

DISSOLUTION RATE OF GYPSUM IN AQUEOUS SALT SOLUTIONS¹

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We measured the dissolution rate of gypsum particles (0.5- to 1.0-mm fraction) in distilled water and in aqueous salt solutions of NaCl, MgCl₂, Na₂SO₄, MgSO₄, and CaCl₂ at salt concentrations of 20, 40, and 60 mmol kg⁻¹. Two gypsum samples were tested, one from a gypsum mine in Egypt and another from New Mexico, United States. We monitored the dissolution rate by measuring Ca concentrations in these solutions with and without shaking. The rate of gypsum dissolution increased with shaking and with increasing concentration of the salt solutions. Neither ion concentration nor species influenced the rate of gypsum dissolution when the rate was normalized by the solubility. The first-order reaction equation was unsuited for describing the dissolution process when Ca concentrations exceeded about 50% of gypsum solubility. The second-order reaction equation described the process well, providing a rate constant independent of ion concentrations or species.

Gypsum (CaSO₄·2H₂O) is a common mineral present in geological strata, as well as in some arid-zone soils (Antolini 1977). Because of its soluble nature, its presence can significantly alter the chemistry of soils and water (e.g., Dutt 1962). For agricultural purposes, gypsum is used as a source of soluble Ca for reclaiming sodic soils (e.g., Oster 1982) and for preventing soil crust formation (Shainberg et al. 1982). Gypsum can also be used to ameliorate water quality and prevent soil sodification (Gobran et al. 1982).

Although extensive information is available concerning gypsum's solubility (e.g., Tanji 1969), information on dissolution rates is scarce. Existing literature shows that the dissolution

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rates are influenced by Ca and/or SO₄ concentrations in solution, by surface area or particle size (Kemper et al. 1975), and by the thickness of the diffusional layer around gypsum particles (Barton and Wilde 1971). The rate of dissolution has been described by the first-order reaction equation (Kemper et al. 1975; Keren and Shainberg 1981; Liu and Nancollas 1971) or by a modified form (Keren and O'Connor 1982).

The rate of gypsum dissolution generally increases with increasing ionic concentration (e.g., Kemper et al. 1975; Keren and Shainberg 1981). However, the effect of ionic species present in solution on the dissolution rates is not fully quantified. The objectives of this study were (1) to determine whether gypsum dissolution rates are dependent on ion species present in solution, (2) to examine the suitability of the first- and second-order reaction equations for describing gypsum dissolution in aqueous salt solutions.

MATERIALS AND METHODS

Crushed gypsum samples were obtained from EL-gharbaniat quarry, Egypt, as well as from Albuquerque, New Mexico. Chemical analyses showed that these samples contain 99% CaSO₄·2H₂O. Complete chemical analyses of the Egyptian gypsum sample can be found elsewhere (Gobran 1980; Gobran et al. 1982). For this study, a size fraction of 0.5 to 1.0 mm was used.

Six different aqueous salt solutions of different concentrations were used (columns 1 and 2, Table 1).

Two sets of experiments were conducted at 20°C ± 1. The first one consisted of flasks containing the gypsum samples (1.0 g) and the solution (25 ml), which were gently shaken by a wrist action shaker. The shaker was maintained at a constant speed throughout the experiment. This set will be referred to as *with shaking*. The second experiment, referred to as *without shaking*, consisted of flasks left undisturbed for pre-set times. The content of each flask was then filtered through two layers of Whatman filter paper (No. 42) and analyzed for Ca concentrations with an atomic absorption spectrophotometer.

