

MECHANO-CHEMICAL ACTIVATION OF DOLOMITE

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Abstract

Mechano-chemical activation is a widely used method for increasing the reaction activity of solids and, consequently, to accelerate solid phase reactions and to reduce the temperature of the subsequent thermal decomposition. Thermal decomposition of triboactivated calcium carbonate is a subject of different studies while dolomite decomposition has limited data.

The present work represents a study of thermal stability and phase transitions of mechano-chemical activated dolomite under different conditions, namely using various amounts and kind of milling balls and the duration of activation. Temperatures of decomposition of MgCO₃ and CaCO₃ are specified. The study includes the determination of the thermal stability and the rate of thermal decomposition of activated dolomite.

Keywords: dolomite, mechano-chemical activation, thermal decomposition

Introduction

One of the processing methods of dolomite is its baking under appropriate conditions to produce carbonate or carbonate-oxide products with various practical applications. The general principle is its de-carbonization to be completed at the lowest possible temperature [1–4, 6–7], as baking at higher temperatures, though accelerating the process, is not desired due to active MgO being transformed into periclase.

It is known that mechano-chemical activation of materials creates defects on the solid surface, which, from a physico-chemical point of view, is the reason for lower thermal stability and increased reaction activity [3–5].

The aim of this paper is to investigate the possibility of intensification of the process of thermal decomposition of dolomite by specifying the conditions appropriate for its preliminary mechano-chemical activation and doping.

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Experimental techniques

This research was carried out with dolomite of composition Ca – 24.07%; Mg – 12.69%; Cr – 0.002%, Na – 0.02%; K – 0.02%. The mechano-chemical activation of dolomite samples (mass 25 g) processed in a planetary mill Pulverisette-5 (Fritsch, Germany) using iron and carbide milling balls for various periods of time. Two series of experiments were performed. In the first one, the effect of the number of milling balls (ranging from 5 to 20) of 20 mm diameter and that of the duration of activation (from 10 to 30 h) without addition of water were studied. In the other, the thermal decomposition of dolomite after its mechanical activation in presence of 12.5 ml distilled water was studied during 15, 30, 45 and 60 min using 50 carbide milling balls.

The thermal analysis was carried out in air at the temperature range 293–1273 K using a MOM derivatograph (Hungary) at a rate of heating of 5 K min^{-1} . The sample mass was 200 mg and the sensitivity of TG curve 100 mg. The X-ray diffraction measurements were performed by a DRON equipment with CuK_α radiation.

Results and discussion

The thermal analysis data of the studied dolomite sample (Fig. 1) show that the decomposition of dolomite proceeds in two distinct steps, the first at 863–1083 K with 12.5% mass loss and the second at 1083–1173 K with 29.5% of mass loss. This behavior of the thermal curves is determined by the decomposition of the binary salt to its carbonate components, MgCO_3 and CaCO_3 , which then dissociates individually. The decomposition of MgCO_3 starts firstly, and then that of CaCO_3 in a higher temperature range. The total mass loss is 42.0% and the shape of the TG curves indicates

