Grinding methods to enhance the reactivity of olivine

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Abstract
The Albany Research Center (ARC) conducted studies of mechanical activation by conventional and ultrafine grinding techniques to enhance olivine reactivity in mineral carbonation reactions. Activated olivine is one of several solid feed materials used at ARC in reactions with carbon dioxide to form carbonate minerals. This paper compares grinding techniques via energy demand data and product characteristics, including particle size distributions, surface areas, full-width-at-half-maximum (FWHM) XRD analyses, and particle morphology by SEM analyses. Reactivity was calculated by percent conversion to carbonate in subsequent carbonation tests. Particle size reduction has the greatest impact on reactivity, and wet grinding is more energy efficient than dry grinding. Large additional inputs of energy to increase surface area or reduce crystallinity do not result in proportional improvements in reactivity.

Key words: Comminution, Ultrafine grinding, Olivine reactivity, Mechanical activation, Reactivity

Introduction
Background. The Albany Research Center (ARC) of the U.S. Department of Energy (DOE), in cooperation with researchers at Los Alamos National Laboratory, Arizona State University, Science Applications International Corporation and the DOE National Energy Technology Laboratory, is addressing sequestration of carbon dioxide (CO_2), a greenhouse gas emitted by burning fossil fuels, by mineral carbonation.

The basis for sequestration by mineral carbonation is a natural reaction that may occur during serpentinization of ultramafic rocks (O'Connor et al., 2002). When these rocks, containing high concentrations of magnesium (Mg^{2+}), calcium (Ca^{2+}) and ferrous iron (Fe^{2+}), are contacted by formation waters containing dissolved CO_2, secondary carbonate minerals are formed in addition to serpentine. This alteration is favored thermodynamically, but the natural reaction rate is slow. Among many parameters investigated at ARC to increase the reaction rate under laboratory conditions is mechanical activation of the mineral reactants.

Prior literature has discussed the mechanisms and nature of mechanical activation. Linn et al. (1975) noted the formation of amorphous surface layers in ground silicates; disruption of mineral structure, especially during dry grinding; and increased dissolution rates in minerals subjected to prolonged dry grinding. Modification of the crystalline structure of magnesium silicates by fine grinding has been suggested as a cause of activation (McKelvy et al., 2001). In leach tests using dry-ground serpentine, Zhang et al. (1997) found a correlation between concentrations of Mg and Si in the leachates and grinding time. Tromans and Meech (2001, 2002) investigated the connection between fine milling and mineral dissolution, especially focusing on microtopography as an indicator of increased dissolution sites. They suggest an upper size limitation of a few micrometers for microtopography-enhanced dissolution.

More than 600 batch experiments in mineral carbonation have been done at ARC's Albany, Oregon facility (O'Connor et al., 2001a, 2001b, 2002) using olivine, serpentine (antigorite and lizardite) and other mineral reactants. This paper focuses on selected results of these tests to investigate the effect of ultrafine grinding on the reactivity of olivine in the mineral-carbonation reaction.

Materials and methods. The feed materials used in this study were prepared from Twin Sisters olivine, a forsterite olivine from Washington State. The raw material was initially ground in pilot-plant rod and ball mills, classified at 200 mesh (75 μm) and then analyzed.

Results of the analyses are presented as major oxides in Table 1. The cations Al, Ca, Mg, K and Na were analyzed by atomic absorption (AA); Cr and Ni were analyzed by inductively coupled plasma (ICP); Fe^{2+} and Fe^{3+} were analyzed by a volumetric (titration) method; and Si was analyzed by a gravimetric method. CO_2 was analyzed by a gas-absorption method, and C was analyzed by a gas-analysis method. The difference between the C analysis and the C analysis calculated from the CO_2

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analysis represents noncarbonate carbon in the sample.

