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THE INFLUENCE OF WATER VAPOUR ON DECOMPOSITION OF MAGNESITE AND BRUCITE

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ABSTRACT

The thermal decomposition of magnesite and brucite is influenced by furnace atmosphere. Variations in the apparent activation energy, in the half-decomposition temperature and in the specific surface of calcinates depend on water vapour content and on the content of other gases present in the furnace atmosphere.

INTRODUCTION

The thermal decomposition of magnesium carbonate and magnesium hydroxide has been described from different views by a number of authors [1-6]. The calcination to oxide is one of the significant stages for the megnesia clinker production. The calcination conditions have a strong effect on bulk density of a final product.

EXPERIMENTAL

Materials: Magnesium carbonate - flotation concentrate of natural magnesite / 44.25 % MgO, 2.66 % Fe₂O₃ and 51.04 % CO₂/; Magnesium hydroxide, brucite - was prepared from pure laboratory chemicals.

Thermal decomposition was studied by the Netzsch 404 thermobalance in the flow atmospheres of air /reference atmosphere/, carbon dioxide and water vapour, as well as in the mixed atmospheres of $CO_2 + H_2O$ / for magnesite/ and air + H_2O / for brucite/, respectively. The flow of furnace atmosphere was 0.64 cm.s⁻¹ through the free furnace cross-section / after calculating to 0°C and 101 kPa/. The weight samples of 200 mg magnesite or of 250 mg of brucite were applied. The heating rate was 2 °C.min⁻¹.

From TG curves the temperature $/T_m/$ for the attained degree of conversion 0,5 was evaluated. Moreover, from the same curves the preexponential terms of the Arrhenius equation and the apparent activation energy of the process / the formal kinetic parameters A and E/ were calculated. To describe kinetics, the Jerofeev - Avrami equation that was previously utilized by Criado and Morales [7,8] for the non-isothermal process, was chosen.

A set of the results was completed by determining the speci-Proceedings of ICTA 85, Bratislava fic surface of calcinates after isothermal firing up to 900°C for 45 min.

The reproducibility of those results varied between \pm 1 K for T_m, ca 17 % for E and 12 % for the specific surface values, respectively.

RESULTS AND DISCUSSION

The decomposition of magnesite and brucite is considerably influenced by the change in composition of the furnace atmosphere /Table 1/. A raise of partial pressure of a furnace gas component of the same quality as guargeous reaction product is responsible for the equilibrium shift to higher values of decomposition temperature expressed as T_m . Thermal decomposition is influenced also by the additional component of the furnace atmosphere. Due to water vapour effect the decomposition temperature of magnesite will decrease by 73 K when compared to air medium. The decomposition temperature of brucite will increase by 55 K, 1f the furnace air medium is alternated by CO_2 atmosphere.

These changes are expressed by formal E and in A values shown in Table 1. Resulting activation energy values of decomposition reactions taking place in the air atmosphere are in acceptable agreement with data presented in the literature for Mg/OH/ $_2$ / 105 - 131 kJ.mole⁻¹/ and for magnesite / 127 - 149 kJ.mole⁻¹/ $_2$ [9 - 11].

Fig.l illustrates the influence of the change in composition of atmospheres on E by dependence of $y^{\#} = f_{/00}/$ upon reduced temperature / $T/T_m/^{-1}$.

The dependence of E on $p_{\rm H2O}$ observable under the decomposition of brucite assumes a logarithic character. The effect of the mixed $\rm SO_2+H_2O$ atmosphere upon decomposition of magnesite has not been found additive. The activation energy was found higher than in pure water vapour, or in $\rm SO_2$ atmosphere.

