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# DEVELOPMENT OF A NON-LINEAR LEAST-SQUARES KINETIC MODEL FOR HEAP LEACH CHEMICAL EXTRACTION USING COLUMN LEACH DATA

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**ABSTRACT.** Mathematical modelling plays a central role in the interpretation of hydrometallurgical extraction processes. Laboratory experiments generate valuable information regarding the dissolution behaviour of minerals; however, meaningful interpretation of experimental results requires quantitative models capable of describing extraction kinetics. In this study, a non-linear kinetic model describing gold extraction by cyanide was developed using experimental column recovery data and parameter estimation through least-squares regression. Experimental recovery measurements obtained from column leach tests were fitted to an exponential extraction model expressed as, $F(t) = K_2 * [1 – \exp(K_1 * t)]$, where F represents fractional extraction, $K_1$ is the kinetic rate constant, $K_2$ represents the asymptotic maximum extraction, and t denotes time. Model parameters were estimated by minimising the sum of squared differences between experimental observations and model predictions using spreadsheet-based optimisation. The resulting model successfully reproduces the non-linear extraction behaviour observed in the experimental dataset and demonstrates the capability of exponential kinetic models to represent the rapid initial dissolution and subsequent asymptotic recovery typical of hydrometallurgical systems. Statistical validation of the fitted model gave squared correlation coefficient ($R^2$) as 0.9904 and root mean square error (RMSE) as 0.0168 in fractional extraction units. Direct comparison with reaction-control and diffusion-control shrinking-core alternatives showed that the selected single-exponential model gave the lowest RMSE for this dataset, and residual analysis showed no persistent bias after the initial ore wetting period.

**Key words:** heap leach, column test work, reaction kinetics, process simulation.

## Introduction

Hydrometallurgical extraction processes involve complex interactions between chemical reactions, mass transfer, and mineralogical characteristics of the ore (Petersen, 2016). Laboratory column leaching experiments are commonly used to evaluate the dissolution behaviour of mineral samples under controlled conditions. These tests generate time-dependent recovery data that reflect the combined effects of reaction kinetics and transport phenomena within the column (Dixon and Hendrix, 1993).

Although experimental data provides important insights into the extraction process, interpretation of such data requires mathematical models capable of describing the observed trends. Kinetic models allow extraction behaviour to be represented using a small set of parameters that describe the rate and extent of metal dissolution. These parameters can then be used to predict recovery behaviour under different conditions and assist in the design and optimisation of metallurgical processes (Sohn and Wadsworth, 1979; Fogler, 2006).

Among the various kinetic models proposed for hydrometallurgical systems, exponential extraction models have proven particularly useful because they capture the characteristic recovery behaviour observed in many leaching experiments: rapid initial dissolution followed by a gradual decrease in reaction rate as the process approaches equilibrium (Crundwell, 2011).

The objective of the present work is to develop a kinetic model describing chemical extraction behaviour using experimental column recovery data. The model parameters are determined using non-linear least-squares regression and implemented in spreadsheet software.

## Materials and methods

### Experimental Conditions and Procedures

The dataset analysed in this study consists of experimental extraction values obtained from oxide gold ore laboratory column leach tests. These measurements represent the percentage of metal recovered from the column under controlled experimental conditions.

In the present study, the available experimental information consisted of cumulative extraction versus time data obtained from the laboratory column test. The original dataset used for regression did not include complete operating descriptors such as column diameter and height, particle size distribution, irrigation rate, or leach solution composition. Therefore, the present paper should be regarded as a kinetic fitting study based on time–extraction data, and these variables should be reported in future work to improve reproducibility and plant-scale interpretation.

A 55 kg charge of sample with $P_{80}$ = 7.7 mm and 2.36 ppm average gold (Au) containing crushed ore sample was placed in a 0.15 m diameter Plexiglas column. Feed material particle size distribution is presented on Figure 1.

Ore bed height in the column was measured before and after leaching. The change in height was used to determine slump during leaching and to calculate the final apparent bulk density of the material in the column. Column slump provides an indication of possible permeability issues in operating heaps. Slump values greater than 10% are accepted as high. The test column showed low slump. The initial and final ore bed heights were 1.951 and 1.932 m, respectively, corresponding to a final apparent dry bulk density of 1.58 t/m³. The column was operated as a continuously drained drip leach test. This test configuration provides a close laboratory representation of heap leach conditions and is commonly used

when the ore contains sufficient fines to limit solution channelling along individual rock surfaces.

