

DIVISION S-2—SOIL CHEMISTRY

Simultaneous Determination of Calcite Surface Area and Content in Soils¹

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ABSTRACT

A method to simultaneously determine calcite surface area and content in soils has been developed. The proposed procedure is based on rates of CO₂ production upon reaction of soil with buffered acid solutions under controlled conditions. A pressure transducer connected to a chart recorder allows determination of soil calcite dissolution rate, which is directly proportional to calcite surface area. Sample size typically ranges from 0.3 to 10.0 g. The coefficient of variation for surface area was 0.05, based on nine replicated analyses of the same soil.

Additional Index Words: dissolution, CO₂, kinetics, pressure transducer, CaCO₃.

Suarez, D.L., and J.D. Wood. 1984. Simultaneous determination of calcite surface area and content in soils. *Soil Sci. Soc. Am. J.* 48:1232-1235.

CALCITE dissolution is likely the major weathering process in irrigated soils of arid and semiarid environments. Recent attempts to relate crusting and dispersion to soil types have included clay type and rate of soil weathering (Shainberg et al., 1981) as important factors. Soil weathering rates often do not correlate well with CaCO₃ content in the soil. We maintain that at least part of this discrepancy is due to differences in calcite particle sizes. Also, secondary or pedogenic calcite coatings on other minerals are commonly observed in soils of semiarid environments. Gile (1961) described a wide variety of ca soil horizons with CaCO₃ forms ranging from thin coatings to indurated layers.

Our objectives were to develop a simple, rapid procedure for determining the concentration and surface area of calcite in soils. There are many existing procedures for determining the CaCO₃ content of soils. For example, Williams (1948) described a widely used method based on acid reaction with soil and measurement of the pressure of generated CO₂ by manometer. Skinner and Halstead (1958) used the differences in dissolution rates to distinguish between calcite and

dolomite in soils. Recently Evangelou et al. (1984) described a method of determining calcite and dolomite contents in soils by acid dissolution and measurement of pressure with a differential pressure transducer connected to a recorder. The above procedures, with modification to keep pH, temperature, and stirring rate constant can be calibrated with calcite standards of known surface area. This enables use of the reaction rate in a quantitative manner for determination of both calcite surface area and content of soils.

PROCEDURE

Apparatus

The experimental setup is shown in Fig. 1. The reaction vessel was constructed from a 500-mL wide-mouth jar fitted with a rubber gasket, plastic screw cap, and 3-way glass stopcock. A small wire tripod with a plastic table was placed in the jar. A no. 4 plastic stopper was attached to the table with a wire loop which acted as a hinge so the stopper could tip and empty its contents. A small teflon-coated stir bar was wedged in a hole near the top of the stopper. A large stir bar was placed in the jar with 100 mL of distilled water and 5 mL of 1.0 mol L⁻¹ Na acetate. A measured amount of calcite standard or soil (0.1 to 10 g dry weight) was placed into the distilled water and allowed to disperse. Next, 5 mL of 2.0 mol L⁻¹ acetic acid was placed in the stopper. The jar was capped and placed in a 1-L water bath on top of an insulated stir-plate in a temperature-controlled room (25°C ± 0.8° in 20 min cycles of heating and cooling, < ± 0.08° from cycle to cycle). The water bath maintained a temperature of 25°C ± 0.1°. Small tubing (1.5 mm i.d.) connected the vessel to a insulated pressure transducer (Sunstrand Model 314D) whose output was recorded on a strip chart. The total air space in the system was 0.465 L. After 5 min of stirring at 280 to 300 rpm (to allow rapid mixing while maintaining a smooth surface on the liquid) the stopcock was closed and stirring was continued. The acid was added by forcing the plastic stopper to tip by placing a large magnet near the vessel. A chart recorder was used for continuous measurement of pressure. The recorder was set at 0.1 V full scale deflection (0–2 kPa) for determination of surface area and then switched to the 1.0 V scale for determination of CaCO₃ content. Maximum pressures were reached within 50 min (3 ks) for the standards. Reaction rate is obtained by determining the maximum slope of the pressure vs. time curve. The maximum dissolution rate should occur almost immediately upon addition of the acid since surface area decreases during dissolution. A slight lag is observed initially

¹ Contribution from the U.S. Salinity Laboratory, USDA, ARS, Riverside, CA 92501. Received 23 June 1983. Approved 21 May 1984.

