THERMAL ANALYSIS OF MAGNESIUM HYDROXIDE

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Natural brucite and two precipitated $Mg(OH)_2$ samples were analysed in a simultaneous TG-DTG-DSC analyser. The initial dehydroxylation temperature of natural brucite is lower than those of the precipitated samples, but the maximum and final temperatures of the former are higher than those of the latter. The maximum temperatures of individual samples obtained from DTG and DSC curves are almost the same. Heats of reaction derived from peak areas for the three samples are not exactly the same, as they are influenced by the specific surface area of the individual sample. Activation energies deduced by Freeman and Carroll's method are very different from one another. This is attributed to the difference in pressure when the sample is crimped. A linear relationship is observed between the deduced activation energy and the specific height of the DSC peak.

In a series of papers [1], Freeman and Carroll's treatment was applied to investigate the kinetic parameters of some reactions in solution. Activation energies and orders of reaction derived therefrom agree very well with the accepted values.

The thermal dehydroxylation of $Mg(OH)_2$ has been investigated by many authors, but agreeing conclusions were not obtained. Thus, Gregg and Razouk [2] found that the rate of dehydroxylation was of two-thirds order. The activation energies for two brucite samples of 10—80 mesh and 100—200 mesh were 21.0 and 27.6 kcal/mole, respectively. The activation energies of several precipitated $Mg(OH)_2$ samples varied from 12.4 to 27.4 kcal/mole. Kenya [3] claimed that the initial stage of dehydration of $Mg(OH)_2$ was a first-order reaction, and an activation energy of 23 kcal/mole was observed. Turner, Hoffman and Chen [4] investigated several preparations of $Mg(OH)_2$ with a thermobalance. Assuming a two-thirds order reaction and taking the first two terms of Schlomich's expansion as the approximation of the integral, they obtained 51.4 and 57.0 kcal/mole for the activation energies of the precipitated $Mg(OH)_2$ and natural brucite, respectively. Their values are much higher than the previous ones. A review has recently been published by Sharp [5]. Activation energies varying from 16 to 95 kcal/mole, and reaction orders varying from 0 to 1.8 have been reported by various authors for the dehydroxylation of different types of $Mg(OH)_2$ samples, using different methods of data treatment. It is desirable, therefore, to apply Freeman and Carroll's method to analyse thermogravimetric data for the dehydroxylation of $Mg(OH)_2$.

Experimental

Three samples were used for investigation. Sample A was a natural brucite obtained from the Mineralogy Section, Soil Research Institute, Department of Agriculture, Experimental Farm, Ottawa, Canada. It was ground to pass through a 100-mesh sieve. Samples B and C were prepared by precipitating $MgCl_2$ solution with equivalent amounts of NaOH and NH_4OH solutions, respectively, in glass-stoppered Erlenmeyer flasks. Water used for preparing solutions had been boiled to expel dissolved carbon dioxide, and cooled under the protection of a soda lime tube. The precipitated mass was allowed to stand in contact with the mother liquid for one week, with occasional shaking. After filtration and washing free from chloride, the precipitate was dried in an oven at 80°. The dried mass was then pulverized to pass through a 100-mesh sieve. About 15 mg of sample was accurately weighed out and inserted in an aluminium pan, covered with a lid, and pressed in a sample crimper. Approximately the same weight of α-Al_2O_3 was treated in the same way and used as the reference sample. Thermal analysis was performed in a combined TG-DTG-DSC analyser, manufactured by the Rigaku Denki Co. Ltd. of Japan. Experimental conditions used were: DSC ± 8 mcal/sec; TG range 10 mg; DTG range 0.2 div; heating rate 5°/min; chart speed 5 mm/min; temperature full scale 20 mV. Exact weights of sample used were 14.75, 15.50 and 15.70 mg for samples A, B and C, respectively.

