KINETICS OF HYDRATION OF MAGNESIUM OXIDE IN AQUEOUS SUSPENSION

I. METHOD OF MEASUREMENT AND EVALUATION OF EXPERIMENTAL DATA

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Magnesium oxide in aqueous suspension is hydrated by the "via solution" mechanism. In the initial stage, there arise brucite nuclei on active centres of the surface of MgO, and this is associated with a rapid increase in the specific surface area of the solid phase. In the subsequent stage, the specific surface area decreases as a result of a slowing down of the nucleation rate, probably due to inactivation of the free active centres that become overgrown by the forming brucite crystals. The time course of the entire process is described by the equation $\ln (1/(1-y)) = (kt)^n$, *where* $\underline{y}$ *is the rate of conversion,* $\underline{t}$ *is time,* $\underline{k}$ *is the rate constant and* $\underline{n}$ *is a constant of the empirical equation, having the value of 2/3. The temperature dependence of the rate constant conforms to the Arrhenius equation and has the activation energy* $\underline{E} = 54.7$ *kJ mol*$^{-1}$.

INTRODUCTION

Lime production for building construction from pure limestones would lead in foreseeable future to exhaustion of their natural deposits. Efforts are therefore aimed at producing the lime from dolomitic limestones whose stocks are substantially larger. However, the conventional slaking of such lime leaves most of the magnesium oxide unhydrated, and its hydration then takes place in the hardened mortar. The additional hydration is associated with an increase in volume, and usually also involves a loss in strength. This risk is eliminated when complete hydration of both calcium and magnesium oxides is achieved in the course of slaking, e.g. by hydration under pressure. Suspensions of dolomitic hydrates exhibit more favourable rheological properties, and as demonstrated by Bláha and Jedlička [1], carbonation of $Mg(OH)_2$ also contributes to the increase in strength due to carbonation of $Ca(OH)_2$.

For this reason, study of hydration of magnesium oxide is not merely a theoretical issue, but a matter of practical interest to the lime industry. This interest is due to the facts mentioned above, namely the much lower rate of reaction of MgO with water compared to that of CaO, and the almost generally incomplete degree of hydration achieved under usual industrial operating conditions.

The mechanism of hydration of magnesium oxide was studies by Kahler [2] who applied Le Chatelier's theory of the formation of magnesium hydroxide by the via solution reaction [3]. The reaction rate of MgO hydration during extensive agitation of the MgO suspension was measured by Smithson and Bakhshi [4]. These authors reached the conclusion that hydration of MgO is controlled by the rate of the chemical reaction. Other authors studied hydration of MgO by steam: mention can be made of Layden and Brindley [5], Bratton and Brindley [6], Johnston [7], and Feitknecht and Braun [8]. The last mentioned authors divided the hydration mechanism into four stages: formation of a layer of physically adsorbed water, transport of OH^- and Mg^{2+} ions through the layers of adsorbed water, formation of an oversaturated solution and $Mg(OH)_2$ nuclei, and finally growth of tabular crystals.

The present paper had the aim of acquainting the readers with the measuring method employed and the evaluation of the experimental results, and with describing the rate at which magnesium oxide reacts with water.

EXPERIMENTAL

Magnesium oxide was prepared by firing magnesium carbonate specified as "carbonate for ferromagnetics" (Lachema Brno) in stationary air atmosphere at 900 °C for 60 minutes. Chemical, X-ray diffraction and gravimetric thermal analyses showed that the substance can be described by the chemical formula $4MgCO_3Mg(OH)_2.4H_2O$. Its specific surface area was 23 m^2 g^{-1}. The habitus of the leaf-shaped crystals arranged in tubular formations is shown in Figures 1 and 2. The specific surface area of all samples was established by the nitrogen adsorption method at the boiling point of nitrogen.

