\alpha_{oi}$ value of 0.16 and k of 0.49 cm/day were estimated from the data obtained

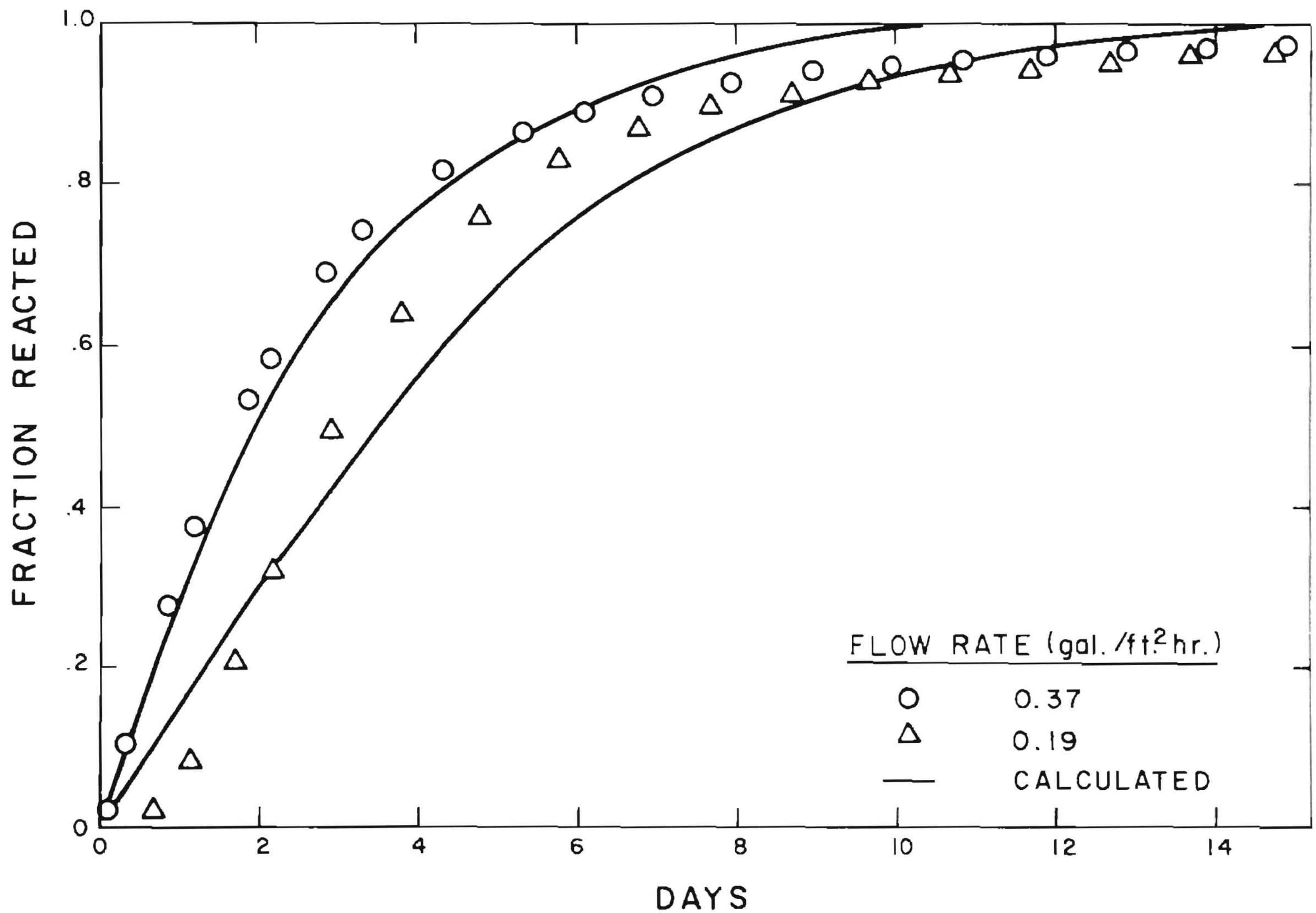


Figure 9. The copper recovery data for 3.36 x 2.36 mm ore. Feed acid was 9.8 gpl $H_2SO_4$.

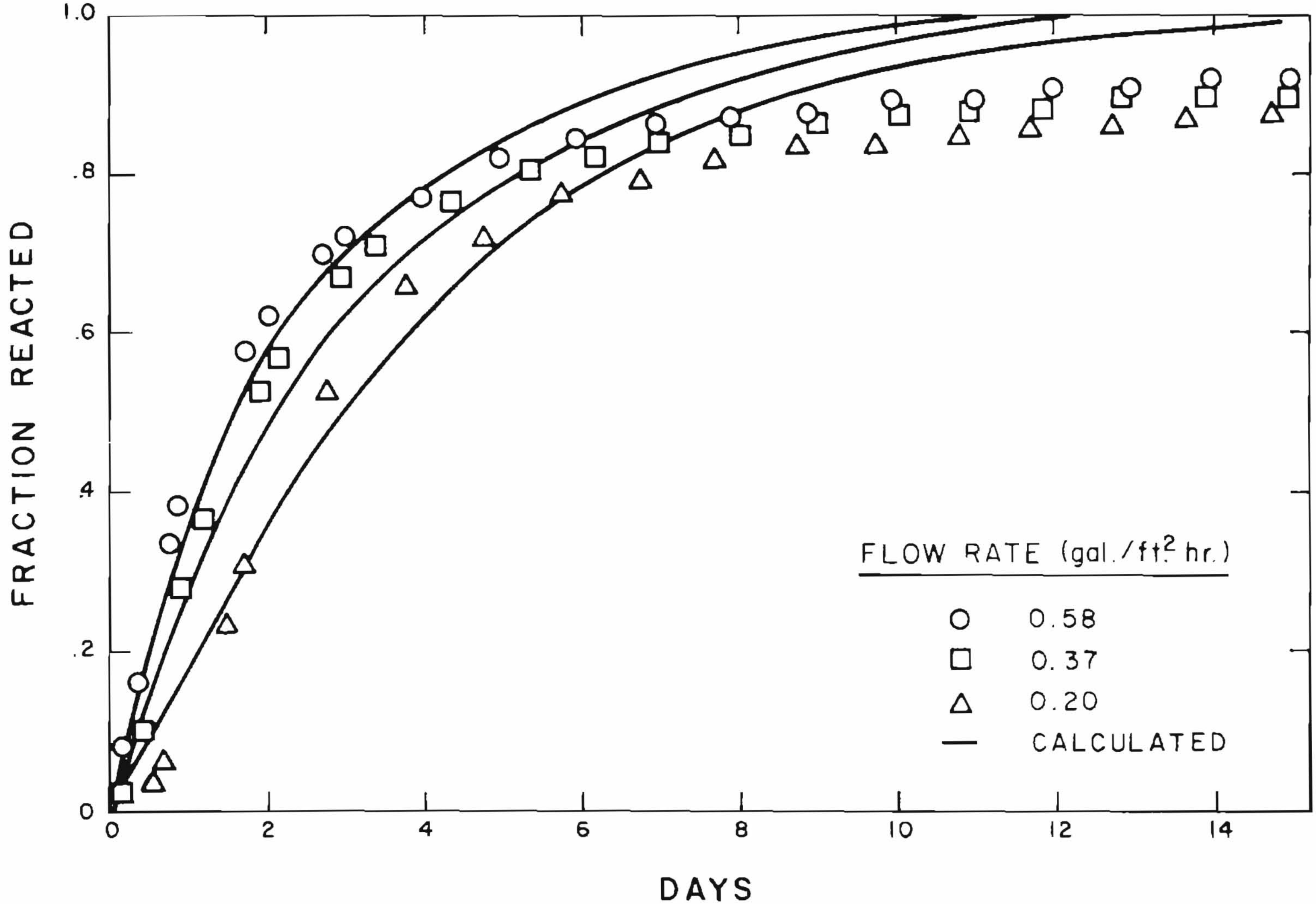


Figure 10. The copper recovery data for 4.76 x 3.36 mm ore. Feed acid was 9.8 gpl $H_2SO_4$.