Forsterite, the Mg-rich end member of the olivine solid-solution series, has an ideal composition of Mg_2SiO_4. The results shown in Table 1 indicate that approximately 8 molar percent of Fe^{2+} substitutes for Mg in this material, although some of this iron may also occur in other alumino-silicate minerals present in trace to minor amounts.

Subsequent grinding of the feed was done in a stirred media detritor mill (SMD) or an attrition mill (AM) to produce the materials shown in Table 2. Samples AM-D and AM-24D were ground dry, and samples SMD-W and AM-W were ground at 50% solids in tap water. Grind times and calculated approximate energy inputs are included in the table.

Grinding energy was determined for the pilot-plant rod/ball mill products using a work index methodology described in the *SME Mineral Processing Handbook* (Bond, 1985). This method permits the determination of a scalable grinding energy or work index for a particular material. Scalable energy determinations were acquired for the SMD mill by use of a laboratory-scale version of an industrial-sized SMD mill. Energy consumption in the attrition mill was determined by applying the SME work index formula, recognizing that it is probably not the most appropriate methodology for that grinding technology. Thus, the attrition mill energy figures are not scalable, but provide relative values for comparison with the other grinding technologies utilized for the study. Some of the calculated grinding energies (Table 2) are clearly excessive for practical application; they were used only to investigate the effects of ultra-fine grinding on reactivity of the mineral.

Surface area was determined by a nitrogen gas absorption method, and particle size distribution was determined by an automated gravitational sedimentation method to characterize bulk properties of the materials related to reactivity. X-ray diffraction (XRD; Cu K_α X-rays) and full-width-at-half-maximum (FWHM) measurements based on the XRD patterns provided an indication of the crystallinity of each ground product. Finally, SEM examinations gave qualitative information about physical shape and surface characteristics of each sample.

The five materials were used as feed in carbonation experiments using test procedures and conditions that have been standardized at ARC (O'Connor et al., 2001a). In these tests, 15%-solids slurry is prepared of the mineral reactant and a solution of 0.64*M* $NaHCO_3$ and 1*M* NaCl. The slurry is sealed in an autoclave. The autoclave is then purged with CO_2 and stirred at 1,000 rpm. The system is heated to 185°C (1-hour heating time) and CO_2 is injected to 150 atm P_{CO2}. These conditions are maintained for 1 hour, after which the system is cooled and brought to atmospheric pressure and the slurry is recovered for filtering, drying, weighing and analysis. Mg content of the feed material is used to calculate CO_2 capture potential; CO_2 content of the solid carbonation product is compared to this number to give a percent stoichiometric conversion of silicate Mg to carbonate Mg (O'Connor et al., 2002). This simplified calculation was used here to compare results. Ca and Fe^{2+} in the feed also contribute to CO_2 capture, and including these cations in the calculations would reduce conversion for each sample by the same small percentage.

Table 1 — Major oxide analysis of minus 200-mesh olivine feed.

Species	Weight percent
Al_2O_3	0.16
CaO	0.20
Cr_2O_3	0.03
FeO	7.64
Fe_2O_3	0.49
MgO	50.68
NiO	0.23
K_2O	0.01
SiO_2	40.50
Na_2O	0.01
CO_2	<0.01
C	0.10
H_2O, dehyd.[1]	0.10
H_2O, chem.[2]	1.05
Total:	101.19

[1] Water of dehydration (free moisture), measured as weight loss after heating for 1 hour at 105°C in air.

[2] Chemically bonded (interstitial) water, measured as the difference between loss on ignition (LOI), at 1,000°C in Ar, and all other analyzed volatiles.

Table 2 — Preparation of samples studied with approximate energy input.

Sample	Method of preparation	Product/ Grinding time	Approximate energy input, kWh/t[1]
Feed	Pilot plant rod/ball mills	-200 mesh	11
SMD-W	Stirred media detritor	25 min. wet[2]	121
AM-W	Attrition mill	1 hr. wet[2]	50
AM-D	Attrition mill	1 hr. dry	729
AM-24D	Attrition mill	24 hr. dry	15,100

[1] Calculations for the four products include 11 kWh/t for initial grinding of the feed.

