How Do Specific Surface Area and Particle Size Distribution Change When Granular Media Dissolve?

Jeffrey W. Bullard^{a,b,*}, Qingxu Jin^{c,d}, Kenneth A. Snyder^c

^aZachry Department of Civil & Environmental Engineering, Texas A&M University, College Station, TX, USA ^bDepartment of Materials Science and Engineering, Texas A&M University, College Station, TX, USA ^cMaterials and Structural Systems Division, Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA

^dSchool of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA, USA

Abstract

The measured dissolution rate of a granular medium depends on its surface area and how the surface area changes during the course of the measurement. Moreover, the assumption that the specific surface area either remains constant or initially increases during dissolution is not always valid. This paper demonstrates that when the particle size distribution has sufficient variance, the instantaneous change in surface area during dissolution can be negative, even before the smallest particles dissolve away. The concept is explained using spherical particles, extended for use with prismatic particles, and demonstrated experimentally with gypsum powder. For the commercial gypsum powder used, the specific surface area decreases by about 50 % during the first 10 % of mass loss in water, so this effect may have practical importance and have a significant impact on the uncertainty in reported dissolution rates measured with batch reactors.

Keywords: dissolution; surface area; granular media

Preprint submitted to Chemical Engineering Journal

^{*}Corresponding author

Email addresses: jwbullard@tamu.edu (Jeffrey W. Bullard), billjin@gatech.edu (Qingxu Jin), kenneth.snyder@nist.gov (Kenneth A. Snyder)

1. Introduction

The dissolution of granular media in aqueous solutions is a central step in a range of natural and engineering processes. Among many examples are the weathering of sediments [1], the environmental release of pharmaceuticals [2–4], pesticides [5], and fertilizers [6], and the manufacture of concrete and gypsum products [7–9]. The primary kinetic property of interest in these processes is their rate per unit surface area. We use the symbol *J* to designated this property, which has the units of a flux. The absolute release rate, *R*, is the product of *J* and the total area, *S*, of actively dissolving surface. The absolute rate therefore changes with changes in *J*, changes in *S*, or both. Changes in *J* typically occur when the mechanism, temperature, or the driving force change during the process, and can remain relatively constant when the conditions of dissolution are controlled. In contrast, *S* changes continuously among a fixed collection of convex particles.

An estimate of geometric surface area is usually used to normalize the absolute rate and infer J. The actual flux is nonuniform over the surface, happening primarily by detachment from surface kink sites [10, 11]. The local concentration (number per unit geometric area) of kink sites is greatest where dislocations or grain boundaries intersect the surface [11]. Therefore, one expects significant variability in observed values of J when the geometric surface area is used to determine the flux. Nevertheless, geometric surface area estimates are almost always used instead because characterization of kink site concentrations is typically not feasible for experimental measurements.

Experimental studies of granular dissolution typically make simplifying assumptions for estimating the surface area and its changes during the process. Most estimate the surface area by assuming that the particles are smooth spheres and using knowledge of the average particle dimension [12–15], although at least one study attempted to account for particle shape effects on the surface area [2]. Some use more direct estimates of specific surface area, *s*, by air permeability measurements [16] or multipoint nitrogen adsorption (BET) isotherms [9].

Measurements of granular dissolution or growth fluxes are complicated by the fact that both the specific surface area and the total area change as the particles dissolve. But measuring such changes in surface area is difficult in practice, and so most experimental studies make simplifying assumptions. Much of the work on dissolution kinetics is performed in the area of geochemistry, and in a survey of that literature over the last 40 years we found one investigation that used a uniformly shrinking core model to estimate changes in particle size and surface area [17] and two others that tracked the change in BET specific surface area as a function of mass loss [9, 18]. However, the vast majority of reported fluxes are obtained by assuming that S remains constant throughout the time interval used to measure the average dissolution flux [12-15]. Given that the volume of particles is always decreasing during dissolution, the implicit assumption is that the specific surface area keeps increasing, at least until the smallest particles dissolve completely. When evaluating granular dissolution of sparingly soluble solids with low dissolution rates, especially over relatively short time intervals, the surface area may remain approximately constant over the duration of the measurement. In fact, most prior studies on such systems do assume a constant surface area. Nevertheless, that assumption should be evaluated for its applicability to more rapidly dissolving systems or longer time intervals. This paper takes a step in that direction by investigating how the surface area of a collection of uniformly shrinking particles depends both on the particle size distribution and on the progress of dissolution.

The nature of the evolution of the specific surface area during dissolution is studied analytically using spherical particles. The results indicate that when expected values of the particle distribution meet certain requirements, the initial change in specific surface is negative. Moreover, the expected values can also be used to estimate the initial slope of the change. To apply this theory to practical materials, the degree to which prismatic particles can be approximated by spheres is studied to identify the range over which the physical parameter estimations remain within approximately 25 %. To demonstrate the occurrence of decreasing specific surface area in practice, gypsum powder is dissolved in water while periodically measuring its particle size (laser diffraction) and specific surface area (BET).