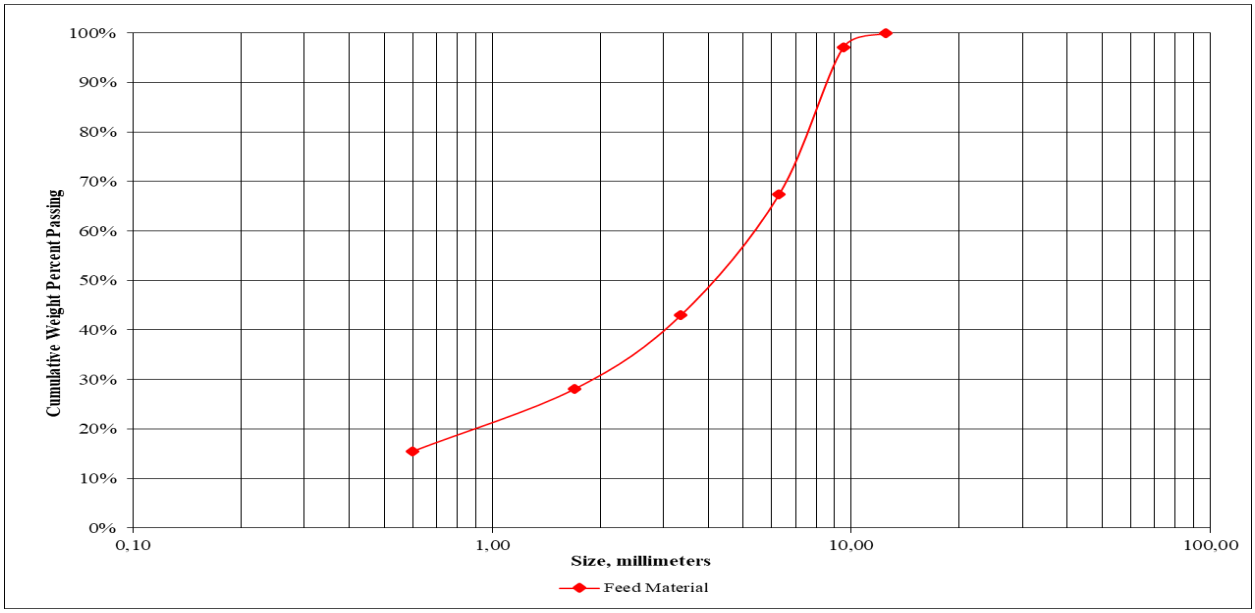



**Fig. 1. Feed material particle size distribution**

Solution was applied as a continuously drained drip leach at 11 L/(h m) using an initial 1.0 g/L sodium cyanide solution; on-flow solution was maintained at 0.5 g/L sodium cyanide and hydrated lime was used to control pH at a target of 10.5.

Protective alkalinity was provided by the initial addition of hydrated lime, and the leach solution was monitored to maintain pH in the range of 10 to 11.

Both sodium cyanide consumption and hydrated lime addition were elevated in this test. Sodium cyanide consumption was 1.04 kg per metric tonne of ore. Total lime addition was 2.7 kg per metric tonne of ore.

Effluent from the column was collected in the bottom floor pregnant leach solution (PLS) tank. During each cycle, the leach solution was analysed for pH, NaCN and Au. The solution was then passed for 24 hours through a bottle of activated carbon to recover dissolved gold. After carbon contact, the solution was re-analysed for pH, NaCN and Au. Sodium cyanide was added as needed to maintain a target concentration of 0.5 g/L NaCN, and the solution was recycled to the ore for another 24-hour leach cycle. Two solution batches were used so that one batch could be applied to the column while the other was treated through carbon. The cumulative extraction increased from 5.63% on day 1 to 67.14% on day 37 of column leaching.

The recovery values of the column leaching experiments are affected by ore mineralogy, permeability differences, and variations in mineral accessibility (Sohn and Wadsworth, 1979; Levenspiel, 1999). Despite the variability observed in individual measurements, the dataset exhibits an overall extraction trend that can be described using a continuous kinetic model. The supporting laboratory test ran for 53 days, but the regression dataset retained in this paper extends through day 37. Column set-up is presented in Figure 2.

Mineralogy influences extraction because gangue composition, oxidation state and the mode of gold occurrence determine how readily reactive surfaces are exposed to the lixiviant. Permeability controls solution distribution and residence time within the packed ore bed; reduced



**Fig. 2. Column set-up (front-left)**

permeability promotes channelling, perched solution, or incomplete wetting. Mineral accessibility represents the fraction of valuable metal that is exposed through pore space, fractures, or liberated surfaces, and limited accessibility contributes directly to the asymptotic approach to the recovery limit.

Initial and final effluent colour and clarity were observed and noted during the column test. The colour and clarity of initial and final column effluent was light yellow / clear and colourless / clear, respectively. A colourless, clear effluent from the column indicates that fines did not migrate through the ore bed. Significant metal accumulation is generally reflected by a noticeable change in solution colour. The lack of colour indicated that metal buildup did not occur during leaching.

**Assaying procedures**

Head assays gold content was performed by fire assaying technique.

Activated carbon used to recover the gold from solution was dried and weighed to analyse the gold content loaded in the carbon. Two samples were split and submitted for assay, and the remaining carbon was retained for reference. The assay samples were roasted to ash and then analysed by conventional fire assay.

Solution assays were completed during each cycle using an atomic absorption spectrophotometer and gold standards. These solution assays were used to monitor column test progress and leaching kinetics presented on the paper.

Sodium cyanide in leach solutions was determined by colorimetric titration using silver nitrate titrant and 5-[p-(Dimethylamino)-benzylidene]-rhodanine indicator. Free cyanide was determined by titrating 25 mL of leach solution to the colorimetric endpoint. Drops of 1N sodium hydroxide were then added to dissociate base-metal cyanide complexes, and titration continued to the final endpoint to determine total cyanide in solution.