[2] 50% solids in tap water.

Results

Characterization. Surface area and particle size data are given in Table 3. Surface area data show that wet grinding in the attrition mill increased surface area by a factor of three over the feed, while the other ultrafine grinding methods increased surface area slightly or in the case of AM-24D caused it to be reduced. The product with the greatest increase in surface area (AM-W) also is the finest product for which data are available. Using D_{50} values for comparison, other grinding methods were nearly as effective at size reduction without concurrent increases in surface area. Some large particles remained after dry attrition grinding, as shown by sample AM-D's D_{80} value of 16.23 μm. This large D_{80} value is thought to be due to trapping of grains in "dead zones" of the mill that have no grinding action.

With 24 hours of dry attrition grinding, the surface area of AM-24D decreased to approximately one-half that of the starting material. This is thought to be due to the phenomenon of "cold welding," which has been well documented in mechanical alloying of metals (Benjamin and Volin, 1974). This would also affect size distribution, but these data are not available for confirmation.

X-ray diffraction patterns and FWHM measurements are graphed in Fig. 1. Amorphous background scatter increased with grinding, but the backgrounds are not shown in the figure to facilitate comparison of the samples. The patterns indicate

Table 3 — Surface area, particle size, and reactivity data for samples studied.

Sample	BET surface area, m^2/g	Particle size distribution D_{80}, μm	D_{50}, μm	D_{10}, μm	Conversion to carbonate, %
Feed	4.60	40.86	19.46	2.77	5.1
SMD-W	6.66	8.48	4.63	0.99	69.9
AM-W	14.21	8.66	3.91	0.69	84.3
AM-D	5.09	16.23	4.34	0.77	70.6
AM-24D[1]	2.65	N/A	N/A	N/A	88.8

[1] Material was not available to conduct particle size distribution analysis for this sample.

