

KINETICS OF HYDRATION OF MAGNESIUM OXIDE IN AQUEOUS SUSPENSION

PART 2 - THE EFFECT OF CONDITIONS OF FIRING BASIC MAGNESIUM CARBONATE ON THE SPECIFIC SURFACE AREA OF MAGNESIUM OXIDE

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Thermal decomposition of basic magnesium carbonate ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) yields porous pseudomorphoses of the original crystals. The specific surface area of the oxide decreases exponentially with increasing firing temperature. The maximum specific surface area of MgO fired at 500 °C amounts to $155 \text{ m}^2 \text{ g}^{-1}$, falling down to $20 \text{ m}^2 \text{ g}^{-1}$ when fired at 1200 °C. Extension of the time of firing affects negligibly the specific surface area. Of the admixtures accompanying magnesium oxide in dolomitic raw materials, the specific surface area of fired magnesia is mostly affected by ferric oxide. Under the same firing conditions, at a content of 2 wt.% of this component, the specific surface area decreases down to one tenth of that of non-doped magnesium oxide.

INTRODUCTION

Studies of hydration of calcium oxide show that the rate of conversion to hydroxide depends on the specific surface area of CaO and it may be assumed that the time course of hydration of MgO will likewise depend on its specific surface area.

The present stage of the study had the aim to examine how the conditions of firing and purity of the raw material affect the specific surface area of magnesium oxide for the purpose of preparing model samples for study of the kinetics of its hydration.

According to Pampouch, Librant and Piekarczyk [1] the shape and size of magnesium oxide crystals is affected by the way the initial raw materials have been heat treated. Coleman and Ford [2] showed that the largest surface area is exhibited by magnesium oxide prepared by firing magnesium oxalate at 400 to 600 °C. Each firing temperature has its own limit value of surface area, as pointed out by Razouk and Mikhail [3], below which it does not fall even after long-term heating and firing of the initial magnesium hydroxide or carbonate. Apart from temperature and time of firing, the specific surface area is significantly affected by the firing atmosphere. Razouk, Mikhail and Ragai [4] found that firing of precipitated magnesium hydroxide and magnesium carbonate in vacuo produces magnesium oxide with a surface area larger several times than that of the oxide fired in air atmosphere. As proved by Razouk and Mikhail [5], 650 °C is the minimum firing temperature for preparing magnesia from magnesite.

EXPERIMENTAL PART

The magnesium oxide was prepared from chemically pure magnesium carbonate (Lachema Brno) [6]. The material was chosen because the temperature of its decomposition is lower than the decomposition temperature of magnesite, because its firing yields MgO with a larger surface area, because among the available magnesium raw materials it shows adequate purity and may thus serve well for studying the effect of contaminating admixtures on the character of the fired oxide. The firing temperatures were in the range from 500 to 1200 °C. The bottom temperature is that at which the carbonate employed begins to decompose, as indicated by differential and gravimetric thermal analysis. The top temperature was chosen as the limit one for firing dolomitic lime while taking into account its trouble-free hydration.

Apart from the firing temperature and time, the specific surface area of MgO is also influenced by its degree of contamination. In natural materials, i.e. magnesite and dolomite, there occur as admixtures oxides of silicon, aluminium and iron. The sintering process proper can also be significantly affected by alkalis and fluorides. In order to assess the effect of these admixtures on the specific surface area values and thus on the course of sintering magnesium oxide, model mixtures were prepared in such a way that the content of the individual admixtures in the fired magnesium oxide amounted to 5 wt.%. The individual admixtures were added in the form of oxides; in the case of fluoride it was introduced

in the form of calcium fluoride, and alkalies were added as sodium carbonate. From the standpoint of their content in natural raw materials, the amounts added were obviously too high, but the purpose was to examine the extent of their effect on the sintering process. On the basis of the orientation measurements performed it was shown that among the naturally occurring contaminating substances, ferric oxide was technologically the most significant one, as it influenced strongly the specific surface area of the fired MgO. The effect of this admixture was therefore studied in more detail by adding such amounts of ferric oxide to the carbonate that after firing the magnesium oxide contained 1, 2, 4 and 6 wt.% of ferric oxide.

In both stages of the study, the samples were fired in a vertical furnace in stationary furnace atmosphere. The fired magnesium oxide samples were characterized by their specific surface area, determined by low-temperature adsorption of nitrogen after Nelsen and Eggertsen [7]. Scanning electron micrographs were taken of some selected samples.