2. Theory

The evolution of specific surface area is first demonstrated using the mathematics describing spherical particles. The degree to which these equations characterize prismatic particles is investigated in preparation for characterizing the results of an experiment conducted on commercial gypsum particles.

2.1. Spherical Particles

Consider a dissolution experiment conducted on a sample of spherical particles. Before the dissolution experiment begins, let the initial particle size distribution be characterized by a continuous probability density function, f(x), such that f(x)dx is the number fraction of particles having a radius between x and x + dx. The corresponding cumulative distribution function F(x),

$$F(x) = \int_0^x f(x') \, \mathrm{d}x'$$
 (1)

is the number fraction of particles having a radius less than or equal to x.

For the random variable *X* that represents the radius of a particle that was drawn from the probability density function f(x), the expected value of its *n*-th power (i.e., a raw moment) is calculated from

$$\langle X^n \rangle_0 = \int_0^\infty x^n f(x) \,\mathrm{d}x \tag{2}$$

where the subscript $\langle \cdot \cdot \cdot \rangle_0$ denotes that the value is calculated from the initial particle size distribution f(x).

The initial specific surface area of the particles is the ratio of the initial expected surface area *S* to the initial expected volume *V*:

$$\frac{S_0}{V_0} = \frac{\int_0^\infty k_s \, x^2 f(x) \, \mathrm{d}x}{\int_0^\infty k_v \, x^3 f(x) \, \mathrm{d}x} = k_{sv} \frac{\langle X^2 \rangle_0}{\langle X^3 \rangle_0} \tag{3}$$

The constants k_s and k_v are shape factors; for spheres, $k_s = 4\pi$ and $k_v = 4\pi/3$. The constant k_{sv} is the ratio of these two shape factors.

As dissolution progresses, the particle radius distribution will change, depending on the degree of dissolution. Let all the particle radii shrink by a constant linear dimension ϵ in a given time interval, which they will do if the molar dissolution flux is constant. The relative number of particles remaining with radius x is a conditional probability $g(x|\epsilon)$ that is proportional to the relative number of particles with dimension $(x + \epsilon)$ from the original distribution: $g(x|\epsilon) \propto f(x + \epsilon)$. The coefficient of proportionality is calculated by ensuring the total integral equals unity:

$$g(x|\epsilon) = \frac{f(x+\epsilon)}{[1-F(\epsilon)]}$$
(4)

where $F(\epsilon)$, according to Eq. (1), is the number fraction of the original particles that are small enough to disappear completely when the radius of all particles shrinks by ϵ . The expectations $\langle X^n \rangle_{\epsilon}$ of the distribution $g(x|\epsilon)$ can be expressed as a function of the original particle size distribution, after a substitution and a change of variables $(Z = X + \epsilon)$:

$$\langle X^n \rangle_{\epsilon} = \int_0^\infty x^n g(x|\epsilon) \, \mathrm{d}x = \int_{\epsilon}^\infty (z-\epsilon)^n \frac{f(z)}{[1-F(\epsilon)]} \, \mathrm{d}z$$
 (5)

By inspection, $\langle X^n \rangle_{\epsilon \to 0} = \langle X^n \rangle_0$. Furthermore, if the dissolution has not completely dissolved any of the particles, ϵ is less than the smallest initial particle (x_{\min}) and $F(\epsilon) = 0$. In this case, the expectations can be calculated from the corresponding expectations of the initial distribution f(x):

$$\langle X^n \rangle_{\epsilon < x_{\min}} = \int_{\epsilon < x_{\min}}^{\infty} (z - \epsilon)^n f(z) dz = \sum_{k=0}^n \binom{n}{k} (-\epsilon)^k \langle X^{n-k} \rangle_0$$
 (6)

The factor $\binom{n}{k}$ is the binomial coefficient.

As dissolution progresses, the radius distribution will change. For all values of $\epsilon < x_{min}$, the corresponding expectations $\langle X^n \rangle_{\epsilon}$ can be calculated from the original distribution function.

The dissolution-dependent specific surface area is the ratio of the expected surface area $S(\epsilon)$ to the expected volume $V(\epsilon)$:

$$s(\epsilon) \equiv \frac{S(\epsilon)}{V(\epsilon)} = \frac{\int_0^\infty k_s \, x^2 g(x|\epsilon) \, \mathrm{d}x}{\int_0^\infty k_v \, x^3 g(x|\epsilon) \, \mathrm{d}x} = k_{sv} \frac{\langle X^2 \rangle_\epsilon}{\langle X^3 \rangle_\epsilon} \tag{7}$$

Two quantities of interest are the initial specific surface area and the corresponding value for $\epsilon < x_{\min}$:

$$s(0) = k_{sv} \frac{\langle X^2 \rangle_0}{\langle X^3 \rangle_0} \tag{8}$$

$$s(\epsilon < x_{\min}) = k_{sv} \left[\frac{\langle X^2 \rangle_0 - 2\epsilon \langle X \rangle_0 + \epsilon^2}{\langle X^3 \rangle_0 - 3\epsilon \langle X^2 \rangle_0 + 3\epsilon^2 \langle X \rangle_0 - \epsilon^3} \right]$$
(9)