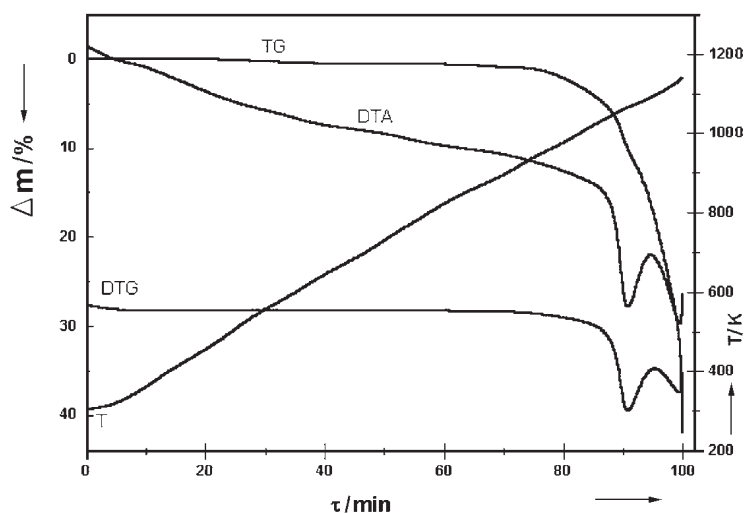


Fig. 1 DTA curve of the starting dolomite sample

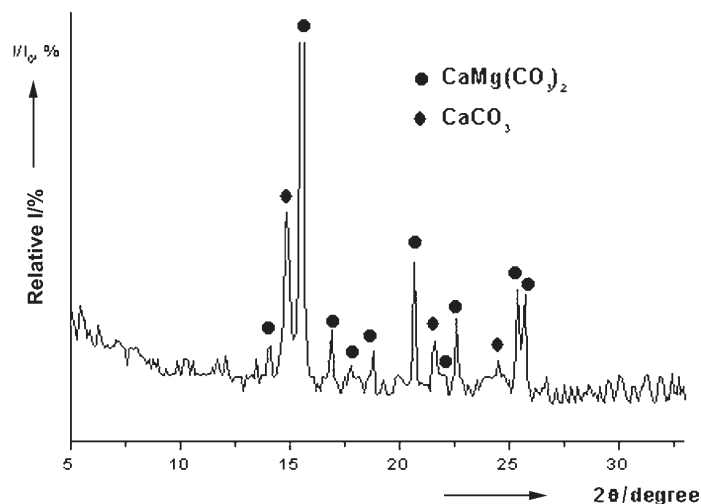


Fig. 2 X-ray diffraction pattern of dolomite sample

that the process is not completed and the decomposition of CaCO_3 starts before that of MgCO_3 has been finished. The X-ray diffraction pattern of the starting dolomite sample (Fig. 2) shows the presence free CaCO_3 associated with dolomite.

The thermal analysis data of dolomite after its mechano-chemical activation (processed in a mill during 10, 20 and 30 h using different amounts of milling balls 5, 10, 15 and 20 balls) are shown in Fig. 3.

Firstly, intensification during the first stage of the process concerned with thermal decomposition of MgCO_3 is observed. In this case appreciable lowering of DTA peak shift of a temperature of decomposition of MgCO_3 by about 200 K with respect to that for the non-activated dolomite is observed independently of the conditions of activation. The mass loss in this range increases indicating the complete dissociation of MgCO_3 and one can separate the two stages of the dolomite decomposition. In the second stage which is related with the decomposition of CaCO_3 the temperature range also drops down by more than 120 K, but the loss of mass decreases by about 5%. The total mass loss also decreases by about 4.5% with increasing the number of milling balls and the duration of activation. The X-ray diffraction patterns of the products of activation of dolomite (Fig. 4) show the characteristic lines of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, clearly indicating that the mechano-chemical activation leads to the formation of regions of local pressures and temperatures that initiate the decomposition of the binary salt into its carbonate components. The formed virgin reaction surface easily absorbs air moisture forming $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$.

By comparing the effects of the amount of milling balls and the duration of activation on the dissociation of dolomite, it is concluded that it is not favoured increasing these parameters, i.e. the temperature of decomposition shift by about 50 K up-