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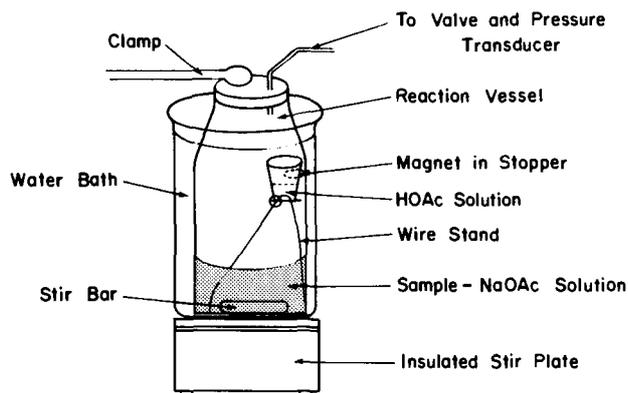


Fig. 1—Experimental setup.

due to the rapid increase in H_2CO_3 and the initial disequilibrium between H_2CO_3 and CO_2 in the solution.

Preparation of Calcite Standards

Standards were prepared from Iceland spar calcite which was crushed and then washed in distilled water. Different size fractions were obtained by sedimentation in water and by wet sieving. The $> 20 \mu\text{m}$ calcite was wet sieved with screens ranging between 50 and $150 \mu\text{m}$. Because the particles are assumed to be equidimensional rhombohedrons passing through square grid openings, a correction was made for the sizes obtained based on the 102° calcite cleavage angle. For example, crystals having edge lengths of 46 to $68 \mu\text{m}$ were caught between the 50- and $74\text{-}\mu\text{m}$ screens. Particles retained between screens were assumed to be uniformly distributed by weight in $2\text{-}\mu\text{m}$ size increments. A value of $0.039 \text{ m}^2 \text{ g}^{-1}$ surface area was calculated by averaging calculated surface areas for each $2\text{-}\mu\text{m}$ size increment between 46 and $68 \mu\text{m}$ (assuming equal weight in each size) and using the calcite density of 2.71 Mg m^{-3} . This surface area corresponds to a particle with an edge length of $56 \mu\text{m}$.

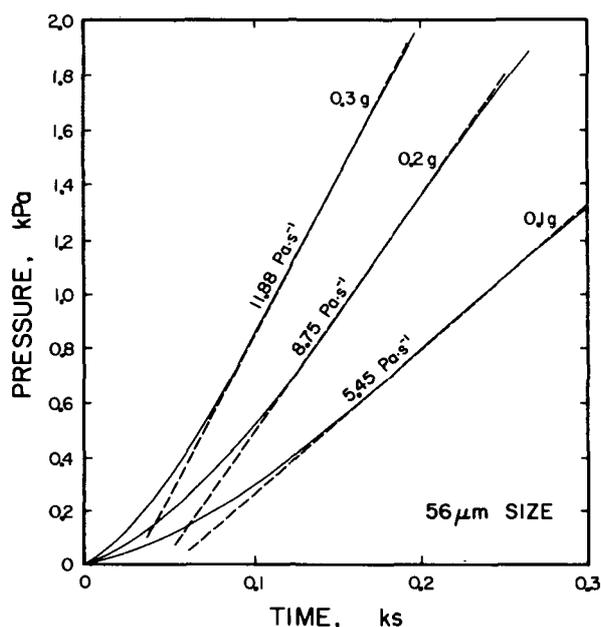


Fig. 3—Pressure vs. time relationship for 0.1 g, 0.2 g, and 0.3 g calcite having a calculated surface area of $0.039 \text{ m}^2 \text{ g}^{-1}$. Dashed lines are the maximum slopes of the curves.

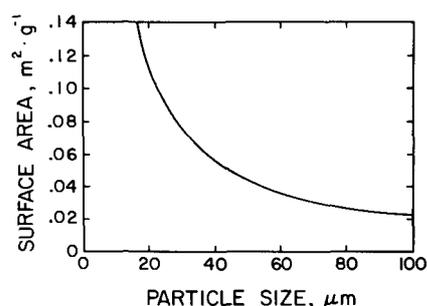


Fig. 2—Relationship between calcite surface area in $\text{m}^2 \text{ g}^{-1}$ and particle size (edge length) in μm .