The initial evolution of the specific surface area during dissolution, while $\epsilon < x_{\min}$, is a function of the moments of the original particle size distribution (on a number basis). The moments are therefore independent of ϵ , so the rate of change of *s* with respect to ϵ , as $\epsilon \rightarrow 0$, is

$$\frac{\mathrm{d}s}{\mathrm{d}\epsilon}\Big|_{\epsilon \to 0} = \lim_{\epsilon \to 0} \frac{s(\epsilon) - s(0)}{\epsilon} = s(0) \left[\frac{3\langle X^2 \rangle_0}{\langle X^3 \rangle_0} - \frac{2\langle X \rangle_0}{\langle X^2 \rangle_0} \right]$$
(10)

The surprising result is that the initial slope in the specific surface (with respect to ϵ) can be positive, zero, or negative, even though the specific surface area of each individual particle increases. Moreover, the magnitude of the slope is proportional to the initial specific surface, so dissolution will initially cause an exponential growth or decay in specific surface area,

$$s(\epsilon \to 0) = s(0) \exp\left[\left(\frac{3\langle X^2 \rangle_0}{\langle X^3 \rangle_0} - \frac{2\langle X \rangle_0}{\langle X^2 \rangle_0}\right)\epsilon\right]$$
(11)

The condition for *s* to increase with ϵ is that the term in parentheses of Eq. (10) be positive. This condition can be rewritten in terms of a dimensionless parameter ζ that must satisfy the following relationship:

$$\zeta \equiv \frac{\langle X^2 \rangle_0^2}{\langle X \rangle_0 \langle X^3 \rangle_0} > \frac{2}{3} \tag{12}$$

If $\zeta = 2/3$, the specific surface area should initially remain constant, and if $\zeta < 2/3$ specific surface area will decrease upon dissolution.

In some applications, particles are described on a volume basis density function

p(y), where p(y) dy is the *volume* fraction of particles having a radius between y and y + dy. The above analysis is more complicated in this basis, and is discussed in the Appendix.

2.2. Discrete Particle Size Distributions

The dynamic behavior of the specific surface can be illuminated by considering a simple discrete particle size distribution. Let there be *N* different particle sizes, each scaled by the smallest particle size, and let the discrete distribution be represented by a sum of Dirac delta functions, $\delta(x)$:

$$f(z) = \sum_{i=1}^{N} \gamma_i \,\delta\left(z - \frac{X_i}{X_{\min}}\right) \tag{13}$$

where γ_i the probability of particle size X_i , and $X_{\min} = X_1$.

A familiar case is that of a collection of perfectly monosized particles, in which case N = 1 and $\gamma_1 = 1$. Application of Eq. (12) leads to the expected result that the collection of monosized particles will increase in specific surface area during dissolution.

More complex behavior is encountered by introducing more particle sizes, however. Consider a size distribution in which a fraction *p* has a size of z = 1 and the rest have a size $z = (X_2/X_1) = \beta$. The particle size distribution for this situation is the sum of two terms:

$$f(z) = p \,\delta(z-1) + (1-p) \,\delta(z-\beta) \tag{14}$$

Application of Eq. (12) to this collection yields a criterion for an increase in specific surface upon dissolution:

$$p^{2} + 2p(1-p)(3\beta^{2} - \beta^{3} - \beta) + \beta^{4}(1-p)^{2} > 0$$
(15)

Figure 1 shows the (β, p) pairs that result in an initial increase or decrease in specific surface area. The points along the curve are the (β, p) pairs for which the specific surface area remains constant as the particles initially dissolve.



Figure 1: Incremental change in specific surface during dissolution for a granular medium with two particle sizes having a size ratio of β , given that the number fraction of smaller particles is p: (a) shows the curve that distinguishes the regions where the change is positive or negative, with a dotted line at p = 1 for comparison; (b) shows the same curve, with the quantity (1-p) on the y-axis. The filled circles in (b) indicate the starting points of the systems considered in Fig. 2, and the arrows indicate the direction of the path taken.

Eq. (15) and the "phase diagram" in Fig. 1 indicate only the limiting behavior in the specific surface area at the onset of dissolution when $\epsilon \to 0$. As dissolution progresses, the ratio of particle sizes β increases while the relative probability p remains constant, and so a point in (β, p) -space moves horizontally to the right from its initial position in Fig. 1. If a path in (β, p) -space crosses the boundary in Fig. 1, the specific surface area may switch between increasing and decreasing specific surface area as dissolution continues. Eq. (9) applies for any degree of dissolution up to $\epsilon = 1$ where the smallest particles disappear, and Fig. 2 shows the various ways that the specific surface area can evolve during dissolution when the ratio of the two particle sizes is $\beta = 10$, depending on the number fraction p of the small particles. As indicated in Fig. 1, the limiting slope of the curves as $\epsilon \to 0$ can be positive, negative or zero. In particular, if one begins somewhere on the curve in Fig. 1, the limiting slope is zero and the curve remains nearly flat as dissolution progresses—the specific surface area remains nearly constant.