**Mathematical Model**

The extraction observed in the experimental dataset was modelled using the exponential kinetic equation (Levenspiel, 1999; Fogler, 2006).

$$F(t) = K_2 * [1 - \exp(K_1 * t)] \quad (1)$$

where,

$F(t)$ = fractional extraction

$K_1$ = kinetic rate constant

$K_2$ = maximum extraction parameter

$t$ = leaching time

For clarity, $F(t)$ is the fractional extraction at time t, $K_2$ is the asymptotic extraction limit, and $K_1$ is the first-order kinetic constant written in sign-convention form.

This model describes a system in which extraction increases rapidly during early reaction stages and gradually approaches an asymptotic recovery limit.

At the start of the reaction ($t = 0$), the model predicts $F(0) = 0$. As time increases, the exponential term decreases and extraction approaches the maximum value $K_2$.

Accordingly, the model predicts,

$$dF/dt = - K_1 * K_2 * \exp (K_1 * t) \quad (2)$$

So, the initial extraction rate is controlled jointly by the magnitude of $K_1$ and the asymptotic extraction level $K_2$.

**Least-squares parameter estimation**

To determine the kinetic parameters $K_1$ and $K_2$, a non-linear least-squares regression method was used. The objective of this method is to minimise the difference between experimental measurements and model predictions. The objective function minimised during the regression process is

$$S = \Sigma_{i=1}^{n} [F_{exp,i} - F_{model,i}]^2 \quad (3)$$

where, n is the number of experimental observations, $F_{exp,i}$ is the measured fractional extraction, and $F_{model,i}$ is the corresponding model prediction.

The spreadsheet model calculates predicted extraction values for each experimental point and then computes the squared residual error. The sum of these squared errors represents the total deviation between the model and the experimental dataset.

Excel Solver was used to iteratively adjust the kinetic parameters until the sum of squared residuals reached a minimum value.

In addition to minimising the sum of squared residuals, the fitted model was evaluated using the squared correlation coefficient, root mean square error, and approximate parameter confidence intervals (CI).

For the spreadsheet fit,

$R^2 = 0.9904$,

$RMSE = \sqrt{[\Sigma(F_{exp} - F_{cal})^2 / n]} = 0.0168$.

Based on the local sensitivity of the fitted equation, the 95% confidence intervals are,

$K_1 = -0.12398\ d^{-1}$ (95% CI: $-0.13139$ to $-0.11656\ d^{-1}$),

$K_2 = 0.67735$ (95% CI: 0.66579 to 0.68890).

## Results

The regression procedure produced a kinetic model capable of reproducing the general extraction trend observed in the experimental dataset.

The data comparison between experimental extraction values and model predictions is presented in Table 1.

A non-linear least-squares kinetic model was developed from the spreadsheet calculations for the analysed column leach dataset. Equation (3) presents the fitted model for the recovery expression. The fitted relation is a single-exponential recovery model.

$$F(t) = 0.67735 * [1 - \exp(-0.12398 * t)] \quad (4)$$

The predicted values follow the overall trend of the experimental data and reproduce the non-linear behaviour observed in the extraction measurements.

Equation (3) indicates that the model asymptotically approaches an ultimate extraction of 67.7% under the test conditions.

The magnitude of the kinetic term, $k = 0.12398\ d^{-1}$, governs how rapidly the system approaches this limit and represents a lumped effect of dissolution kinetics, wetting behaviour, and internal mass-transfer resistance.

For the selected model,

$k = 0.12398\ d^{-1}$ gives a leaching half-time of $t_{1/2} = \ln(2)/k =$ 5.6 days.

The calculated times to reach 90% and 95% of the fitted asymptotic recovery are 18.6 and 24.2 days, respectively.

These values show that $K_1$ quantifies the apparent speed at which the column approaches $K_2$ under the stated test conditions.

**Graphical Model**

The relationship between experimental extraction values and model predictions is illustrated in Figure 3. Extraction vs time curve showed exponential recovery behaviour.

The figure illustrates that extraction increases rapidly during the early stages of the reaction and then gradually approaches a limiting value. This behaviour is typical of hydrometallurgical dissolution systems where the reaction rate decreases as reactive mineral surfaces become depleted.

In this plot, the modelled values closely follow the experimental data, indicating that the exponential kinetic model provides a reasonable representation of the extraction process.

The kinetic model developed in this study successfully reproduces the extraction behaviour observed in the column leach experiments. The exponential form of the model captures the characteristic recovery trend commonly observed in hydrometallurgical systems that is the rapid initial extraction followed by a gradual decrease in reaction rate as the system approaches equilibrium.

Relative to alternative heap-leach modelling approaches reported in the recent literature, the present formulation is deliberately simple. Its advantage is that only time and extraction data are required for calibration; its limitation is that it does not explicitly represent lift height, solution holdup, preferential flow, climatic effects, or downstream inventory delays (Ghorbani et al., 2015; Marsden and Botz, 2017; Botz and Marsden, 2019).