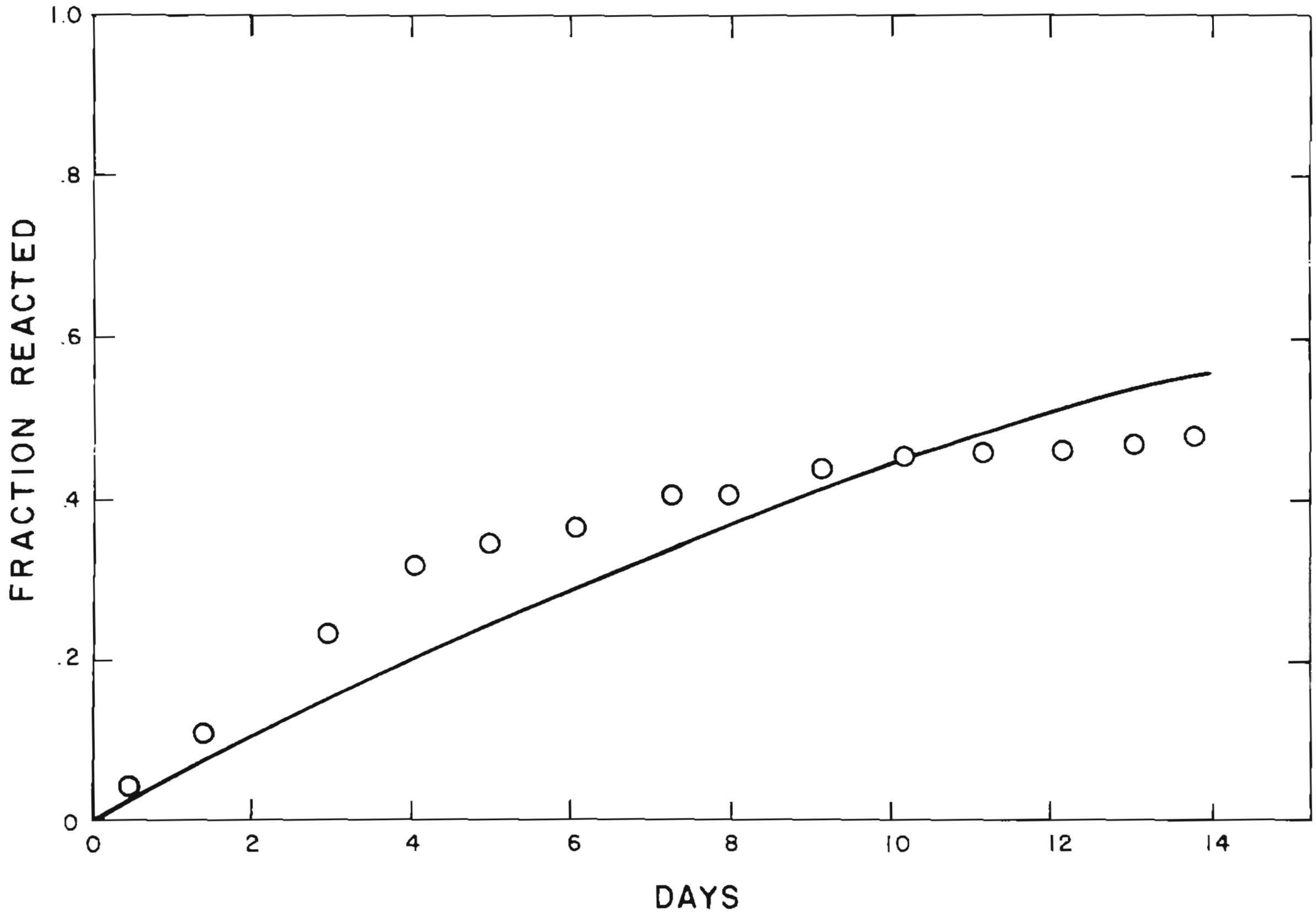


Figure 11. The copper recovery data for 13.5 x 4.76 mm ore at 0.2 gal/ft.$^2$hr. flow rate.

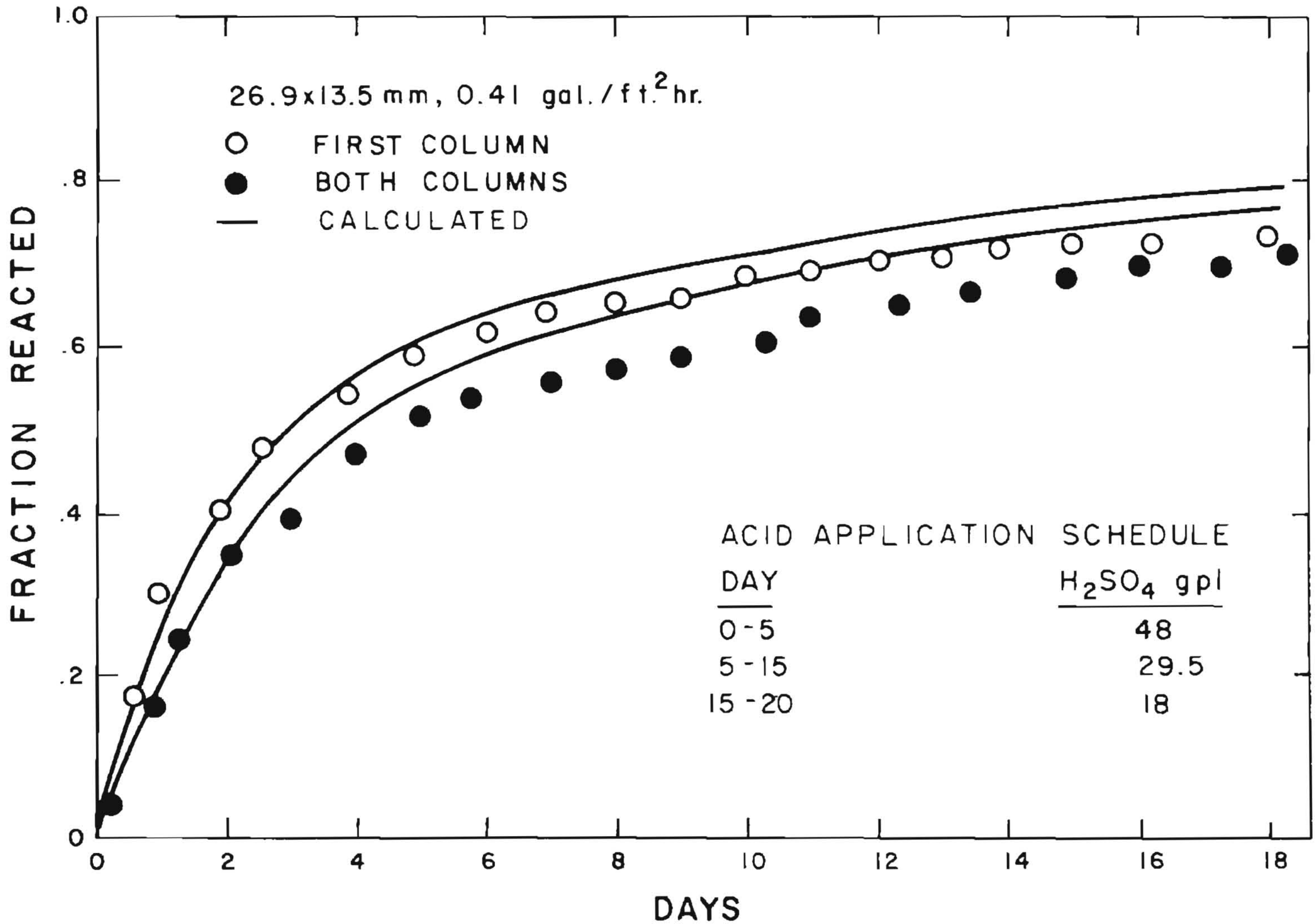


Figure 12. The copper conversion data for two columns operated in series.

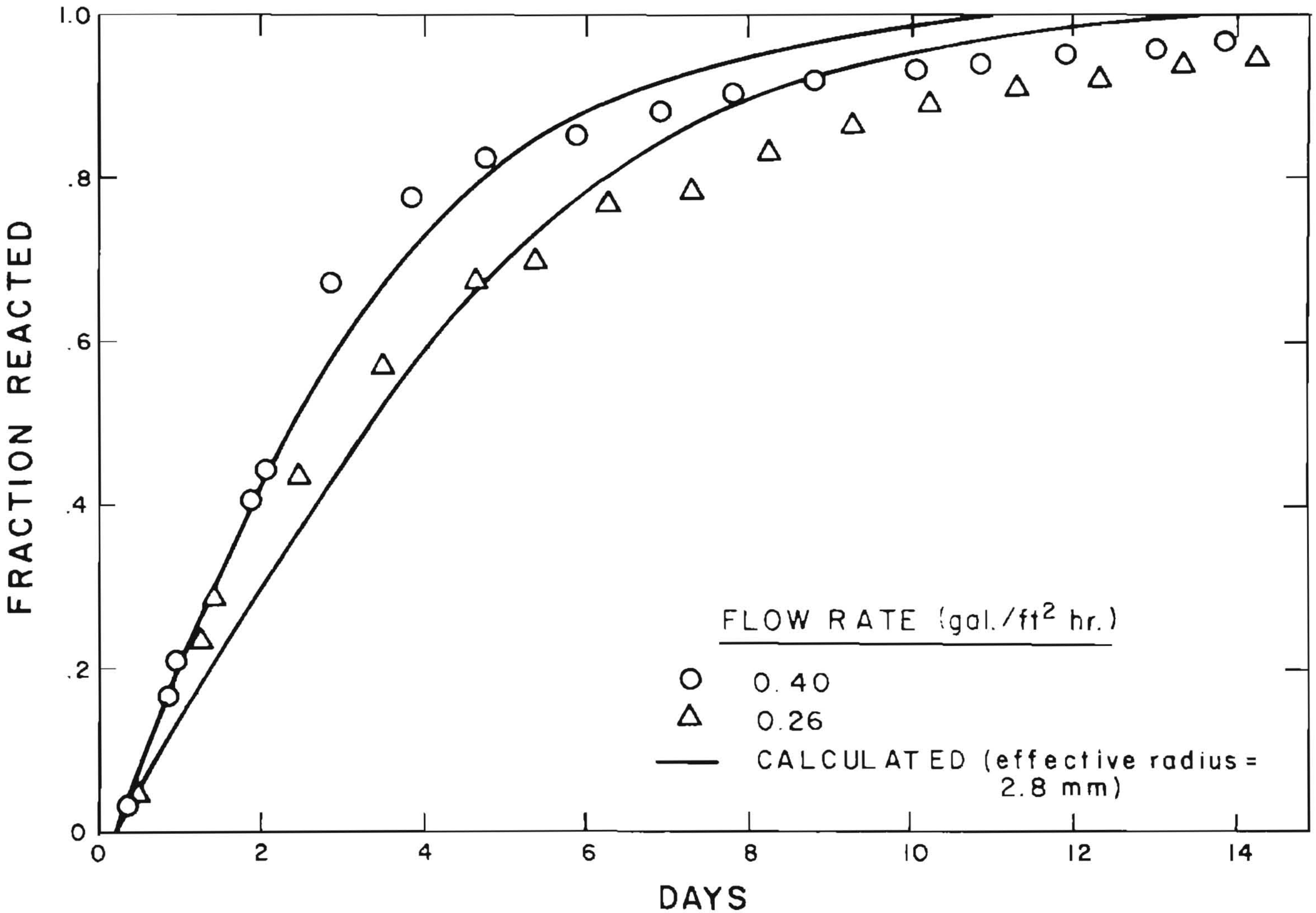


Figure 13. Inundated column leach data for two flow rates. Feed acid was 9.8 gpl $H_2SO_4$.

for the 3.35 x 2.36 mm ore. The same thickness ($r_{io} - r_i$) for $\alpha_{io} = 0.16$ from the 3.35 x 2.36 mm ore was used to estimate $\alpha_{io}$ of other sizes. Figure 14 shows the relationship between the actual initial size of ore and the effective initial size used in the calculation. A smaller difference between the two sizes is expected for large sizes. The surface reaction term is also expected to be less important for larger sizes. The profile of hydrogen ion concentration and that of copper recovery in the column calculated according to the model are depicted in Figures 15 and 16 for two cases indicated in the figures. The same type of behavior is obtained for other cases. The apparent steady-state condition is reached sooner and a higher hydrogen ion concentration of effluent solution is obtained for faster flow rates. This can be seen in Figures 6, 7, and 8.