Figure 2: Predictions of the evolution in scaled specific surface area ($S = s(\epsilon)/s(0)$) during uniform dissolution of a bimodal particle size distribution. The left plot shows the influence of the number fraction of the smaller particles for a fixed initial size ratio of $\beta = 10$. The right plot shows the influence of that initial size ratio for a fixed number fraction p = 0.999 of the smaller particles. The initial behavior, whether increasing, decreasing, or remaining relatively constant, is indicated by the diagram in Fig. 1.

2.3. Continuous Distributions

Although continuous probability distributions that have finite values near x = 0 are used to approximate particle size distributions, there is often a practical lower limit (X^*) such that $F(x < X^*) \approx 0$. Therefore, for values of $\epsilon \le X^*$, the previous analysis holds. This lower limit can often be inferred from some acceptably small probability for having particles smaller than X^* .

Several continuous probability density functions are commonly used to describe particle size distributions. The logarithmic normal (log-normal) distribution is sometimes used as a model for crushed powders, and it is examined here for illustration purposes:

$$f(x) = \left(\frac{1}{x \,\sigma \sqrt{2\pi}}\right) \exp\left[-\frac{1}{2} \,\left(\frac{\ln(x/x_m)}{\sigma}\right)^2\right] \tag{16}$$

where x_m is the median value and σ is a distribution width parameter. The moments of the log-normal distribution are

$$\langle X^n \rangle = x_m^n \, \exp\left[\frac{n^2 \sigma^2}{2}\right] \tag{17}$$

If there is a practical lower limit X^* , the corresponding partial expectation $h(X^*)$

is expressed as a function of the normal cumulative distribution function Φ :

$$h(X^*) = \int_{X^*}^{\infty} x f(x) dx = \langle X \rangle \Phi\left(\frac{\ln(x_m/X^*)}{\sigma} + \sigma\right)$$
(18)

Therefore, as long as $x_m/X^* \ge 10$ and $\sigma \le 1$, the correction required to $\langle X \rangle$ will be less than 0.1 % when the log-normal distribution is truncated at a lower limit of X^* ; higher moments will be less effected by this truncation.

During initial dissolution for which $\epsilon < X^*$, satisfying Eq. (12) gives the following criterion for the specific surface to increase:

$$\sigma < \sqrt{\ln(3/2)} \approx 0.6368 \tag{19}$$

Therefore, a collection of particles characterized by a log-normal particle size distribution and having a width parameter σ greater than this value will exhibit a *decreasing* specific surface at the onset of dissolution.

This result is particularly interesting because it is independent of whether the lognormal distribution characterizes the number density function or the volume density function. If the number density function is log-normal, so is the corresponding volume density function, and vice-versa. Moreover, the width parameter σ is unchanged (the curve merely shifts on a semi-log plot), which is why the above mentioned criterion applies to either the number density or the volume density distribution for a lognormal distribution. Further details of this result are discussed in the Appendix.

2.4. Prismatic Particles

In the subsequent experiment, the gypsum powder being analyzed were manufactured by precipitation from a supersaturated solution. As a result, the particles have a prismatic shape indicative of the underlying crystal structure. Another consequence of this manufacturing technique is that upon dissolution, the particles are expected to dissolve in such a way as to maintain their general shape (the ratio of lengths describing the size of the particle).

Particles in the shape of a rectangular prism can be uniquely described by a triplet representing the length, width, and height of the particle: (x, y, z). To simplify further analysis, the *y* and *z* lengths can be expressed as a product of the *x* length and a scaling factor: (x, wx, hx). Thus, the shape of the particle can be characterized by the tuple (w, h), with the following classifications: cube - w = h = 1; prolate - w = h < 1; oblate - w = h > 1.

For these particles to dissolve in such a way as to retain their shape, each dimension must lose a thickness of material that is in proportion to the length of that dimension. Letting ϵ represent the characteristic depth of material dissolved away, the volume $V(\epsilon|w, h)$ and surface area $S(\epsilon|w, h)$ of a particle with initial size x and shape (w, h) are as follows:

$$V(\epsilon|w,h) = (x-\epsilon) (wx - w\epsilon) (hx - h\epsilon)$$

= $wh(x-\epsilon)^3$ (20)

$$S(\epsilon|w,h) = 2[(x-\epsilon)(wx-w\epsilon) + (x-\epsilon)(hx-h\epsilon) + (wx-w\epsilon)(hx-h\epsilon)]$$

= 2(w+h+wh)(x-\epsilon)² (21)

The significance of this result is that the particle volume is a product of two independent terms - one is a function of only the shape (w, h), and the other only the particle size x and dissolution depth ϵ .

Furthermore, the expectations $\langle X^n \rangle_{\epsilon}$ have the same form as Eq. 5, and as a result, one recovers Eqs. 8 & 9, with the following shape factor

$$k_{sv} = \frac{2(w+h+wh)}{wh}$$
(22)

This means that the ratio $s(\epsilon \to 0)/s(0)$ (Eq.11) is a function of ϵ and the initial size distribution f(x), but does not depend on shape.