The column labelled as $K_1$ on Table 1 contains pointwise back-calculated rate constants obtained from

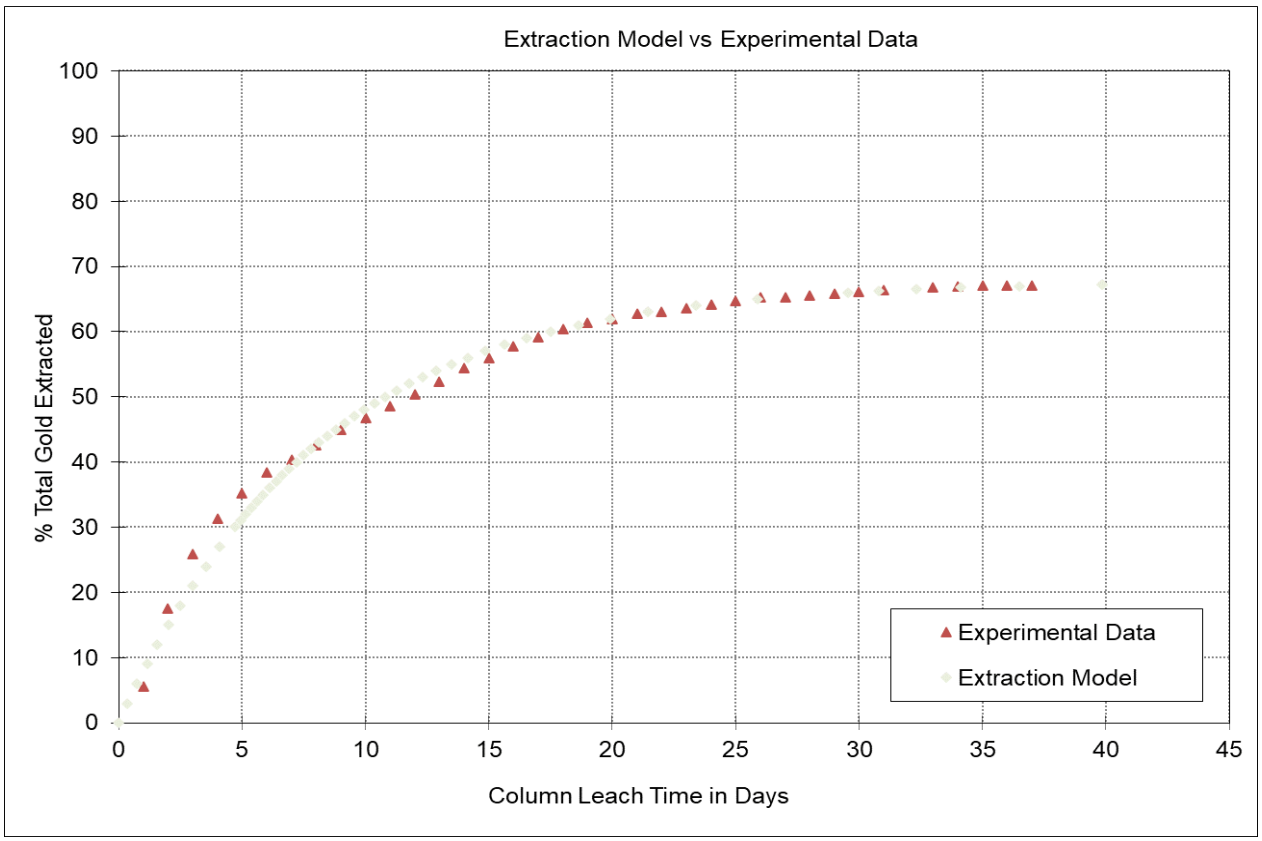



**Fig. 3. Comparison of experimental and modelled extraction values**

$$K_1 = \ln (1 - F / K_2) / t, \quad (5)$$

and these values are negative because the exponential term is written using, $K_1 < 0$.

The term, $\Sigma(K_1 - K_{1avg})^2$ gives the contribution of each point to the spreadsheet objective used to stabilise the average rate constant. The column "t given F" is the inverse-model solution for time at a specified extraction level, whereas "F estimated" and "F calculated" are model-predicted fractional extractions generated for prescribed times and for the actual experimental times, respectively (day 32 is absent because no experimental observation was available for that day in the original dataset). The $R^2$ value reported in the table refers to the goodness of fit between experimental and model-calculated extraction values in the spreadsheet regression.

**Kinetic model comparison**

A comparison with higher-complexity models was prepared as part of this study. In the tiered heap-leach framework, the present equation is closest to a Level 1–2 empirical description because it uses column extraction data directly and does not include explicit in-heap solution inventory, heap geometry, or downstream process constraints. By contrast, Level 3 spreadsheet models adjust production for solution holdup and recovery delays within the heap, which becomes increasingly important in multi-lift systems as inventory grows with heap height (Ghorbani et al., 2015; Botz and Marsden, 2019).