Each the different rate and temperature interval of decomposition were leading to the change in crystallinity and aggregation of solid product being characterized in this paper by specific surface / the method of adsorption from solution/ /Table 2 /. Based on comparisons of the results one may deduce that the thermal decomposition of carbonate and hydroxide, proceeding in the atmosphere being qualitatively equal to the gaseous decomposition product, yields calcinates of lower specific surface than it does

TABLE 1

Magnesite				Brucite			
Firing atmosphere	™ _m ∕ĸ	EX	lņ A	Firing atmosphere	T _m /K	EX	ln A
air water vapour + 25 % CO ₂ + 50 % CO ₂ + 75 % CO ₂ 100 % CO ₂	857.5 779 851 871 893 935.5	152 236 461 474 505 450	12.3 14.2 17.7 17.9 18.2 17.6	air + 5 % H ₂ O + 20 % H ₂ O + 40 % H ₁ O water vapour CO ₂	668 673 685 698 713 723	107 185 148 205 209 221	13.3 21.7 24.9 29.7 29.7 32.2

XRemark: E in kJ mole⁻¹; for equation parameter m = 0.5 [8]and for conversion of 0.10 up to 0.75.

TABLE 2 Specific surface of calcinates after firing up to 900 $^{\rm O}{\rm C}$

Firing atmosphere	specific surface of a magnesite	brucite
air water vapour carbon dioxide	9 4	46 10 41

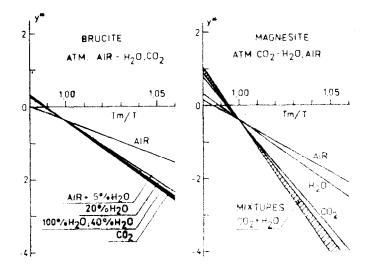


FIG.) Dependence of $f_{/3Q'}$ (= y^{*}) on related tempers are / $1/T_{\rm m}^{-11}$

in the neutral medium / air / or in the "third" furnace atmosphere. The influence of the atmosphere composition on specific surface is in accordance with studies dealing with decomposition mechanism and morphology of calcination products [12 - 14].

CONCLUSIONS

Changes in composition of the furnace atmosphere cause changes in the rate and in the temperature of decomposition reactions; with decomposition of magnesite taking place in the mixed CO_2+H_2O atmospheres. the activation energy was found higher than in pure water vapour, or in CO_2 .

The change in composition of the furnace atmosphere affects the magnitude of specific surface of calcinates. By firing in the medium corresponding to the gaseous decomposition product, the calcinate of lower surface than that in the medium of other gases was obtained.

REFERENCES

1 Bron V.A., Desperova M.J., Sudakova L.P., Neorg.Mat. <u>10</u>, 1870 / 1967 / 2 Guillat J.F., Brett N.H., Trans. Brit. Cer. Soc. <u>69</u>, 1 /1970/ 3 Pampuch R., Librant Z., Piekarzyk J., Ceramurgia Int. <u>1</u>, 14 / 1975 / 4 Cimino A., Porta P., Valigi M., J.Am. Cer. Soc. <u>49</u>, 152,/1966/ 5 Mansour N.A.L., Ceramurgia Int. <u>4</u>, 24 /1978/ 6 Koishi M., Meguro K., Bull.Chem.Soc. of Japan <u>37</u>,1570/1964/ 7 Hancock J.D., Sharp J.H., J.Am. Cer. Soc. <u>55</u>, 74/ 1972 / 8 Criado J.M., Morales J., Thermochimica Acta <u>41</u>, 125 / 1980 / 9 Kissinger H.E., J. Research Nat.Bur.Stand. <u>57</u>, 217 / 1956 / 10 Kissinger H.E., Anal. Chem., <u>29</u>, 1702 / 1957/ 11 Blečič D., Živkovič Z.D., Thermochica Acta <u>60</u>, 69 / 1983/ 12 Phillips V.A., Opperhauser H., J. Am. Cer. Soc. <u>61</u>, 75 / 1978/ 13 White J., Refr. Res. J. Austr. Cer. Soc. <u>9</u>, 60 / <u>1973</u>/ 14 Cremer E., Bachmann L., Z. f. Elektrochemie <u>59</u>, 407 / 1955 /