This is also true if the sample comprises of a collection of different shapes. The expected volume of a discrete distribution of shapes can be expressed as

$$V_0 = \int_0^\infty \sum_i \phi_i w_i h_i \ x^3 f(x) \,\mathrm{d}x \tag{23}$$

where ϕ_i is the number fraction of particles having shape (w_i, h_i) . The summation is independent of the integral, and is multiplicative; this is true for the dissolution dependent expectation as well. Thus, for prismatic particles that dissolve in a shape preserving manner and that are characterized by Eq. 23, one does not have to know the specific distribution of shapes present.

3. Experiments

3.1. Materials

A synthetic gypsum powder was used to study the relationship between the change of specific surface area, relative to its initial value, and the fraction of powder mass consumed after partial dissolution in deionized water. The synthetic gypsum was reagent grade calcium sulfate dihydrate (Sigma Aldrich, St. Louis, MO¹. The certificate of analysis reports a purity of \geq 99 %, with the most concentrated impurity being chlorine at \leq 100 mg kg⁻¹. Examination of the powder particles by scanning electron microscopy (SEM) reveals the large particles to be decorated with smaller particles, as shown in Fig. 3. The synthetic gypsum was partially dissolved in the deionized water for varying fractions of initial powder mass. In the dissolution experiments, cold ionized water (< 3 °C) was used to avoid the precipitation and increase the solubility of

¹Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

gypsum powder. The residual powder was collected for further characterization. The SEM image of powder particles after partial dissolution exhibits fewer smaller particles and the surface of large particles are roughened during the dissolution compared to the particles observed before dissolution. This indicates that smaller particles likely have completely dissolved, as reported previously for silica nanoparticles [19].



Figure 3: Gypsum particles at different amounts of dissolution, reported here as a percent dissolved by mass. (a) Initial powder particles; (b) 9% dissolved; (c) 16% dissolved; (d) 28% dissolved.

3.2. Characterization

Both the specific surface area, *s*, and the discrete particle size distribution (PSD) of the gypsum powder were measured before dissolution and after varying degrees of dissolution. Brunauer-Emmett-Teller (BET) nitrogen adsorption and desorption isotherms were used to estimate *s*. Approximately 1.5 g of powder were used in a gas analyzer (Micromeritics ASAP 2020) over a pressure range of 0.01 atm to 0.99 atm. The powder was degassed at 1 mPa for 12 h prior to the analysis. The PSD measurements

were made using laser diffraction of a dilute suspension of particles in isopropanol; the results are on a volume basis, which were transformed into a number basis using the procedure outlined in the Appendix. All BET and PSD measurements were made on three separate samples, except for the PSD after dissolution for which only one sample was measured. However, six sequential replicate PSD measurements were made on each PSD sample to calculate a mean value, and the uncertainty was estimated from the three measurements made on the sample before dissolution.

The PSDs obtained by this method are based on particle sizes that correspond to equivalent sphere diameters. Therefore, the true value of k_v is the one required to transform from the assumed spherical geometry of the PSD measurement to the actual particle shape. This is somewhat of a semantic detail because the analysis is based largely on ratios, in which the shape constants factor out.

4. Results

The specific surface was calculated from BET estimates for the total surface area per mass of specimen. More specifically, assuming that the powders had a constant density, the ratio of instantaneous specific surface for mass m to the initial specific surface at m_0 is equal to the relative change in the BET result.

The specific surface area of the gypsum particles, normalized by its initial value, is plotted as a function of the fractional change in mass, $(1 - m/m_0)$, as shown by the points in Fig. 4. The specific surface area decreases as the particles start to dissolve. An empirical exponential model was recently used to account for observed changes in specific surface area by dissolving gypsum powders [9]:

$$\frac{s}{s_0} = 1 + a \left[1 - e^{-b[1 - m(t)/m_0]} \right]$$
$$= 1 + a \left[1 - e^{-bVM(c - c_0)/m_0} \right]$$
(24)

where s_0 is the initial specific surface area and $\{a, b\}$ are experimentally-determined parameters. The values of a and b obtained by nonlinear regression, together with their standard errors, are indicated in the plot.

Fig. 4 compares this exponential model with the shrinking core model described in the previous section and based on the initial PSD. The shrinking core model is just as consistent with the data as the exponential fit, the only difference being a modestly different rate of decrease at low mass loss where there are no experimental data for comparison.



Figure 4: Measured dependence on dissolved mass fraction of the relative specific surface area of the gypsum powder. The solid curve was produced by nonlinear regression using Eq. (24), yielding coefficients and standard errors of $a = 0.57 \pm 0.02$ and $b = 21 \pm 7$. The error bars were produced by propagating the measured sample standard deviation of three BET measurements of the initial powder, $39 \text{ m}^2 \text{ kg}^{-1}$.