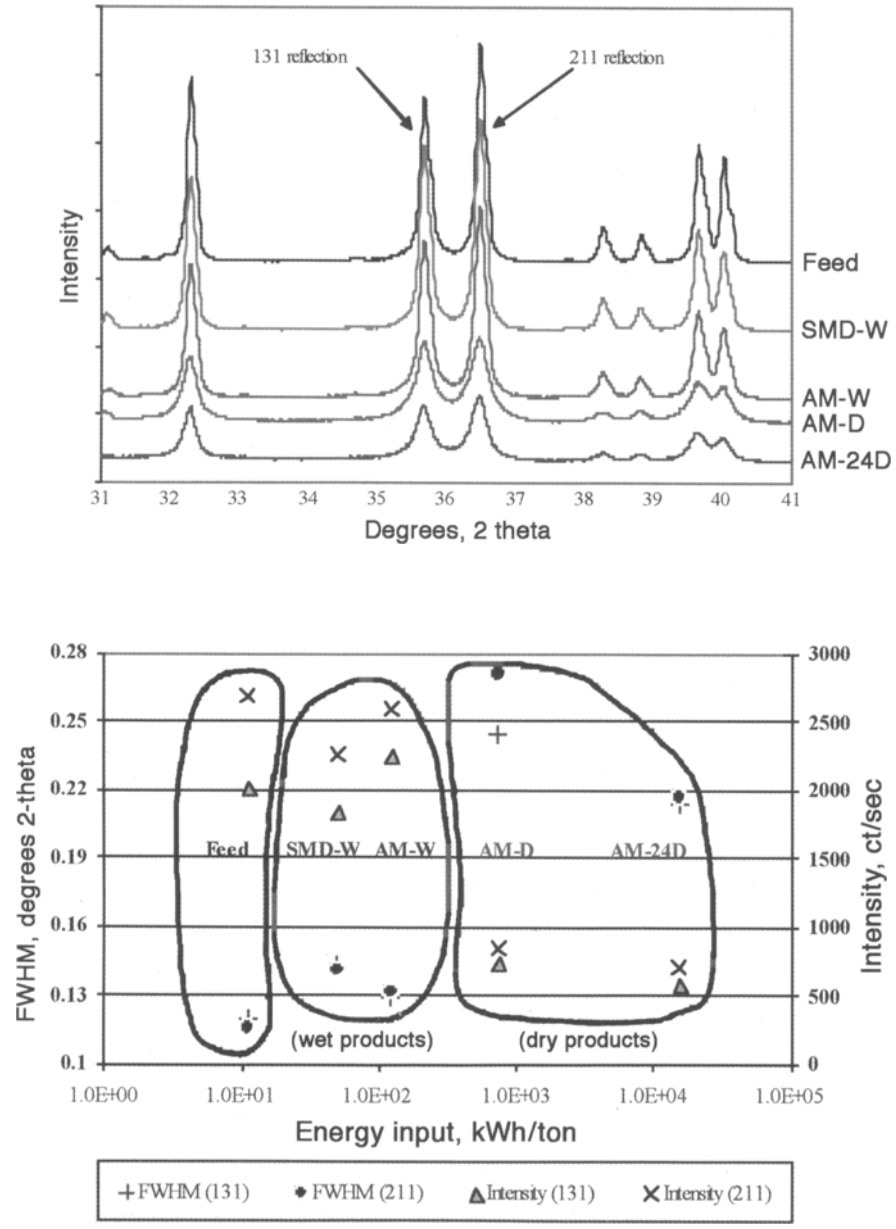


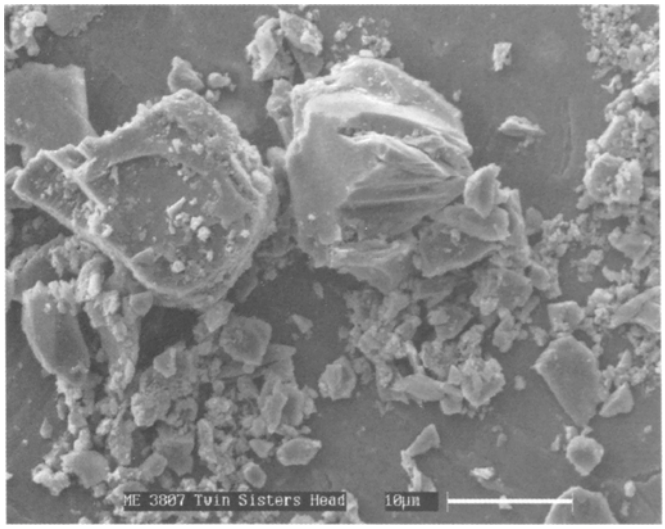
Figure 1 — X-ray diffraction scan results for the olivine feed material and four ultra-fine ground products. Top: XRD patterns (Cu K_α X-rays). Bottom: Full-width at half-maximum (FWHM) and intensity data plotted against estimated energy input.

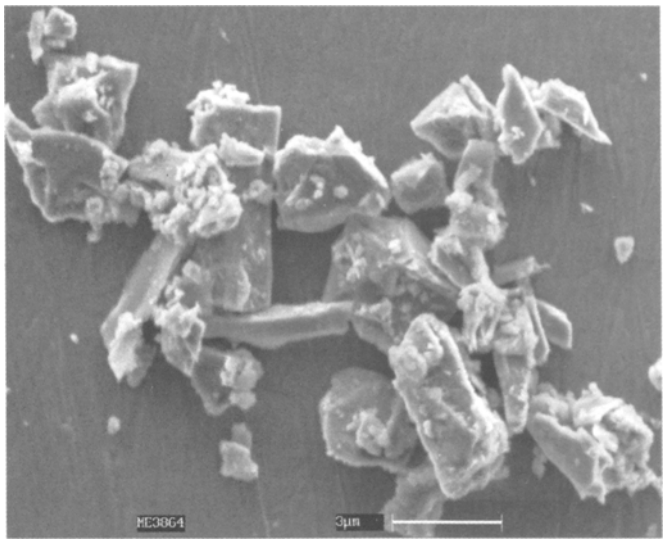
a pronounced loss of crystallinity with dry attrition grinding. This is especially clear in the lower graph in Fig. 1, where plotted FWHM measurements are considerably greater and intensities are much lower for dry-ground products as compared to wet-ground products. The FWHM data correlate crudely with the calculated energy input, but the difference between wet and dry grinding is much more apparent.