Table 1. *Experimental and modelled extraction data*

| Rate of Chemical Extraction Model Equations: | | | | | | | | | | $R^2$ = 0.9904 |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $F = K_2 (1-e^{k1t})$ | | | | | | | |
| F= 0.677 -0.124 | | | $t\ (days) = (Ln(1-F)/K_2) / K_{1avg}$ | | | | | | | |
| | | | $K_1 = (Ln(1-F) / K_2) / t_{days}$ | | | | | | | |
| Column recovery (%) | Time (t) days | $K_1$ | $K_2$ | $(\bar{K_1}-K_1)^2$ | Solve for t given F | Chemical extraction model F estimated | | Solve for F given t | Chemical extraction model F calculated | $(F_{act}-F_{cal})^2$ |
| 5.629 | 1 | -0.08676 | 0.677348 | 0.00138498 | 0.000 | 0.000 | 0.0 | 1.0 | 0.079 | 0.00051475 |
| 17.581 | 2 | -0.1502517 | 0.677348 | 0.00069045 | 0.365 | 0.030 | 3.0 | 2.0 | 0.149 | 0.00073236 |
| 25.868 | 3 | -0.1603664 | 0.677348 | 0.00132431 | 0.748 | 0.060 | 6.0 | 3.0 | 0.210 | 0.00233251 |
| 31.344 | 4 | -0.1553176 | 0.677348 | 0.00098234 | 1.150 | 0.090 | 9.0 | 4.0 | 0.265 | 0.00236262 |
| 35.216 | 5 | -0.1467575 | 0.677348 | 0.00051903 | 1.573 | 0.120 | 12.0 | 5.0 | 0.313 | 0.00153935 |
| 38.418 | 6 | -0.1395747 | 0.677348 | 0.00024334 | 2.019 | 0.150 | 15.0 | 6.0 | 0.355 | 0.00082738 |
| 40.335 | 7 | -0.1292942 | 0.677348 | 0.00002829 | 2.492 | 0.180 | 18.0 | 7.0 | 0.393 | 0.00010803 |
| 42.559 | 8 | -0.1237131 | 0.677348 | 0.00000007 | 2.993 | 0.210 | 21.0 | 8.0 | 0.426 | 0.00000028 |
| 44.933 | 9 | -0.1209756 | 0.677348 | 0.00000900 | 3.529 | 0.240 | 24.0 | 9.0 | 0.455 | 0.00003689 |
| 46.827 | 10 | -0.1175481 | 0.677348 | 0.00004131 | 4.102 | 0.270 | 27.0 | 10.0 | 0.481 | 0.00016939 |
| 48.515 | 11 | -0.1145158 | 0.677348 | 0.00008948 | 4.719 | 0.300 | 30.0 | 11.0 | 0.504 | 0.00036075 |
| 50.431 | 12 | -0.1137242 | 0.677348 | 0.00010509 | 4.935 | 0.310 | 31.0 | 12.0 | 0.524 | 0.00040114 |
| 52.350 | 13 | -0.1140167 | 0.677348 | 0.00009917 | 5.158 | 0.320 | 32.0 | 13.0 | 0.542 | 0.00034902 |
| 54.467 | 14 | -0.1164465 | 0.677348 | 0.00005668 | 5.387 | 0.330 | 33.0 | 14.0 | 0.558 | 0.00017617 |
| 55.928 | 15 | -0.1164643 | 0.677348 | 0.00005642 | 5.623 | 0.340 | 34.0 | 15.0 | 0.572 | 0.00015825 |
| 57.765 | 16 | -0.1197508 | 0.677348 | 0.00001785 | 5.865 | 0.350 | 35.0 | 16.0 | 0.584 | 0.00004246 |
| 59.170 | 17 | -0.1216459 | 0.677348 | 0.00000543 | 6.116 | 0.360 | 36.0 | 17.0 | 0.595 | 0.00001106 |
| 60.428 | 18 | -0.1237084 | 0.677348 | 0.00000007 | 6.374 | 0.370 | 37.0 | 18.0 | 0.605 | 0.00000012 |
| 61.352 | 19 | -0.1243143 | 0.677348 | 0.00000011 | 6.641 | 0.380 | 38.0 | 19.0 | 0.613 | 0.00000017 |
| 61.992 | 20 | -0.1233796 | 0.677348 | 0.00000035 | 6.917 | 0.390 | 39.0 | 20.0 | 0.621 | 0.00000046 |
| 62.732 | 21 | -0.1240792 | 0.677348 | 0.00000001 | 7.202 | 0.400 | 40.0 | 21.0 | 0.627 | 0.00000001 |
| 63.053 | 22 | -0.1214518 | 0.677348 | 0.00000637 | 7.499 | 0.410 | 41.0 | 22.0 | 0.633 | 0.00000639 |
| 63.675 | 23 | -0.1223688 | 0.677348 | 0.00000258 | 7.806 | 0.420 | 42.0 | 23.0 | 0.638 | 0.00000217 |
| 64.193 | 24 | -0.1229519 | 0.677348 | 0.00000105 | 8.126 | 0.430 | 43.0 | 24.0 | 0.643 | 0.00000074 |
| 64.676 | 25 | -0.1239085 | 0.677348 | 0.00000000 | 8.459 | 0.440 | 44.0 | 25.0 | 0.647 | 0.00000000 |
| 65.256 | 26 | -0.1272228 | 0.677348 | 0.00001055 | 8.806 | 0.450 | 45.0 | 26.0 | 0.650 | 0.00000477 |
| 65.295 | 27 | -0.1230925 | 0.677348 | 0.00000078 | 9.169 | 0.460 | 46.0 | 27.0 | 0.654 | 0.00000033 |
| 65.614 | 28 | -0.1237155 | 0.677348 | 0.00000007 | 9.549 | 0.470 | 47.0 | 28.0 | 0.656 | 0.00000002 |
| 65.834 | 29 | -0.1232145 | 0.677348 | 0.00000058 | 9.947 | 0.480 | 48.0 | 29.0 | 0.659 | 0.00000017 |
| 66.137 | 30 | -0.1248939 | 0.677348 | 0.00000084 | 10.367 | 0.490 | 49.0 | 30.0 | 0.661 | 0.00000020 |
| 66.337 | 31 | -0.1251877 | 0.677348 | 0.00000147 | 10.809 | 0.500 | 50.0 | 31.0 | 0.663 | 0.00000029 |
| 66.762 | 33 | -0.1285868 | 0.677348 | 0.00002127 | 11.277 | 0.510 | 51.0 | 32.0 | 0.665 | 0.00000957 |
| 66.936 | 34 | -0.1305798 | 0.677348 | 0.00004362 | 11.774 | 0.520 | 52.0 | 33.0 | 0.666 | 0.00001111 |
| 67.138 | 35 | -0.1351754 | 0.677348 | 0.00012544 | 12.304 | 0.530 | 53.0 | 34.0 | 0.667 | 0.00001626 |
| 67.138 | 36 | -0.1314205 | 0.677348 | 0.00005543 | 12.871 | 0.540 | 54.0 | 35.0 | 0.669 | 0.00000821 |
| 67.138 | 37 | -0.1278686 | 0.677348 | 0.00001516 | 13.481 | 0.550 | 55.0 | 36.0 | 0.670 | 0.00000337 |