Results and discussion

Separate thermal curves for samples A, B, and C are shown in Figs 1, 2 and 3, respectively. In each Figure curve ACD represents the TG curve, EFG the DTG curve, HIJ the DSC curve, and line LM the temperature of the sample. The instrument has a three-pen recorder. One pen records both the TG and DTG data; DTG data are recorded continuously, and TG data intermittently. The line AB
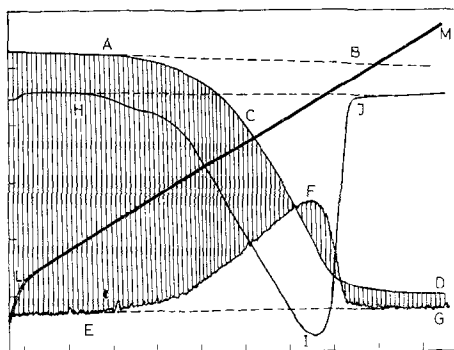

Fig. 1. Thermal curves for sample A (natural brucite)

represents the baseline of the TG curve. It was drawn manually by inspection of the initial part of the TG data. Weight changes were read from the differences between the TG curve and its baseline. α values were calculated from the weight changes and the theoretical total weight loss. Freeman and Carroll's plots are shown in Fig. 4. Activation energies were found to be 210.0, 351.0 and 273.6 kJ/mole (50.2, 83.9 and 65.4 kcal/mole) for samples A, B and C, respectively. The order of reaction was found to be approximately 2 in all cases. Other information found from the curves is listed in Table 1.
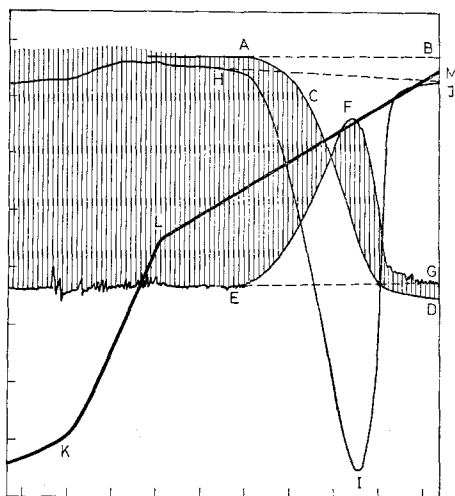

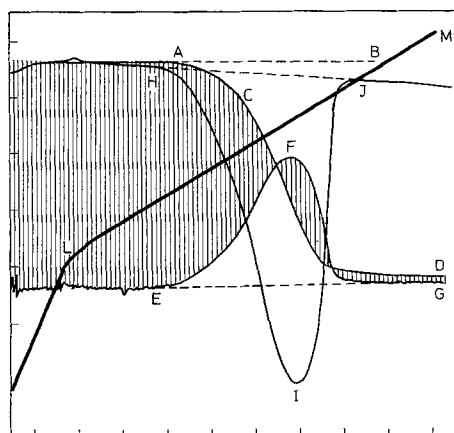Fig. 2. Thermal curves for sample B (precipitated $Mg(OH)_2$)

Fig. 3. Thermal curves for sample C (precipitated $Mg(OH)_2$)

Table 1

Dehydroxylation of $Mg(OH)_2$ by thermal analysis

Sample	DSC peak height, cm*/mg	$\Delta E^{\neq}$		ΔH		t_i °C (DSC)	t_m, °C		t_f °C (DSC)
		kcal/mole	kJ/mole	kcal/mole	kJ/mole		DSC	DTG	
A (brucite)	0.73	50.2	210.0	20.9	87.4	313	424	425	451
B $(MgCl_2 + NaOH)$	1.12	83.9	351.0	21.4	89.5	320	388	389	429
C $(MgCl_2 + NH_4OH)$	0.87	65.4	273.6	19.7	82.4	320	389	390	425

* 1 cm = 0.32 mcal/sec.

The initial temperature of the DSC curve for the two precipitated $Mg(OH)_2$ samples was found to be 320°, whereas that of the brucite sample was 313°. Hashizume and Amita [6] investigated $Mg(OH)_2$ samples by both DSC and DTA tech-
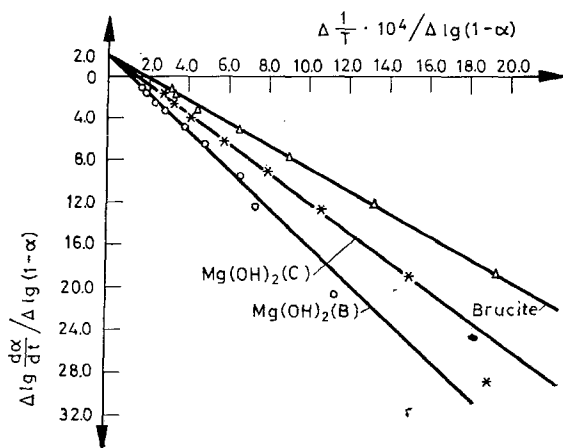