Figure 5 shows the experimentally measured particle size distributions initially and after about 28 % mass loss by dissolution, plotted as probability density functions on a volume basis (Fig. 5a) or on a number basis (Fig. 5b). They show that the changes in PSD are only modestly greater than the uncertainty in the data, which is approximately indicated by the size of the symbols.

The minor details of the particle size distribution can influence the interpretation of the expected behavior. Inspection of the data in Fig. 5a indicates small but non-



Figure 5: Particle size distribution of gypsum particles initially (circles) and after 28 % volume loss by dissolution (squares). The plots are given as probability density functions (a) on a volume basis and (b) on a number basis. Each data point is the mean of six sequential measurements, and the sample standard deviation of the mean is about the size of the symbols used.

zero volume fraction below approximately 10 µm. Approximating the distribution in Fig. 5a by fitting a log-normal to only the portion of the distribution greater than 10 µm would yield erroneous results (the width parameter σ would be less than 0.6). The particles in Fig. 5a greater than 10 µm appear as a barely discernible peak beyond 10 µm in Fig. 5b. By separating the area under the distribution on either side of 10 µm in Fig. 5b, the number density function before dissolution can be approximated by one particle size at 0.5 µm with probability 0.999, and another particle size at 20 µm with probability 0.001. This corresponds to $\zeta \approx 0.1$, corroborating the experimental evidence that the specific surface decreases dramatically upon dissolution.

5. Discussion

The shrinking core model predicts that some particle size distributions may display an initial decrease in specific surface area upon dissolution even though each individual particle's specific surface area must be increasing. This can happen even before the smallest particles begin to disappear, although the disappearance of those particles can intensify the decrease in specific surface area. In practical experimental situations it may be difficult to separate the influence of these two effects. However, this study shows that significant changes in specific surface area can occur, not to mention changes in the total surface area, over time intervals for which the particle size distribution does not change perceptibly, as can be seen by a comparison of Fig. 5 and Fig. 4. That is, small changes in PSD are not sufficient to justify the assumption that the surface area changes are negligible, as is often done in the literature.

The model assumes that the particles dissolve in a shape preserving manner, and does not account for changes in surface roughness that might occur by dissolution. Dissolving particles may undergo some apparent smoothing of their corners and edges, although it is not clear that that apparent smoothing actually correlates to a decrease in local kink site density [20]. Moreover, dissolving particles can also experience local surface roughening due to etch pit formation at surface defects. Neither smoothing nor roughening are taken into account by the shrinking core model, and their absence may adversely affect the actual changes in surface area during powder dissolution. However, such effects are quite difficult to predict without resorting to a detailed characterization of the surface defect density and particle shape, and even then would probably require molecular-scale simulations to model the changes with time. That kind of characterization and analysis may by beyond the reach of most laboratories for the time being, but in any event is beyond the scope of this paper.

Although the shrinking core model has the theoretical shortcomings just mentioned, it does seem to do an excellent job of predicting the surface area changes that were measured experimentally (Fig. 4) for dissolving gypsum powder when the initial particle size distribution was input. That powder seemed to suffer no significant changes in roughness during the experiment, at least at the scale that can be resolved by the SEM images in Fig. 3. The model should be tested in the future on powders that may undergo more significant roughening to check for the broadness of its applicability. In any event, such a simplified model is a substantial improvement over the usual assumption that the either the total surface area or the specific surface area remain constant throughout the experiment, especially for rapidly dissolving granular media which can undergo such changes over short time intervals.

6. Conclusion

The specific surface area of an ordinary commercial gypsum powder decreases by about 50 % during the first 10 % of mass loss in water, which happens at room temperature within about ten seconds. The same effect is predicted by a relatively simple mathematical model of particles dissolving in such a way as to preserve their shape. That model also suggests that the magnitude, and even the sign, of the change in surface area depend sensitively on the details of the particle size distribution. Assuming that the surface area remains constant can potentially introduce an error in the inferred dissolution flux. Based on the data for gypsum shown in Fig. 4, the error in that particular case would be at least a factor of two. Significantly better estimates of powder dissolution rates can be made by measuring the number-based particle size distribution and using it in a model like that reported here to estimate the changes in surface area over the course of the dissolution measurement.

Acknowledgments

Qingxu Jin gratefully acknowledges financial support from National Science Foundation INTERN DCL program via Grant No. CMMI-1362843. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

- S. R. H. Worthington, G. J. Davies, E. C. Alexander, Enhancement of bedrock permeability by weathering, Earth-Science Reviews 160 (2016) 188–202.
- [2] M. Mosharraf, C. Nyström, The effect of particle size and shape on the surface specific dissolution rate of microsized practically insoluble drugs, Inter-

national Journal of Pharmaceutics 122 (1–2) (1995) 35–47. doi:10/1016/0378-5173(95)00033-F.

