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DEHYDRATION OF BRUCITE*

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ABSTRACT

Even though a number of investigators have concluded that the dehydration of $Mg(OH)_2$, either precipitated or in its mineral form brucite, follows one or another of the orthodox kinetic equations in which $k_T = f(\alpha)$, there is clear evidence that the process is stepwise, the reaction occurring initially at the surface, then preferentially at fresh surfaces exposed by cracking.

Crushed or cleaved brucite crystals are shown to evolve water at rates which rise and fall in manners consistent with the dehydration-and-cracking mechanism but inconsistent with any of the behaviors described by nucleation-and-growth or diffusion mechanisms.

INTRODUCTION

The kinetics of thermal decomposition of brucite, mineral magnesium hydroxide, has been described in terms of orthodox equations by a number of workers[1–10]. The descriptions include order-of-reaction, contracting geometry, and nucleation-and-growth models, even though some[2, 7, 11] had reported the systematic cracking of well-crystallized brucite into crystallites about one micron in size during thermal decomposition. Also, the pressure dependence of the dehydration has been clearly demonstrated both by equilibrium P–T curves[8, 12–16] and by dynamic measurements[7, 17].

The variation of the temperatures of DTA peaks under well-controlled pressures of water vapor in the 1–8 atm range and the location of these temperatures between those in vacuo and at much higher pressures[8, 12–16] indicates that the dependence exists at all pressures, the P_{H_2O} in experiments in vacuo arising from the (unknown and uncontrolled) pressure gradient within the particle and/or collection of particles.

The existence of an atmosphere dependence indicates per se that the expressions based simply on geometry or order of reaction equations which contain no pressure

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term are inadequate and any kinetic parameters calculated from them are suspect. One of us[18] has pointed out the ease of ascertaining the existence of an atmosphere dependence even in apparatus not designed for atmosphere control by use of greatly different sample sizes and geometries. This present paper reports specific evidence that brucite has a unique dehydration behavior which is not describable by a single equation related to any of the customary models.

In dynamic studies of the temperature of the dehydration of brucite as a function of the pressure, Weber and Roy[8] found a double peak in DTA curves. Whether or not the behavior was consistent in form and magnitude was not specified, but the curve illustrated shows very clear resolution. In extending the studies of Garn and Freund[17] to verify the suspected discontinuity of mechanism in the 6–8 atm range and to examine further the tunnelling mechanism, similar observations were made on a commercial magnesium hydroxide. The peaks were not clearly resolved, but the secondary peak appeared on *both* sides of the main peak, on the low temperature side at the lower pressures. Indeed, the most frequent manifestation was a bulge in the peak rather than an obvious shoulder. The relative crystallinity and homogeneity of Weber and Roy's samples would be expected to lead to superior resolution because of the special nature of the dehydration process. Nonetheless, evidence for a second peak can be seen even on relatively less crystalline samples without deliberate selection of particle size.

Examination by Freund and Garn[19] of a number of differential thermal analysis (DTA) curves from several different laboratories led to the conclusion that there was, in many cases, an initial rhythmic pattern superimposed on the overall peak. The evidence comprised a set of smaller peaks spaced fairly regularly in time or temperature and diminishing in resolution. This behavior could be ascribed to the dehydration of the surface followed by cracking (due to the misfit of magnesia and brucite) which exposed fresh hydroxide surface. This was in agreement with earlier hypotheses by Freund and Nägerl[20–22] which ascribed the relative ease of surface dehydration compared with intracrystalline dehydration to a tunnelling mechanism made possible by the greater amplitude of the wagging vibration of the surface hydroxyl compared with the corresponding intralattice vibration.

As a test of the hypothesis, Freund et al.[23] pulverized magnesium hydroxide to a size ($< 1\ \mu m$) intended to avoid the intrusion of the dehydrate–crack–dehydrate–crack sequence and observed the decomposition in vacuo in a mass spectrometer. They found that the water was evolved irregularly over the temperature interval 200–700 °C, maxima appearing ca. 330, 460, and 570 °C. They concluded that their curves could only be obtained from very minute samples having a small number of particles. As the number of particles increases, so does the tendency of the superpositioning of the many more-or-less-rhythmic individual curves to coalesce into a smooth envelope. The dehydration reaction is known to be reversible so their heating above 600° in vacuum without complete dehydration is surprising considering that the reaction is generally complete below 500° at ambient or even elevated pressures of water vapor[17]. This may reflect yet another unusual behavior of magnesium hydroxide but it is probable that similar behavior in other materials is not uncommon. It is observable without much difficulty in magnesium hydroxide because of the relative simplicity of the $Mg(OH)_2$ structure.