Introduction of the three stages simplified the calculation and the use of an effective initial size and effective surface area made it possible to evaluate the column leach results based upon the batch tests. In spite of the simplicity of the model the agreement with the experimental data is reasonable without the difficulty noted by Shafer et. al. [13] on the variation of acid consumption of the ore as a function of copper extracted. For copper oxide leaching, a simplified version of the general formulation derived in the previous section may be used to model the leaching behavior for small scale column tests using mono-sized particles. The application of the model appears to be straight forward for multi-particle sized ore and extension to field conditions. The general formulation may also be applied to sulfide leaching and uranium leaching with appropriate modification for the leaching parameters.

It must be noted that the parameters $B_2$ were determined based upon the experimental data on the effluent acid concentration for every case. $B_0$ and $B_1$ were determined to provide a suitable data fit. As seen in Table XII there may be certain relationships between $B_2$ and $B_0$, and $B_2$ and $B_1$. Except one case (data from reference 2) $B_0/B_2$ and $B_1/B_2$ turned out to be around 12.5 and 2.1 respectively. For the ideal case, the parameters B may be proportional to (retained liquid volume x ore mass)/(solution flow rate x colume volume).

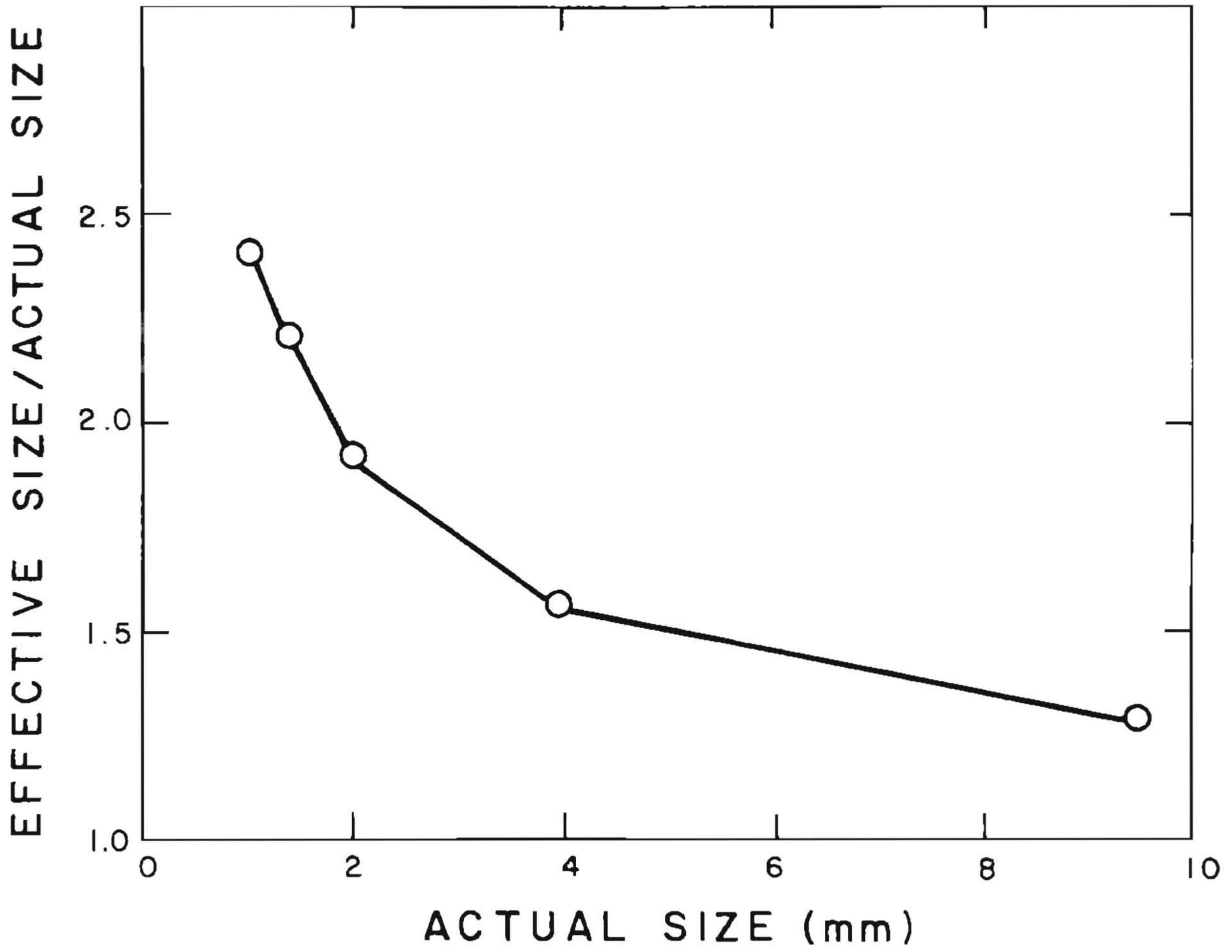


Figure 14. The relationship between the actual initial size and the effective initial size used for the calculations.

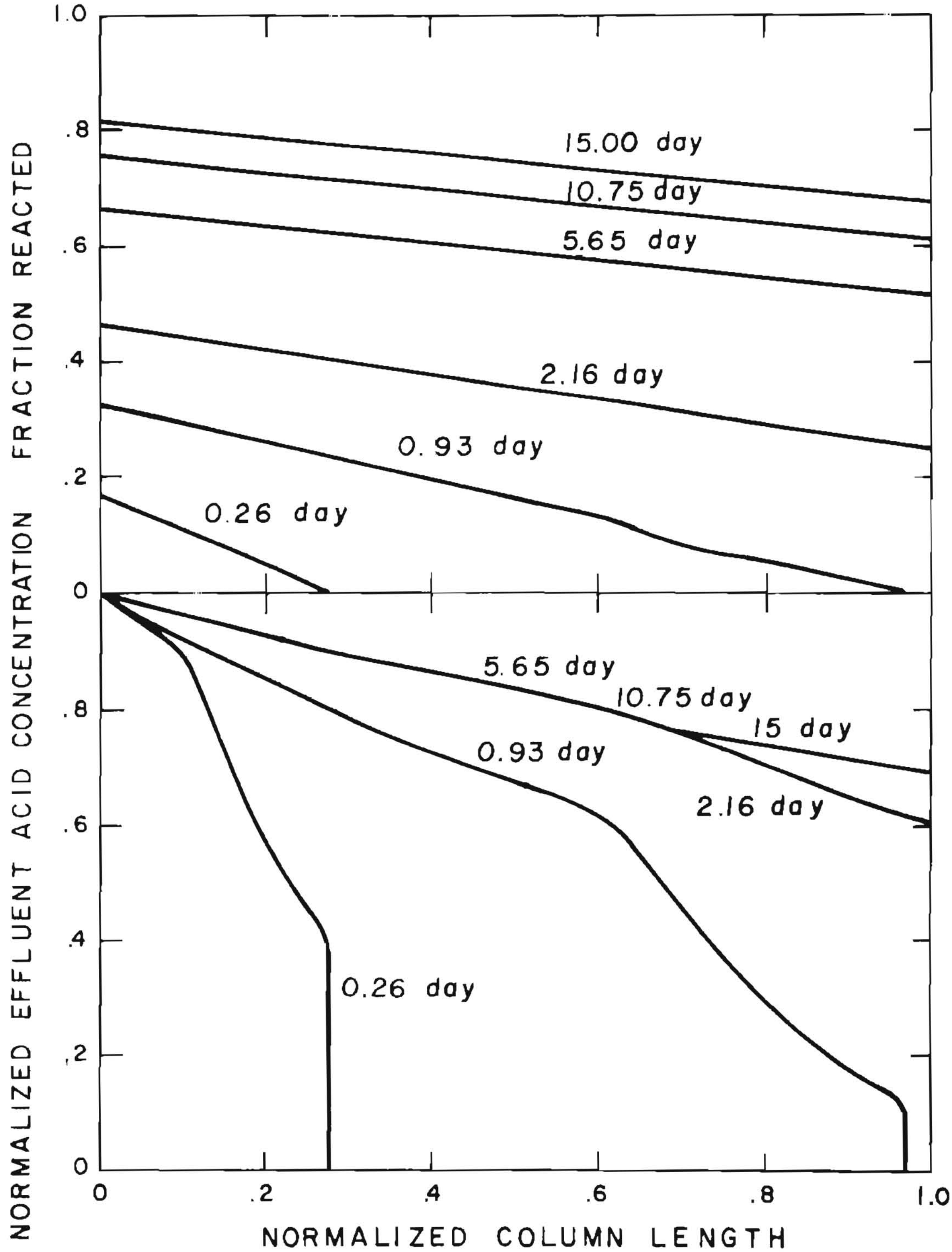


Figure 15. The copper recovery and normalized acid concentration profile calculated according to the model for the condition shown in Figure 12.