RESULTS AND DISCUSSION

Tables 1 and 2 and figure 1 present a survey of the fired samples jointly with the respective specific surface area values. The accuracy of the specific surface measurement is 5 %.

Table 1. The effect of firing temperature and type of admixture on the specific surface area of MgO.

Time of firing is 60 minutes, content of admixtures is 5 wt. %.

temperature (°C)	specific surface area (m ² g ⁻¹)			
	Al ₂ O ₃	Fe ₂ O ₃	CaF ₂	Na ₂ O
650		93	120	75
900		22	8	8
1200	15	1.5	2	3

Table 2. Specific surface area of MgO samples doped with various amounts of ferric oxide vs. temperature and time of firing.

temperature (°C)	time (min.)	specific surface area (m ² g ⁻¹) content of ferric oxide (wt.%)				
		0	1	2	4	6
500	60	155				
650	15	129				
650	60	93				
900	5	56	35	36	41	43
900	60	33	28	25	22	21
1200	5	22	15	11	7	6
1200	60	20	6	2	1.5	1.1

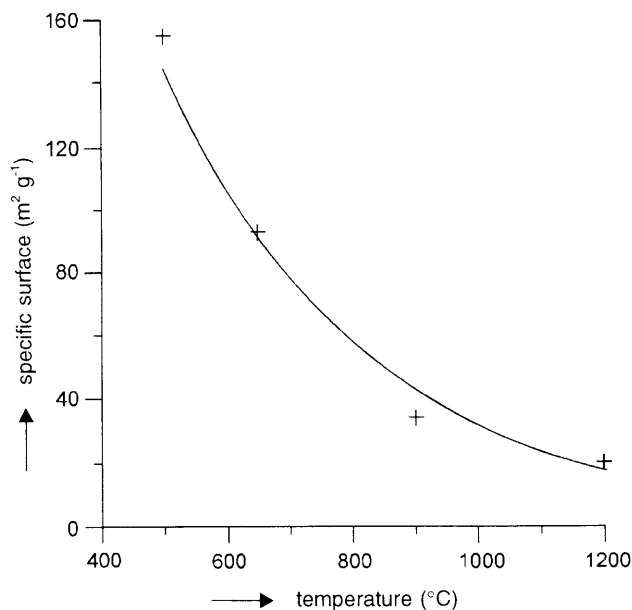


Figure 1. Specific surface area of MgO vs. temperature of firing. Time of firing is 60 minutes.

As far as the effect of firing temperature on the change in specific surface area of magnesium oxide is concerned, figure 1 shows that the surface area decreases with increasing temperature. The time of firing has no substantial effect on the specific surface area.

Tables 1 and 2, summarizing the effects of admixtures on the specific surface area value and thus on the sintering degree, indicate that aluminium oxide does not affect the sintering of magnesium oxide over the temperature range in question. With regard to the other three contaminating components it may be concluded that their influence starts only at 900 °C, and becomes distinct at a firing temperature of 1200 °C. On the basis of data contained in table 2, the following conclusions can be formulated with respect to the effects of ferric oxide: at 900 °C and after a short time of firing (5 minutes) the specific surface area somewhat decreases as compared to that of non-doped samples, but changes very little with increasing additions of Fe₂O₃. For longer periods of firing at 900 °C and at 1200 °C, the effect becomes more distinct, in particular in the case of firing at 1200 °C for 60 minutes, where in comparison with zero addition, the specific surface area has fallen down to one third as a result of a 1 wt.% ferric oxide content, and down to one twentieth of the original value in consequence of a 6 % ferric oxide content.

The morphological changes of the magnesium oxide crystals in terms of temperature, time of firing and type of contaminating admixture are illustrated by the electron micrographs. Crystals of the original magnesium carbo-