SEM photos show that the products of dry attrition grinding differ remarkably in particle morphology from those of wet grinding in both the SMD and the attrition mill. Products of the wet fine-grinding procedures, though reduced significantly in size and containing particles well below 1 μm in diameter, show fracture characteristics and particle shapes much like the feed material (Fig. 2). The dry attrition-ground samples, in contrast, demonstrate significant alteration of morphology. This is especially true for AM-24D (Fig. 3, middle and bottom), in which the resulting particles are rounded, appear to have a narrow size distribution, and to be well-bonded aggregates of much finer grains. Such characteristics have been described in mechanically alloyed metals (Guerrero-Paz and Jaramillo-Vigueras, 1998) and again indicate that cold welding has occurred during dry grinding of olivine.

Reactivity in carbonation. The conventionally ground olivine and the four products of ultrafine grinding were used as feed materials in batch carbonation tests. Reactivity is represented by the conversion of magnesium silicate in feed materials to magnesium carbonate. Table 3 presents conversion numbers based on Mg concentration in the feed and CO_2 concentration in reaction product solids; Fig. 4 compares these conversion percentages to the grinding energy used to prepare each of the samples.

There is a positive relationship between grinding energy and reactivity. All of the ultrafine grinding methods significantly increased the reactivity during carbonation, but the extreme energy inputs of the dry attrition grinding did not lead to proportional improvements in reactivity during carbonation. In fact, the 15-fold increase in energy input from AM-W to AM-D yielded a product that was less reactive under the carbonation conditions used. Thus, although there is generally a positive relationship between energy input and conversion percentage, the return in reactivity decreases as energy input goes up.