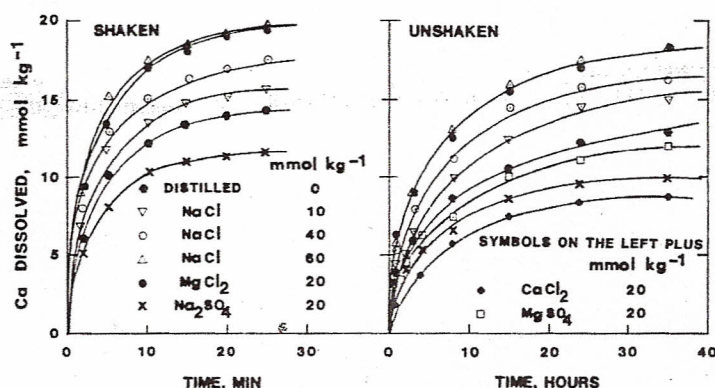
In a supplemental experiment, the crushed

TABLE 1
Equilibrium concentrations of dissolved Ca in various aqueous salt solutions and distilled water at 20°C

Solutions	Initial salt concentration	Measured		Predicted ^a
		Egypt mmol kg ⁻¹	New Mexico mmol kg ⁻¹	
Distilled water	0	14.8 ± 0.5	15.1 ± .2	15.3
NaCl	10	16.8 ± 0.5	—	16.2
	40	18.2 ± 0.4	18.8 ± 0.4	18.3
	60	20.2 ± 0.3	—	19.4
MgCl ₂	20	20.5 ± 0.7	20.7 ± 0.3	21.2
CaCl ₂	20	10.5 ± 0.8	11.0 ± 0.2	11.3
Na ₂ SO ₄	20	11.7 ± 0.1	12.1 ± 0.2	11.3
MgSO ₄	20	13.7 ± 0.7	—	12.9

^a Predicted by a computer model of Tanji and Doneen (1966).

FIG. 1. Dissolved Ca concentrations in various salt solutions for a gypsum sample (0.5 to 1.0 mm) from Egypt with shaking (left) and without shaking (right).



gypsum samples were first washed with distilled water until the weight was reduced by about 10%, in an attempt to remove fine gypsum particles and irregular particle surfaces. Excess water was then removed by placing the washed sample on a sheet of absorption paper; the sample was then air-dried and used for the dissolution test as described above.

All the experiments were triplicated, and the mean separation was performed using Duncan's multiple range (DMR) test at the 5% level.

RESULTS AND DISCUSSION

Dissolution characteristics of the gypsum sample from Egypt in NaCl and MgCl₂ solutions are shown in Fig. 1. The data from the New Mexico gypsum sample were virtually identical and thus are not shown. Gypsum dissolved faster with shaking than without shaking. This trend can be expected from the theory of transfer-controlled gypsum dissolution (Barton and Wilde 1971). Gypsum dissolution also increased with increasing salt concentrations, as can be

expected from increasing ionic strength (e.g., Tanji 1969; Nakayama 1971).

At an equal equivalent concentration of NaCl and MgCl₂ solutions (e.g., 40 mmol kg⁻¹ NaCl solution versus 20 mmol kg⁻¹ MgCl₂ solution in Fig. 1), gypsum dissolved faster in MgCl₂ solution than in NaCl solution. However, the difference in dissolution rate was not statistically significant at the 5% level. Theoretically, gypsum solubility is higher in MgCl₂ solutions than in equivalent concentrations of NaCl solution (e.g., Tanji and Doneen 1966).

The amounts of gypsum dissolved at given times in Na₂SO₄ and MgSO₄ solutions were about 30% smaller than those in equivalent solutions of NaCl and MgCl₂ (e.g., Fig. 1). Obviously, this is due to the common ion effects (e.g., Kemper et al. 1975). Gypsum also dissolved at a slower rate in CaCl₂ solution for the same reason.

Dissolved Ca concentrations (*C*) were normalized by the equilibrium value (*C_e*) (Fig. 2). The measured values of *C_e* in different salt so-