Fig. 4. Freeman and Carroll's plot for thermal dehydroxylation of $Mg(OH)_2$

niques. $Mg(OH)_2$ samples were prepared by calcining hydrated magnesium carbonate at different temperatures and then hydrolysing the MgO obtained. The crystal size of the $Mg(OH)_2$ thus prepared depends on the temperature of calcination. They found that the initial temperature of the DSC peaks of different $Mg(OH)_2$ samples was $327 \pm 3°$, independently of the crystal size. The initial temperature of their DTA peaks was $340 \pm 3°$. Theoretically, the two techniques should yield the same result for the same material. The big difference between their DTA and DSC data apparently lies in the different experimental conditions. Their DTA thermal curves were run in a Rigaku Denki apparatus, using a heating rate of 5°/min and a sample weight of 300 mg, possibly under a static atmosphere, while

their DSC curves were run in a Perkin-Elmer apparatus, using a heating rate of 10°/min and a sample weight of 2 mg, the experiments being carried out under a current of nitrogen. The initial temperature of decomposition reported by Girgis [7], using a DTA technique, was 323°, which is close to the present value. Pechkovskii et al. [8] reported an initial temperature of 351°, which is markedly different from the value mentioned above. We do not know their experimental conditions, but their value was derived from thermogravimetry. The maximum temperature of the DSC curve for precipitated $Mg(OH)_2$ is about 389°, while that for brucite is 424°. Hashizume and Amita [6] found that the maximum temperature of their prepared $Mg(OH)_2$ samples depended very much on the crystal size and varied from about 371 to 379°. Pirmatov and Altykis [9] reported an endothermic effect at 390° and 420° with micro- and macro-crystalline $Mg(OH)_2$, respectively. These are probably the maximum temperatures. They ascribed the shift of the endothermic effect toward 420° as due to the decomposition of complex aggregates of $Mg(OH)_2$ to more simple species, with their subsequent dehydration. The maximum temperature of precipitated $Mg(OH)_2$ reported by Girgis [7] was 383°, which is about six degrees lower than the present value. The final temperatures of the three samples are all different. This temperature is seriously affected by the experimental conditions and does not have any important significance. Not many values could be found from the literature, except that of 396° reported by Pechkovskii et al. [8], using thermogravimetric analysis. The final temperatures of the two precipitated $Mg(OH)_2$ samples are lower than that of the brucite, reflecting their ease of dehydroxylation. The ease of a chemical reaction is usually indicated by the initial temperature of a DSC or DTA peak, as this temperature is not much affected by experimental conditions. In the present investigation, experimental conditions are kept as close as possible. The initial temperature of the brucite is lower than that of the precipitated $Mg(OH)_2$, implying that the former undergoes dehydroxylation more easily than the latter. This seems rather peculiar at first glance, as naturally-occurring substances are usually more stable than artifically-prepared ones. The reason here could be attributed to the imperfections created during pulverization. Chemical reactions are more easily initiated on the broken edges of a crystal. In the two precipitated $Mg(OH)_2$ samples, the crystallites are smaller than 100 mesh. Grinding of the big lump merely separates the agglomerates of small crystallites and does not create broken edges. Therefore, the above-mentioned initial temperature differences should reflect different sample preparations. The DSC peak temperature is almost the temperature of the maximum reaction rate. It should also relate to the ease of a reaction. However, at this temperature a large proportion of the molecules undergo decomposition. Therefore, it is not much affected by crystal defects. Different maximum temperatures reported by various authors should be attributed to differences in crystal size, as mentioned by Hashizume and Amita [6]. In general, the peak is broader and lower for natural brucite than for the precipitated $Mg(OH)_2$. It is noted that the peak heights and the activation energies for the three samples investigated bear a linear relationship, as shown by Fig. 5. The reproducibility of the peak height is estimated to be

