# Enhanced Dissolution Following Extended Milling

**N. H. Fletcher**
Dept. of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia

**N. J. Welham**
Dept. of Applied Mathematics, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia

Extended ball-milling has been shown to provide enhanced rates of solubility in a variety of mineral systems (Balaz et al., 1992, 1999; Balaz, 1996; Tkacova et al., 1996; Welham, 1996, 1997a,b; Welham and Llewellyn, 1998). For the metal sulphides (Balaz et al., 1992, 1999; Balaz, 1996) this may be partially or wholly accounted for by oxidation (Welham, 1996, 1997a).

There have been a few earlier investigations (Tkacova et al., 1996; Welham, 1997b; Welham and Llewellyn, 1998) into the effect of extended milling time on the solubility of a mineral that does not apparently undergo phase change during extended milling. Because of the potential commercial importance of this type of enhanced solubility, this article presents a model of the dissolution of milled ilmenite in a sulphuric acid leach.

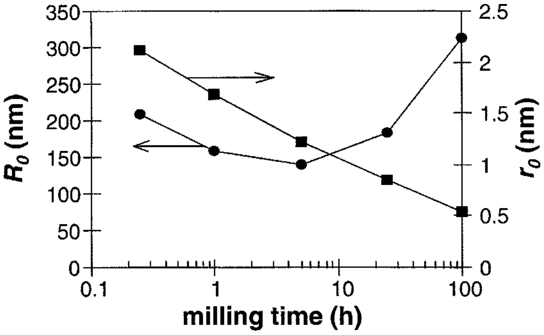

**Figure 1. Experimental cluster radius $R_0$ (●) and crystallite size $r_0$ (■) as functions of milling time.**

$R_0$ was derived from the BET surface area, and $r_0$ was determined by X-ray diffraction.

## Structure of Milled Materials

The structure of milled material can be examined by a combination of BET absorption and X-ray diffraction. The results of this, as previously published (Welham and Llewellyn, 1998), are shown in Figure 1. The material appears to consist of compact clumps that are impervious to nitrogen and have mean radius $R_0$ in the range 150 to 300 nm. Embedded within these clumps are microcrystalline grains with average radius $r_0$ in the range 0.5 to 2.5 nm. The clumps are presumably cemented together with amorphous material generated during the milling process. While it would be straightforward to simply parameterize this description, it is instructive to see how it might arise physically.

Consider first the breakdown of crystalline particles during the milling process. This probably involves the fracture of large particles, the probability of fracture during a ball impact being proportional to some positive power $n$ of the particle radius $r_0$. The relative rate of decrease in particle volume $V$, namely $-V^{-1}dV/dt$, is thus proportional to $r_0^n$, and this leads to an equation of the form

$$r_0(t) = r_0(0)(1 + at)^{-1/n}, \tag{1}$$

where $a$ is a constant describing the mill efficiency, and $r_0(0)$ is the crystallite radius at time $t = 0$. It is an interesting feature of such an equation that, particularly if $n > 1$, it is well approximated by a simple logarithmic dependence of the form

$$r_0(t) = A - B \log t \tag{2}$$

over a range of as much as two decades in $t$ around the value $t = (2^n - 1)/a$. This agrees with the experimental data in Figure 1, and from this the numerical values of $A$ and $B$ can be determined. Because Eq. 2 is valid over only a limited range of time, the constants $A$ and $B$ have no direct physical meaning. For simplicity, we adopt the form Eq. 2 in the subsequent development.

Because crystallites are assumed to break apart during the milling process, their number increases with increasing milling

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Correspondence concerning this article should be addressed to N. H. Fletcher.

time. The increase in crystallite number, however, is accompanied by the generation of amorphous material that effectively coats the crystallites and binds them together into clumps. The rate at which this amorphous material is generated during the milling process can be described in a similar way. Suppose that the amorphous fraction of the total material is $F$, then we expect that

$$F(t) = 1 - (1 + bt)^{-1/m}, \tag{3}$$

where $b$ and $m$ are new constants. We shall find later that this expression, with $m = 3.4$, fits the derived experimental data well.

There is a further hidden parameter that specifies the concentration of crystallites, but this is effectively determined by Eqs. 1–3 and the law of conservation of mass, and is not actually required in the analysis. The one remaining descriptive parameter is the radius $R_0$ of the composite clumps. Since these are cemented together by amorphous material, we should expect their size to remain nearly constant over the milling period, except perhaps in the first stages when the amount of amorphous material is very low. From Figure 1, the clump radius $R_0$ does not show any clear trend with milling time, but does vary significantly. The best that can be done is to parameterize this curve directly.