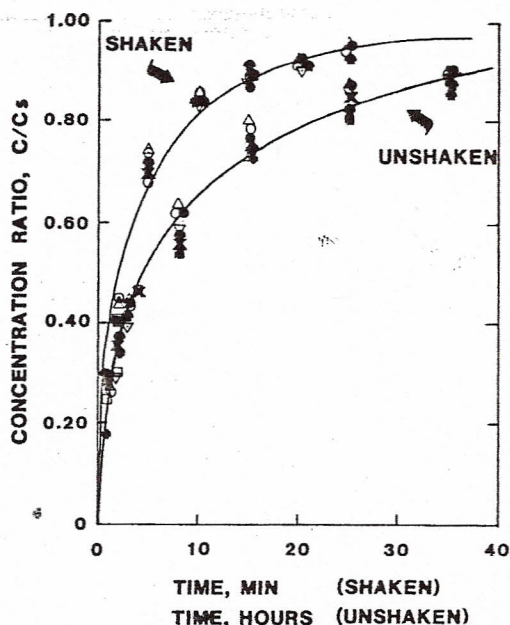


FIG. 2. The ratio of dissolved Ca concentration (C) to its equilibrium value (C_s) as a function of time. Symbols are the same as those of Fig. 1.

lutions are listed in Table 1, along with the predicted C_s with the computer model of Tanji and Doneen (1966). The Debye-Huckel equation was used for estimating the activity coefficient. The plots followed two sets of curves, one with shaking and another without shaking. We observed no significant difference in normalized dissolution rate among the salt solutions or between the two gypsum samples. The apparent differences in gypsum dissolution rates presented in Fig. 1 were largely related to the difference in the solubility of gypsum in various salt solutions.

The first-order reaction equation has been used to describe the gypsum dissolution process (e.g., Kemper, et al. 1975; Keisling et al. 1978; Keren and Shainberg 1981)

$$dC/dt = k_1(C_s - C) \quad (1)$$

where C is the Ca concentration in solution at a given time t , C_s is the equilibrium Ca concentration, and k_1 is the first-order kinetic constant with a dimension of T^{-1} .

The integral form of Eq. (1) with the initial condition of $C = C_0$ at $t = 0$ is

$$\ln[(C_s - C_0)/(C_s - C)] = k_1 t \quad (2)$$

The plot of $\ln[(C_s - C_0)/(C_s - C)]$ versus t should give a straight line, if Eq. (1) is applicable. This equation, when used with the present data, however, produced curvilinear relationships (Fig. 3), showing high dissolution rates for the first approximately 5 min (or $C/C_s < 0.5$), followed by slower rates. Liu and Nancollas (1971) pointed out that the deviation from the linear relationship can be caused by a reduction in the surface area of gypsum particles. In our experiments, 1 g of gypsum was applied to 25 ml of the solutions, causing no more than 86 mg of gypsum dissolution (or 8.6% of the applied). The reduction in the exposed surface area, assuming a uniform dissolution in three dimensions, would be about 6%. The gypsum samples, initially washed to reduce their weight by 10%, provided a slower dissolution rate by about 5%, yet the same type of curvilinear trend persisted. It seems that the reduction in the exposed surface area cannot be cited as the major cause of the deviation from the linearity. Alternatively, it is possible that the agitation created at the time of gypsum application and during filtration have partly contributed to the high initial dissolution rate. This factor, however, should be small under the shaken conditions.

We then assumed that the rate of gypsum dissolution follows the second-order reaction equation

$$dC/dt = k_2(C_s - C)^2 \quad (3)$$

where k_2 is the second-order kinetic constant

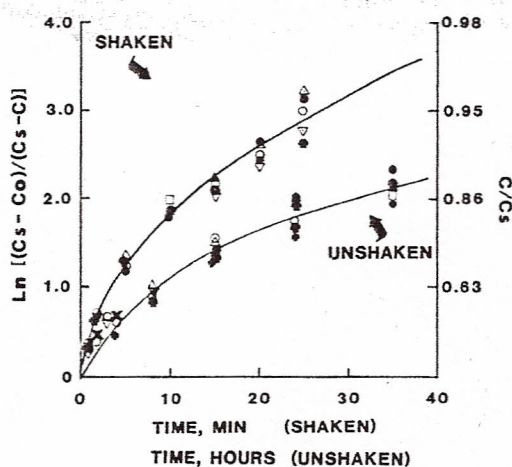


FIG. 3. Plots of the first-order equation given by Eq. (2) for gypsum dissolution with and without shaking. Symbols are the same as those of Fig. 1.