The information relatable to the present study is that the dehydration can involve catastrophic steps on a micro scale. The high vacuum, however, provides a special condition for a reversible reaction, enabling the (reversible) decomposition to proceed rapidly at 200°C. (The rapid beginning may have been due, in part, to strains introduced in the grinding.)

This senior author (PDG) prefers not to use high vacuum experiments for reversible reactions because of the increased uncertainty of the water pressure at the actual reaction site. This present report is on the irregular rates of dehydration of single crystals of brucite obtained from larger, well-crystallized pieces by crushing and by cleaving and cracking. In the first case, the exposed faces are poorly controlled, whereas the cleaving enables a predominant exposure of the cleavage plane, the 0001 face. The existence of such a well-defined cleavage plane inhibits the study of other faces because of the tendency of samples having relatively large areas perpendicular to the 0001 plane to cleave even without imposed stress. Hence, the present data offer a limited, rather than definitive, test of the anisotropy of the process.

These experiments on brucite crystals are a part of a more general study of the effect of structure on thermal decomposition kinetics and mechanisms.

EXPERIMENTAL

The brucite crystal was from Lancaster County, Pennsylvania, U.S.A., and was supplied by the Smithsonian Institute. Crushing (without grinding) was used to provide more-or-less random distribution of surface exposure. The 0001 face was common but not predominant. Crushed samples weighed ca. 3 mg, cleaved samples ca. 8 mg.

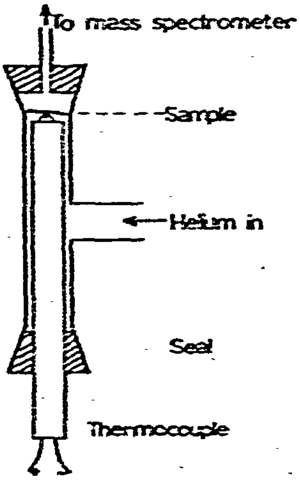

Fig. 1. Sample holder for the measurement of temperature and water evolution from single particles.

The first sample holder was constructed from a standard tee fitting arranged (Fig. 1) so that the particle was supported in part by the wall and in part by the end of the thermocouple entering from the bottom of the tee. The upper end was connected to the capillary inlet valve to a Finnigan Quadrupole Mass Spectrometer Model 1015 SL. The inlet valve is part of the associated gas chromatograph. The sample holder assembly was within the gas chromatograph oven using the gas supply normally used for the capillary column. This enabled use of the chromatograph oven controls to heat the sample and maintain a constant temperature or program the temperature as needed. The gas stream passed through tubing within the oven, thereby being heated to the oven temperature, before entering the side opening of the tee.

In later experiments, this arrangement was varied to enable sampling of a portion of the gas stream rather than introduction of the whole gas stream into the mass spectrometer.

The scan control was set to measure only the water peak at mass 18 and the total ion monitor output was connected to one channel of a two-pen recorder, the other channel being connected to the sample thermocouple. In this way, the recorder not only related the water evolution to time and temperature, but also monitored the temperature control.

In a typical experiment, the sample was dried at ambient temperature or ca. 100°C in the sample holder. When the total ion monitor indicated that no more water was coming into the mass spectrometer, the oven temperature was programmed rapidly upward to the preselected temperature. The water evolution was monitored until its rate had approached zero, whereupon the temperature was raised to ca. 400°C to make certain the dehydration was complete.

RESULTS

Even though the exact form of the water evolution curve or the DSC curve was not highly reproducible because of variations in shape of the particle or heat transfer to the particle, the characteristic pattern discloses the non-agreement between the experimental evidence and any of the theoretical descriptions of solid decompositions. Either or both of two events are shown. There is an abrupt and short-lived increase in the evolution of water some time after reaching the control temperature and/or there is an apparently “normal” decrease in rate of water evolution for a period of time followed by an increase to a new level (5–20%) higher) which subsequently decays.

