Dynamics of particle-size distributions in continuous leaching reactors and autoclaves

F.K. Crundwell *, N. du Preez, J.M. Lloyd

CM Solutions (Pty) Ltd, Office Suite 119, Killarney Mall, 60 Riviera Road, Killarney, 2193, South Africa

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A B S T R A C T

Leaching plays a central role in hydrometallurgical processing. However, frequently it is the leaching step that is the least efficient part of the hydrometallurgical process. Part of any drive to improve the efficiency of the operation therefore requires an understanding of the behaviour of leaching reactors. Surprisingly little work has been done on studying the effect of the particle-size distribution on the performance of leaching reactors. The objective of this work is to examine the impact of the mean and standard deviation of several different functional forms of the particle-size distribution on the performance of the reactor. Previous work showed that the Leaching Number, defined as \((\text{linear rate of shrinkage}) \times (\text{residence time}) / (\text{mean particle size})\), is a key parameter in the performance of leaching reactors. The results of these calculations demonstrate the following: (i) the number distribution of the particles leaving the reactor reflects the interaction between particle-size distribution in the feed and the residence-time distribution, which is correctly described by the population balance; (ii) the mean size of the particles leaving the reactor can either increase or decrease, depending on the variance of the particle-size distribution of the feed; (iii) changing the variance over a wide range, from 0.1 to 1.8, increases the conversion by about 10%; and (iv) the Leaching Number is the primary variable in determining the performance of leaching reactors.

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1. Introduction

Leaching and dissolution play a central role in most hydrometallurgical processes (Crundwell, 2010, 2011; Crundwell et al., 2011). Consequently, the performance of these operations impacts greatly on the performance of the process as a whole. Thus, improving the understanding of the chemistry and chemical engineering of leaching and dissolution can contribute significantly to improving the performance of many metallurgical facilities. The modelling and simulation of leaching operations could contribute in the improvement of designs, but more readily in the increasing of throughput in existing operations. It is well known that the particle-size distribution of the feed material plays an important role in the performance of the reactor. However, surprisingly little work has been published on the effect of the particle-size distribution on the performance of leaching reactors, and even less on the nature of the particle-size distribution leaving the reactor.

The purpose of this paper is to examine the effect of particle-size distribution on the performance of leaching reactors. The theory of leaching reactors is presented in the next section, following which the effect of different particle-size distributions is presented. It is shown that the mean of the particle-size distribution of the exit slurry depends on the variance of the feed size distribution. In addition, it is demonstrated that the Leaching Number, developed previously by Crundwell (2005), plays a central role in determining the performance of leaching reactors. The main focus of the paper is to investigate how the particle-size distribution changes with leaching. In particular, it is shown that the covariance of the distribution affects the outlet distribution in a manner that has not been reported previously.

2. Theory of continuous leaching reactors

2.1. Mass balances for continuous processes

The mass balance for a component in solution in a continuous stirred tank reactor is written as follows:

\[
QC_{\text{in}} = QC_{\text{out}} - rV
\]

where \( Q \) is the volumetric flow rate, \( C \) is the concentration of the component, \( r \) is the rate of formation of the component, and \( V \) is the volume of the tank. This well-known equation accounts for two factors: (i) the kinetics of the reaction through the expression for \( r \), and (ii) the state of mixing, through the assumption that the concentration of the component in the exit stream is the same as that in the tank. This assumption is that of “maximum mixedness” (Zwietering, 1959).
2.2. Mathematical models of leaching

Two models of leaching have emerged to describe leaching:

(i) The population-balance approach (Crundwell and Bryson, 1992; Herbst, 1979; Papangelakis et al., 1990; Sepulveda and Herbst, 1978), and


At first sight these two approaches might appear to be unrelated. However, Crundwell (1994, 2005) demonstrated that they are both population balances, with the first corresponding to the maximum-mixedness assumption and the second to the segregated-flow mixing assumption (Zwietering, 1959). Since the conditions of mixing in these reactors are more likely to be described by maximum-mixedness, which is the usual assumption of the well-mixed contents of a stirred tank, the population balance approach is the preferable approach.

2.3. Population balance model of leaching

In addition to the factors that are accounted for in Eq. (1), there is an additional factor that affects the performance of leaching reactors: the particle-size distribution of the feed. Since small particles dissolve faster than larger ones, this is a critical factor. The population balance accounts for the effect of size on the performance of the reactor. The population balance is given as follows:

$$\frac{d n_{\text{in}}}{d \ell} = Q n_{\text{out}} - \rho \frac{d n_{\text{in}}}{d \ell}$$

(2)

where $r_{\text{in}}$ is the linear rate of particle shrinkage in m/s, $\ell$ is the particle size, $V$ is the tank volume, and $Q$ is the slurry feed rate to the tank. The terms $n_{\text{in}}$ and $n_{\text{out}}$ represent the inlet and outlet size functions, respectively. More formally, $n$ represents the particle size density function on a number basis. The relationship between particle distributions on a number and on a mass basis is presented later in this section.