Dynamic flowsheet models go further by linking ore stacking, solution storage, recycle, and plant limitations in a time-dependent mass balance, allowing evaluation of PLS tenor, make-up water demand, and downstream bottlenecks (Muller and Newton, 2008).

To address model selection quantitatively, the same extraction dataset was also fitted with chemical reaction-control and diffusion-control shrinking-core formulations - equations (6 - 8).

The reaction-control form was evaluated as,

$$F(t) = F\infty \{1 - [1 - k_r t]^3\} \quad (6)$$

where $k_r$ - intrinsic chemical reaction rate at the surface of the unreacted core, $F\infty$ - the fractional extraction at infinite time.

The diffusion-control form was evaluated as,

$$F(t) = F\infty X \quad (7)$$

where,

$$k_d t = 1 - 3 (1 - X)^{(2/3)} + 2 (1 - X) \quad (8)$$

where $k_d$ - the overall rate constant that accounts for the diffusion in the product layer, X - the fractional conversion of the solid particle, i.e., the reacted fraction.

These equations represent idealised spherical-particle controls and are used here as comparison models rather than as complete heap simulators.

The model comparison was carried out using the same experimental column-leach extraction dataset for all three kinetic expressions. For each model, calculated extraction values were generated at the same leach times as the measured data, and the residual for each point was calculated as the difference between the experimental extraction and the model-predicted extraction

For the two alternative models, the shrinking-core reaction-control model and the shrinking-core diffusion-control model (SCM diffusion) the data were expressed in terms of reacted fraction, (X), and then converted to predicted extraction by $F(t) = F\infty X$ , so that all three models were compared on the same fractional extraction basis.

For the shrinking-core reaction-control model (SCM reaction) case, the relationship (6) was rearranged to calculate (X) directly at each time step.

For the diffusion-control case, the relationship (8) was solved numerically for (X), because this expression is not conveniently rearranged into an explicit form for (X). The fitted constants were selected by minimising the sum of squared errors between measured and calculated extraction values.

For a direct quantitative comparison, the shrinking-core alternatives were fitted to the same fractional extraction dataset by minimising the sum of squared errors. To isolate the effect of the kinetic form, $F\infty$ was fixed at 0.677348 for the two shrinking-core alternatives.

The selected single-exponential model was evaluated using

$$F(t) = F\infty [1 - \exp(-k t)] \quad (9)$$

where F∞ represents the fitted ultimate extraction and (k) is the apparent first-order rate constant.

Model performance was then compared using the squared correlation coefficient $R^2$, root mean square error, mean absolute error, sum of squared errors, and maximum absolute residual. This procedure allowed the single-exponential model to be evaluated against two mechanistically based alternatives using identical experimental data and identical error criteria.

The comparison (Table 2) shows that the selected single-exponential equation has the best statistical performance for this dataset (the highest $R^2$ and lowest RMSE among the tested alternative models); however, the alternative shrinking-core models remain useful for mechanistic interpretation when additional particle-scale data are available.

The model reliability also depends on the defining ore type, particle-size distribution, leach kinetics, and solution hydrodynamics.