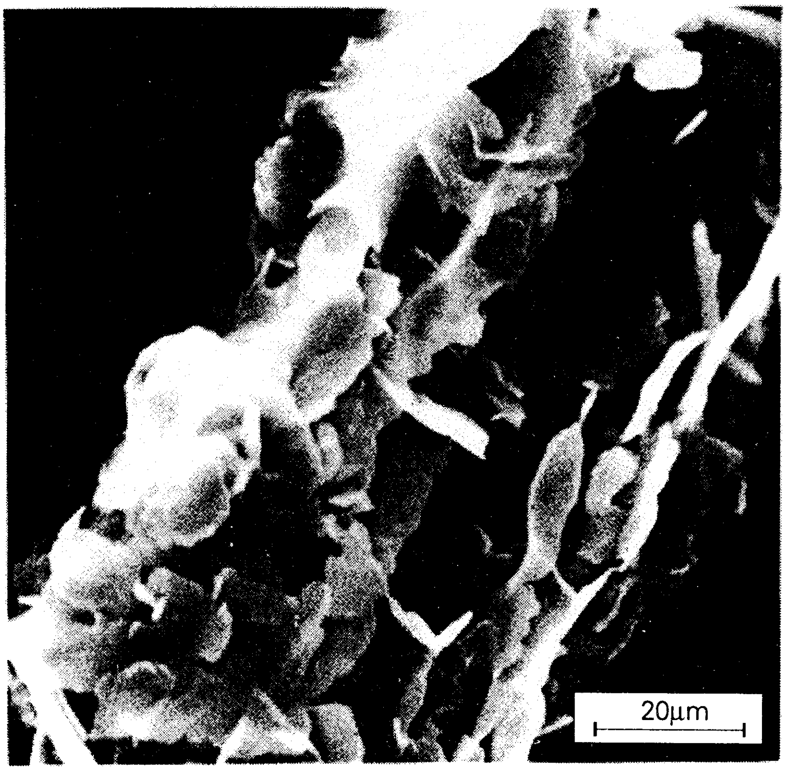

Figure 1. Leaf-shaped form of basic magnesium carbonate for ferromagnetics

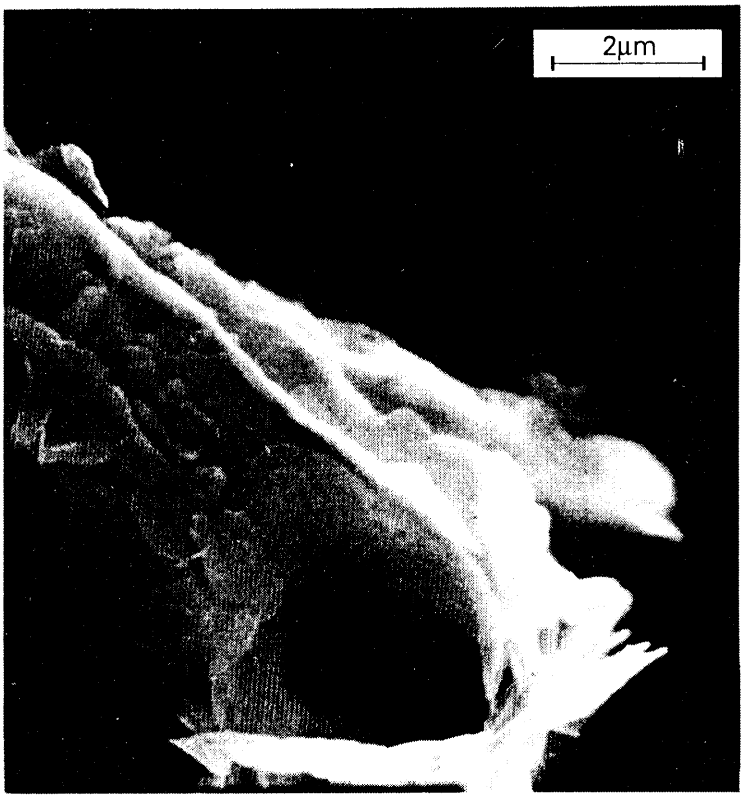

Figure 2. Tubular arrangement of leaf-shaped crystals of basic magnesium carbonate for ferromagnetics