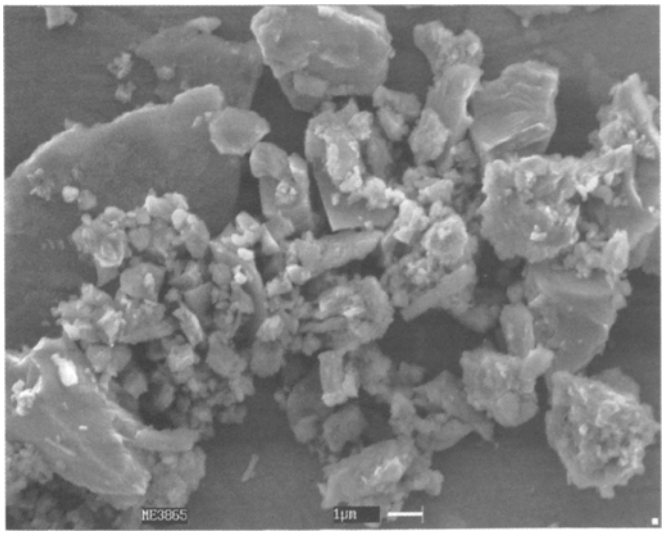
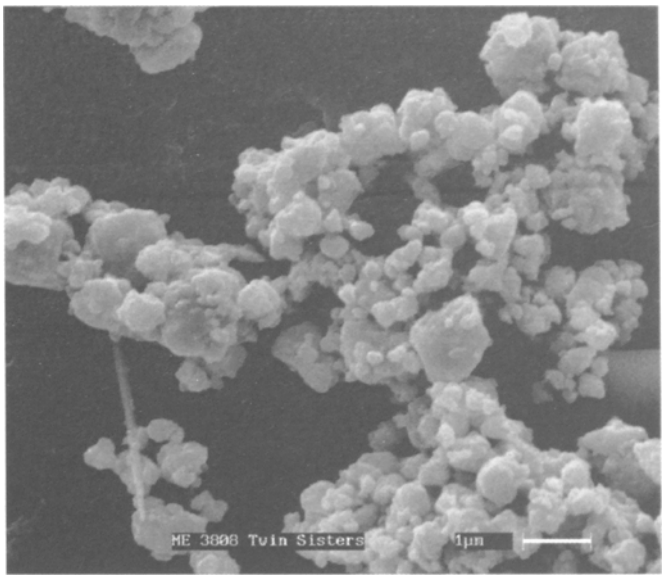
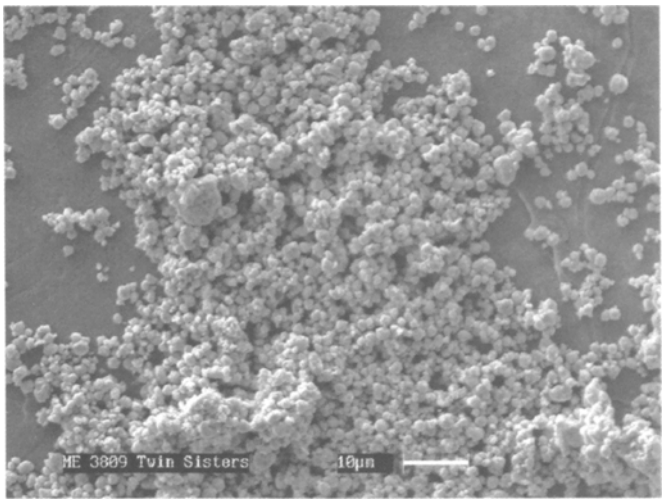


Figure 2 — Top: Conventionally ground olivine (Feed). Scale bar 10 µm. Middle and bottom: Products of ultra-fine grinding under wet conditions. The scale bar in the middle image (SMD-W) is approximately 3 micrometers long; the scale of the bottom image (AM-W) is similar. To the limits of resolution, particles in all three photos are similarly angular. Some particle surfaces are smooth, and others have some roughness that is characteristic of conchoidal fracture.





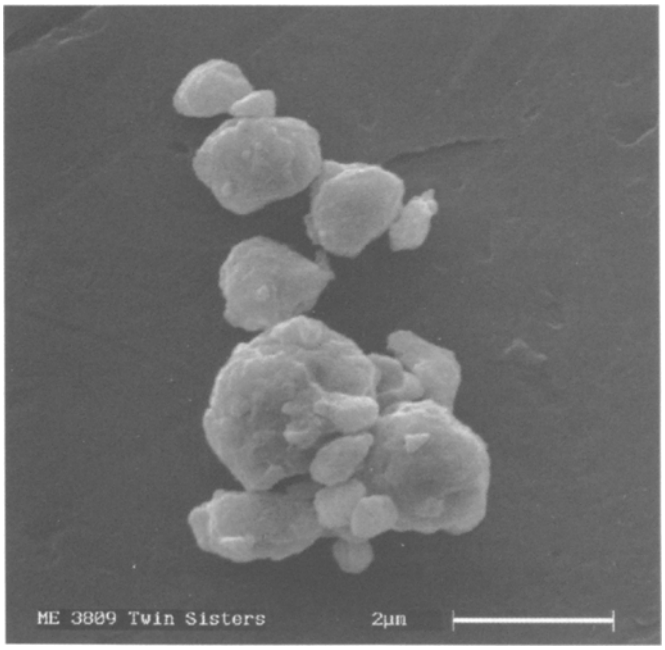


Figure 3 — Dry attrition-ground products. Top: AM-D; scale bar 1 micrometer. Middle and bottom: AM-24D; scale bars 10 and 2 micrometers, respectively. Particles are rounded and rich in microtopography in comparison to those in Fig. 2.