Table 1. *Quantitative comparison of kinetic models fitted to the same fractional extraction dataset*

| Model | Model expression / fitting basis | Fitted or fixed parameters | $R^2$ | RMSE | Selection comment |
|---|---|---|---|---|---|
| Single exponential model | $F(t) = F\infty\ [1 - \exp(-k\ t)]$ | $F\infty = 0.677348$<br>$k = 0.12398\ d^{-1}$ | 0.9905 | 0.0168 | Best fit; lowest RMSE and highest $R^2$ among the tested models. |
| Shrinking core -Diffusion controlled model | $F(t) = F\infty X$<br>$k_d * t = 1 - 3\ (1 - X)^{(2/3)} + 2\ (1 - X)$<br>Product-layer diffusion control<br>X was capped at 1 | $F\infty$ fixed = 0.677348<br>$k_d = 0.02599\ d^{-1}$ | 0.9879 | 0.0265 | Intermediate fit; better than reaction-control SCM but still less accurate than the single-exponential model. |
| Shrinking core - Reaction controlled model | $F(t) = F\infty X$<br>$F(t) = F\infty\ \{1 - [1 - k_r\ t]^3\}$<br>Surface reaction at the shrinking interface control<br>X was solved by Newton iterations | $F\infty$ fixed = 0.677348<br>$k_r = 0.03302\ d^{-1}$ | 0.9823 | 0.0329 | Poorest of the three tested fits; the curve reaches completion too sharply for the observed gradual asymptote. |

The fitted kinetic parameters provide quantitative insight into the extraction system. In this dataset, $K_1$ should be interpreted as an apparent first-order leaching-rate parameter rather than a pure intrinsic reaction constant.

Because the fitted response is based on solution recovered from the column, $K_1$ includes the effects of chemical dissolution at exposed mineral surfaces, diffusion through partially reacted particles, wetting and percolation through the packed ore bed, and solution transport to the effluent. Under the fixed test conditions summarised above, it is best described as an apparent or lumped rate constant. Separating the individual contributions of reaction control, diffusion control, permeability, and solution transport would require additional tests at multiple particle sizes, irrigation rates, column heights, or reagent concentrations.

One of the main advantages of the modelling approach used in this work is its simplicity. The exponential extraction model requires only two parameters yet can describe a wide range of extraction behaviours. This simplicity allows the model to be implemented easily using spreadsheet software and makes it suitable for rapid analysis of experimental datasets.

However, it should be noted that the model represents an empirical approximation rather than a fully mechanistic description of the extraction process. In real hydrometallurgical systems, additional factors such as diffusion limitations, surface passivation, changes in reagent concentration, and in-heap solution inventory may influence reaction kinetics and recovery behaviour (Habashi, 1999).

More complex shrinking-core, diffusion-controlled, or inventory-adjusted heap models can incorporate these effects when mineralogical, hydraulic, and operating data are available (Muller and T. Newton, 2008; Ghorbani et al., 2015; Botz and Marsden, 2019).

Mechanistic or phenomenological models are also more complex than the present formulation. These approaches may couple unsaturated flow, diffusion, and reaction kinetics and, in advanced cases, represent gas and liquid flow, reagent balance, bacterial effects, and thermodynamic or temperature responses (Muller and T. Newton, 2008). The shrinking-core type treatment is therefore more physically explicit for heterogeneous ore particles than the single-exponential equation used here, but it also requires more detailed characterisation and calibration (Dixon and Hendrix, 1993). The fitted relation in Equation (4) should therefore be interpreted as an empirical kinetic baseline for the present column data rather than as a complete mechanistic heap-leach simulator.

The contribution of the present work is therefore not the proposal of a new kinetic law, but the demonstration that a transparent spreadsheet-based nonlinear least-squares workflow can be used to fit column-leach extraction data, quantify model error, and interpret the fitted parameters in a way that is useful for preliminary metallurgical screening.

Accordingly, the scientific contribution of the present paper is not the development of a more comprehensive heap simulator, but the demonstration that the single-exponential fit

can provide a practical first-pass kinetic interpretation of column leach data and can serve as an initial benchmark against which more complex models may later be tested

**Proposed model residuals plot**

Residuals were calculated as experimental extraction minus calculated extraction. The largest residuals occur during the first four days, which is consistent with initial wetting and rapid early dissolution effects that are not explicitly represented by the single-exponential empirical model. After approximately day 8, residuals remain small and show no persistent directional bias.

The residual plot in Figure 4 should be read as a signed model-error plot. Points above the zero-residual line mean that the experimental extraction was higher than the calculated value, so the model underpredicted recovery at those times. Points below the zero-residual line mean that the calculated value was higher than the experimental extraction, so the model overpredicted recovery. Therefore, Figure 4 is a diagnostic plot used to evaluate whether the fitted equation (4) leaves systematic error, not a separate recovery model.

The residual pattern shows the largest positive deviations during the early leaching period and the largest negative deviations during the transition toward the asymptotic region. This indicates that the single-exponential equation slightly underpredicts part of the rapid early extraction stage and then slightly overpredicts the mid-test approach to the recovery limit. After approximately day 18, the residuals cluster close to zero, indicating that the later portion of the column-leach response is described without persistent positive or negative bias.