within $\pm 2\%$. The reproducibility of the activation energy is roughly estimated to be within $\pm 10\%$. The linear relationship between the two quantities may be explained as follows. The activation energy is related to the temperature coefficient of the rate constant. For two substances of the same quantity, the one with higher activation energy will be exhausted within a narrower temperature range and also within a shorter time interval if they are heated at the same rate. This implies that the base of the DSC peak would be narrower for the substance with higher activation energy. If the two substances had approximately the same heat of reaction, i.e. the same peak area, then the one with the shorter baseline would naturally have the higher peak height.
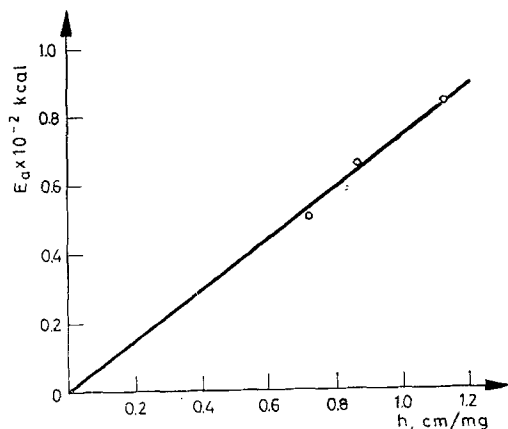

Fig. 5. Linear relationship between activation energy and peak height

The maximum temperatures derived from the DSC and DTG curves are about the same. The DSC peak temperature is the one at which the rate of transmission of heat from the furnace and auxiliary heater less the rate of absorption of heat by the sample due to chemical reaction is equal to the rate of transmission of heat from the furnace to the reference sample, while the DTG peak represents the temperature of maximum reaction rate. These two temperatures may not be equal, depending on the reaction systems investigated. Heat can be transmitted from the furnace to the sample and reference sample in two ways, by convection and by radiation. Heat is transmitted from the surface to the interior by conduction. Heat transfer from the auxiliary heater outside the sample holder to the sample is also by conduction. In the absence of instrumental error, if the thermal conductivities of the starting material and the final product were the same, then the DTA or DSC peak should coincide with that of the DTG. If the thermal conductivity of the starting material were higher than that of the final product, then the thermal conductivity of the sample would decrease as the reaction proceeds; the rate of transmission of heat to the sample would also decrease. At the temperature of the maximum reaction rate, the rate of transmission of heat from the furnace to the

sample less the rate of absorption of heat would still be smaller than the rate of transmission of heat from the furnace to the reference sample. The temperature of the sample relative to the reference sample, would continue dropping until more reactant had been consumed and the rate of heat absorption decreased. Therefore, the DSC peak temperature will be higher than the DTG peak temperature, and vice versa. In the present case, the thermal conductivities of $Mg(OH)_2$ and MgO may be approximately the same. The initial and final temperatures of the DTG curve are difficult to read because of the large noise.
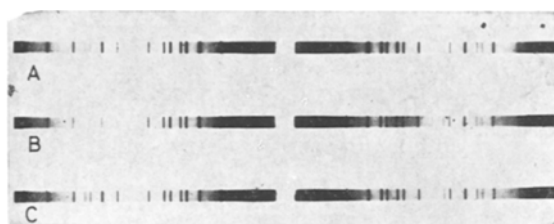

Fig. 6. X-ray diffraction patterns of $Mg(OH)_2$ samples

The mechanism of thermal dehydroxylation of $Mg(OH)_2$ involves two stages [10]. The first stage consists in tunnelling of protons from the electron clouds of their own $O^=$ ions to those of their neighbours. The second stage is the removal of water by diffusion. Anderson and Horlock [11] claimed an additional stage of crystallization of the product, MgO, which is slightly exothermic. The diffusion of water in the crystal lattice proceeds in the plane of the hexagonal layers, not in the C axis. This step is slower than proton tunnelling. The activation energies of the three samples investigated differ markedly. The crystallinities of these samples are more or less the same when examined by X-ray diffraction, as shown in Fig. 6. This implies that the rate-determining step for the overall dehydroxylation reaction is the diffusion of water vapor through the grain boundary, rather than through the crystal lattice. The differences in the activation energies of the three samples are attributed to the pressure exerted on the crimper when the sample pan is pressed. The greater the pressure, the more tightly the sample is packed, the more difficult it will be for water vapor to diffuse out, and therefore, the higher the activation energy, and vice versa. This conclusion is in accord with that of Sharp [5]. He claimed that "the higher activation energies observed from DTA than from isothermal thermogravimetry in vacuo are due to build-up in the partial pressure of water vapor in the vicinity of the sample". Investigation of the effect of the pressure used to prepare the sample on the activation energy is under progress. Preliminary results show that when the sample is heavily pressed, both peak temperature and peak height increase.