DISCUSSION

Calibration

Figure 2 shows the relationship between particle size (edge length) and surface area for calcite. Figure 3 shows the initial pressure vs. time relationship for 0.1, 0.2, and 0.3 g of calcite having a mean edge length of $56 \mu\text{m}$ and a surface area of $0.039 \text{ m}^2 \text{ g}^{-1}$. The dashed lines represent maximum CO_2 release rates. There is an initial lag in pressure response after which there is a maximum rate for about 100 s. Beyond this point the CO_2 pressure vs. time relationship is not linear due primarily to decreasing surface area with time. The maximum slopes of the curves were 5.45, 8.75, and 11.88 Pa s^{-1} for 0.1, 0.2, and 0.3 g CaCO_3 , respectively, demonstrating an increasing reaction rate with increasing surface area. A calibration of the system is required to relate total calcite surface area in each sample to maximum rate of P_{CO_2} release (slope of pressure-time line). As shown in Fig. 4, using calcite standards of known size and surface area, an accurate calibration can be made. The curve drawn is slightly "S" shaped; however, a straight line regression equation, $y = (1.069 \times 10^{-3})X - 1.473 \times 10^{-3}$ fits the data well ($r^2 = 0.998$) above a rate of 2 Pa s^{-1} . The relationship is nonlinear below that point, possibly due to nonlinear transducer response. The transducer was calibrated at zero, one-half, and full scale recorder settings using a water manometer. After the calibration curve is obtained, only the slope of the pressure-time line is needed to calculate total surface area of calcite

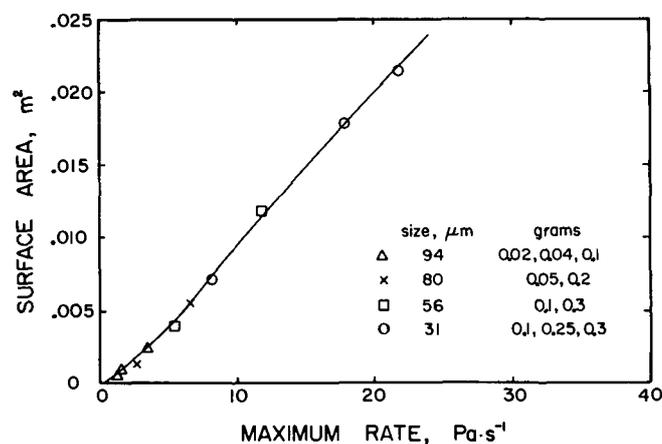


Fig. 4—Relationship between surface area and maximum slope of the pressure/time lines for calcite standards of different sizes and surface areas.

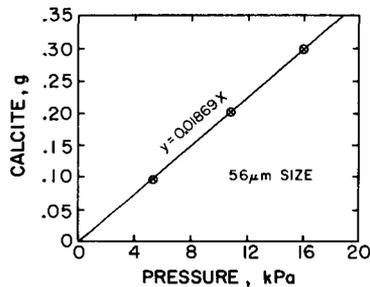


Fig. 5—Calibration curve relating total calcite (g) and final pressure (kPa).

present. The correlation was found not to be affected by variations in quantity of calcite or particle size for the ranges examined.

The final pressure is expected to be linearly proportional to the mass of CaCO_3 present, since all CaCO_3 should be dissolved and $\text{H}_2\text{CO}_3 \rightleftharpoons \text{P}_{\text{CO}_2}$ equilibrium should exist. The data shown in Fig. 5 shows the expected linear relationship with zero intercept. The slight deviation from the 1:1 slope is due to the small quantity of H_2CO_3 remaining in solution and at equilibrium with the P_{CO_2} . The calcite (grams) vs. pressure curve is thus dependent on the liquid/gas ratio used in the experimental setup. The relationship shown is for the setup described earlier.

Once the total calcite surface area (from Fig. 4) and mass of calcite present (from Fig. 5) in a soil sample is determined, the specific calcite surface area can be calculated ($\text{m}^2 \text{g}^{-1}$). It should be noted that Fig. 4 is applicable only to the setup previously described. Any change in stirring rate, gas volume, or surface area/volume ratio of the liquid phase caused by using different liquid volumes, container sizes, or tubing changes the calibration.