An expression for the linear rate of particle shrinkage can be obtained from the shrinking-core model, which describes the mechanism of particulate dissolution. Other models, such as the electrochemical model (Crundwell, 1988a,b) and models of passivation (Crundwell and Godorr, 1997) can be included by incorporating them into the expression for the linear rate of shrinkage.

The term on the left-hand side of Eq. (2) represents the material coming into the reactor with size $\ell$, while the first term on the right-hand side represents the material leaving the reactor with size $\ell$, and the second term on the right-hand side represents the change in particle size as a result of the reaction. The rate of reaction is dependent on particle size, which has been made explicit in the term $\frac{d n_{\text{in}}}{d \ell}$.

The correspondence between Eqs. (1) and (2) is obvious: Eq. (2) is a linear first-order differential equation that can be easily solved by analytical and numerical methods.

The model is completed by determining the conversion from the change in the size distribution. The conversion in the leaching reactor is calculated by determining the mass of the mineral leaving the reactor from the size distribution shown by Eq. (3).

$$X = 1 - \frac{\int_0^\infty \ell^3 n_{\text{out}}(\ell) d\ell}{\int_0^\infty \ell^3 n_{\text{in}}(\ell) d\ell}$$

(3)

Thus, the solution of Eqs. (2) and (3) describes the leaching of particles in a continuous stirred tank reactor.

2.4. Mass and number density functions

The particle-size distribution up till now has been described on a number basis, that is, $n(\ell)d\ell$ is the number of particles with a size between $\ell$ and $\ell+d\ell$. However, the particle distribution is usually described on a mass basis, where $m(\ell)d\ell$ is the mass of particles with a size between $\ell$ and $\ell+d\ell$. The number density function is converted to the mass density function in the following manner:

$$m(\ell) = \frac{\ell^3 n(\ell)}{\int_0^\infty \ell^3 n(\ell) d\ell}$$

(4)

The particle-size distributions are frequently described by standard functions. The functional forms of the more common distributions are given in Table 1.

2.5. Incorporating the shrinking-core model

Expressions are required for the rate of particle shrinkage and for the particle-size distribution. Analytical solutions can be obtained for a limited number of cases.

The linear rate of shrinking can be obtained from the shrinking-core model. For the reaction

$$a A(s) + b B(aq) \rightarrow \text{products}$$

(5)

the rate of shrinkage of a particle, $r_s$, for reactions described by the shrinking-core model is given by:

$$r_s = \frac{d \ell}{dt} = -2a[B(aq)]k_s \frac{k_s}{b \rho_s}$$

(6)

for a reaction that is of order 1 in B and controlled by the rate of reaction. $\rho_s$ is the molar density of A, $k_s$ is the rate constant for the reaction, and $a$ and $b$ are stoichiometric coefficients. Upon integration, Eq. (6) yields the familiar $1 - (1 - X)^{1/3} = k_s t$ for a batch reactor if the concentration of B(aq) is constant and the particles are initially of uniform size (note that $k_s$ is the right-hand side of Eq. (6) divided by the particle size).

<table>
<thead>
<tr>
<th>Function</th>
<th>Mass density function, $m(\ell)$</th>
<th>Mean</th>
<th>Variance, $\sigma^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dirac-delta</td>
<td>$\delta(\ell - L)$</td>
<td>$L$</td>
<td>0</td>
</tr>
<tr>
<td>Gamma</td>
<td>$\frac{\ell^{\alpha-1}}{\Gamma(\alpha)}$</td>
<td>$\alpha \beta$</td>
<td>$\alpha \beta^2$</td>
</tr>
<tr>
<td>Log-normal</td>
<td>$\frac{1}{\sqrt{2\pi \sigma^2}} \exp\left(-\frac{(\ell - \mu)^2}{2\sigma^2}\right)$</td>
<td>$\exp(\mu + q^2/2)$</td>
<td>$\sqrt{\exp(q^2) - 1} \exp(2\mu + q^2)$</td>
</tr>
<tr>
<td>Rosin-Rammler</td>
<td>$\frac{1}{\sqrt{2\pi \sigma^2}} \exp\left(-\frac{(\ell - \mu)^2}{2\sigma^2}\right)$</td>
<td>$\mu \left(\frac{q}{\mu}\right)^{1/2}$</td>
<td>$q^2 \left[1 - \left(\frac{q}{\mu}\right)^2\right]$</td>
</tr>
</tbody>
</table>
This completes the requirements for the model. The conversion can be calculated from Eqs. (2) and (3) for a reaction that is described by the shrinking-particle model, given by Eq. (6).