Overall heats of reaction calculated from peak areas were found to be 87.4, 89.5 and 82.4 kj/mole (20.9, 21.4 and 19.7 kcal/mole) for samples A, B and C, respectively. The instrument was calibrated with both pure $KClO_4$ and zinc sam-

ples. The values for natural brucite and one sample of precipitated Mg(OH)$_2$ do not differ much. They are somewhat higher than the value of 18.9 kcal/mole reported by Girgis [7]. The heat of reaction of the other precipitated Mg(OH)$_2$ sample is about 1 kcal/mole lower and is in good agreement with the Girgis value. This difference should be attributed to the difference in the specific surface areas of the samples as pointed out by Hashizume and Amita [6]. The heat of reaction calculated from the standard heats of formation of the products and the reactant is 20.4 kcal/mole at 25°.

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RÉSUMÉ — La brucite naturelle et deux échantillons de Mg(OH)$_2$ précipités ont été étudiés par TG-TGD et DSC simultanées. La température initiale de la déshydroxylation de la brucite naturelle est plus faible que celle des deux échantillons précipités, mais les températures maximale et finale de déshydroxylation de la brucite sont plus élevées que celles des échantillons précipités. Les chaleurs de réaction déduites de l'aire des pics DSC des trois échantillons ne sont pas exactement les mêmes, puisqu'elles sont influencées par l'état de surface des échantillons individuels. Les énergies d'activation trouvées en appliquant la méthode de Freeman et Carroll sont très différentes les unes des autres. Elles sont attribuées à la différence de pression au niveau de l'échantillon. On a observé une relation linéaire entre l'énergie d'activation déduite et la hauteur spécifique du pic DSC.

ZUSAMMENFASSUNG — Natürlicher Brucit und zwei gefällte Mg(OH)$_2$-Proben wurden in einem simultanen TG-DTG-DSC-Analysator geprüft. Die Anfangstemperatur der Dehydroxylierung des natürlichen Brucits ist niedriger als die der gefällten Proben, doch sind Maximal- und Endtemperaturen des ersteren höher als jene der letzteren. Die an Hand von DTG und DSC-Kurven erhaltenen Maximaltemperaturen der einzelnen Proben sind fast identisch. Die aus den Peakflächen der drei Proben errechneten Reaktionswärmen sind nicht genau dieselben, da sie von der spezifischen Peakfläche der einzelnen Proben beeinflußt werden. Die mittels der Methode von Freeman und Carroll abgeleiteten Aktivierungsenergien sind von einander sehr verschieden. Sie werden den Unterschieden im Druck bei dem Schrumpfen der Probe zugeschrieben. Ein linearer Zusammenhang zwischen der abgeleiteten Aktivierungsenergie und der spezifischen Höhe der DSC-Peaks wurde beobachtet.

Резюме—Природный бруцит и два образца осажденного Mg(OH)$_2$ были проанализированы с помощью одновременного ТГ—ДТГ—ДСК анализатора. Первоначальная температура дегидроксилирования природного бруцита ниже, чем осажденных образцов, но максимальная и конечная температуры для него выше, чем для последних. Максимальные температуры индивидуального образца, полученные из ДТГ и ДСК, почти одинаковые. Теплоты реакции, установленные из площади пика, для этих трех образцов, не совсем одинаковые, так как они обусловлены удельной площадью поверхности индивидуального образца. Энергии активации их, выведенные по методу Фримэна—Кэрролла, очень отличаются друг от друга, что обусловлено различием в давлении при обжимании образца. Наблюдается линейная взаимосвязь между выведенной энергией активации и удельной высотой пика ДСК.