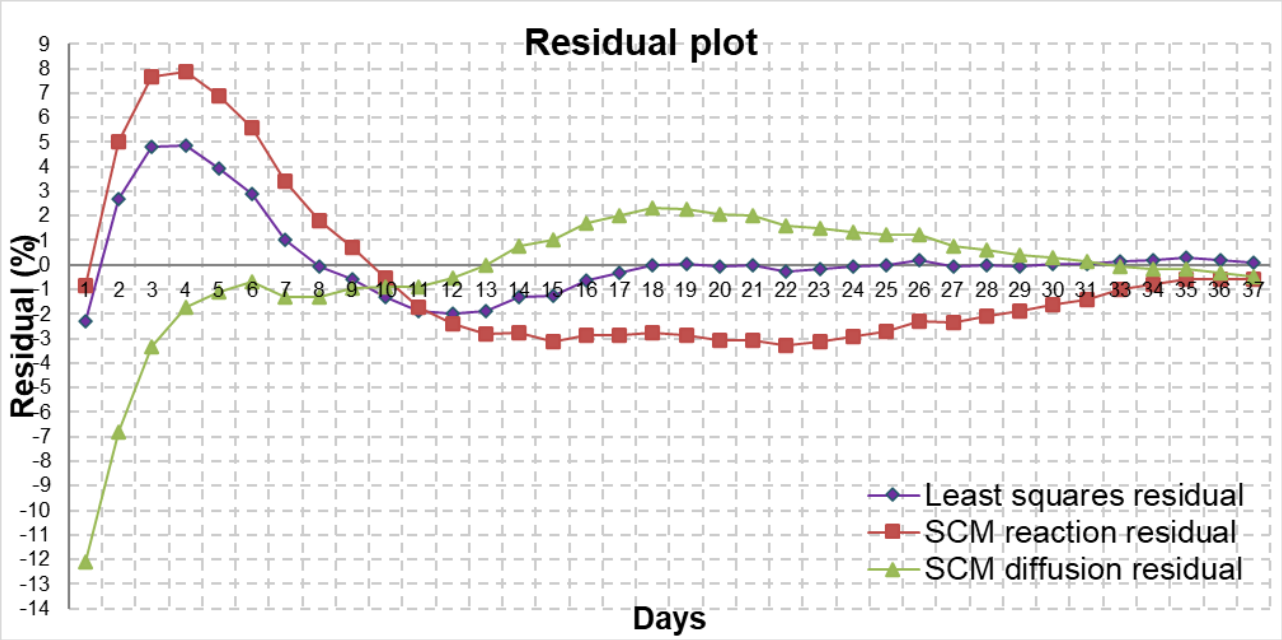



**Fig. 4. Residual plots of the kinetic models**

## Conclusion

A non-linear kinetic model describing chemical extraction behaviour was developed using experimental column recovery data and least-squares regression.

The results demonstrate that

- The exponential extraction model successfully describes the non-linear recovery behaviour observed in the experimental dataset.
- Least-squares regression provides an effective method for estimating kinetic parameters from laboratory extraction data.
- Spreadsheet-based optimisation tools provide a convenient platform for performing kinetic modelling and parameter estimation.
- The resulting model can be used to predict extraction behaviour and assist in the interpretation of hydrometallurgical experiments.

The model is best suited for preliminary kinetic description of column-leach behaviour rather than direct prediction of full-scale heap performance.

This model comparison with shrinking core reaction and diffusion-controlled approach also addresses effectiveness and precision of the least squares model. The model presented in this paper produced explicit, reproducible translation of experimental column extraction data into fitted kinetic parameters and statistical error measures. It can be used as an interpretable baseline model that is simple enough for rapid metallurgical screening.

The comparison showed that the selected single-exponential model provided the best overall statistical fit to the column-leach data. The single-exponential model gave the highest coefficient of determination and the lowest error terms, with ($R^2$) of approximately 0.9905 and RMSE of approximately 0.0168. The shrinking-core diffusion-control model gave the next closest fit, while the shrinking-core reaction-control model showed larger deviations, particularly in the early-to-intermediate leaching period. These results indicate that the

observed extraction trend is better represented by a smooth asymptotic first-order recovery form than by the sharper reacted-core progression predicted by the reaction-control shrinking-core model. The comparison therefore supports the use of the exponential model as a practical empirical representation of the column-leach extraction data, while recognising that the shrinking-core models provide useful mechanistic alternatives for systems where particle-scale reaction or diffusion control can be independently demonstrated.

The novelty claim of the model presented in the paper is limited. The work does not claim a new leaching law, but it provides a reproducible spreadsheet-based workflow that,

- Fits the extraction curve.
- Reports confidence intervals and residual statistics.
- Compares the selected model against shrinking core model reaction and diffusion control alternatives.
- Identifies the fitted model as a practical baseline for preliminary column-leach screening.

Furthermore, the developed kinetic model provides a useful tool for interpreting and predicting extraction behaviour in column leach hydrometallurgical systems.

By determining the kinetic parameters $K_1$ and $K_2$, the model allows estimation of both the apparent extraction rate and the ultimate extraction achievable under the stated column conditions. Such information is valuable for evaluating metallurgical performance, comparing the leachability of different materials, and estimating the time required to reach a target recovery.

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