## Kinetics of Dissolution

The kinetics of dissolution can be regarded as proceeding in two separate stages. Pictorially this is analogous to the dissolution of a sugar lump in a cup of hot coffee—first the intergranular material dissolves and the lump falls rapidly apart, following which there is slower dissolution of the crystalline grains. (The analogy should not be pressed too far!) In reality the two stages overlap, but the difference in time scales is sufficiently great that this can be ignored in the interest of simplicity.

Consider first a composite lump of radius $R$ immersed in acid, and assume that the dissolution is reaction-rate limited rather than diffusion limited. Let the reaction rate for amorphous material be $G$, and that for crystalline material $H$, with $G \gg H$. Since a fraction $F$ of the exposed surface is amorphous, the rate of dissolution would appear to be

$$\frac{d}{dt}\left(\frac{4}{3}\pi R^3\right) = -4\pi R^2 F G, \tag{4}$$

but, when the intercrystalline amorphous material is dissolved away, the crystalline grains, which constitute a fraction $(1 - F)$ of the clump, fall away as well, so that the factor $F$ can be removed from Eq. 4. The result, after a little manipulation, is that

$$R = R_0 - Gt \tag{5}$$

and the fraction of total material dissolved is

$$D_1 = F\left(1 - \frac{(R_0 - Gt)^3}{R_0^3}\right). \tag{6}$$

After a time $t = R_0/G$, all the fraction $F$ is dissolved and the rate $D_1$ must be set equal to zero.

The dissolution process for the crystallite grains proceeds in the same manner, except that the initial complication of partial composition is avoided. The fraction of total material dissolved by this process, assuming it to begin after a negligibly small delay, is

$$D_2 = (1 - F)\left(1 - \frac{(r_0 - Ht)^3}{r_0^3}\right), \tag{7}$$

and the total dissolution after time $t$ is $D = D_1 + D_2$, so that

$$D(t) = F\left(1 - \frac{(R_0 - Gt)^3}{R_0^3}\right) + (1 - F)\left(1 - \frac{(r_0 - Ht)^3}{r_0^3}\right). \tag{8}$$

For initial values of $R_0$ and $r_0$ as given in terms of the milling time by the experimental data of Figure 1, this equation has only two unknown parameters, the reaction rates $G$ and $H$, and the unknown function $F$, which we expect to have the form of Eq. 3. Clearly $G$ and $H$ must remain the same for all milling times and depend only upon temperature, while $F$ must be the same for all temperatures and depend only upon milling time.

## Results

The extent of dissolution as a function of leaching time for these milled powders is shown in Figure 2. There is clearly a

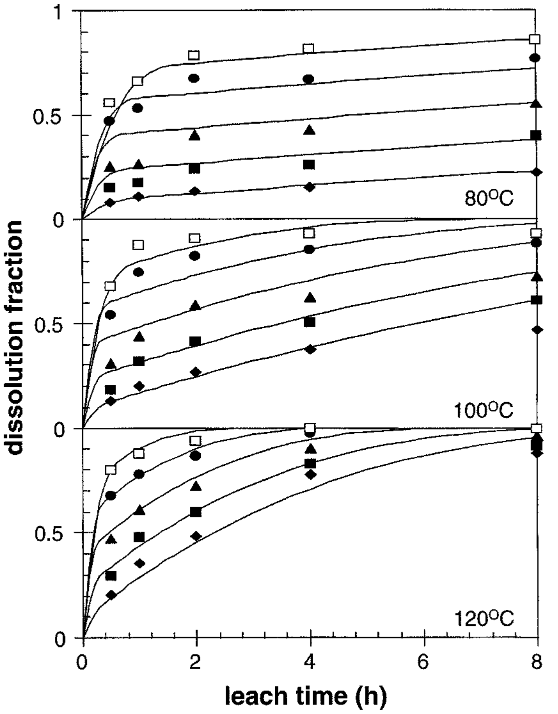

**Figure 2. Optimum fit of the model (lines) to the data at 80, 100 and 120°C for milling times of 0.25 (♦), 1 (■), 5 (▲), 25 (●), and 100 h (□).**

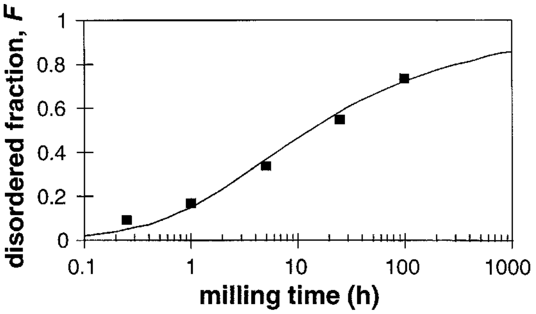

**Figure 3. Values of *F* derived from the initial fitting of the model to the experimental data.**

substantial increase in the rate of dissolution at all temperatures with increasing milling time.