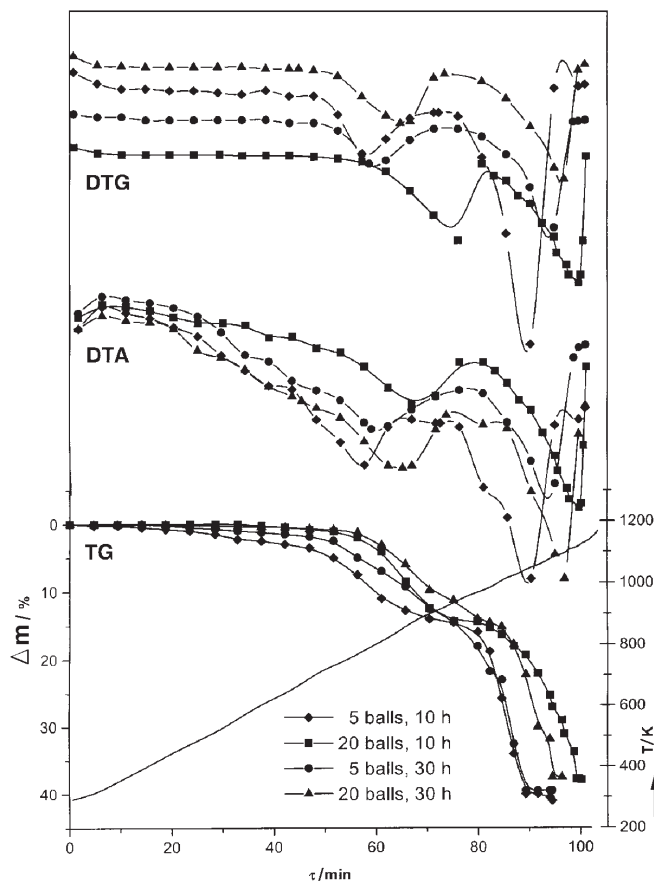


Fig. 3 DTA curves of dolomite samples activated in a planetary mill under different conditions

wards, and both the total mass loss and the rate of decomposition of CaCO_3 decreases. This fact can be explained that upon long-time mechanical-chemical treatment, agglomeration of particles occurs (Fig. 4) leading to the difficulty of diffusion at later stages of treatment. Our results, as well as such of others [2], show that the reaction capacity of the activated dolomite maximizes and then decreases with increasing either the duration of activation or the amount of milling balls. Thus, on the basis of the results obtained it is concluded that the suitable conditions of preliminary mechanical-chemical activation of dolomite are 10 h of milling using 5 milling balls.

The second series of experiments studies the intensification of the decomposition of dolomite by its mechano-chemical activation treatment in the presence of distilled water. This treatment was expected to accelerate the decomposition of the binary salt to carbonates and to accelerate the hydration and possibly hydroxide formation, consequently to change the kinetics of the process and to reduce the corresponding temperature of their decomposition. Due to the relatively short time of activation

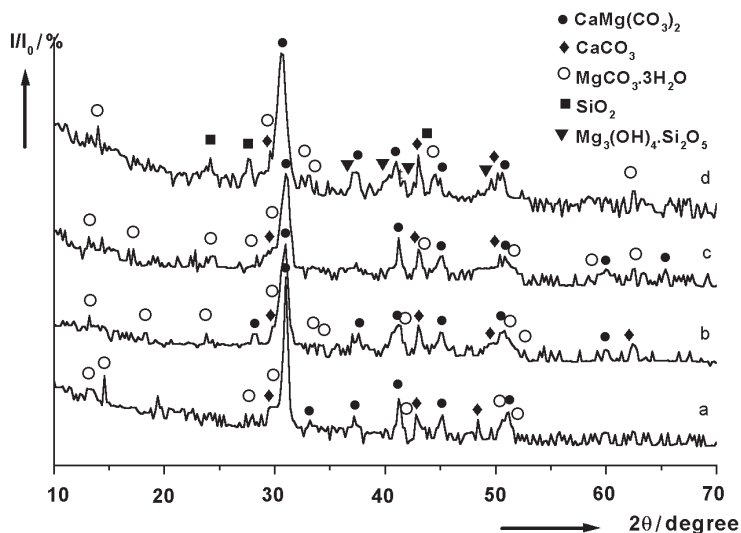


Fig. 4 X-ray diffraction patterns of dolomite mixed with distilled water and treated in a planetary mill with a – 5 milling balls for 10 h; b – 5 milling balls for 30 h; c – 20 milling balls for 10 h; d – 20 milling balls for 30 h

of these experiments, the amount of milling balls was increased up to 50 balls. The experimental X-ray diffraction and thermal analysis data are shown in Figs 5 and 6 and confirm the suggestions already proposed.