- [3] P. A. Mountford, M. A. Borden, On the thermodynamics and kinetics of superheated fluorocarbon phase-change agents, Advances in Colloid and Interface Science 237 (2016) 15–27.
- [4] A. C. F. Rumondor, S. S. Dhareshwar, F. Kesisoglou, Amorphous solid dispersions or prodrugs: Complementary strategies to increase drug absorption, Journal of Pharmaceutical Sciences 105 (9) (2016) 2498–2508.
- [5] T. J. Strathmann, A. T. Stone, Reduction of the pesticides oxamyl and methomyl by Fe-II: Effect of pH and inorganic ligands, Environmental Science and Technology 36 (4) (2002) 653–661.
- [6] I. P. Abrol, I. S. Dahiya, D. R. Bhumbla, On the method of determining gypsum requirement of soils, Soil Science 120 (1) (1975) 30–36.
- [7] P. Juilland, E. Gallucci, Morpho-topological investigation of the mechanisms and kinetic regimes of alite dissolution, Cement and Concrete Research 76 (2015) 180–191.
- [8] P. Juilland, L. Nicoleau, R. S. Arvidson, E. Gallucci, Advances in dissolution understanding and their implications for cement hydration, RILEM Technical Letters 2017 (2) (2017) 90–98.
- [9] J. Tang, J. W. Bullard, L. N. Perry, P. Feng, J. Liu, An empirical rate law for gypsum powder dissolution, Chemical Geology 498 (2018) 96–105.
- [10] W. K. Burton, N. Cabrera, Crystal growth and surface structure, part I, Discussions of the Faraday Society 5 (1949) 33–39.
- [11] A. Lasaga, A. Lüttge, Variation of crystal dissolution rate based on a dissolution step wave model, Science 291 (2001) 2400–2404.

- [12] A. L. Lebedev, Kinetics of gypsum dissolution in water, Geochemistry International 53 (9) (2015) 811–824.
- [13] A. Jeschke, K. Vosbeck, W. Dreybrodt, Surface controlled dissolution rates of gypsum in aqueous in solutions exhibit nonlinear dissolution kinetics, Geochimica et Cosmochimica Acta 65 (2001) 27–34.
- [14] D. Damidot, F. Bellmann, T. Sovoidnich, B. Möser, Measurement and simulation of the dissolution rate at room temperature in conditions close to a cement paste: From gypsum to tricalcium silicate, Journal of Sustainable Cement-Based Materials 1 (3) (2012) 94–110.
- [15] L. Nicoleau, A. Nonat, D. Perrey, The di- and tricalcium silicate dissolutions, Cement and Concrete Research 47 (2013) 14–30.
- [16] F. Bellmann, T. Sowoidnich, H.-M. Ludwig, D. Damidot, Dissolution rates during the early hydration of tricalcium silicate, Cem. Concr. Res. 72 (2015) 108–116.
- [17] J. Christoffersen, M. R. Christoffersen, The kinetics of dissolution of calcium sulphate dihydrate in water, Journal of Crystal Growth 35 (1) (1976) 79–88.
- [18] Q. Jin, L. N. Perry, J. W. Bullard, Temperature dependence of gypsum dissolution rates, Cement and Concrete Research 129 (2020) 105969. doi:10.1016/j.cemconres.2019.105969.
- [19] T. Diedrich, A. Dybowska, J. Schott, E. Valsami-Jones, E. H. Oelkers, The dissolution rates of SiO₂ nanoparticles as a function of particle size, Environmental Science and Technology 46 (2012) 4909–4915. doi:10.1021/es2045053.
- [20] L. Briese, R. S. Arvidson, A. Lüttge, The effect of crystal size variation on the rate of dissoltuion—-a kinetic Monte Carlo study, Geochimica et Cosmochimica Acta 212 (2017) 167—175. doi:10.1016/j.gca.2017.06.010.

Appendix A Volumetric Particle Size Distribution

It is common to express a particle size distributions on a volume bases, rather than a number basis. The most common volumetric particle size distribution is from a sieve analysis, whereby one reports the mass fraction of particles resting on a sieve having an opening size 2y. Assuming uniform particles, the mass fractions are equal to the volume fractions. For a continuous distribution p(y) of spherical particles, the quantity p(y) dy is the *volume* fraction of particles having a radius between y and y + dy.

For the random variable *Y* from the distribution p(y), the expected values for the powers of *Y* (the raw moments) are calculated from

$$\langle Y^n \rangle_0 = \int_0^\infty y^n \, p(y) \, \mathrm{d}y \tag{A.1}$$

where the subscript $\langle \cdots \rangle_0$ denotes that the value is calculated from the initial distribution p(y).

As dissolution progresses, the corresponding particle size distribution will become a conditional probability distribution $t(y|\epsilon)$ that depends on the degree of dissolution, by analogy to the number density case. In this case, however, there is no simple translational relationship between p(y) and $t(y|\epsilon)$ because the relative volume fractions are changing as a function of the particle size. Instead, the conditional probability must be calculated from the transformation from the number density distribution.