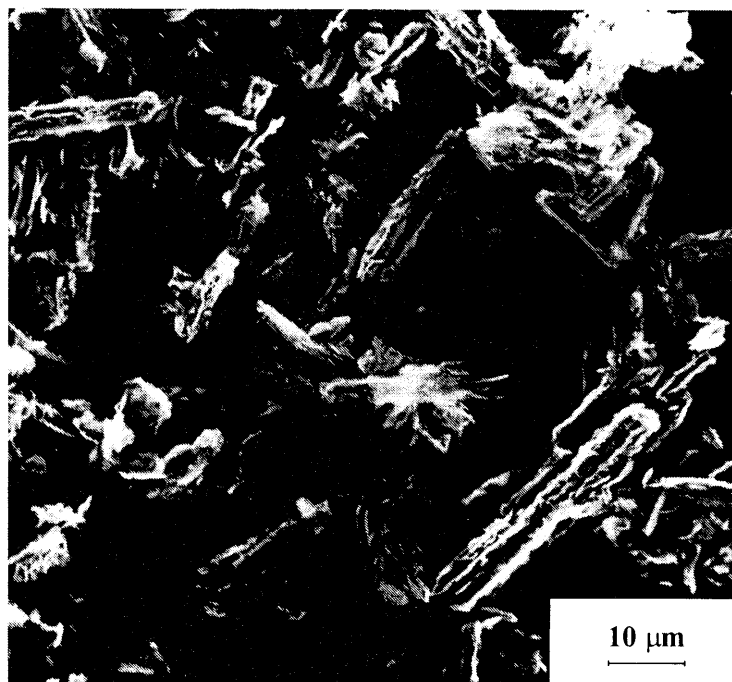


Figure 2. SEM: 4MgCO₃.Mg(OH)₂.4H₂O.

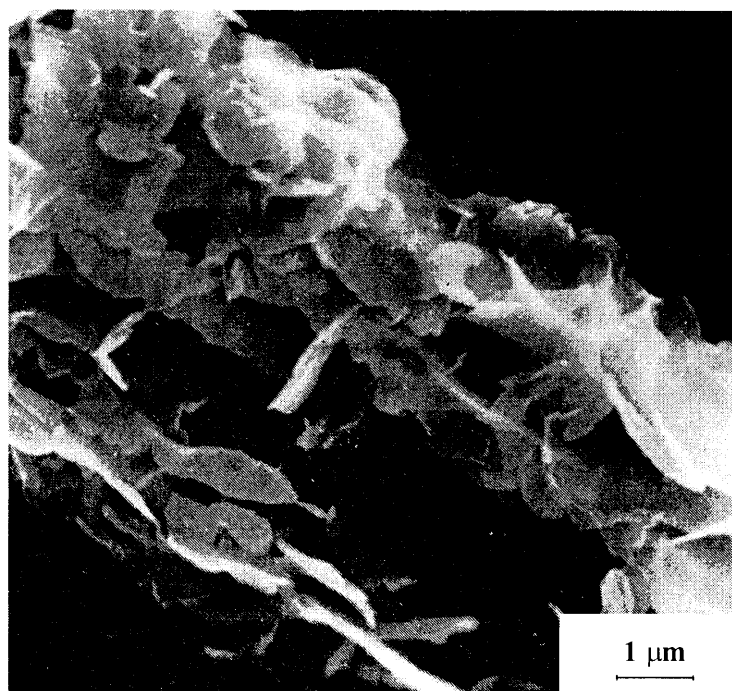


Figure 3. SEM: 4MgCO₃.Mg(OH)₂.4H₂O.

nate are leaf-like. The individual scales are arranged in tubular formations shown in figures 2 and 3. Firing turns the original crystals into pseudomorphoses (figures 4, 5, 6, 7 and 8) which are obviously MgO microcrystals

intergrown into a continuous porous lattice. This also corresponds to the specific surface area value which indicates that the MgO particles forming this lattice are 0.01 μm in size.