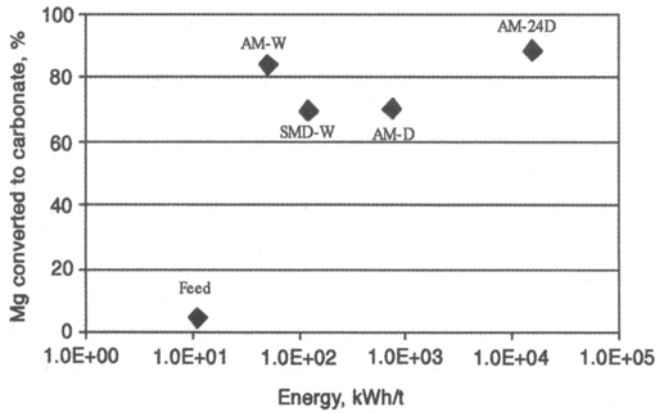


Figure 4 — Stoichiometric conversion of Mg in ultra-fine products to carbonate vs. energy input. The two most energy-intensive processes offered little benefit in added reactivity.

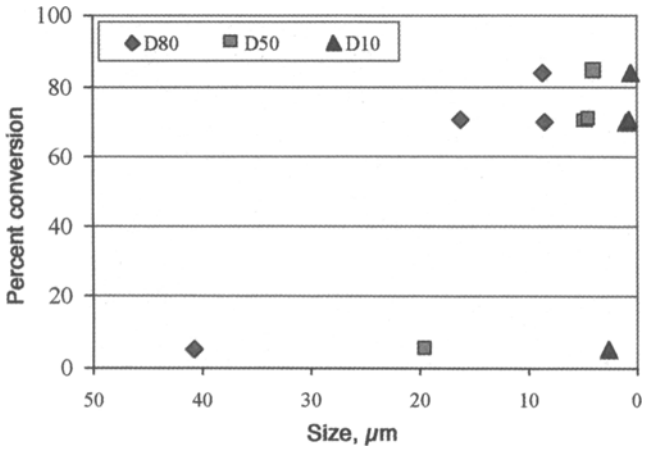


Figure 5 — The relationship between percent conversion to carbonate and size distribution.

Discussion

Surface area determination, particle size analysis, full width at half maximum (FWHM) XRD analysis, and particle morphology by SEM analysis are all common methods for characterizing ultrafine grinding products. No one analytical technique accurately predicted reactivity of the products in this study, but taken together, the data are informative.

Particle size data (Table 3), available for four of the five samples, indicate significant size reduction by all ultrafine grinding methods, and the D_{50} and D_{10} data show an inverse relationship with conversion (Fig. 5). As would be expected, conversion improved with finer grinding, but there were significant differences in conversion with similarly sized materials. This suggests that other factors in addition to size reduction contribute to reactivity in the carbonation reaction.

Both XRD data and SEM photographs show that the large energy inputs for dry attrition grinding (Table 2) resulted in significant structural damage to the mineral particles. Previous research leads one to believe that this degradation of crystallinity greatly enhances solubility and reactivity of the particles. The rough microtopography of the dry-ground particles could also be an indicator of increased dissolution sites (Tromans and Meech, 2001). In contrast, the energy put into wet attrition grinding (Table 2) yielded a product with a significant increase in surface area, an effect not seen in the dry ground products (Table 3). This also leads to an expectation of increased solubility and reactivity.

All of the ultrafine grinding methods greatly improved conversion over conventional grinding for a number of reasons. If reactivity of the olivine particles is limited by the diffusion rate through a depleted outer rim, size reduction increases reactivity by creating more particles that react completely in a shorter period of time. Increasing surface area through wet grinding results in more dissolution sites per unit mass. Structural damage caused by dry grinding improves reactivity by increasing the diffusion rate.