Figure 3. Magnesium oxide - pseudomorphosis of basic magnesium carbonate

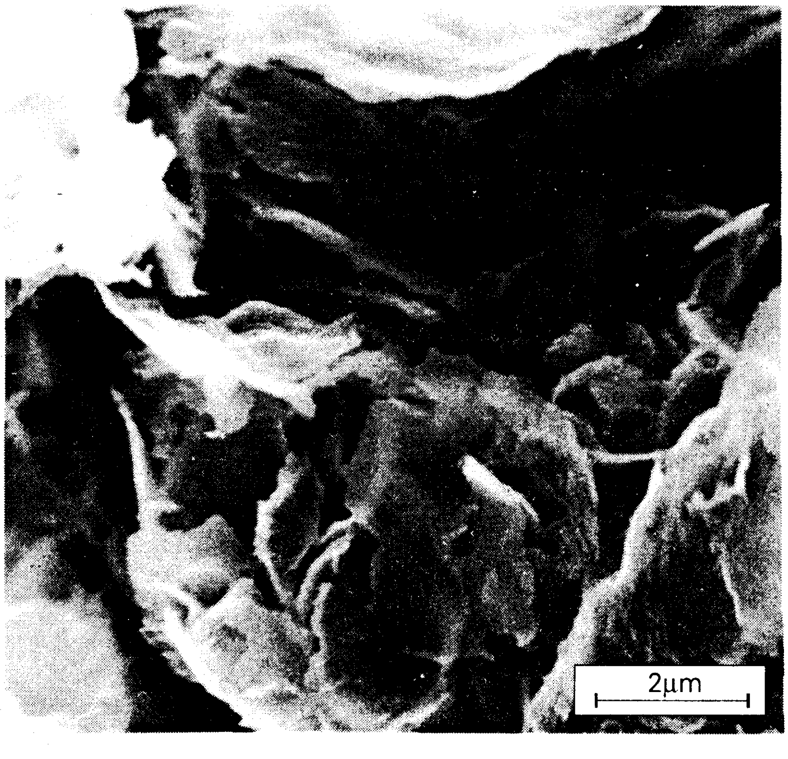

Figure 4. Magnesium oxide

The crystalline character of the fired magnesium oxide is shown in Figures 3 and 4. Its specific surface area was 33 $m^2 g^{-1}$.

The oxide was hydrated in a teflon vessel covered with a lid and placed in an aluminium block. The temperatures at which the course of the process was monitored, were maintained constant by a water thermostat, and chosen so as to make the reactions proceed at suitable rates for measuring the conversion degree. In all instances, 1.5 g of the oxide was hydrated in 9 ml of water. Samples were taken at suitable intervals chosen with respect to kinetic data processing, blended with a 1:1 mixture of ethyl alcohol and acetone to stop the reaction, and filtered off in vacuo. After drying at 90 °C, they were subjected to gravimetric thermal analysis, and the conversion degree y was established from the loss in weight over the temperature range of 340 to 420 °C, where the loss corresponded to the amount of water bound to magnesium hydroxide. The measuring results are listed in Table I.

Table I. Degree of conversion of magnesium oxide to hydroxide in terms of time and temperature of hydration

Time of hydration (min.)	Conversion degree for hydration temperature of 36 °C	46 °C	56 °C
3.5	0.01	0.02	0.05
7	0.02	0.04	0.07
15	0.04	0.11	0.21
30	0.09	0.25	0.51
60	0.23	0.48	0.76
120	0.52	0.75	0.89
240	0.74	0.92	

The rate of hydration of magnesium oxide was evaluated by means of the equation suggested by Jerofeev:

$$\ln (1/(1-y)) = (kt)^n. \tag{1}$$

This is an empirically established general form of the kinetic equation for isothermally proceeding heterogeneous processes.

Equation (1) was logarithmized for the purpose of obtaining the respective constants k and n:

$$\ln (\ln (1/1-y)) = n \ln (kt) \tag{2}$$

On defining the half-time $t_{0.5}$ of the given process as the time when the conversion degree just attains the value of 0.5, Equation (2) acquires the following form:

$$\ln \ln 2 = n \ln (kt_{0.5}), \tag{3}$$

where k is a proportionality constant whose physical significance is not precisely defined. Substitution of Equation (3) into Equation (2) yields an expression where n is the sole correlation parameter without any defined physical significance. If $n = 1$, then Equation (1) is an integrated form of a first-order differential kinetic equation.

To obtain the values of $t_{0.5}$ and those of constant n, the values of ln (ln (1/(1-y))) were plotted vs. ln t as follows from Equation (4):

$$\ln (\ln (1/(1-y))) = n \ln t + (\ln \ln 2 - n \ln t_{0.5}). \tag{4}$$

The expression in brackets on the right-hand side of Equation (4) corresponds to the length of the segment on ordinate Y, and parameter n is determined from the gradient of the straight line. The equation rearranged in this way has the advantage of allowing the half-time value to be calculated from known n values, and designated $(t_{0.5})_{calc}$. The value can be compared to that read off the graphic plot of the time course of the experimentally established conversion degrees (Figure 5).