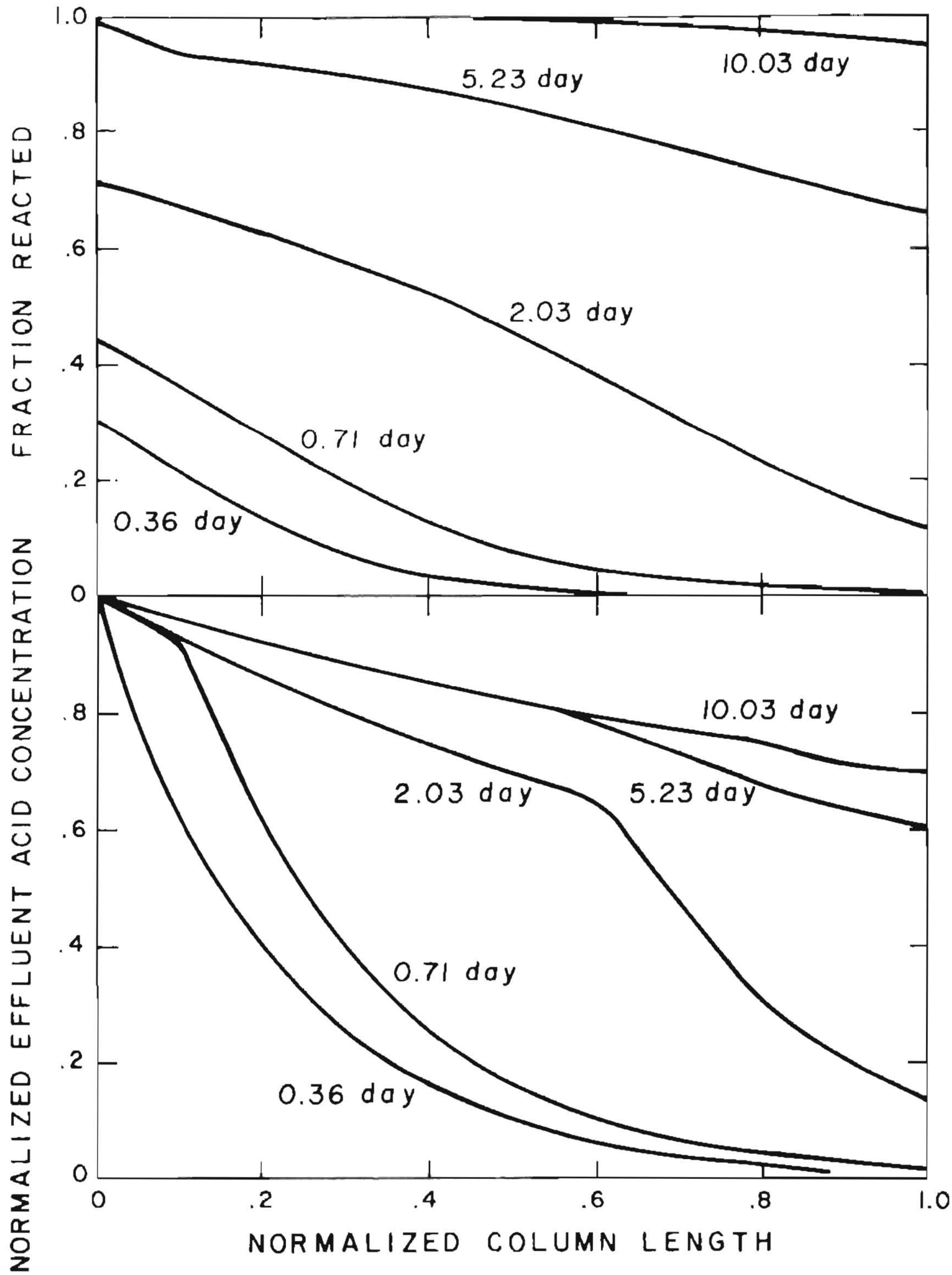


Figure 16. The copper recovery and normalized acid concentration profile calculated according to the model for an inundated system of 3.36 x 2.36 mm ore, 0.40 gal/$ft^2$hr, and 9.8 gpl $H_2SO_4$.

## CONCLUSIONS

A model based upon the equation of continuity for mass transport is developed. A simplified version of the model has been examined for percolation leaching of copper oxide ore. Essentially, the model involves quasi-steady state diffusion of the lixiviant through the previously reacted portion of the ore particles, followed by chemical reaction at the surface of the unreacted core. The leaching behavior can reasonably be explained by the following mechanism; (i) flushing of the ore with the highest rate of lixiviant consumption, (ii) penetration of lixiviant to react with copper mineral and gangue constituents, (iii) slow lixiviant consumption, mostly by gangue materials. The mechanism can be applied to both batch systems and flow systems. The major difference in reaction rate between the two systems may be attributed to an effective surface area and subsequent effective initial size of the ore due to clustering of the ore particles and by-pass of the lixiviant in packed columns. The model provides a means to explain field test studies for copper oxide ores.

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# APPENDIX A

## CALCULATIONS

A procedure of calculation is presented for monosize system. In the following no index indicating particle size is employed.

(a) Batch system. Because of x-independence and because the concentration was allowed to vary, from Equation (11)

$$\frac{\partial c(t)}{\partial t} = -\frac{B_j}{r_o} c(t) \qquad \text{(A-1)}$$

As discussed in the text only $B_1$ and $B_2$ are necessary in the period of time considered. Integrating (A-1) yields

$$\frac{c(t)}{c^o} \begin{cases} = \exp(-\frac{B_1}{r_o} t), & t<t_1 \\ = \exp(-\frac{1}{r_o}(B_1 - B_2)\, t_1 - \frac{B_2}{r_o} t), & t>t_1 \end{cases} \qquad \text{(A-2)}$$

From Equations (14) and (15)

$$\alpha(t) = \frac{3k\ c^o}{\rho\sigma\ r_o}\int_0^t \frac{c(t)}{c^o}\, dt = T(t), \quad t<t_o \qquad \text{(A-3)}$$

$$DK(\alpha') = T(t), \quad \alpha(t) = \alpha_o + (1-\alpha_o)\alpha'(t), \quad t>t_o$$

$$DK(\alpha') = \frac{3kr_o}{2D_e}(1-\frac{2}{3}\alpha'(t)-(1-\alpha(t))^{2/3}) + 3(1-(1-\alpha'(t)))^{1/3}$$

where $t_o$ is the time when $\alpha(t_o) = \alpha_o$. That is, during $t_o$ the leaching is in flushing stage. Batch tests revealed that $t_o < t_1$, which may be ascribed to the gangue constituents consuming acid as well as copper mineral as discussed in the text. Using (A-2), $\alpha(t)$ can easily be obtained.

(b) Column flow system. For i-th increment Equation (11) may be rewritten as

$$\frac{\partial c_i(x,t)}{\partial t} + \frac{v}{\varepsilon}\frac{\partial c_i(x,t)}{\partial x} = -\frac{B'_j}{r_o} c_i(x,t) \qquad \text{(A-5)}$$

$0 \leq x \leq \Delta x$, length of an increment

$t = t^i + t_r(i - 1), \; t_r = \varepsilon\Delta x/v,$

where $t^i$ is the time measured from the moment when the lixiviant reaches top of the i-th increment. In this study the right hand side of (A-5) is always negative, the time derivative of concentration is positive, and the derivative with respect to x is negative. Hence the second term in the left hand side of (A-5) is always greater than the first term in magnitude. Solution to (A-5) may be given as

$$c_i(x,t) = c_i^o \exp(-\frac{B_j}{r_o} x)\, S_{\frac{\varepsilon x}{v}}(t^i), \qquad c_1^o = c^o \qquad \text{(A-6)}$$

where $c_i^o$ is the lixiviant concentration at top of i-th increment, which may be represented by $c_{i-1}(\Delta x,t)$, $B_j = B'_j/v$, and

$$S_{\frac{\varepsilon x}{v}}(t^i) \begin{cases} = 0, & t^i < \frac{\varepsilon x}{v} \\ = 1, & t^i > \frac{\varepsilon x}{v} \end{cases}$$

The average concentration over the increment, $\bar{c}_i(t)$ is given by

$$\bar{c}_i(t) = \frac{1}{\Delta x}\int_0^x c_i(x,t)\, dx$$

The integration can be carried out resulting in

$$\bar{c}_i(t) = c_i^o \frac{1 - \exp(-\frac{B_j}{r_o} x_{min})}{\frac{B_j}{r_o} \Delta x} \qquad \text{(A-7)}$$

$$x_{min} = \min(\frac{v\ t^i}{\varepsilon}, \Delta x)$$

From (14) and (15) noting that i stands for i-th increment,

$$\bar{\alpha}_i(t) = \frac{3c^o k}{\rho \sigma r_o} \int_0^t \frac{\bar{c}_i(t)}{C^o}\, dt = T_i(t), \qquad t^i < t_o \qquad \text{(A-8)}$$

$$DK(\bar{\alpha}_i') = T_i(t), \quad \bar{\alpha}_i(t) = \alpha_o + (1 - \alpha_o)\, \bar{\alpha}_i'(t), \quad t^i > t_o \qquad \text{(A-9)}$$

At a given time $T_i(t)$ can be computed by using (A-7). $\bar{\alpha}_i'(t)$ can then be estimated from a table prepared for $DK(\alpha)$ as a function of $\alpha$. A computer scheme for the calculation is presented in the following.

t and x are given, and initially $n = 0$.

step 1. $n = n + 1$ and $i = 0$ ( n for time, i for increment).

step 2. $i = i + 1$ and $t^i(n) = n\Delta t - t_r(i - 1)$ $(n\Delta t = t)$

if $t^i(n) < 0$, set $\bar{c}_i(n) = 0$ and $\bar{\alpha}_i(n) = 0$ and go to step 1, otherwise go to step 3.

step 3. (a) if $t^i(n) \leq t_r$, set $c_{i+1}^o(n) = 0$ and

$$\bar{c}_i(n) = c_i^o(n)\ (1 - \exp(-\frac{B_1}{r_o} \Delta x\ t^i(n)/t_r)/(\frac{B_1}{r_o} \Delta x),$$

$$\Delta\alpha_i(n) = \frac{3c_i^o(n)\ k}{B_1\ x}((t^i(n) - t^i(n-1)) - \frac{t_r r_o}{B_1 \Delta x}\ (\exp(-\frac{B_1}{r_o} \Delta x\ t^i(n-1)/t_r) - \exp(-\frac{B_1}{r_o} \Delta x\ t^i(n)/t_r)))$$

$$\bar{\alpha}_i(n) = \sum_{m=1}^{n} \Delta\alpha_i(m)\ , \quad \text{then go to step 1.}$$

Note that it is easy to take $\Delta x$ such that $t^i(1) < t_r$, otherwise extra term has to be taken into account in (b).