Appropriate blank runs were made to make certain that none of the effects could have been caused by instrumental artifacts, for example, overshoot by the temperature controller. This overshoot would tend to be reproducible in its time constant and hence easily identifiable even if the temperature of the sample was not monitored. Noise from any part of the system or other aberrations of behavior have never caused any abrupt change other than the usual almost-instantaneous pulse. The

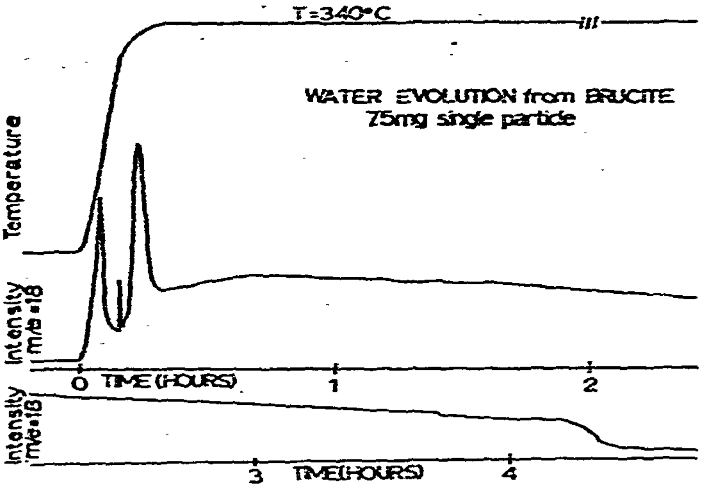

Fig. 2. Temperature and water evolution versus time for a 0.0075 g single particle obtained by crushing a larger crystal.

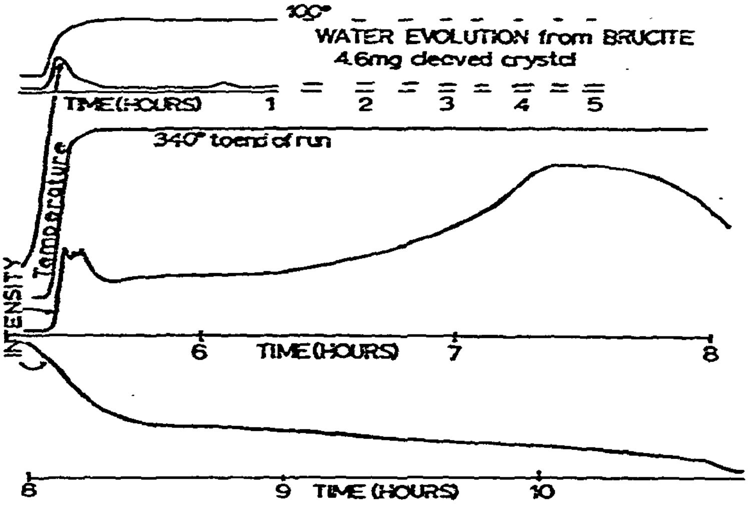

Fig. 3. Temperature and water evolution versus time for a 0.0046 g cleaved crystal.

total ion monitor and the scan control of the mass spectrometer operate at an excellent level of stability. The effects measured clearly arise from the sample.

Microscopy on a hot stage discloses major cracking, but it is not certain that this observable cracking is on the same scale as that detected by the other techniques.

DISCUSSION

The results are in accord with the hypothesis previously stated, the stepwise dehydration and cracking of the mismatched, strained lattice, exposing fresh surfaces. The detection of abrupt changes is not easy because of the time lag between the sample and the transducer. Consequently, the observed increase in rate due to concurrent cracking after a period of surface dehydration is not surprising. There is no real periodicity for single particles because each set of fresh surfaces is in a different environment from the last and the characteristics of the cracking can hardly be expected to be uniform. From this, the pattern of concurrent cracking can be expected to degenerate rapidly. This rapid degeneration was also observed in the DTA curves which led to this investigation.

New apparatus to bring the sample closer to the detector, both in space and in time, is being constructed, not only to examine this behavior more closely, but to ascertain whether or not this is a very limited phenomenon or a characteristic behavior of a multitude of materials. It is easy to hypothesize that any easily decomposed material, whether hydroxide, hydrate, carbonate or others, whose residue tends to have strong bonds to, but substantially different spacings from, the parent crystal will show such behavior. Whether or not cleavable crystals are particularly likely to show such behavior is another important question.

It is worth nothing that the acoustical method reported by Lønvik[24] discloses mechanical events during heating of brucite[25]. Because the water vapor environment was not controlled, the lack of clear agreement in temperatures of acoustical activity and water loss is not necessarily significant. Garn and Freund[17] have already shown that the pressure of water vapor influences the dehydration temperature and have noted that an apparent discontinuity between their data in the 1–8 atm region and extrapolated values from the pressures suggested a changing mechanism, or at least a changing rate-limiting parameter.

CONCLUSIONS

The proposed discontinuous dehydration of magnesium hydroxide by surface dehydration followed by cracking to expose fresh surfaces is confirmed by discontinuities in the water loss from single particles and in consumption of energy during differential scanning calorimetry.

The behavior may be common to a variety of materials.

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