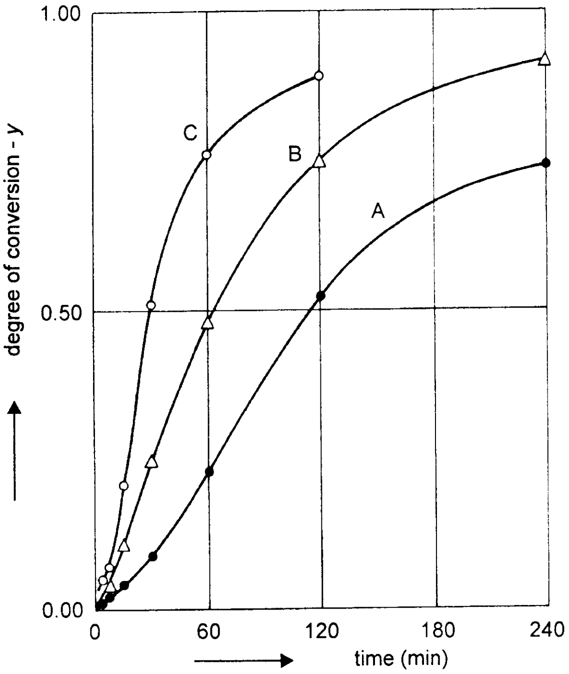

Figure 5. Degree of conversion of magnesium oxide to hydroxide The time of hydration at: ● - 36 °C, △ - 46 °C, ○ - 56 °C

Figure 6 shows the graphic plots of Equation (4) in linear ordinates for various hydration temperatures.

The Arrhenius equation was used in calculating the apparent activation energy of the heterogeneous reaction of magnesium oxide with water from the half-time values. The activation energy established was 54.7 kJ mol^{-1}. For the given temperature range, exponent n was constant and equal to 2/3.

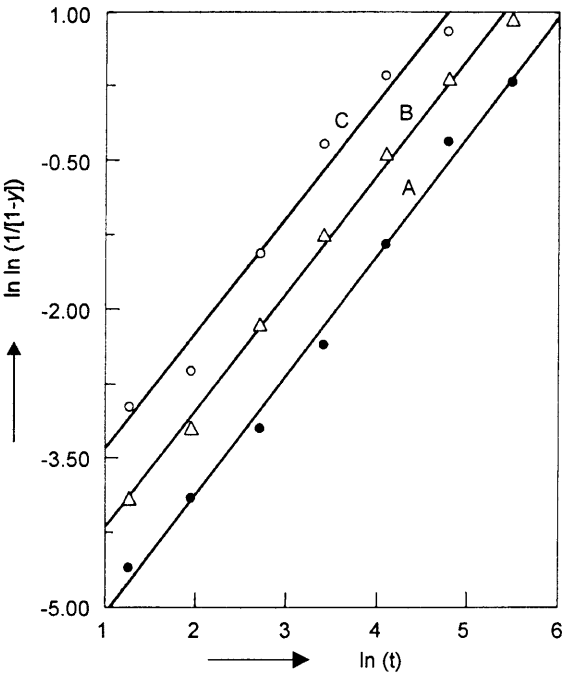

Figure 6. Graphic plot of Equation (4)
The time of hydration at: ● - 36 °C, Δ - 46 °C, ○ - 56 °C

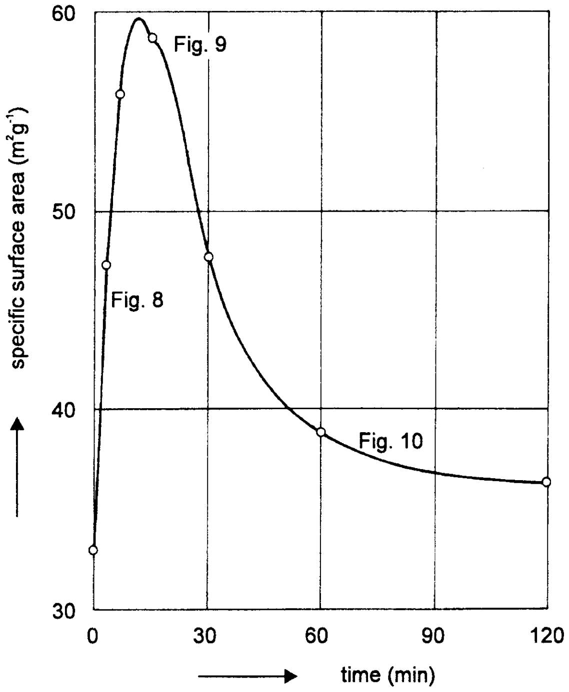

Figure 7. Specific surface area of magnesium hydroxide vs. the time of hydration at 56 °C

Apart from measuring the rate of hydration, the dependence of the specific surface area of hydrated magnesium oxide on the time of hydration was also determined. The measuring results are plotted in Figure 7. Scanning electron micrographs of some selected samples are shown in Figures 8 through 10.