(b) if $t_r < t^i(n) \leq t_o$, set

$$c^o_{i+1}(n) = c^o_i(n) \exp(-\frac{B_1}{r_o}\Delta x)$$

$$\bar{c}_i(n) = c^o_i(n) \ (1 - \exp(-\frac{B_1}{r_o}\Delta x))/(\frac{B_1}{r_o}\Delta x)$$

$$\Delta\alpha_i(n) = \frac{3c^o_i(n)\ k}{\rho\sigma\ B_1\ \Delta x}\ (1 - \exp(-\frac{B_1}{r_o}\Delta x)\ (t^i(n) - t^i(n-1))$$

$$\bar{\alpha}_i(n) = \sum_{m=1}^{n}\Delta\alpha_i(m)\ ,$$ then go to step 2.

(c) if $t_o < t^i(n) \leq t_1$, set

$$\bar{c}_{i+1}(n) = c^o_i(n) \exp(-\frac{B_1}{r_o}\Delta x)$$

$$\bar{c}_i(n) = c^o_i(n) \ (1 - \exp(-\frac{B_1}{r_o}\Delta x)/(\frac{B_1}{r_o}\Delta x)$$

$$\Delta T_i(n) = \frac{3c^o_i(n)\ k}{\rho\sigma\ B_1\Delta x}\ c^o_i(n)\ (1 - \exp(-\frac{B_1}{r_o}\Delta x)\ \Delta t$$

$$DK(\bar{\alpha}'_i(n)) = \sum_{m=1}^{n}\Delta T_i(m)$$

$\bar{\alpha}_i(n) = \alpha_o + (1 - \alpha_o)\ \bar{\alpha}_i(n)$, then go to step 2.

(d) if $t_1 < t^i(n) \leq t_2$,

same as in (c) with substitution of $B_2$ into $B_1$, and then go to step 2.

(e) if $t_2 < t^i(n)$,

same as in (c) with $B_3$ instead of $B_1$, if $i < i_{max}$ (last increment) go to step 2, otherwise go to next step.

step 4. if $n < n_{max}$ (desired time period) go to step 1.

step 5. end.

Detailed computer FORTRAN code is listed in Appendix B.

# APPENDIX B

## FORTRAN CODE

In the FORTRAN code there are twenty input variables used which are listed below as follows:

RO : initial effective radius of ore in cm,
DAYMAX: maximum number of days considered,
DEFF : effective diffusivity of ore in $cm^2$/day,
RWB : density of ore x Cu-grade x stoichiometry factor in moles/$cm^3$,
FAIS : shape factor of ore (dimensionless),
RKC : surface reaction rate constant in cm/day,
DX : length of each increment in cm,
RLN : packed column length in cm,
FLØW : volumetric flow rate in $cm^3$/day,
VRT : retained liquid volume in column in $cm^3$,
CO : feed concentration of lixiviant in moles/liter,
DELTT : time increment in day,
DELTA : increment in fraction reacted (dimensionless),
AHAF : arbitrary value, for example 0.5, of fraction reacted,
(DELTA and AHAF are used to obtain time as function of Alfa, fraction reacted, to have non-uniform time increments up to Alfa=AHAF; small time increments are necessary at early stage of leaching.),
AO : fraction reacted at $t_o$,(see page 29 in text)
A1 : fraction reacted at $t_1$,
A2 : fraction reacted at $t_2$,
BO : coefficient related to reaction rate constant in cm/day, (see pages 12 and 33 in text),
B1 : same as above,
B2 : same as above.

The FORTRAN CODE listing follows on the next pages.

```
      DIMENSIØN T(700), C2(122),C(122),A(122),SUMT(122),LL(122),
       X(22),DK(104),DAY(30),AT(30),CT(30),ACID(30),CEFF(30),
       ALØ(22,30),CLØ(22,30)
   10 FØRMAT(8F10.0)
C*** INPUT VARIABLES
      READ 10, RO,DAYMAX,DEFF,RWB,FAIS,RKC
      READ 10, DX,RLN,FLOW,VRT,CO,DELTT,DELTA,AHAF
      READ 10, AO,A1,A2, BO,B1,B2
C*** CHANGE CO IN MØLES PER CUBIC CENTIMETER
      CO = CO/1000.0
      TR = VRT*DX/FLOW/RLN
      BETAZ = BO/RO *DX
      BETAØ = B1 /RO *DX
      EXBZ = EXP(-BETAZ)
      EXBØ = EXP(-BETAØ)
      EXBBZ = (1.0 - EXBZ)/BETAZ
      EXBBØ = (1.0 - EXBØ)/BETAØ
      BETAT = B2/RO *DX
      EXBT = EXP(- BETAT)
      EXBBT = (1.0 - EXBT)/BETAT
      DKR = RKC *RO/DEFF
      GAMA = 3.0 *RKC/FAIS/RWB/RO
      TEXT = (TR - TR *EXBBZ)*GAMA/BETAZ
      IMAX = RLN/DX + 1.000001
      IMAX = IMAX - 1
      IMX = AHAF/DELTA + 1.000001
      IMXX = 1.0/DELTA + 1.000001
      T(1) = 0.0
      DK(1) = 0.0
      DATA K1,KMAX/2,21/
      DØ 60 N = 2,IMXX
      ALF = (N -1)*DELTA
      ACB = CBRT(1.0 -ALF)
      DK(N) = (1.0-2.0*ALF/3.0 -ACB*ACB)*1.5*DKR+3.0*(1.0-ACB)
      DDT = (DK(N) -DK(N-1))*0.75/CO/GAMA
   60 T(N) = T(N-1) + DDT
      NAM = (DAYMAX - T(IMX))/DELTT + 0.000001
      IF(NAM.LT. 0) NAM=0
      NMAX = IMX + NAM
      NMØ = (NMAX-1)/20.0 + 0.000001
      NMØD = NMØ + 1
C
      DØ 65 N=IMX,NMAX
   65 T(N+1) = T(N) + DELTT
C***
C*** INITIALIZATIØN ØF DEPENDENT VARIABLES
      DØ 70 I=1,IMAX
      C2(I) = 0.0
      A(I) = 0.0
      LL(I) = 0
   70 SUMT(I) = 0.0
      CTØT = 0.0
```

```
      ATØT = 0.0
      SUMC = 0.0
      C1 = 0.0
C***  CALCULATION BEGINS
      J=1
      N=1
C***  STEP 1
 100  N = N + 1
      C2(1) = CO
      I = 0
C***  STEP 2
 200  IF (I .GT. IMXM) GØ TØ 110
      TI = T(N) - TR*(I-1)
      IF(TI .GT. TR) GØ TØ 320
      IF (TI .LT. 0.0) GØ TØ 110
C*    STEP 3(A)
      TPR = T(N-1) -TR*(I-1)
      KK = A(I)/DELTA
 201  KK = KK +1
      IF (KK-1) 202,202,203
 202  DT = T(2)
      GØ TØ 205
 203  DT = T(KK) - T(KK-1)
 205  TC = TPR + DT
      IF (TC-TI) 206,206,207
 207  DT = TI - TPR
      TC = TI
 206  TIN = TC - DT
      IF (TIN .LT. 0.0) TIN = 0.0
      EXTR =BETAZ*TC/TR
      EXPR = EXP(-EXTR)
      EXTØ = BETAZ*TIN/TR
C***  AVERAGE CØNCENTRATIØN ØVER AN INCREMENT
      C(I) =C2(I)*(1.0 - EXPR)/BETAZ
      DAI=TC-TIN-TR*(EXP(-EXTØ)-EXPR)/BETAZ
C***  AVERAGE CØNVERSIØN ØVER AN INCREMENT
      A(I) =A(I)+DAI*GAMA/BETAZ *C2(I)
      TPR =TPR+DT
      IF(TPR .LT. TI) GØ TØ 201
      GØ TØ 110
 320  IF(A(I) .GT. AO) GØ TØ 330
C***  STEP 3 (B)
      TPR = T(N-1)
      KK= A(I)/DELTA
      C2(I+1)=C2(I)*EXBZ
      C(I)=C2(I)*EXBBZ
 321  KK=KK+1
      IF(KK-1) 322,322,323
 322  DT=T(2)
      GØ TØ 324
 323  DT=T(KK)-T(KK-1)
 324  TC=TPR + DT
```

```
      IF(TC - T(N)) 325, 325, 327
  327 DT = T(N)-TPR
  325 DAI= GAMA*C(I)*DT
      IF(A(I) .LT. 0.000001) DAI=DAI+TEXT*C2(I)
      A(I)=A(I) + DAI
      TPR=TPR+DT
      IF(TPR .LT. T(N)) GØ TØ 321
      GØ TØ 200
C*******
  330 IF(A(I) .GT. A1) GØ TØ 340
C***  STEP 3 (C)
      TPR=T(N-1)
      KK=A(I)/DELTA
      C2(I+1)=C2(I)*EXBZ
      C(I)=C2(I)*EXBBZ
  331 KK=KK+1
      DT=T(KK) - T(KK-1)
      TC=TPR+DT
      IF(TC-T(N)) 335, 335, 336
  336 DT=T(N)-TPR
  335 DELT=C(I)*GAMA*DT
      SUMT(I)=SUMT(I)+DELT
      SUMTA=SUMT(I)
      LLL=LL(I)
      CALL FINDA(DK,AP,SUMTA,LLL,IMXX,DELTA)
      A(I)=AO+(1.0-AO)*AP
      LL(I)=AP/DELTA +0.2
      TPR=TPR+DT
      IF(TPR .LT. T(N)) GØ TØ 331
      GØ TØ 200
C********
  340 IF(A(I) .GT. A2) GØ TØ 350
C***  STEP 3 (D)
      C2(I+1)=C2(I)*EXBØ
      C(I)=C2(I)*EXBBØ
      TPR=T(N-1)
      KK=A(I)/DELTA
  341 KK=KK+1
      DT=T(KK)-T(KK-1)
      TC=TPR+DT
      IF(TC-T(N)) 345, 345, 346
  346 DT=T(N)-TPR
  345 DELT=C(I)*GAMA*DT
      SUMT(I)=SUMT(I)+DELT
      SUMTA=SUMT(I)
      LLL=LL(I)
      CALL FINDA(DK,AP,SUMTA,LLL,IMXX,DELTA)
      A(I)=AO+(1.0-AO)*AP
      LL(I)=AP/DELTA +0.2
      TPR=TPR+DT
      IF(TPR. LT. T(N)) GØ TØ 341
      GØ TØ 200
```

```
C***  STEP 3 (E)
  350 C2(I+1)=C2(I)*EXBT
      C(I)=C2(I)*EXBBT
      TPR=T(N-1)
      KK=A(I)/DELTA
  351 KK=KK+1
      DT=T(KK)-T(KK-1)
      TC=TPR+DT
      IF(TC-T(N)) 355,355,356
  356 DT=T(N)-TPR
  355 DELT=C(I)*GAMA*DT
      SUMT(I)=SUMT(I)+DELT
      SUMTA=SUMT(I)
      LLL=LL(I)
      CALL FINDA(DK,AP,SUMTA,LLL,IMXX,DELTA)
      A(I)=AO+(1.0-AO)*AP
      LL(I)=AP/DELTA +0.2
      IF(A(I) .GT. 0.999999) GØ TØ 347
      TPR=TPR+DT
      IF(TPR .LT. T(N)) GØ TØ 351
  347 IF(I .LT. IMXM) GØ TØ 200
      SUMC=SUMC+(C2(IMAX)+C1)*(T(N)-T(N-1))/2.0
      C1=C2(IMAX)
C*******
  110 IF(N .EQ. NMØD) GØ TØ 400
C***  STEP 4
      IF(N.LT.NMAX) GØ TØ 100
C***  FØR PRINT ØUT AT DESIRED TIME INTERVALS
  400 J=J+1
      DAY(J)=T(N)
      DØ 410 M=1,I
      ATØT=ATØT+A(M)
  410 CTØT=CTØT+C(M)
      AT(J)=ATØT/IMXM
      CT(J)=CTØT/IMXM
      ATØT=0.0
      CTØT=0.0
C********
      DØ 420 K=1,KMAX
      I=(K-1)*K1+1
      IF(K .EQ. KMAX) I=IMXM
      ALØ(K,J)=A(I)
  420 CLØ(K,J)=C(I)/CO
      ACID(J)=(CO*DAY(J)-SUMC)*FLØW-VRT*CT(J)
      CEFF(J)=C2(IMAX)/CO
      NMØD=NMØD+NMØ
C***  IF TIME IS LESS THAN DAYMAX GØ BACK TØ STEP 1
      IF(N .LT. NMAX) GØ TØ 100
      DØ 430 K=1,KMAX
      I=(K-1)*K1+1
  430 X(K)=(I-1)*DX/RLN
      CO=CO*1000.0
```

```
C*************
C*****PRINT OUT*****
      PRINT 500, DEFF, FLOW, CO, RO
      PRINT 501, DX, RKC
      PRINT 510
      PRINT 511,X(1),X(2),X(3),X(4),X(5),X(6),X(7),X(8),X(9),
                X(10)
      PRINT 511,X(11),X(12),X(13),X(14),X(15),X(16),X(17),X(18),
                X(19),X(20),X(21)
      PRINT 520
      PRINT 521,(DAY(M),AT(M),ALO(1,M),ALO(2,M),ALO(3,M),ALO(4,M)
       ,ALO(5,M),ALO(6,M),ALO(7,M),ALO(8,M),ALO(9,M),ALO(10,M),
        M=2,J)
      PRINT 522
      PRINT 521,(DAY(M),ALO(11,M),ALO(12,M),ALO(13,M),ALO(14,M),
        ALO(15,M),ALO(16,M),ALO(17,M),ALO(18,M),ALO(19,M),
        ALO(20,M),ALO(21,M), M=2,J)
      PRINT 530
      PRINT 521,(DAY(M),CT(M),CLO(1,M),CLO(2,M),CLO(3,M),CLO(4,M)
       ,CLO(5,M),CLO(6,M),CLO(7,M),CLO(8,M),CLO(9,M),CLO(10,M),
        M=2,J)
      PRINT 531
      PRINT 521,(DAY(M),CLO(11,M),CLO(12,M),CLO(13,M),CLO(14,M),
        CLO(15,M),CLO(16,M),CLO(17,M),CLO(18,M),CLO(19,M),
        CLO(20,M),CLO(21,M), M=2,J)
      PRINT 540
      PRINT 541,(DAY(M),ACID(M),CEFF(M),AT(M), M=2,J)
C********************
  500 FORMAT(/,16H EFFECTIVE DIFF=,E12.5,11H FLOW RATE=,E12.5,
       14H INITIAL CONC=,E12.5,18H EFFECTIVE RADIUS=,E12.5)
  501 FORMAT(11H INCREMENT=,E10.5,24H SURFACE REACTION CONST=,
       E10.5,/)
  510 FORMAT(/,75H  COLUMN LENGTH INCREMENTS WHERE CONVERSIONS
      AND CONCENTRATIONS ARE PRINTED,/)
  511 FORMAT(11F10.5)
  520 FORMAT(/,46H  DAY  AVERAGE ALFA AND ALFA AT EACH INCREMENT,
      /)
  521 FORMAT(12F10.5)
  522 FORMAT(/,32H  DAY AND ALFA AT EACH INCREMENT,/)
  530 FORMAT(/,64H  DAY  AVERAGE CONCENTRATION AND CONCENTRATION
      AT EACH INCREMENT,/)
  531 FORMAT(/,41H  DAY AND CONCENTRATION AT EACH INCREMENT,/)
  540 FORMAT(/,88H  DAY   ACID CONSUMPTION IN MOLES AND EFFLUENT
      NORMALIZED CONCENTRATION AND AVERAGE ALFA,/)
  541 FORMAT(4(3X,F12.5))
      STOP
      END
C****
C***  ESTIMATE OF ALFA PRIME IN EQUATION (A-9)
      SUBROUTINE FINDA(DK,AP,SUMTA,L,IMXX,DELTA)
      DIMENSION DK(104)
      NM=0
```

```
      L=L+1
      IF (L .GT. IMXX) L=IMXX
    1 DIFF=SUMTA-DK(L)
      IF(DIFF) 2, 3, 4
    2 IF(NM .EQ. 0) GØ TØ 5
    7 AP=(L - 2)*DELTA+DELTA*(SUMTA-DK(L-1))/(DK(L)-DK(L-1))
      RETURN
    4 L=L+1
      IF(L .GT. IMXX) GØ TØ 3
      NM=1
      GØ TØ 1
    5 L=L-1
      DIFF=SUMTA - DK(L)
      IF(DIFF)  5,3,6
    6 L=L+1
      GØ TØ 7
    3 AP=(L-1)*DELTA
      RETURN
      END
```