2.6. Numerical solution of the population balance

The population balance given in Eq. (2) is a non-linear first order differential equation. Eq. (2) can be integrated by parts to give the following expression:

$$n_{\text{out}}(\ell) = \frac{1}{F \tau} \int_{0}^{\ell} n_{\text{in}}(\ell') \tau \, d\ell$$

(7)

where $F$ is the integrating factor given by:

$$F = \exp \left( \int_{0}^{\ell} \frac{d\ell'}{\tau} \right).$$

(8)

Eqs. (7) and (8) can be integrated analytically for a limited number of cases. In this work, these integrals are evaluated numerically using standard numerical techniques (Crundwell, 1994; Crundwell and Bryson, 1992).

2.7. The Leaching Number

The rearrangement of equations into their dimensionless form often reveals their essence; so it is with leaching. The dimensionless form of Eq. (2) is as follows:

$$n_{\text{in}}(\ell') = n_{\text{out}}(\ell') - \frac{d(n_{\text{in}}(\ell') n_{\text{out}}(\ell'))}{d\ell'}$$

(9)

where $\tau$ is the mean residence time, $L$ is a characteristic value of the particle-size distribution of the feed, and $\ell'$ is $\ell/L$. In most cases, it is convenient to take the mean size of the feed as the value for $L$. The terms $n_{\text{in}}(\ell')$ and $n_{\text{out}}(\ell')$ represent the dimensionless forms of the inlet and outlet size functions, respectively.

The only parameter in Eq. (9) is the Leaching Number (Crundwell, 2005), and is given by the expression:

$$N_{L} = \frac{\tau}{L}.$$ 

(10)

The Leaching Number can be expressed in words as follows:

Leaching Number = \frac{\text{(linear rate of shrinkage) \times (mean residence time)}}{\text{(mean particle size)}}.

The significance of the Leaching Number is that in order to increase the conversion, the Leaching Number must increase. All the factors affecting the chemistry are accounted for in the term for the linear rate of shrinkage, which as stated earlier, is given by the shrinking-core or shrinking-particle models. For example, if the temperature rises, or the concentration of reactant rises, this will increase the rate of dissolution, and hence the Leaching Number will increase, resulting in an increase in conversion.

The other two factors, the mean residence time and the mean particle size of the feed, are physical parameters that influence the conversion. If the mean particle size decreases, the Leaching Number and the conversion will increase. If the mean residence time increases, the Leaching Number and the conversion will increase.

3. Results

As stated in the introduction, the purpose of this work is to determine the effect of the particle-size distribution on the performance of the leaching reactor. Five different functional forms of the particle-size distribution are examined: the Dirac-delta (or spike) distribution, the normal, (iii) log-normal, (iv) Rosin-Rammler, and (v) beta distributions. The impact of these distributions will be discussed in turn in the sections that follow.

3.1. Dirac-delta distribution

The simplest possible distribution is that all particles entering the reactor are of the same size. This means that they are described by a Dirac-delta function, in other words, a spike at a particular value. The Dirac-delta function has infinite height, zero width and an area of one. If the feed size distribution is described by a Dirac-delta function, all the particles in the feed are of the same size. In this case, the solution to the population balance with the shrinking-particle model is given by:

$$n_{\text{out}}(\ell) = \frac{1}{k_{s} \tau} \exp \left( \frac{(L-1)}{k_{s} \tau} \right) \quad 0 \leq \ell \leq L.$$ 

(11)

The number Eq. (11) represents an exponential decay in the number density function, representing the residence-time distribution of a single tank reactor, which is an exponential decay. The exponential distribution of the outlet number density function is shown in Fig. 1. The values for the parameters used in these calculations are as follows: $k_{s}$ is $-5 \text{ mm}^{2}/\text{h}$, $\tau$ is 10 h, and $L$ is 95 μm. These values are used in all subsequent calculations in this section.

This result shows that feeding the particles of the same size into the reactor is the same as a tracer test commonly used in plant trials to determine the form of the residence-time distribution. That the solution to the population balance reflects the residence-time distribution is emphasised because recent work (Kotsiopolous et al., 2008) has incorrectly stated that the population balance does not account for the residence time.