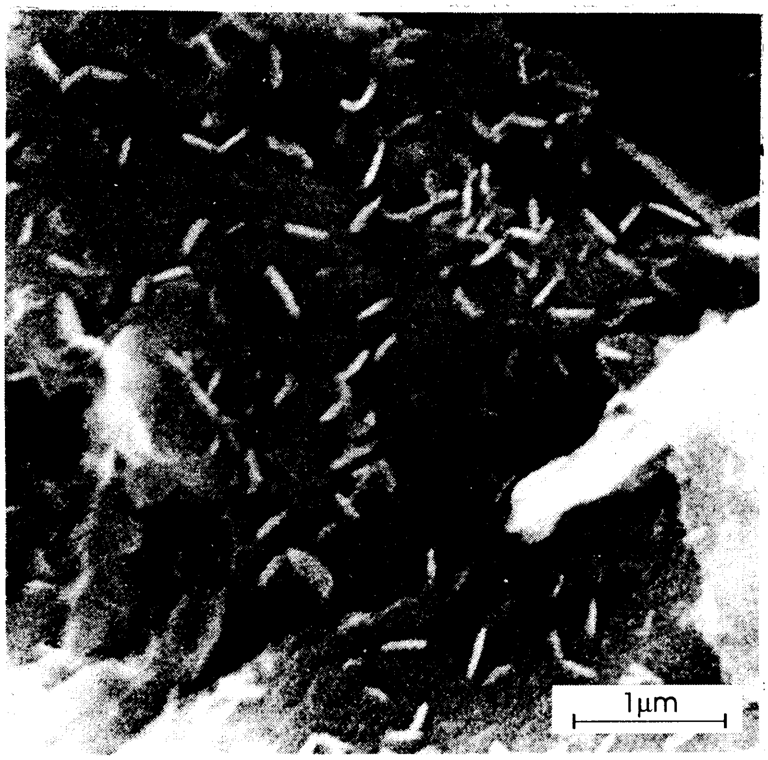

Figure 8. Initial stage of growth of magnesium hydroxide crystals on crystals of magnesium oxide, time of hydration 3.5 minutes, temperature 56 °C

Figure 9. Crystals of magnesium hydroxide, time of hydration 15 minutes, temperature 56 °C

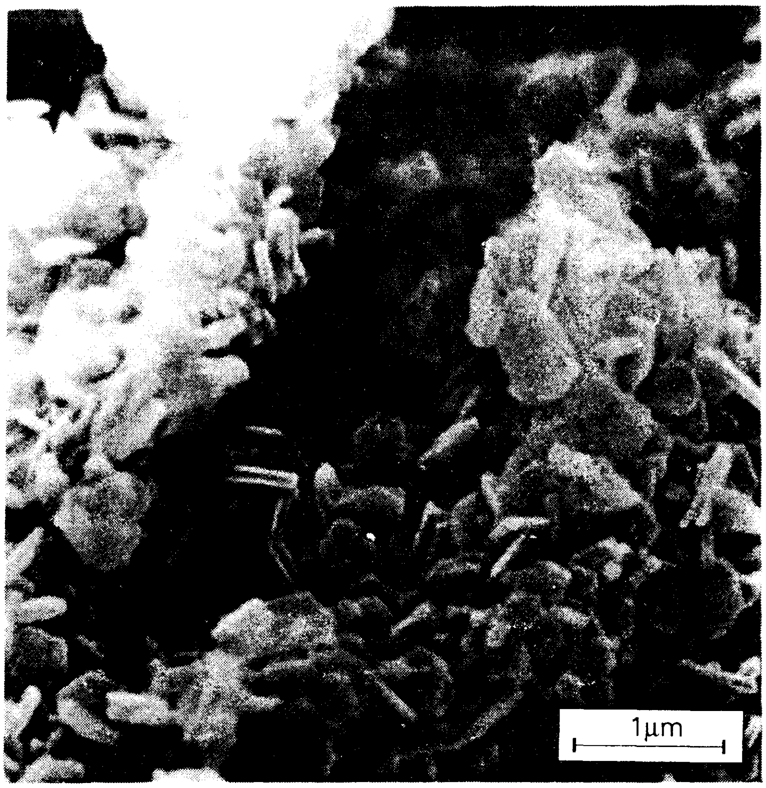

Figure 10. Crystals of magnesium hydroxide, time of hydration 60 minutes, temperature 56 °C

DISCUSSION

Purity and adequate fineness were the main criteria for selection of the initial material for the preparation of magnesium oxide. Among the compounds available, both these requirements were met only by the basic magnesium hydroxide intended for the manufacture of ferromagnetic materials. The firing temperature and time were chosen with respect the the possibility of transferring the results obtained to the similar conditions of industrial firing of dolomitic limestones. This was the lowest possible firing temperature, in particular with respect to calcium carbonate.