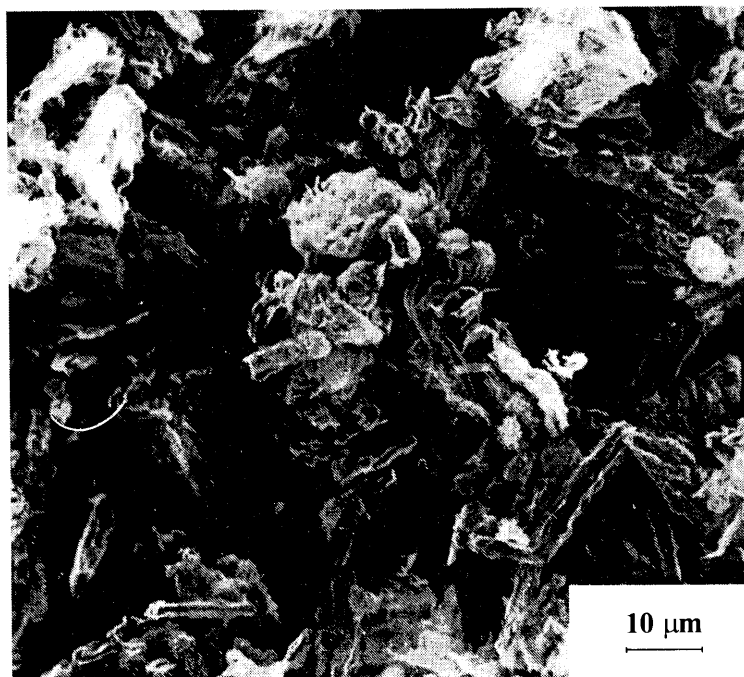


Figure 4. SEM: MgO fired at 900 °C for 60 minutes.

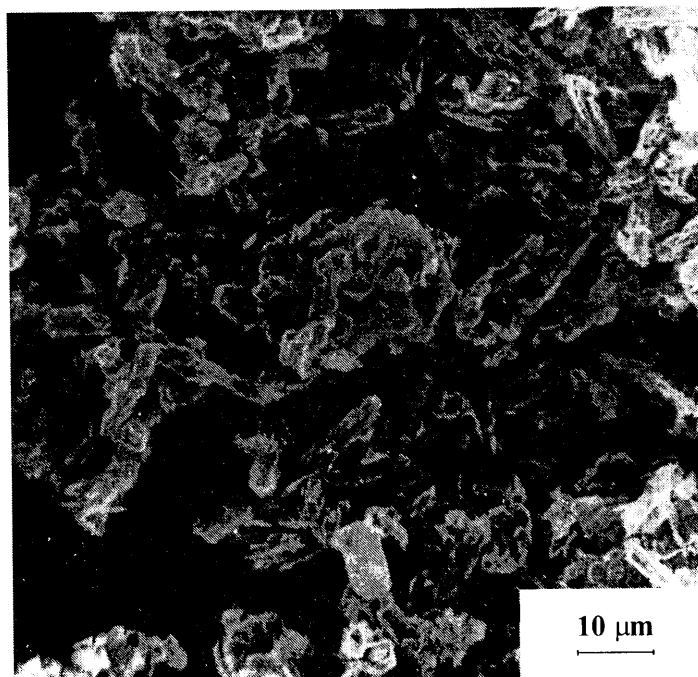


Figure 5. SEM: MgO doped with 5 wt.% Fe₂O₃, fired at 900 °C for 60 minutes.

The samples with admixtures of sodium carbonate and in particular those containing calcium fluoride lose the character of the original magnesium carbonate particles, as demonstrated by figures 6 and 9.

A larger magnification of the samples reveals disintegration of the scaly particles, porous pseudomorphoses, and their transformation into corpuscular crystals of magnesium oxide 0.2 to 0.4 μm in size.

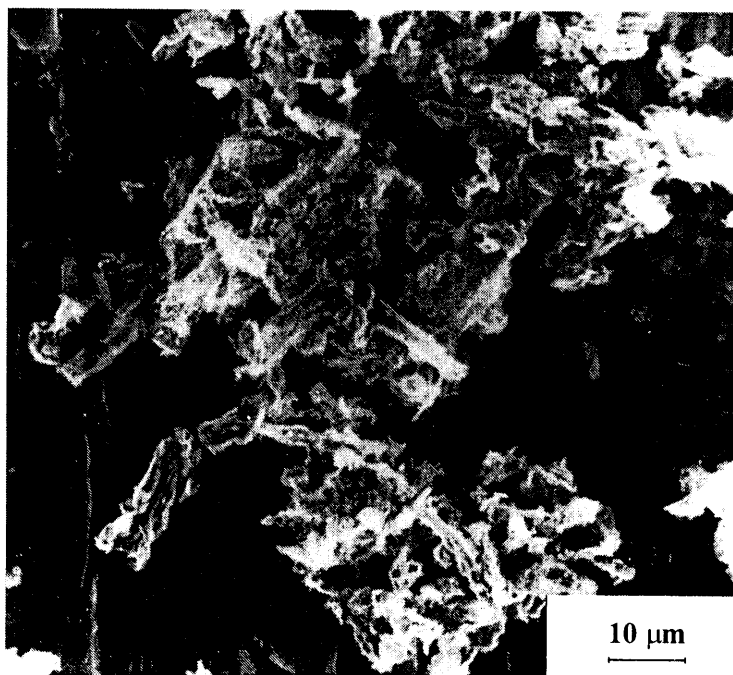


Figure 6. SEM: MgO doped with 5 wt.% Na₂CO₃, fired at 900 °C for 60 minutes.