This point is worth discussing in further detail. Zwietering (1959) showed in a seminal paper that the residence-time distribution of a CSTR is imbedded in the component mass balance. In order to expose this information, a tracer test can be performed. For the component balance, Eq. (1) is written in its dynamic form, and solved with a boundary condition that represents the injection of the tracer. The solution to this dynamic balance is a concentration-time profile that exposes the underlying residence-time distribution, in this case, that of a single CSTR.

![Fig. 1. The number density function of the particles in the outlet from a leaching reactor which is fed with particles that are all of the same size. Note that the scale of the y-axis is logarithmic.](image-url)
Crundwell (1994) showed that the population balance contains the same assumptions as the component balance. While it appears on the surface that the population balance does not account for the residence-time distribution, it is embedded in the assumptions of mixing subtly contained in the formulation, just as these same assumptions are embedded in the component balance of Eq. (1). Just as a tracer test exposes this embedded residence-time distribution for the component balance, so the input of a very narrow size distribution to the leaching reactor exposes the residence-time distribution of the population balance.

The mass density function that corresponds with the number density function given in Fig. 1 is shown in Fig. 2. Unlike the number density function given in Eq. (11), the mass density function is not an exponential decay, due to the transformation of the particle-size distribution from a number basis to a mass basis (Eq. (4)).

In the case of the Dirac-delta distribution, the mean of the outlet size distribution is always smaller than that of the inlet size. The change in mean size of the outlet distribution with Leaching Number is shown in Fig. 3. This result concurs with the expectations of a leaching process: leaching is the dissolution of a mineral, which reduces the particle size; hence the mean particle size should decrease through a continuous tank reactor.

The development of the particle-size distribution through a series of tanks is shown in Figs. 4 and 5. The change in particle-size distribution reflects the residence-time distribution for a series of tanks.

The conversion through a series of tanks each with the same values of the Leaching Number is shown in Fig. 6. These results demonstrate the primary importance of the Leaching Number in determining the conversion of the leaching system, and the product distribution reflects the residence time distribution of the system.

The conversion for a single tank reactor fed with particles of a single size can be solved analytically. This solution was used to validate the numerical results. The solution is given by the following expression:

$$X = -3N_l - 6N_l^2 - 6N_l^3 + 6N_l^3 \exp \left( \frac{1}{N_l} \right).$$  \hspace{1cm} (12)

More significant than the validation of numerical techniques, which have been validated elsewhere (Crundwell, 1994; Crundwell and Bryson, 1992), is the observation that the conversion is only affected by the Leaching Number if the reactor is fed with particles of a single size. This observation makes the calculation of the conversion rather trivial.

A feed size distribution similar to the Dirac-delta distribution would be a rare occurrence in an industrial environment. In the next section, the effect of other, more realistic, feed distributions on the performance of the leaching reactor is investigated. In particular, the effect of their mean and variance is examined.

3.2. Gamma distribution

The functional form of the gamma distribution is given in Table 1. Fig. 7 shows the effect of changing covariance, given as

$$\text{COVAR} = \frac{\sigma^2}{\mu}.$$  \hspace{1cm} (13)

on the shape of the density function. The average particle size has been maintained at a value of 100 μm for all the particle-size distributions shown in Fig. 7.
The effect of changing the covariance of the particle-size distribution of the feed is shown in Figs. 8 and 9. The results for three tanks of equal size arranged in series are shown. Fig. 8 shows that the particle-size distribution decreases through the continuous series of tanks, while Fig. 9 indicates that it increases. As indicated earlier, the expectation is for the particle-size distribution to move to smaller sizes during leaching. For the results shown in Fig. 8, this occurs. However, under similar conditions of leaching rate, residence time and mean size of the feed, the mean size increases through the series of tanks. This result is unexpected.

The difference between the cases shown in Figs. 8 and 9 is the spread of the particle-size distribution of the feed. In the case of a relatively narrow size distribution the particles leaving the reactor are on average smaller than those entering. However, if the particle-size distribution spreads, the size of the particles leaving the reactors gets larger. Clearly, it is the variance (or covariance) of the particle-size distribution of the feed that is influencing this behaviour.

The ratio of the mean size leaving a single tank to the mean size in the feed as a function of the covariance of the particle-size distribution of the feed is shown in Fig. 10. These results indicate that if the covariance is less than 0.5, the mean size of the particles leaving the reactor is smaller than the mean size of the particles in the feed. However, if the covariance is greater than 0.5, the mean size of the particles leaving the reactor is greater than the mean size of the feed.

The effect of the changes to the mean size of the particle-size distribution of the feed on the performance of the reactor, measured by the conversion, is shown in Fig. 11. The effect of the change in the mean size is expressed in terms of the Leaching Number. The covariance was maintained at a value of 0.71 in these calculations.

