

## HYDRATION KINETICS OF MAGNESIUM OXIDE

## PART 3 - HYDRATION RATE OF MgO IN TERMS OF TEMPERATURE AND TIME OF ITS FIRING

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The rate of hydration of magnesium oxide depends on the temperature and time of its firing. To describe the kinetics of hydration over the entire temperature range measured, use can be made of the equation  $\ln(1/(1-\alpha)) = (kt)^n$ , which was proposed for similar heterogeneous systems by Yerofeyev. The temperature dependence of rate constants conforms to the Arrhenius equation. The activation energy also depends on temperature and the time of firing of MgO, and its values range from 50 to 93 kJ mol<sup>-1</sup>.

## INTRODUCTION

The previous communication [1] was concerned with the mechanism and rate of hydration of MgO and showed that the rate of hydration is decisively affected by the specific surface area.

The present study had the aim to investigate the effect of temperature and time of firing magnesium hydroxide carbonate on the hydration rate of the oxide formed.

## EXPERIMENTAL PART

Magnesium hydroxide carbonate was used in the preparation of magnesium oxide for reasons explained in the previous paper [1]. The firing was effected in a vertical furnace in stationary air atmosphere. The fired samples of magnesium oxide were characterized by the method of low-temperature adsorption of nitrogen after Nelssen and Eggertsen [3]. The fired oxides were hydrated by the method described in the first part of the present study [1]. The hydration temperatures were chosen according to the character of the oxide, over the range of 6 to 86 °C.

A survey of the samples, their designation and their specific surface areas is presented in table 1. The results of experimental determination of the kinetics of their hydration are summarized in table 2.

The established values of the conversion degree were evaluated from the point of view of kinetics by means of the Yerofeyev equation [1]. The calculated rate constants were plotted vs. the respective reciprocal values of temperature (K). The graphic plot is shown in figure 1. The half-time method, described in the previous study [1], was used in calculating the apparent activation energies for the individual magnesium oxide samples in terms of the time and temperature of their firing. The respective values of apparent activation energy are listed in table 3.

Table 1. Designation of magnesium oxide samples with regard to firing temperature and time, and to specific surface area.

designation	firing temperature (°C)	time (min)	specific surface area (m <sup>2</sup> g <sup>-1</sup> )
M500/30	500	30	155
M650/15	650	15	129
M650/60	650	60	93
M900/5	900	5	56
M900/60	900	60	34
M1200/60	1200	60	19
M1400/60	1400	60	11

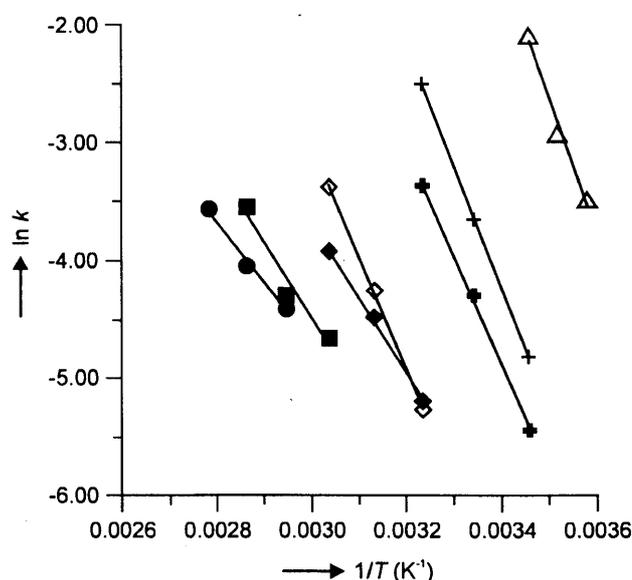


Figure 1. Logarithm of the rate constant vs. reciprocal value of absolute temperature of MgO hydration.

Δ – MgO, 500 °C, 30 min; + – MgO, 650 °C, 15 min; – – MgO, 650 °C, 60 min; ◊ – MgO, 900 °C, 5 min; ◆ – MgO, 900 °C, 60 min; ■ – MgO, 1200 °C, 60 min; ● – MgO, 1400 °C, 60 min.