APPENDIX C. SUMMARY OF EXPERIMENTAL DATA

TABLE I

COLUMN TEST DATA PRESENTED IN FIGURES 2 AND 3

Conditions:

Ore: 2.36 x 1.70 mm Cerrillos
Flow rate: 0.39 gal/ft$^2$-hr
Feed acid: 9.8 gpl $H_2SO_4$
Retained volume: 14.3 % of column volume

| DAYS | RECOVERY | NORMALIZED ACID CONCENTRATION | CUM. ACID CONSUMPT. / TOTAL ORIGINAL Cu |
|---|---|---|---|
| 0.022 | 0.000 | 0.000 | 0.031 |
| 0.050 | 0.000 | 0.000 | 0.067 |
| 0.300 | 0.016 | 0.000 | 0.382 |
| 0.800 | 0.218 | 0.0004 | 1.015 |
| 1.116 | 0.375 | 0.002 | 1.417 |
| 1.800 | 0.664 | 0.028 | 2.325 |
| 2.050 | 0.734 | 0.178 | 2.579 |
| 2.802 | 0.838 | 0.359 | 3.223 |
| 3.272 | 0.863 | 0.467 | 3.527 |
| 4.258 | 0.901 | 0.544 | 4.068 |
| 5.258 | 0.915 | 0.607 | 4.544 |
| 6.057 | 0.928 | 0.648 | 4.888 |
| 6.883 | 0.935 | 0.678 | 5.249 |
| 7.887 | 0.944 | 0.708 | 5.613 |
| 8.887 | 0.950 | 0.724 | 5.982 |
| 9.887 | 0.956 | 0.740 | 6.334 |
| 10.804 | 0.960 | 0.740 | 6.620 |
| 11.804 | 0.964 | 0.756 | 6.927 |
| 12.821 | 0.968 | 0.773 | 7.208 |
| 13.821 | 0.972 | 0.789 | 7.475 |
| 14.821 | 0.975 | 0.789 | 7.752 |
| 15.821 | 0.978 | 0.798 | 8.005 |
| 16.804 | 0.980 | 0.807 | 8.248 |

TABLE II

BATCH TEST DATA PRESENTED IN FIGURES 3, 4, AND 5

Conditions:

| | | |
|---|---|---|
| Ore: | Cerrillos 77 gm | |
| Solution: | 450 ml | |
| A: | 3.35 x 2.36 mm, | initial $H_2SO_4$ 19.6 gpl |
| B: | 3.35 x 2.36 mm, | initial $H_2SO_4$ 9.8 gpl |
| C: | 3.35 x 2.36 mm, | initial $H_2SO_4$ 4.9 gpl |
| D: | 4.75 x 3.35 mm, | initial $H_2SO_4$ 4.9 gpl |

| TIME | A | | | B | | | C | | | D | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| min | a | b | c | a | b | c | a | b | c | a | b | c |
| 5 | .213 | .013 | .62 | .169 | .021 | .52 | .144 | .034 | .44 | .106 | .030 | .36 |
| 10 | .278 | .020 | .93 | .227 | .036 | .86 | .197 | .057 | .71 | .149 | .053 | .62 |
| 15 | .323 | .027 | 1.22 | .264 | .043 | 1.03 | .229 | .067 | .82 | .178 | .062 | .72 |
| 20 | .352 | .031 | 1.37 | .290 | .047 | 1.11 | .258 | .082 | .98 | .203 | .067 | .77 |
| 25 | .377 | .034 | 1.51 | .313 | .051 | 1.19 | .280 | .092 | 1.08 | .220 | .077 | .86 |
| 30 | .399 | .034 | 1.51 | .334 | .055 | 1.26 | .290 | .102 | 1.18 | .232 | .082 | .91 |
| 60 | .479 | .041 | 1.78 | .396 | .066 | 1.49 | .354 | .121 | 1.34 | .290 | .113 | 1.18 |
| 90 | .528 | .049 | 2.05 | .433 | .083 | 1.79 | .390 | .137 | 1.48 | .325 | .129 | 1.31 |
| 120 | .568 | .056 | 2.31 | .468 | .087 | 1.86 | .419 | .162 | 1.68 | .351 | .145 | 1.43 |
| 150 | .586 | .060 | 2.43 | .497 | .091 | 1.93 | .440 | .176 | 1.78 | .375 | .154 | 1.49 |
| 180 | .610 | .064 | 2.56 | .522 | .096 | 2.00 | .459 | .190 | 1.87 | .393 | .162 | 1.55 |
| 210 | .623 | .072 | 2.79 | .531 | .104 | 2.20 | .479 | .204 | 1.96 | .404 | .171 | 1.61 |

a: RECOVERY OF COPPER
b: pH - INITIAL pH
c: CUMULATIVE ACID CONSUMPTION DIVIDED BY TOTAL AMOUNT OF ORIGINAL COPPER IN THE ORE