It should be noted that, for the samples leached for 8 h at 120°C, hydrolysis of the solubilized titanium had occurred, precipitating $TiO_2$ (Welham and Llewellyn, 1998). The uncertain amount of this phase precipitated for each milling time is unknown and the fraction of ilmenite dissolution for the longest leach time is therefore uncertain. A high temperature is more likely to lead to hydrolysis, and therefore the 8-h data points for the 100 and 120°C runs were not used during the fitting process.

Initially, the values of $G$ and $H$ were determined by successive approximations, allowing the value of $F$ to be determined for each separate milling time. Figure 3 shows the deduced variation of $F$ with milling time, while the plotted curve is given by Eq. 3, with $m = 3.4$ and $b = 0.73\ \mathrm{h}^{-1}$. This explicit form of the relationship (Eq. 3) was then inserted into the calculations and the values of the rate constants, $G$ and $H$, were iteratively refined to give best fit to the experimental data for all three leaching temperatures.

From the rate constants derived from the model, an Arrhenius plot can be used to estimate the activation energy of each stage; this plot is shown in Figure 4. The activation energies of the two stages are 22 and 70 $\mathrm{kJ \cdot mol^{-1}}$ for the first and second stages, respectively. These values are in reasonable agreement with the values of 15 and 70 $\mathrm{kJ \cdot mol^{-1}}$ previously derived from the same experimental data (Welham and Llewellyn, 1998). These data were calculated assuming two stages of reaction, an initial stage that was assumed to be completed in the first half hour of leaching, and a first-order chemical-reaction-controlled stage beyond this. The presented data fit for the second stage of dissolution (Welham and Llewellyn, 1998, fig. 3b) suggests that the second stage does not occur until $>1$ h of leaching. Recalculating the activation energy of the initial step based on the initial step lasting 1 h, gave an activation energy of 21 $\mathrm{kJ \cdot mol^{-1}}$, which is closer to the value derived from the present model.

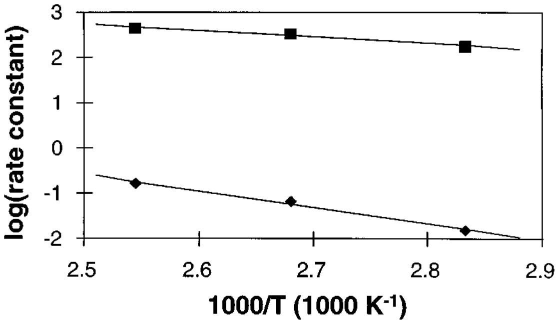

**Figure 4. Arrhenius plot for the rate constants *G* (♦) and *H* (■) derived from the model.**

## Discussion

The use of a two-stage process is in accord with the previous results, that indicate a rapid initial stage of dissolution followed by a slower second stage (Welham, 1997b; Welham and Llewellyn, 1998), even for unmilled powders (Duncan and Metson, 1982a,b; Welham and Llewellyn, 1998). The experimentally determined activation energies of the two reactions are similar to those derived from the model, suggesting that the model is a good approximation to reality.

The evidence from other systems is that the ilmenite will eventually become amorphous with extended milling (Koch, 1990), that is, $r_0 \rightarrow 0$ and $F \rightarrow 1$, thereby removing the term for the slower reaction $H_2$ from Eq. 8. Under these circumstances the rate of dissolution will be determined by the size of the clumps, with smaller clumps dissolving much more rapidly than large clumps, because of the greater specific surface area. Thus, since the effect of milling is to decrease $r_0$ and increase $F$, it is necessary to also minimize $R_0$ to ensure the maximum rate of dissolution. It is clear from Figure 1 that dry milling for longer than about 5 h results in an increase in $R_0$, indicating that the rate of rewelding of particles under impact is greater than the rate of breakage. Thus, it is necessary to decrease the rewelding to minimize the value of $R_0$. In industrial practice this is simply achieved by wet milling, which increases the proportion of fines (Taggart, 1954; Wills, 1992). Indeed, there is also evidence that small ($<0.1\%$) amounts of other chemicals in the water also aids the formation of surface area, with increases of up to 70% reported (El-Shall, 1985).

## Conclusions

A model has been formulated to explain the two-stage dissolution of a phase that has undergone extended milling. The model is based on the measured specific surface area and crystallite size of the milled powders along with the fraction of amorphous material around the crystallites, which could not be measured. The model agrees well with experimental results, with close agreement between the kinetic and thermodynamic parameters indicating that the model is a good representation of the dissolution process. The critical parameters for the model were found to be the crystallite size and the fraction of material in the disordered layer, with minimization of the former and maximization of the latter giving the most rapid dissolution. The size of the clumps, each comprising numerous crystallites with their amorphous coatings, also needs to be minimized.

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