Table 2. Conversion degree for the individual samples of magnesium oxide in terms of hydration temperature and time.

sample	hydration temperature (°C)	conversion degree after time of hydration (min.)					
		3.5	7	15	30	60	120
M500/30	6	0.17	0.29	0.41	0.56	0.83	0.89
	11	0.28	0.41	0.55	0.78	0.87	
	16	0.40	0.58	0.86	0.89		
M650/15	16	0.08	0.17	0.25	0.34	0.45	0.60
	26	0.18	0.23	0.38	0.61	0.77	0.87
	36	0.30	0.48	0.75	0.83		
M650/60	16	0.03	0.06	0.10	0.16	0.27	0.46
	26	0.10	0.12	0.25	0.45	0.57	0.75
	36	0.17	0.28	0.45	0.68	0.80	
M900/5	36	0.02	0.05	0.10	0.15	0.23	0.52
	46	0.06	0.08	0.25	0.45	0.57	0.75
	56	0.11	0.28	0.45	0.68	0.80	
M900/60	36	0.01	0.02	0.04	0.09	0.23	0.52
	46	0.02	0.04	0.11	0.25	0.48	0.75
	56	0.05	0.07	0.21	0.51	0.76	0.89
M1200/60	56	0.01	0.04	0.11	0.18	0.42	0.62
	66	0.03	0.08	0.20	0.34	0.58	0.75
	76	0.10	0.25	0.49	0.68	0.80	0.87
M1400/60	66	0.02	0.06	0.14	0.35	0.53	0.68
	76	0.05	0.10	0.27	0.47	0.72	0.78
	86	0.08	0.20	0.41	0.59	0.76	0.77

Table 3. Values of apparent activation energy of the hydration reaction for the individual samples of MgO.

Sample	Apparent activation energy (kJ mol <sup>-1</sup> )
M500/30	93.3
M650/15	86.1
M650/60	85.5
M900/5	80.0
M900/60	54.7
M1200/60	52.4
M1400/60	50.3

## DISCUSSION

The experimental results showed that the hydration rate of magnesium oxide depends on the temperature of hydration, as well as on the temperature and time of firing. However, a decisive influence on the hydration rate is exhibited by the degree of crystallization and sintering of magnesium oxide, whose measure is its specific surface area. These conclusions are identical with the findings of Smithson and Bakhshi [4] who reported that the hydration rate was directly proportional to the surface area of the magnesium oxide particles.

An account of the morphological changes of magnesium oxide crystals depending on firing temperature was given in the previous part of the study [1].

The effect of firing temperature and time on specific surface area and the hydration rate can be illustrated by comparing the conversion degrees attained at a hydration temperature of 56 °C within 30 minutes of hydration. At the firing temperature of 900 °C, sample M900/5 with a specific surface area of 56 m<sup>2</sup> g<sup>-1</sup> attained a conversion degree of 0.68. Extension of the time of firing to 60 minutes (sample M900/60) caused the specific surface area to decrease to 34 m<sup>2</sup> g<sup>-1</sup> and the conversion degree down to 0.51. When the firing temperature was raised up to 1200 °C and the time of firing prolonged to 60 minutes (sample M1200/60), the specific surface area was reduced to 22 m<sup>2</sup> g<sup>-1</sup> and the conversion degree under the same conditions was as low as 0.18.

Increases in hydration temperature accelerated the course of hydration. For example, hydration of sample M900/60 for 30 minutes at 36 °C resulted in a conversion degree of 0.09, at 46 °C in one of 0.25, and hydration at 56 °C yielded a value of as much as 0.51.

The temperatures at which the individual samples were hydrated were chosen with respect to the processing of results for the purpose of establishing the kinetics of hydration. With increasing firing temperature and thus

with decreasing specific surface area of the fired magnesium oxides, the hydration was carried out at higher temperatures to achieve the maximum conversion degree within 120 minutes. A not too high temperature of hydration could not be chosen because the initial hydration period would be too short.