# TABLE III

COLUMN TEST DATA PRESENTED IN FIGURES 3, 6, AND 9

Conditions:

Ore: 3.35 x 2.36 mm Cerrillos
Flow rate: 0.37 gal/ft$^2$-hr
Feed acid: 9.8 gpl $H_2SO_4$
Retained volume: 12.8 % of column volume

| DAYS | RECOVERY | NORMALIZED ACID CONCENTRATION | CUM. ACID CONSUMPT. / TOTAL ORIGINAL Cu |
|---|---|---|---|
| 0.029 | 0.004 | 0.0009 | 0.034 |
| 0.113 | 0.022 | 0.005 | 0.152 |
| 0.363 | 0.102 | 0.032 | 0.489 |
| 0.863 | 0.276 | 0.124 | 1.098 |
| 1.179 | 0.372 | 0.227 | 1.423 |
| 1.863 | 0.535 | 0.330 | 2.033 |
| 2.113 | 0.580 | 0.420 | 2.244 |
| 2.865 | 0.693 | 0.489 | 2.805 |
| 3.335 | 0.747 | 0.557 | 3.097 |
| 4.321 | 0.818 | 0.611 | 3.640 |
| 5.321 | 0.865 | 0.650 | 4.096 |
| 6.119 | 0.887 | 0.664 | 4.547 |
| 6.946 | 0.908 | 0.710 | 4.873 |
| 7.949 | 0.925 | 0.724 | 5.225 |
| 8.949 | 0.938 | 0.741 | 5.588 |
| 9.949 | 0.945 | 0.773 | 5.909 |
| 10.866 | 0.954 | 0.759 | 6.171 |
| 11.866 | 0.960 | 0.791 | 6.467 |
| 12.883 | 0.966 | 0.791 | 6.732 |
| 13.883 | 0.971 | 0.800 | 7.004 |
| 14.883 | 0.975 | 0.810 | 7.290 |
| 15.883 | 0.977 | 0.810 | 7.521 |
| 16.866 | 0.980 | 0.826 | 7.829 |

TABLE IV

COLUMN TEST DATA PRESENTED IN FIGURES 3, 6, AND 9

Conditions:

Ore: 3.35 x 2.36 mm Cerrillos
Flow rate: 0.19 gal/$ft^2$-hr
Feed acid: 9.8 gpl $H_2SO_4$
Retained volume: 13.8 % of column volume

| DAYS | RECOVERY | NORMALIZED ACID CONCENTRATION | CUM. ACID CONSUMPT. / TOTAL ORIGINAL Cu |
|---|---|---|---|
| 0.052 | 0.000 | 0.000 | 0.034 |
| 0.174 | 0.0004 | 0.000 | 0.093 |
| 0.691 | 0.024 | 0.0003 | 0.383 |
| 1.129 | 0.086 | 0.0003 | 0.654 |
| 1.691 | 0.209 | 0.001 | 1.015 |
| 2.151 | 0.325 | 0.002 | 1.326 |
| 2.926 | 0.500 | 0.008 | 1.823 |
| 3.777 | 0.645 | 0.048 | 2.327 |
| 4.750 | 0.760 | 0.161 | 2.834 |
| 5.788 | 0.838 | 0.305 | 3.345 |
| 6.788 | 0.874 | 0.392 | 3.782 |
| 7.702 | 0.898 | 0.433 | 4.127 |
| 8.723 | 0.916 | 0.472 | 4.463 |
| 9.724 | 0.930 | 0.511 | 4.781 |
| 10.726 | 0.941 | 0.546 | 5.089 |
| 11.728 | 0.945 | 0.556 | 5.376 |
| 12.726 | 0.954 | 0.569 | 5.666 |
| 13.733 | 0.959 | 0.587 | 5.927 |
| 14.753 | 0.965 | 0.616 | 6.214 |
| 15.757 | 0.968 | 0.634 | 6.489 |
| 16.736 | 0.972 | 0.634 | 6.700 |
| 17.760 | 0.975 | 0.634 | 6.919 |
| 18.747 | 0.978 | 0.641 | 7.162 |
| 19.733 | 0.981 | 0.654 | 7.372 |

TABLE V

COLUMN TEST DATA PRESENTED IN FIGURES 3, 7, AND 10

Conditions:

Ore: 4.76 x 3.35 mm Cerrillos
Flow rate: 0.58 gal/$ft^2$-hr
Feed acid: 9.8 gpl $H_2SO_4$
Retained volume: 12.0 % of column volume

| DAYS | RECOVERY | NORMALIZED ACID CONCENTRATION | CUM. ACID CONSUMPT. / TOTAL ORIGINAL Cu |
|---|---|---|---|
| 0.219 | 0.084 | 0.064 | 0.426 |
| 0.372 | 0.160 | 0.148 | 0.705 |
| 0.750 | 0.336 | 0.260 | 1.299 |
| 0.875 | 0.381 | 0.372 | 1.464 |
| 1.719 | 0.580 | 0.533 | 2.319 |
| 2.018 | 0.623 | 0.637 | 2.565 |
| 2.709 | 0.702 | 0.710 | 3.021 |
| 2.962 | 0.719 | 0.741 | 3.177 |
| 3.969 | 0.772 | 0.789 | 3.641 |
| 4.969 | 0.817 | 0.826 | 4.012 |
| 5.969 | 0.836 | 0.844 | 4.353 |
| 6.966 | 0.853 | 0.844 | 4.666 |
| 7.913 | 0.867 | 0.866 | 4.949 |
| 8.969 | 0.875 | 0.880 | 5.245 |
| 9.969 | 0.888 | 0.880 | 5.518 |
| 10.969 | 0.896 | 0.880 | 5.741 |
| 11.969 | 0.905 | 0.880 | 5.967 |
| 12.969 | 0.909 | 0.880 | 6.215 |
| 13.969 | 0.914 | 0.912 | 6.431 |
| 14.969 | 0.918 | 0.912 | 6.586 |
| 15.969 | 0.922 | 0.957 | 6.663 |
| 16.969 | 0.930 | 0.957 | 6.752 |
| 17.969 | 0.934 | 0.957 | 6.842 |
| 18.969 | 0.939 | 0.938 | 6.980 |
| 19.969 | 0.943 | 0.957 | 7.075 |
| 20.969 | 0.947 | 0.938 | 7.211 |

TABLE VI

COLUMN TEST DATA PRESENTED IN FIGURES 3, 7, AND 10

Conditions:

Ore: 4.76 x 3.35 mm Cerrillos
Flow rate: 0.37 gal/$ft^2$-hr
Feed acid: 9.8 gpl $H_2SO_4$
Retained volume: 12.0 % of column volume

| DAYS | RECOVERY | NORMALIZED ACID CONCENTRATION | CUM. ACID CONSUMPT. / TOTAL ORIGINAL Cu |
|---|---|---|---|
| 0.032 | 0.005 | 0.006 | 0.035 |
| 0.115 | 0.024 | 0.031 | 0.141 |
| 0.365 | 0.098 | 0.060 | 0.443 |
| 0.865 | 0.277 | 0.113 | 1.001 |
| 1.181 | 0.368 | 0.204 | 1.318 |
| 1.865 | 0.530 | 0.317 | 1.905 |
| 2.115 | 0.574 | 0.402 | 2.094 |
| 2.867 | 0.672 | 0.471 | 2.719 |
| 3.338 | 0.710 | 0.545 | 2.964 |
| 4.324 | 0.762 | 0.622 | 3.458 |
| 5.324 | 0.806 | 0.649 | 3.907 |
| 6.122 | 0.822 | 0.694 | 4.205 |
| 6.949 | 0.839 | 0.741 | 4.490 |
| 7.952 | 0.850 | 0.727 | 4.805 |
| 8.952 | 0.861 | 0.757 | 5.129 |
| 9.952 | 0.870 | 0.774 | 5.428 |
| 10.869 | 0.876 | 0.791 | 5.722 |
| 11.869 | 0.882 | 0.791 | 5.955 |
| 12.886 | 0.889 | 0.809 | 6.208 |
| 13.886 | 0.893 | 0.809 | 6.447 |
| 14.886 | 0.896 | 0.809 | 6.678 |
| 15.886 | 0.900 | 0.809 | 6.940 |
| 16.869 | 0.904 | 0.855 | 7.133 |

TABLE VII

COLUMN TEST DATA PRESENTED IN FIGURES 3, 7, AND 10

Conditions:

Ore: 4.76 x 3.35 mm Cerrillos
Flow rate: 0.20 gal/ft$^2$-hr
Feed acid: 9.8 gpl $H_2SO_4$
Retained volume: 12.0 % of column volume

| DAYS | RECOVERY | NORMALIZED ACID CONCENTRATION | CUM. ACID CONSUMPT. / TOTAL ORIGINAL Cu |
|---|---|---|---|
| 0.080 | 0.001 | 0.000 | 0.056 |
| 0.169 | 0.004 | 0.000 | 0.113 |
| 0.549 | 0.041 | 0.0003 | 0.366 |
| 0.670 | 0.062 | 0.001 | 0.451 |
| 1.507 | 0.236 | 0.0014 | 0.960 |
| 1.757 | 0.307 | 0.010 | 0.115 |
| 2.750 | 0.530 | 0.100 | 1.831 |
| 3.757 | 0.663 | 0.281 | 2.407 |
| 4.757 | 0.726 | 0.411 | 2.833 |
| 5.757 | 0.771 | 0.503 | 3.262 |
| 6.754 | 0.795 | 0.577 | 3.615 |
| 7.701 | 0.820 | 0.624 | 3.881 |
| 8.757 | 0.835 | 0.651 | 4.159 |
| 9.757 | 0.843 | 0.660 | 4.425 |
| 10.757 | 0.852 | 0.681 | 4.663 |
| 11.757 | 0.860 | 0.682 | 4.919 |
| 12.757 | 0.864 | 0.688 | 5.185 |
| 13.757 | 0.871 | 0.702 | 5.418 |
| 14.757 | 0.876 | 0.702 | 5.614 |
| 15.757 | 0.880 | 0.717 | 5.800 |
| 16.757 | 0.884 | 0.717 | 5.980 |
| 17.757 | 0.888 | 0.737 | 6.153 |
| 18.757 | 0.891 | 0.751 | 6.313 |
| 19.757 | 0.895 | 0.787 | 6.474 |
| 20.757 | 0.900 | 0.787 | 6.634 |

TABLE VIII

COLUMN TEST DATA PRESENTED IN FIGURES 3, 8, AND 13

Conditions:

Ore: 3.35 x 2.36 mm Cerrillos
Flow rate: 0.40 $gal/ft^2$-hr
Feed acid: 9.8 gpl $H_2SO_4$
Retained volume: 38.9 % of column volume

| DAYS | RECOVERY | NORMALIZED ACID CONCENTRATION | CUM. ACID CONSUMPT. / TOTAL ORIGINAL Cu |
|---|---|---|---|
| 0.882 | 0.157 | 0.000 | 0.436 |
| 0.962 | 0.201 | 0.000 | 0.548 |
| 1.854 | 0.502 | 0.110 | 1.459 |
| 2.052 | 0.531 | 0.197 | 1.705 |
| 2.854 | 0.671 | 0.468 | 2.381 |
| 3.823 | 0.776 | 0.534 | 3.102 |
| 4.823 | 0.820 | 0.574 | 3.657 |
| 5.917 | 0.849 | 0.653 | 4.164 |
| 6.889 | 0.876 | 0.653 | 4.488 |
| 7.861 | 0.899 | 0.667 | 4.905 |
| 8.847 | 0.916 | 0.667 | 5.314 |
| 10.056 | 0.931 | 0.680 | 5.814 |
| 10.889 | 0.939 | 0.680 | 6.104 |
| 11.955 | 0.948 | 0.693 | 6.476 |
| 13.063 | 0.957 | 0.706 | 6.921 |
| 13.906 | 0.963 | 0.719 | 7.218 |
| 15.750 | 0.975 | 0.732 | 7.941 |
| 18.111 | 0.986 | 0.745 | 8.528 |

TABLE IX

COLUMN TEST DATA PRESENTED IN FIGURES 3, 8, AND 13

Conditions:

Ore: 3.35 x 2.36 mm Cerrillos
Flow rate: 0.26 gal/$ft^2$-hr
Feed acid: 9.8 gpl $H_2SO_4$
Retained volume: 38.9 % of column volume

| DAYS | RECOVERY | NORMALIZED ACID CONCENTRATION | CUM. ACID CONSUMPT. / TOTAL ORIGINAL Cu |
|---|---|---|---|
| 0.448 | 0.034 | 0.000 | 0.014 |
| 0.479 | 0.041 | 0.000 | 0.049 |
| 0.604 | 0.045 | 0.000 | 0.170 |
| 1.250 | 0.231 | 0.0001 | 0.609 |
| 1.406 | 0.284 | 0.0004 | 0.821 |
| 2.444 | 0.437 | 0.120 | 1.395 |
| 3.493 | 0.567 | 0.317 | 1.993 |
| 4.674 | 0.674 | 0.317 | 2.432 |
| 5.444 | 0.697 | 0.242 | 2.648 |
| 6.326 | 0.765 | 0.506 | 3.136 |
| 7.295 | 0.781 | 0.506 | 3.334 |
| 8.302 | 0.826 | 0.525 | 3.927 |
| 9.264 | 0.862 | 0.574 | 4.259 |
| 10.253 | 0.888 | 0.574 | 4.627 |
| 11.363 | 0.906 | 0.587 | 4.936 |
| 12.333 | 0.921 | 0.601 | 5.315 |
| 13.413 | 0.935 | 0.614 | 5.685 |
| 14.285 | 0.944 | 0.640 | 5.952 |
| 15.503 | 0.954 | 0.653 | 6.254 |
| 16.292 | 0.961 | 0.653 | 6.475 |
| 18.510 | 0.976 | 0.667 | 6.982 |

TABLE X

COPPER RECOVERY AND NORMALIZED ACID CONCENTRATION PROFILE, CALCULATED, PRESENTED IN FIGURE 15

Conditions: See Figure 12

| DAYS | NORMALIZED COLUMN LENGTH 0.0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1.0 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | COPPER RECOVERY | | | | | | | | | | |
| 0.26 | .171 | .117 | .057 | .000 | .000 | .000 | .000 | .000 | .000 | .000 | .000 |
| 0.93 | .320 | .289 | .259 | .232 | .200 | .171 | .135 | .089 | .065 | .025 | .000 |
| 2.16 | .489 | .446 | .425 | .405 | .382 | .362 | .339 | .316 | .294 | .273 | .252 |
| 5.65 | .674 | .657 | .641 | .625 | .608 | .593 | .576 | .560 | .544 | .529 | .514 |
| 10.75 | .761 | .746 | .730 | .716 | .700 | .686 | .671 | .656 | .642 | .627 | .613 |
| 15.00 | .817 | .803 | .788 | .775 | .760 | .747 | .732 | .718 | .704 | .690 | .677 |
| 18.00 | .837 | .823 | .810 | .796 | .782 | .769 | .755 | .741 | .727 | .714 | .701 |
| | NORMALIZED ACID CONCENTRATION | | | | | | | | | | |
| 0.26 | .997 | .906 | .566 | .000 | .000 | .000 | .000 | .000 | .000 | .000 | .000 |
| 0.93 | .997 | .921 | .851 | .786 | .726 | .671 | .620 | .449 | .281 | .175 | .000 |
| 2.16 | .999 | .962 | .927 | .893 | .861 | .829 | .800 | .760 | .703 | .649 | .602 |
| 5.65 | .999 | .962 | .927 | .893 | .861 | .829 | .800 | .770 | .742 | .715 | .690 |
| 10.75 | .999 | .962 | .927 | .893 | .861 | .829 | .800 | .770 | .742 | .715 | .690 |
| 15.00 | .999 | .962 | .927 | .893 | .861 | .829 | .800 | .770 | .742 | .715 | .690 |
| 18.00 | .999 | .962 | .927 | .893 | .861 | .829 | .800 | .770 | .742 | .715 | .690 |

TABLE XI

COPPER RECOVERY AND NORMALIZED ACID CONCENTRATION PROFILE, CALCULATED, PRESENTED IN FIGURE 16

Conditions: See Figure 16

| DAYS | NORMALIZED COLUMN LENGTH 0.0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1.0 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | COPPER RECOVERY | | | | | | | | | | |
| 0.36 | .316 | .222 | .140 | .076 | .041 | .022 | .010 | .004 | .001 | .000 | .000 |
| 0.71 | .460 | .377 | .288 | .205 | .136 | .083 | .049 | .029 | .018 | .010 | .007 |
| 2.03 | .727 | .682 | .635 | .583 | .527 | .466 | .394 | .308 | .235 | .171 | .123 |
| 5.23 | .962 | .944 | .924 | .901 | .875 | .846 | .814 | .778 | .741 | .700 | .669 |
| 10.03 | 1.008 | .999 | .999 | .999 | .999 | .997 | .994 | .987 | .976 | .963 | .951 |
| | NORMALIZED ACID CONCENTRATION | | | | | | | | | | |
| 0.36 | .947 | .608 | .390 | .251 | .161 | .103 | .066 | .043 | .027 | .000 | .000 |
| 0.71 | .991 | .925 | .623 | .400 | .257 | .165 | .106 | .068 | .044 | .028 | .019 |
| 2.03 | .991 | .925 | .863 | .805 | .751 | .701 | .654 | .484 | .311 | .199 | .135 |
| 5.23 | .996 | .961 | .927 | .894 | .863 | .833 | .787 | .734 | .685 | .639 | .602 |
| 10.03 | .996 | .961 | .927 | .894 | .863 | .833 | .804 | .775 | .748 | .722 | .700 |

TABLE XII

THE PARAMETERS $B_o$, $B_1$, AND $B_2$

| ORE SIZE mm | $B_2$ | $B_o/B_2$ | $B_1/B_2$ | FLOW RATE gal/ft$^2$-hr |
|---|---|---|---|---|
| 3.36 x 2.36 | 0.0021 | 2.0853 | 12.5118 | 0.37 |
| | 0.00445 | 2.0831 | 12.5011 | 0.19 |
| 2.36 x 1.70 | 0.0019 | 2.1474 | 12.4789 | 0.39 |
| 4.76 x 3.36 | 0.0025 | 2.1600 | 12.8000 | 0.37 |
| | 0.0040 | 2.1625 | 12.8750 | 0.20 |
| | 0.0014 | 2.1631 | 12.8794 | 0.58 |
| 13.50 x 4.76 | 0.0065 | 1.7385 | 7.8462 | 0.20 |
| 26.90 x 13.50 | 0.00129 | 2.1318 | 12.6357 | 0.41 |