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CHANGE IN STRUCTURE AND ENTHALPY OF MAGNESITE ACCOMPANYING GRINDING IN AERIAL AND AQUEOUS ENVIRONMENT

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ABSTRACT

The influence of aqueous medium on the change in enthalpy and structure of magnesite has been investigated. The determination of the increase in enthalpy by the method of dissolution heats as well as the study of structural transformations by the X-ray diffraction and EPR-method has shown that the energetic excitation of the structure in the process of its destruction proceeds with equal intensity in the course of grinding in aqueous and aerial media. The dispergation effect of grinding is, however, superimposed in aerial medium by aggregation owing to which a part of now arising surface becomes inaccessible to the determination by the adsorption method.

INTRODUCTION

The mechanical stress of brittle substances in the course of grinding brings about dispergation and accumulation of defects in the volume of disperse particles. The change in energetic state of the structure in the process of its destruction is manifested by activation of heterogeneous chemical reactions. It is known from literature /1 - 3/ that an addition of surface - active substances as well as grinding in water environment increases the efficiency of dispergation. The mechaniam of the effect of active grinding medium and its influence on the change in enthalpy of the ground substances have not yet been unambiguously explained. The aim of this study has been to contribute to elucidation of the mentioned problems by investigating the relationship between the change in structure of magnesite and enthalpy accompanying the grinding in aerial and active aqueous environment.

EXPERIMENTAL

The process of vibratory grinding of natural magnesite (locality Miková, 42,33 % MgO, 3,20 % CaO, 2,88 % FeO, 0,99 % SiO_2)

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was investigated. The weighed amounts of 100 g (granularity 1 - 3 mm) were ground in a laboratory vibration ball mill with an amplitude 6,1 mm and 18,5 s^{-1} revolutions. The grinding tests were carried out in aerial as well as aqueous medium. The grinding times increased in geometric series from 0,125 to 8 hours.

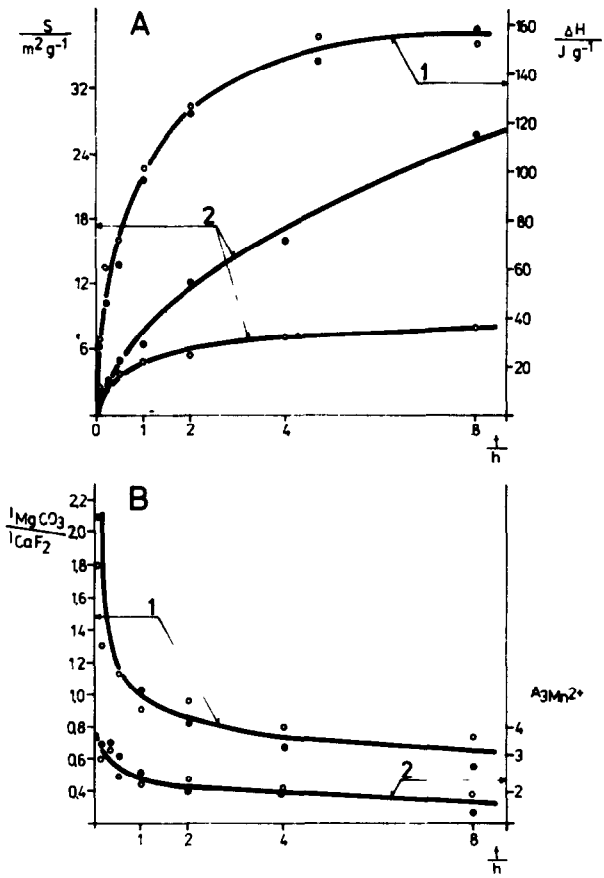

Fig. 1 A Increase in enthalpy Δ H (1) and specific surface area S (2) as a function of grinding time t

Fig. 1 B Ratio of relative intensities of diffraction lines I_{MgCO_3}/I_{CaF_2} (1) and amplitude of the resonance line $A_{3Mn^{2+}}$ (2) as a function of grinding time t

Full points - grinding in water; empty points - grinding in air

The process of dispergation was investigated by the BET method. The specific surface area was determined from the adsorption isotherms of benzene vapour.

The formation of new surface area is accompanied by changes in the crystal space arrangement. The decrease in the structure arrangement results in a decrease in relative intensity of the diffraction lines. The method of additional reference component /1/ for quantitative identification of this effect was chosen. The change in ratio of the relative intensities of the diffraction lines of magnesite (d = 27,42 nm) to this of fluorite (d = = 31,53 nm) due to prolongation of grinding time was determined by using an X-ray apparatur Dron 2,0. The isomorphic admixture of the Mn^{2+} ions gives rise to colour centres in non-ground samples of magnesite. The structure deffects act as source of resonance of the Mn^{2+} ions in their vicinity. The accumulation of structure deffects brings about a decrease in amplitude of the resonance signal of the Mn^{2+} ions with prolongation of the grinding time. The change in amplitude of the Mn^{2+} line was measured by a spectrometer ERS - XQ. A sample of synthetic periclase was used as standard for the measurements of the $3Mn^{2+}$ spectral line amplitude.

The decrease in the structure arrangement degree of magnesite in the course of grinding brings about an increase in enthalpy of the ground samples. The increase in enthalpy was determined from the difference of the heats released by dissolution of activated and inactive samples in 5 M HCl. An adiabatic microcalorimeter made in the Mining Institute of SAS served for indication of heat changes during dissolution.

DISCUSSION AND CONCLUSIONS

In literature, the effect of the active grinding medium is explained on the basis of two contradictory ideas. According to Rebinder /2/, the molecules of active medium migrate into arising internal surface of subcritical cracks and thus reduce the work of cracking. This mechanism causes a decrease in strength of the disintegrated material and enables an elastic-brittle disintegration even under conditions of cyclic loading during long-termed grinding. Provided this assumptions is valid, higher values of specific surface area may be expected in case of grinding in acti-

ve medium but lower degree of structure destruction and lower increase in enthalpy occur than in case of grinding in air.

According to the ideas of the second group of authors /3/, the active medium acts as a lubricant which prevents aggregation of fine grained particles and sticking of ground material to the mill shell and grinding bodies. This assumption holds under the condition of experimental identification of the intensification effect of the active aqueous environment on all particular processes causing energetic excitation of the structure.

The experimental study of vibratory grinding of magnesite has shown that the energetic excitation of the structure in the process of its destruction proceeds with equal intensity during grinding in water and air. The experiments enable tu assume that the dispergation effect of grinding is superimposed by aggregation during grinding in air owing to which a part of arising surface becomes inaccessible to the determination by adsorption method. This assumption was verified by an experiment in which magnesite was subjected to short-termed grinding in water after 8 hours' grinding in air. The specific surface area increased from the original value of 7,5 m^2g^{-1} to 26,3 m^2g^{-1} after 10 minutes' grinding in water. The relative intensity of the X-ray line and the value of the increase in enthalpy was not changed by the disaggregation procedure.

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