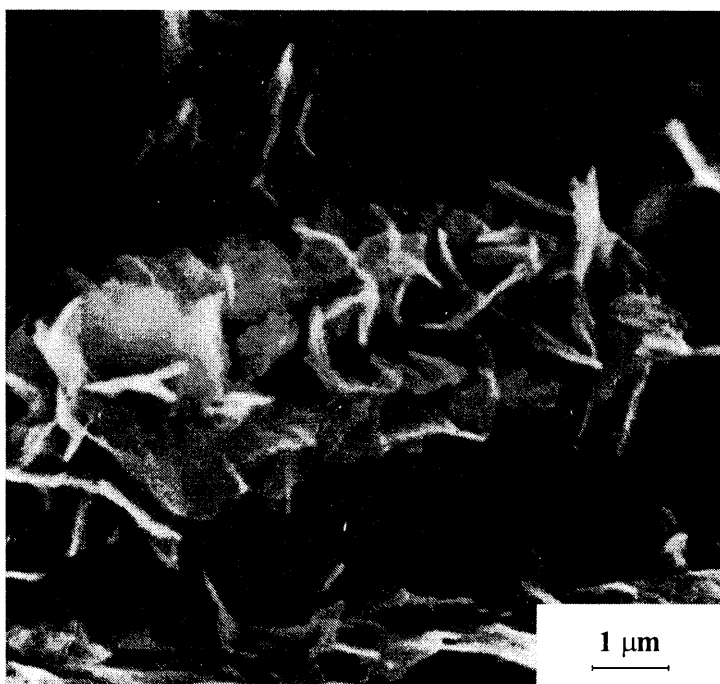


Figure 7. SEM: MgO fired at 650 °C for 60 minutes.

Calculation based on the assumption of spherical formations with a mean particle size of 0.3 μm yielded a specific surface area of 5.6 m² g⁻¹. This value is in good agreement with the value of 8 m² g⁻¹ deter-

mined by the method of low-temperature nitrogen adsorption.

In order to assess the question whether samples doped with calcium fluoride and sodium carbonate sinter

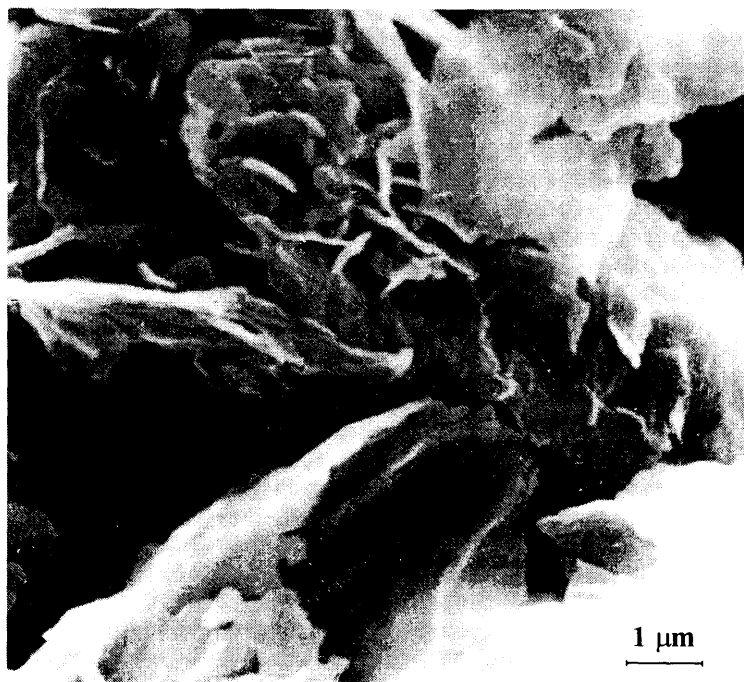


Figure 8. SEM: MgO doped with 5 wt.% Na_2CO_3 , fired at 650 °C for 60 minutes.