Firing at a relatively high temperature for basic magnesium carbonate will yield an oxide having a specific surface area larger by almost one half compared to the original carbonate, and in addition to this, retaining the structure of the original carbonate, as demonstrated by Figures 1 and 3.

If the hydration is effected in the way described above and in particular at temperatures of about 46 °C, its course will be very satisfactory with respect to the conversion degree achieved. The way of stopping the reaction and the method of determining the content of magnesium hydroxide by the gravimetric thermal analysis have been proved fully successful. In this connection it may be pointed out that there is no other method which would give more correct and sensitive results in determining the content of magnesium hydroxide. The content of hydrates measured was used to calculate the conversion degree, and the latter to calculate the half-times of the given process. The equation proposed by Jerofeev was employed in describing the system. In view of possible utilization of the results in technological practice, a formal mathematical description of the time course of the process should be sufficient. The calculated constant n of the equation is merely a parameter describing the given time dependence of the conversion degree.

A single-parameter equation with constant n is obtained by defining the half-time and by rearranging Equation (1) to Equation (4). This treatment permits the values of $t_{0.5}$ and $(t_{0.5})_{\mathrm{calc}}$ to be mutually compared.

Using the Arrhenius equation, calculation was made of the apparent activation energy, which in this case is in fact merely a measure of the temperature dependence of the half-time. Its value is in a good agreement with that published by Smithson and Bakhshi.

The growth of brucite crystals on the oxide particles in the course of the crystallization is well illustrated by the series of scanning electron micrographs (Figures 8 through 10). At first, individual leaf-formed crystals 0.05 × 0.25 μm in size begin to appear on the surface of the oxide crystals. Their amount and size increases with the time of hydration, until, after 60 minutes of hydration when the conversion degree has attained the value of 0.76, the well-developed tabular crystals of magnesium hydroxide cover the entire surface of the original magnesium oxide crystal.

The course of formation and growth of magnesium hydroxide crystals described above is also well illustrated by the time dependence of the specific surface area of the hydrating magnesium oxide (Figure 7). The increase in the specific surface area from the original value for the oxide is due to starting crystallization of the hydroxide, where the experimentally established specific surface area value is a sum of the surface area of the oxide and that of the hydroxide. With increasing time of hydration the oxide is transformed into hydroxide, the initially formed small hydroxide crystals grow and this is the cause of the decrease and final settling of the specific surface area value at that corresponding to the size, shape and number of magnesium hydroxide crystals present in the final product.

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KINETIKA HYDRATACE OXIDU HOŘEČNATÉHO VE VODNÍ SUSPENZI

I. METODIKA MĚŘENÍ A VYHODNOCENÍ EXPERIMENTÁLNÍCH HODNOT

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Mechanizace ve stavebnictví je spojena s výrobou suchých hydrátů. Některé z vápenek budou muset v budoucnu vyrábět vápno z dolomitického vápence a to proto, že zásoby kvalitních vápenců se pomalu vyčerpávají. Hydratace oxidu hořečnatého v provozních podmínkách je z technologické stránky procesu náročná a za běžných podmínek neprobíhá.

Byla vypracována metodika studia hydratace a způsobu vyhodnocení stupně přeměny oxidu hořečnatého na hydroxid. Proces hydratace oxidu hořečnatého vypáleného při teplotě 900 °C po dobu 60 minut a hydratovaného v rozmezí teplot 36 až 56 °C je možno popsat rovnicí $\ln(1/(1-y)) = (kt)^n$, kde $n = 2/3$, závislost k na teplotě vystihuje Arrheniova rovnice a zdánlivá aktivační energie je 54,7 kJ mol^{-1}.

Průběh hydratace je dokumentován sérií snímků SEM a hodnotami měrného povrchu. Výsledky svědčí o tom, že proces probíhá ve dvou krocích: po heterogenní nukleaci $Mg(OH)_2$ na povrchu MgO následuje růst krystalů brucitu.