Given the initial number density distribution f(x), the corresponding initial volume density distribution p(y) is a volume weighted quantity, normalized to ensure unit probability:

$$p(y) = \frac{y^3}{\langle X^3 \rangle_0} f(y) \tag{A.2}$$

The moments of Y^n can be calculated directly from the moments of the number density

distribution:

$$\langle Y^n \rangle_0 = \int_0^\infty \frac{y^{3+n}}{\langle X^3 \rangle_0} f(y) \, \mathrm{d}y = \frac{\langle X^{3+n} \rangle_0}{\langle X^3 \rangle_0} \tag{A.3}$$

where the random variable *X* refers to the number density distribution f(x). By analogy, the conditional volume density distribution $t(y|\epsilon)$ can be calculated from the conditional number density distribution $g(x|\epsilon)$:

$$t(y|\epsilon) = \frac{y^3}{\langle X^3 \rangle_0} g(y|\epsilon) = \frac{y^3}{\langle X^3 \rangle_0} \frac{f(y+\epsilon)}{[1-F(\epsilon)]}$$
(A.4)

The moments Y^n as the dissolution progresses are calculated in the same manner as for the number density, using a change in variables:

$$\langle Y^n \rangle_{\epsilon} = \int_{\epsilon}^{\infty} \frac{(z-\epsilon)^{3+n}}{\langle X^3 \rangle_0} \frac{f(z)}{[1-F(\epsilon)]}$$
 (A.5)

The two limiting cases of interest are

$$\langle Y^n \rangle_{\epsilon=0} = \frac{\langle X^{3+n} \rangle_0}{\langle X^3 \rangle_0}$$
 (A.6)

and the case of minimal dissolution ($\epsilon < x_{\min}, F(\epsilon) = 0$), where the result is similar to the number density result:

$$\langle Y^n \rangle_{\epsilon < x_{\min}} = \frac{1}{\langle X^3 \rangle_0} \sum_{k=0}^{3+n} \binom{3+n}{k} (-\epsilon)^k \langle X^{3+n-k} \rangle_0 \tag{A.7}$$

Appendix B Calculating the ζ Criterion from Volumetric Data

The ζ parameter has been expressed as a function of raw moments of the number density function f(x). To calculate ζ as a function of the raw moments of p(y), the raw moments of f(x) must be expressed as a function of the p(y) moments. This begins by expressing f(x) as a function of p(y).

Given a probability on a volume basis, one can determine the corresponding den-

sity function on a number basis by the algebraic inversion of Eq. A.2 above:

$$f(x) = \langle X^3 \rangle_0 \, \frac{p(x)}{x^3} \tag{B.1}$$

By noting that the integral over f(x) must be unity, one discovers that $\langle X^3 \rangle_0 = 1/\langle Y^{-3} \rangle_0$:

$$f(x) = \left(\frac{1}{\langle Y^{-3} \rangle_0}\right) \frac{p(x)}{x^3}$$
(B.2)

Following the development for the volume density relations above, the raw moments for the two distributions are related as follows:

$$\langle X^n \rangle_0 = \frac{\langle Y^{n-3} \rangle_0}{\langle Y^{-3} \rangle_0} \qquad \qquad \langle Y^n \rangle_0 = \frac{\langle X^{n+3} \rangle_0}{\langle X^{+3} \rangle_0} \tag{B.3}$$

Using these equations and Eq. (17), one can show that for the log-normal distribution the dimensionless ratios of the moments for the number basis PDF ($\langle X \rangle_0^2 / \langle X^2 \rangle_0$, $\langle X \rangle_0^3 / \langle X^3 \rangle_0$) are the same as for the volume basis PDF. Therefore, not only does the distribution remain log-normal upon transformation, the width parameter σ remains the same.

In addition, one can calculate the ζ parameter using the moments of either distribution:

$$\zeta = \frac{\langle X^2 \rangle_0^2}{\langle X \rangle_0 \langle X^3 \rangle_0} \equiv \frac{\langle Y^{-1} \rangle_0^2}{\langle Y^{-2} \rangle_0} > 2/3$$
(B.4)

Appendix C Estimating ϵ from Mass Measurements

During dissolution, the ratio of $m(t)/m_0$ is equivalent to the ratio of the time varying total volume to the initial total volume. These quantities depend on the number of particles n (n_0 – the initial number; $n(\epsilon)$ – the number after dissolution to a depth $\epsilon)$ and the expected particle volume $\langle V \rangle$:

$$\frac{m(t)}{m_0} = \frac{n(\epsilon)}{n_o} \frac{\langle V \rangle_{\epsilon}}{\langle V \rangle_0} = [1 - F(\epsilon)] \frac{\int_0^\infty x^3 g(x|\epsilon) \, \mathrm{d}x}{\int_0^\infty x^3 f(x) \, \mathrm{d}x}$$
$$= \frac{\int_{\epsilon}^\infty (z - \epsilon)^3 f(z) \, \mathrm{d}z}{\langle X^3 \rangle_0} \tag{C.1}$$

For a given measurement of m/m_0 , the value of ϵ is determined from the equation above for particles that dissolve in a shape preserving manner such as spheres and collections of prismatic shapes characterized by Eq. 23.