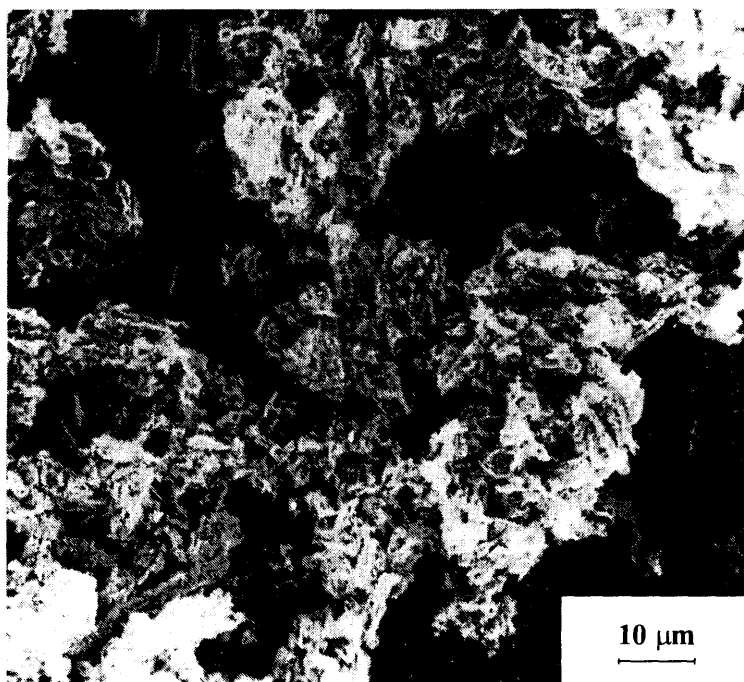


Figure 9. SEM: MgO doped with 5 wt.% CaF_2 , fired at 650 °C for 60 minutes.

in the same way even at lower firing temperatures, firing was carried out at 650 °C for 60 minutes. Virtually no

sintering takes place under these conditions, as shown by figures 8 and 9 and by the values of specific surface

area, namely 120 and 75 m² g⁻¹ respectively, in contrast to 93 m² g⁻¹ of the sample free of admixtures. The course of recrystallization and sintering of magnesium oxide, illustrated by the scanning electron micrographs, is in a satisfactory agreement with the specific surface areas established.

References

1. Pampuch, Librant, Piekarczyk: *Physics of Sintering* 5, 263 (1973).
2. Coleman D.S., Ford W.F.: *Trans.Brit.Ceram.Soc.* 63, 365 (1964).
3. Rayouk R.I., Hikhal R.Sh.: *J.Phys.Chem* 61, 886 (1956).
4. Razouk R.I., Mikhail R.Sh., Ragai J.: *J.Applied Chem. and Biotechnology* 23, 51 (1973).
5. Razouk R.I., Mikhail R.Sh.: *J.Phys.Chem.* 63, 1050 (1959).
6. Bláha J.: *Ceramics-Silikáty* 39, 45 (1995).

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KINETIKA HYDRATACE OXIDU HOŘEČNATÉHO VE VODNÍ SUSPENZI

ČÁST 2 - VLIV PODMÍNEK VÝPALU ZÁSADITÉHO KARBONÁTU
HOŘEČNATÉHO NA MĚRNÝ POVRCH OXIDU HOŘEČNATÉHO

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Při výpalu oxidu hořečnatého ze zásaditého karbonátu hořečnatého tvoří oxid hořečnatý pórovité pseudomorfózy po struktuře výchozího karbonátu. Tato skutečnost je potvrzena serií snímků ze scanovacího elektronového mikroskopu.

Kriteriem stupně slinutí vypáleného oxidu hořečnatého je jeho měrný povrch stanovený metodou nízkoteplotní adsorpce dusíku. Jeho hodnota exponenciálně klesá s teplotou výpalu a to z maximálních 155 m².g⁻¹ pro teplotu 500 °C na 20 m².g⁻¹ pro MgO pálený při 1200 °C.

Na stupeň slinutí mají vliv i některé příměsi. Z těch, které doprovázejí oxid hořečnatý v dolomitických surovinách, měrný povrch nejvíce ovlivňuje oxid železitý. Měřením bylo prokázáno, že při stejných podmínkách výpalu MgO poklesne jeho měrný povrch již při 2 hmot.% obsahu této minoritní složky na desetinu hodnoty nedopovaného oxidu hořečnatého.