More than 80% conversion to carbonate was achieved in one product of wet grinding (AM-W) and one product of dry grinding (AM-24D), but the energy demand was dramatically greater for dry grinding. Thus, the increase in surface area achieved by wet grinding was equally productive but less costly than the loss of crystallinity by dry grinding. The beneficial effects of increasing disorder in the crystalline structure are limited and offset by the energy cost to achieve them.

Conclusions

The data indicate that reactivity increased most significantly as a result of size reduction. Large additional energy inputs in grinding, wet or dry, greatly affected surface area and crystallinity; such inputs in dry grinding caused cold welding and altered particle morphology. However, the additional energy applied did not improve reactivity concordantly. Energy inputs beyond 100 kWh/ton were not necessarily beneficial from the standpoint of improving conversion in the carbonation tests, and lower numbers were sufficient to achieve similar degrees of conversion.

References

Benjamin, J.S., and Volin, T.E., 1974, "The mechanism of mechanical alloying," Metallurgical Trans., Vol. 5, pp. 1929-1934.

Bond, F.C., 1985, "Testing and calculations," in Sec. 3A, General Aspects of Comminution, *SME Mineral Processing Handbook*, Weiss, N.L., ed., Society of Mining Engineers of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., New York, pp. 3A-16-3A-27.

Guerrero-Paz, J., and Jaramillo-Vigueras, D., 1998, "Particle size evolution in Cu-15%Al mechanically alloyed," *NanoStructured Materials*, Vol. 10, pp. 1209-1222.

Lin, I.J., Nadiv, S., and Grodzian, D.J.M., 1975, "Changes in the state of solids and mechano-chemical reactions in prolonged comminution processes," *Minerals Sci. Eng.*, Vol. 7, pp. 313-336.

McKelvy, M.J., Chizmeshya, A.V.G., Bearat, H., Sharma, R., and Carpenter, R.W., 2001, "Developing mechanistic understanding of CO_2 mineral sequestration reaction processes," *Proc. 26th International Tech. Conference on Coal Utilization & Fuel Systems*, Clearwater, Florida, March 5-8, 2001, pp. 777-788.

O'Connor, W.K., Dahlin, D.C., Rush, G.E., Dahlin, C.L., and Collins, W.K., 2001, "Carbon dioxide sequestration by direct mineral carbonation: process mineralogy of feed and products," Preprint No. 01-009, presented at the SME Annual Meeting, Feb. 26-28, 2001, Denver, Colorado, 9 pp.

O'Connor, W.K., Dahlin, D.C., Nilsen, D.N., Gerdemann, S.J., Rush, G.E., Walters, R.P., and Turner, P.C., 2001, "Research status on the sequestration of carbon dioxide by direct aqueous mineral carbonation," Paper 35-1, *Proc. 18th Annual Inter. Pittsburgh Coal Conference*, Newcastle, NSW, Australia, December 3-7, 2001, 11 p.

O'Connor, W.K., Dahlin, D.C., Nilsen, D.N., Gerdemann, S.J., Rush, G.E., Penner, L.R., Walters, R.P., and Turner, P.C., 2002, "Continuing studies on direct aqueous mineral carbonation for CO_2 sequestration," *Proc. 27th International Tech. Conference on Coal Utilization & Fuel Systems*, Clearwater, Florida, March 4-7, 2002.

Tromans, D., and Meech, J.A., 2001, "Enhanced dissolution of minerals: Stored energy, amorphism and mechanical activation," *Minerals Engineering*, Vol. 14, pp. 1359-1377.

Tromans, D., and Meech, J.A., 2002, "Enhanced dissolution of minerals: Conjoint effects of particle size and microtopography," *Minerals Engineering*, Vol. 15, pp. 263-269.

Zhang, Q., Sugiyama, K., and Saito, F., 1997, "Enhancement of acid extraction of magnesium and silicon from serpentine by mechanochemical treatment," *Hydrometallurgy*, Vol. 45, pp. 323-331.