The X-ray diffraction patterns of dolomite mixed with distilled water and activated in a planetary mill show the presence of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, in spite of its processing for time intervals between 15 and 60 min. The DTA data (Fig. 5) show four stages of the decomposition of dolomite in the following temperature ranges: 673–873, 873–1033, 1033–1088 and 1088–1173 K. These stages correspond to the dehydration $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, formed as a free phase during the preliminary sample tribo-chemical activation. The second represents the decomposition of this free MgCO_3 . The third and the fourth stages represent the decomposition of MgCO_3 and CaCO_3 in the dolomite structure. In contrast to the first series of experiments here the dolomite decomposition was found to be shifted to higher temperatures (Fig. 5) due most probably to the shorter treatment time in the planetary mill. The dissociation of MgCO_3 is also shifted to higher temperatures resulting most probably from the overlapping of the stages of decomposition of free MgCO_3 and that combined with CaCO_3 in dolomite structure. The results obtained (Fig. 5) show that high decomposition rate of dolomite is attained at lower temperature range by its activation during 30 min using 50 balls.

These results are similar to that obtained from preliminary mechano-chemical activation processing of dolomite during 10 h using 5 balls.

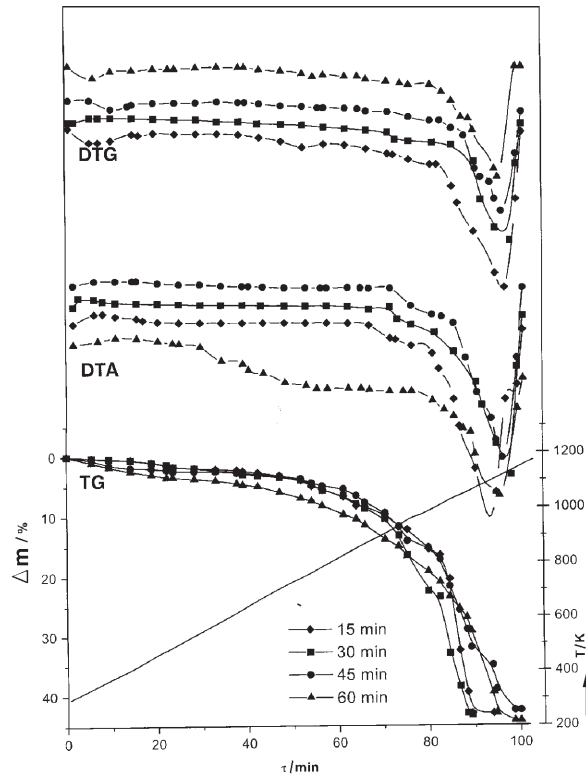


Fig. 5 DTA curves of dolomite samples activated from 15 to 60 min in a planetary mill with 50 carbide milling balls of 10 mm size

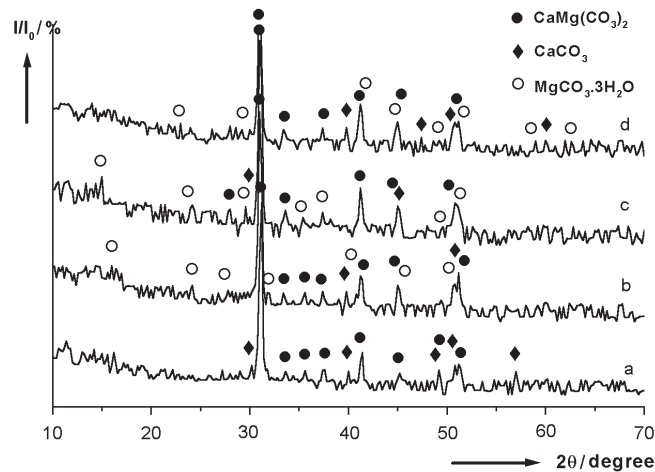


Fig. 6 X-ray diffraction patterns of dolomite mixed with distilled water and treated in a planetary mill for: a – 15 min; b – 30 min; c – 45 min; d – 60 min

Conclusions

The study proves the possibility of intensification of decomposition of dolomite by its preliminary mechano-chemical activation and doping. The most appropriate conditions of activation are its processing in a mill during 10 h and using 5 balls. This leads to the decrease of the decomposition temperature by approximately 200 K and to separation of the stages of decomposition of MgCO_3 and CaCO_3 . Thus, the baking of dolomite can be performed under more appropriate economic conditions of production of the desired end products such as dolomite lime, dolomite concrete, etc.

The results obtained may be applied to the processing of the dolomite used in the Bulgarian metallurgical plants for the production of lime.

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