These results are similar to those published previously (Crundwell, 1994, 1995, 2000, 2001, 2005; Crundwell and Bryson, 1992) as a function of residence time. The equivalent axes for the residence time and the inverse of the mean particle size of the feed are also shown in Fig. 11.

The Leaching Number can also be changed by changing the mean size of the particles in the exit while at the same time resulting in an increase in conversion. Thus, mean size (and hence the Leaching Number) is the primary variable, and the covariance is a secondary variable that is of lesser impact.

3.3. Rosin Rammler and log normal distributions

Similar calculations have been performed for log-normal and Rosin–Rammler distributions. The results of these calculations indicate that these other distributions produce results that are substantially similar to those shown in Figs. 7 to 12. The effect of the
covariance of the feed distribution on the mean size of the particles leaving the reactor is shown in Fig. 13. These results are calculated for gamma, Rosin–Rammler and log-normal distributions functions. All of these results demonstrated similar results, that is, that if the covariance is below 0.5 the mean size of the exit slurry is less than that of the feed, while if it is greater than 0.5, the means size is greater than the feed.

4. Discussion

Little attention in both research and operations has focused on the particle-size distribution. The result that the mean size might increase on passing through a tank reactor was briefly mentioned by Sepulveda and Herbst (1978). However, the authors’ attention was drawn to this phenomenon through our consulting practice when a client showed that the particle-size distribution through their autoclave increased by about 40 μm. Because this result runs counter to the intuition of even the most experienced practitioners in leaching, this investigation was undertaken.

The results presented in this study, particularly the result that the mean size might increase in some cases and decrease in others, have implications for design. For example, operations are frequently designed on the basis of batch experiments, in which the particles always decrease in size. Filtration and thickening tests are then conducted on these residues. However, the size distribution achieved in the batch test work might be significantly different from that in the continuous plant. Consequently, the downstream operations might be incorrectly specified. Also, the size distribution of the material tested in batch tests for the purposes of the design is often poorly specified, in that a single point is given, and not the whole distribution.

The result that the conversion is mainly influenced by the Leaching Number has consequences for design, operations and the improvements in operations. Fig. 14 shows the conversion as a function of the Leaching Number for two different particle-size distributions. The first is the Dirac-delta function, which has a covariance of zero, and the
second is the gamma distribution with a large variance and covariance. Because this difference is relatively small, it can be concluded that this curve adequately describes leaching in a single tank reactor. If this is the case, then a curve such as this can be used for the design and optimization of leaching reactors.

An example of the profitable use of this curve is the following. A design engineer wishes to determine the consequences of reducing the residence time from 10 h to 5 h, with all other conditions remaining the same. If the design engineer calculates the Leaching Number to have a value of 0.5 at a residence time of 10 h, the Leaching Number curve, shown in Fig. 15, gives the conversion to be about 68%. Decreasing the residence time to 5 h decreases the Leaching Number by 10/5 to a value of 0.25. The conversion at a Leaching Number of 0.25 in Fig. 15 is 53%.

As part of the same design, the engineer wishes to determine the effect of reducing the mean particle size from 100 μm to 50 μm. The Leaching Number at 100 μm is 0.5. Changing the mean size from 100 μm to 50 μm changes the Leaching Number from 0.5 to 0.5 × (100/50) = 1. The conversion at a Leaching Number of 1 is 82%.

In a similar manner, the plant metallurgist might be operating at a conversion of 68%. Under pressure from production, the residence time is reduced by 20%. The metallurgist wishes to determine the effect that this might have on the performance of the reactor. The Leaching Number at 68% is 0.5 (from Fig. 15). Reducing the residence time by 20% will reduce the Leaching Number to 0.5 × 0.8 = 0.4. The conversion at a Leaching Number of 0.4 is approximately 62%, which, depending on the operation, may be an unacceptable decline.

5. Conclusions

The following conclusions are drawn from this work:

(i) The number distribution of the particles leaving the reactor reflects the interaction between particle-size distribution in the feed and the residence-time distribution. This interaction is correctly described by the population balance. The conclusion drawn recently by Kotsiopolous et al. (2008) that the population balance does not include the effect of the residence time distribution is erroneous and false.

(ii) The mean size of the particles leaving the reactor can either increase or decrease, depending on the covariance of the particle-size distribution of the feed. This is a remarkable result, and is quite counter-intuitive.

(iii) The effect of changing the covariance over the wide range of 0.1 to 1.8 increases the conversion by about 10%.

(iv) The Leaching Number is the primary variable in determining the performance of leaching reactors.

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