Testing of Soils

Six soils were tested to evaluate the degree to which calcite surface area or particle size may vary among soils. The soils were screened to < 1 mm. The total amount of soil added was adjusted such that the slopes were within the linear portion of the calibration curve determined earlier. Surface areas were calculated from the regression equation given above and CaCO_3 content from the equation given in Fig. 5. Table 1 shows the soil type, maximum slope, final pressure, calculated surface area, CaCO_3 content, % CaCO_3 in soil, and specific surface area in $\text{m}^2 \text{g}^{-1}$. As shown in Table 1 there are differences in specific surface areas ranging from 0.029 to $0.066 \text{ m}^2 \text{g}^{-1}$. The soils range from 3.3

to 73% CaCO_3 content by mass. Based on nine sequential replicate analyses of one soil, the coefficient of variation (SD/mean) was 0.05. Large differences were obtained when the soils were screened to < 2 or < 5 mm rather than < 1 mm (data not shown). It was concluded that sample preparation is important since even slight crushing produced small amounts of high surface area calcite. It appears preferable not to sieve and instead insure that the soil is not aggregated when the acid is released.

Factors Affecting the Dissolution Rate

During the reaction the pH increased from 4.22 initially to ≈ 4.3 to 4.9 (for 0.3 of calcite) at the end of the reaction. The surface area is determined from the initial reaction rate (always before 15% of the calcite is dissolved). The maximum variation of pH during the determination of surface area is ≈ 0.05 . That the surface area determinations were not affected by pH differences is evident from Fig. 4. The surface area of the 0.1, 0.2, and 0.3 g of calcite of 56- μm size fall on a straight line. If pH was not constant during the determination of surface area (initial slope), the calibration curve would curve upward with increasing surface area. Changes in pH could be reduced by increasing the concentration or volume of acetic acid used. It should be noted that pH constancy, while desirable, is not a requisite for the determination of surface area. The change in pH would be accounted for in the calibration. Since we are using standards of known surface area rather than calculating theoretical reaction rates, changes in pH and acetic acid concentration are comparable for standards and samples with the same surface area.

The P_{CO_2} varied between 0.032 kPa initially and 12.0 kPa at the end of the reaction; thus activity of H_2CO_3 varied between 1.07×10^{-5} and 4.02×10^{-2} . The predicted dissolution rate was initially $1.6 \times 10^{-6} \text{ mmol}^{-1} \text{ cm}^{-2} \text{ s}^{-1}$ using the model of Plummer et al. (1978). The predicted increase in reaction rate due to increasing P_{CO_2} (approximately two-fold) during the reaction is almost matched by the decrease in reaction rate due to the increase in pH during the reaction. The dissolution rate could be made independent of P_{CO_2} by using a lower pH; however, this was not judged desirable. Since reaction rate is inversely proportional to pH, use of an unbuffered solution would also require a much lower pH to provide sufficient H^+ for the reaction. A low pH is not desirable due to the increased rate of reaction. At pH = 2 over 50% of the reaction is completed in 30 s. This does not allow

Table 1—Calcite surface area and content in selected arid lands soils.

Soil no.	Location	Soil mass	Evolution rate of CO_2	Final pressure	Calcite content		Calcite surface area	
		g	Pa s^{-1}	kPa	g	% by mass	$\text{m}^2 \times 10^3$	$\text{m}^2 \text{g}^{-1}$
1	West Nabariya, Egypt†	0.35	11.67	13.77	0.257	73.4	11.00	0.043
2	Tacna, AZ‡	4.00	8.17	13.51	0.253	6.3	7.26	0.029
3	San Joaquin, CA§	5.00	9.50	8.80	0.164	3.3	8.68	0.053
4	Redlands, CA¶	4.35	10.21	7.65	0.143	3.3	9.44	0.066
5	Imperial Valley, CA#	3.10	7.36	8.72	0.163	5.3	6.39	0.039
6	Pomona, CA††	1.70	13.62	12.75	0.238	14.0	13.09	0.055

† Calcic Aridisols.

‡ Indio, coarse-silty, mixed (calcareous) hyperthermic Typic Torrifluvents.

§ Twistleman, fine mixed calcareous thermic Typic Torriorthents.

¶ San Emigdio, coarse loamy, mixed (calcareous) thermic Typic Xerofluvents.

Indio, coarse-silty, mixed (calcareous) hyperthermic Typic Torrifluvents.

†† Diablo, fine montmorillonitic thermic Chromic Pelloxererts.

sufficient time to ensure that the acid is well mixed when the slope of the pressure-time curve is determined. Also, the faster the dissolution rate, the greater the dependence on stirring rate and more importantly, the greater the disequilibrium between H_2CO_3 and P_{CO_2} . Since surface areas are determined from initial rates at low P_{CO_2} (pressures of 0.4 to 1.6 kPa above atmospheric), H_2CO_3 should not be a major influence on surface area measurements. Also this effect is taken into account by the calibration curve (Fig. 4).