In this case, the apparent activation energy is merely a measure of the temperature dependence of the reaction half-life. In spite of this fact it may be stated that the values of this quantity depend on the sintering degree of the initial magnesium oxide. Whereas the apparent activation energy of oxides fired at low temperature and thus sintered to a lower degree varies over the range of 80 to 93 kJ mol<sup>-1</sup>, and its value with more strongly sintered oxides falls to the region of 50 kJ mol<sup>-1</sup>.

Comparison of the experimentally established values of apparent activation energy with the those published by other authors shows that the values for magnesium oxide prepared by firing at 900 and 1200 °C are in good agreement with the data given by Smithson and Bakhshi who found the value of 59 kJ mol<sup>-1</sup>.

To assess the effect of specific surface area of the starting magnesium oxide on the rate of its hydration, logarithms of rate constants corresponding to a hydration temperature of 50 °C ( $k_{50}$ ) were calculated (for all MgO samples) by means of the Arrhenius equations of temperature dependence of hydration rate constants. The plot in figure 2 shows the dependence of specific surface

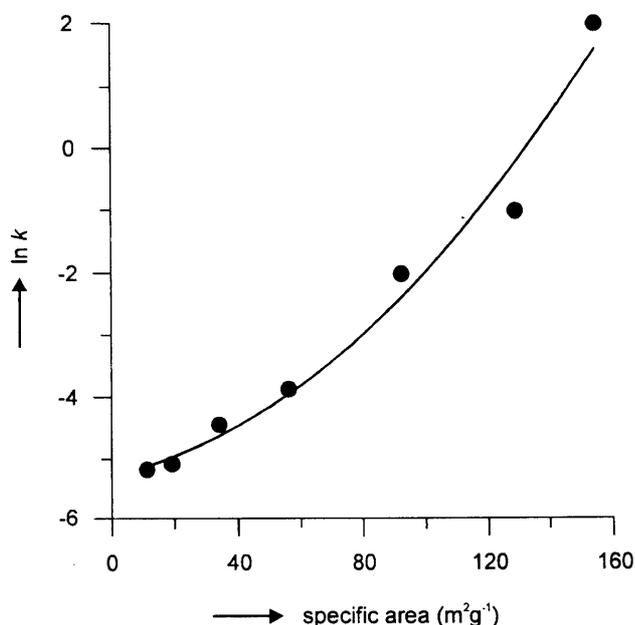


Figure 2. Logarithm of the rate constant for hydration temperature of 50 °C vs. specific surface area of MgO.

area on logarithm of the rate constant ( $k_{50}$ ). The plot indicates that there is an exponential relation between the two quantities.

## CONCLUSION

The dependence of the degree of conversion of magnesium oxide to hydroxide shows that the temperature and time of its firing, and thus the sintering degree of MgO, which can be described by the specific surface area, affect not only the rate of its hydration, but also the value of its apparent activation energy.

## References

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## KINETIKA HYDRATACE OXIDU HOŘEČNATÉHO

ČÁST 3 - ZÁVISLOST RYCHLOSTI HYDRATACE MgO  
NA TEPLITĚ A DOBĚ JEHO VÝPALU

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Možnost využití dolomitických vápen ve stavebnictví je vázána na požadavek úplné hydratace oxidu hořečnatého a to proto, že přítomnost volného oxidu je spojována s možnou objemovou nestálostí dolomitických hydrátů. V provozních podmínkách se doporučuje použití tlakové hydratace dolomitických vápen. Tento proces je však jak z technologického tak ekonomického hlediska náročný.

Tyto praktické důvody byly podnětem pro rozsáhlou studii hydratace oxidu hořečnatého s ohledem na jeho dobu a teplotu výpalu. Na základě výsledků měření lze konstatovat, že proces hydratace oxidu hořečnatého vypáleného při teplotách 500 až 1400 °C a hydratovaného v rozmezí teplot 6 až 86 °C je možno popsat rovnicí  $\ln(1/(1 - \alpha)) = (kt)^n$ , kterou navrhl pro obdobné heterogenní reakce Jerofejev. Závislost rychlostních konstant se řídí Arrheniovým vztahem a vypočítané aktivační energie leží v rozmezí 50 až 93 kJ mol<sup>-1</sup>.