($\text{mmol}^{-1} \text{kg h}^{-1}$). Integration of Eq. (3) with the initial condition of $C = C_0$ at $t = 0$ yields

$$1/(C_s - C) - 1/(C_s - C_0) = k_2 t \quad (4)$$

When $C_0 = 0$, Eq. (4) reduces to

$$(C/C_s)/(C_s - C) = k_2 t \quad (5)$$

When C is expressed as the Ca dissolved (e.g., the measured Ca minus that initially present in solution), instead of the Ca concentrations in solution, Eq. (4) also reduces to Eq. (5).

The second-order plot gave linear relationships for both shaken and unshaken conditions (Fig. 4). In the case of gypsum dissolution in CaCl_2 solution, C was expressed as the measured minus the initially present. The data points scattered considerably from the best-fit lines. However, the deviation was not significant, because a small difference in measured Ca concentrations magnifies itself in this plot. The dissolution rate constants, given by the slope of the lines ($k_2 = 0.900 \text{ mmol}^{-1} \text{kg h}^{-1}$ and $= 0.007 \text{ mmol}^{-1} \text{kg h}^{-1}$ for shaken and unshaken conditions, respectively) were statistically independent of salt concentrations or species, but depended on shaking conditions.

Considering the widespread use of the first-order equation (e.g., Kemper et al. 1975; Keren and Shainberg 1981; Liu and Nancollas 1971), the good agreement with the second-order equation was unexpected. We then applied the second-order equation to the published data of Keren and Shainberg (1981). The results showed

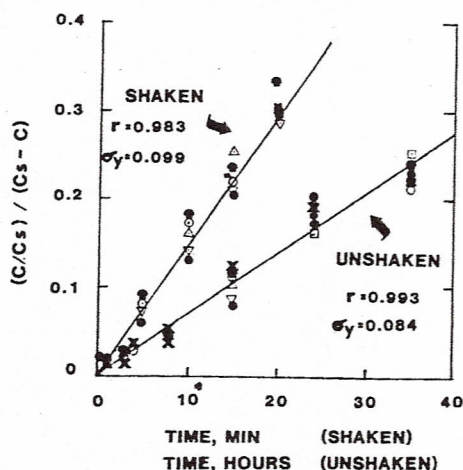


FIG. 4. Plots of the second-order equation given by Eq. (5) for gypsum dissolution with and without shaking. Symbols are the same as those of Fig. 1.

excellent linear relationships with the second-order equation in the entire range of the measurements, whereas the first-order equation began to deviate from the linear relationship at a C/C_s of about 0.3. The first-order equation did produce an excellent linear relationship in the range of $C/C_s < 0.3$, as shown by Keren and Shainberg (1971). The application of the second-order equation to other published data was not feasible for various reasons. Kemper et al. (1975) and Keisling et al. (1978), for example, simply assumed the first-order, and the data of Liu and Nancollas (1971) included the rapid change in surface areas of gypsum seed crystals.

Applying the first- and second-order equations to the data of Keren and Shainberg (1981), as well as to our own data, indicates that the first-order equation is suitable at C/C_s less than 0.3 to 0.5, but that the second-order can describe the entire range, including the low range of C/C_s . This finding is mathematically logical, because the second-order equation converges to the first-order at the limit of C approaching 0. Similarly, the first-order equation converges to the zero order at the limit of C approaching 0. In fact, Barton and Wilde (1971) found that the rate of gypsum dissolution is zero order when $C/C_s < 0.02$.

The agreement with various reaction equations does not necessarily provide insight into the mechanisms involved in dissolution. However, a general discussion can be made based on published literature. When C/C_s is extremely small, as in Barton and Wilde's experiments, the rate-controlling factors should be exclusively physical ones, such as exposed surface areas, the thickness of the diffusion layer, and the rate at which the dissolved Ca is transferred. With increasing Ca concentrations in solution, the dissolution rate begins to be affected by its concentration, while the physical factors still remain important. At higher Ca concentrations, SO_4 ions might come into play. The second-order equation shown by Eq. (3) is merely the special case where Ca and SO_4 are dissolving at equal rates.

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