The presence of dolomite in the samples does not affect the determination of surface area but can result in overestimation of quantity of calcite present. The dissolution rate of dolomite is sufficiently slow that in the presence of calcite the initial CO_2 pressure increase can almost always be attributed to calcite dissolution alone. This is demonstrated by the initial reaction rates of equal weights of calcite and dolomite of 50- to 73- μm size. Assuming similar particle shape and similar surface areas, the calcite dissolution rate in Pa s^{-1} was 70 times that of dolomite. Since soil dolomites are not generally pedogenic but rather transported materials, and since dolomite is relatively resistant to weathering, it can also be expected to occur in larger size particles than calcite. This further reduces the effect of dolomite on the surface area measurements. Substantial errors of calcite surface area determinations will thus occur only at very large dolomite/calcite ratios. If significant amounts of dolomite are present, then the CO_2 contribution of dolomite to the final pressure must be determined. Determination of the quantities (percent) of dolomite and calcite present in a soil can better be obtained by using the procedures described by Evangelou et al. (1984) or Petersen et al. (1966), among others, where strong acids are used. The relative quantities of calcite and dolomite can be obtained from the pressure-time data of our method using the procedure described by Evangelou et al. (1984). However, it requires reaction times of several hours to ensure complete dolomite dissolution.

The proposed procedure assumes that soil calcite reacts at the same rate as pure calcite. The major differences are that soil calcites usually contain a few percent Mg substitution and are likely to have adsorbed ions such as phosphate on the surface, and may also be coated by organic material or precipitated oxides. Detailed information on the dissolution kinetics of high magnesium calcite is not available; however, some decrease in reaction rate is likely since Busenberg and Plummer (1982) observed that removal of the MgCO_3 component was the rate-limiting step in dolomite dissolution. Since the majority of soil carbonates are of low magnesium content, Mg substitution is not likely to be a substantial problem. A sea urchin shell with 1.3 mol % Mg substitution crushed, sieved, and washed to the same particle size as the pure calcite standard gave the same calculated surface area using our procedure. Other crystal impurities are also unlikely to reduce dissolution rates. The presence of inhibiting adsorbed ions such as phosphate likely have a negligible effect on dissolution, at the levels of undersaturation and pH of the present procedure. For example, extrapolation of the rate data of Morse and Berner (1979) indicate that phosphate inhibition of

calcite dissolution becomes negligible at ion activity product/ k_{sp} ratios of < 0.2 . In our experiments at $\text{pH} = 4.2$ and 100 kPa P_{CO_2} (≈ 1 atm) $a_{\text{CO}_3^{2-}} = 10^{-9.75}$. Since the slope of the pressure-time curve is determined before 0.1 g of CaCO_3 have dissolved, $\text{Ca} \leq 10^{-2}$ M, $\gamma_{\text{Ca}} \approx 0.28$ in 0.1 M solution, thus $a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}} \leq 4.09 \times 10^{-13}$. Since $k_{\text{sp}} = 3.3 \times 10^{-9}$ (Plummer and Busenberg, 1982), $(a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}} / k_{\text{sp}}) \leq 1.2 \times 10^{-4}$, which is three orders of magnitude more undersaturated than the point at which phosphate inhibition is expected to slow the reaction.

The low surface area/mass values obtained for soil calcite may be more an indication of surface coatings on the calcite rather than an indication that the particles are in the medium-large silt size. We do not consider this a drawback of the procedure since calcite surface coated with oxides, etc., should not properly be counted as calcite surface area. Studies of phosphate adsorption on calcites in soils as well as prediction of soil salt release rates require information on reactive or available calcite surface area. The proposed procedure determines the surface area of the reactive surface. Even if a physical measurement of calcite particle size were available, conversion of that value to a surface area would not be as relevant as a measurement of the uncoated surface area.

CONCLUSIONS

The proposed procedure for determination of calcite surface area in soils is relatively quick and reproducible. The surface area is determined from the maximum rate of P_{CO_2} release (slope of pressure-time line) during the dissolution of soil CaCO_3 in an acid-aqueous-closed system. The calibration curves are linear over the range examined, thus relatively few calibration points are required.

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