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The decrepitation of dolomite and limestone

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Abstract

The degrees of decrepitation of a limestone and of a dolomite were determined by an industrially accepted procedure called the Pilkington test, and by a TG method. A good correlation in decrepitation trend with change in particle size between the two methods was apparent for the dolomite, and the maximum degree of decrepitation was found to be in the 180–250 μm (60–80 mesh) fraction by both methods. The correlation was less evident for the limestone, and the change in degree of decrepitation with particle size was different for the two tests. The TG method gave much larger values for the degree of decrepitation relative to the Pilkington test, and so can be considered a more sensitive test.

INTRODUCTION

Dolomite and limestone are minerals that are widely used in the glass-manufacturing industry. Limestones are sedimentary rocks primarily consisting of calcium carbonate, although substitution of calcium by magnesium may occur. A limestone containing between 5% and 35% magnesium is termed a magnesian limestone, whereas if the level is below 5% it is classed as a high-calcium limestone. The dolomite family includes dolomite, $CaMg(CO_3)_2$, kutnahorite, $CaMn(CO_3)_2$, and ankerite, $CaFe(CO_3)_2$.

During glass production, the minerals are heated to temperatures well above their decomposition temperatures, and are incorporated into the glass as the oxide. The decomposition reactions of both minerals have been extensively studied by thermal methods of analysis. High-calcium limestones decompose at temperatures in the vicinity of 800°C in one stage with the formation of calcium oxide and carbon dioxide. The temperature of decomposition is dependent on the partial pressure of carbon dioxide. The dissociation proceeds gradually from the outside surface inwards, with the reaction taking place at an interface between calcite and the residual oxide which may be in a metastable form [1–3].

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Dolomite decomposes in a single stage if the partial pressure of CO_2 is low (variously reported to be between 3 and 260 Torr [4–6])

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2$$

If the carbon dioxide pressure is higher than the above limits, the decomposition occurs as a two-step process, usually written as

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2$$

$$CaCO_3 \rightarrow CaO + CO_2$$

The temperature of both steps is affected by the partial pressure of carbon dioxide, although the temperature of the first step initially decreases as the CO_2 pressure increases from 0 to 20%, and then increases again [7]. However, even in an atmosphere of 100% CO_2, it does not reach the value observed in nitrogen. The second step follows the more expected behaviour of an increase in temperature with increase in CO_2 pressure. It is suggested that a more correct representation of the decomposition is

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgCO_3$$

The magnesium carbonate is metastable at this temperature and decomposes immediately, with the rate of decomposition being dependent on the CO_2 pressure. The $CaCO_3$ phase decomposes at a higher temperature.

An additional feature that sometimes appears on the TG curve for the decomposition of dolomite is several irregular weight losses that occur in the vicinity of 400°C and have been attributed to decrepitation. McCauley and Johnson [8] have used TG to assess quantitively the decrepitation of dolomite and have found that there is a relationship between particle size and the extent of decrepitation. The particles in the 150–250 μm (60–100 mesh) range showed the maximum (about 80%) decrepitation, with decreasing tendency on either side of this range. Below 106 μm (140 mesh) and above 1180 μm (16 mesh), no decrepitation was observed. The cause of the decrepitation was suggested to be the result of water trapped in the dolomite structure, which at the temperature of decrepitation would produce a water vapour pressure that was similar to the pressure required to break bars of the dolomite. No direct evidence of the role of water vapour was obtained.

This work reports an investigation into the use of TG as a means of assessing the degee of decrepitation of dolomite and limestone and correlates the results with the standard test. The effect of particle size is also examined.

EXPERIMENTAL

Limestone and dolomite samples were characterised by chemical analysis (see Table 1) and by X-ray diffraction. The samples were split into several

TABLE 1

Chemical analyses (%) of limestone and dolomite

	Limestone	Dolomite
CaO	55.13	30.17
MgO	0.45	21.80
Free carbon	0.38	0.05
Insoluble + SiO_2	0.62	0.13
SiO_2	0.30	0.09
Fe_2O_3	0.046	0.049
Al_2O_3	0.32	0.07
Na_2O	0.02	0.04
K_2O	0.02	0.01
SO_3	0.07	0.02
Loss on ignition	43.71	47.70
Moisture	0.02	0.03

different particle size ranges by sieving. The sieve sizes quoted on the graphs are the average value for the cut. Thus if the fraction is 106–150 μm (100–140 mesh) then the point plotted is 120 mesh.

TG experiments were carried out on a Du Pont 1090 thermal analyser. Approximately 40 mg samples were weighed accurately into an open-ended cylindrical platinum pan, and heated at 10°C in air to 900°C. Both TG and DTG signals were recorded.

RESULTS

The Pilkington test

The Pilkington test is an empirical method adopted by the glass industry as a measure of the degree of decrepitation in limestone and dolomite. The procedure is to dry a sample at 100°C to constant weight and then place 9 g into a metal trough. A tray and lid are placed in a muffle furnace heated to 1040°C and left for 10 min to reach a steady temperature. The trough containing the sample is placed on the tray in the furnace and immediately covered with the lid. Carbonate which can decrepitate out of the trough is trapped in the closed system by the lid so that it falls on the tray. After 10 min, the apparatus is removed and allowed to cool. The weight of the material on the tray and remaining in the trough is measured, and the percentage weight remaining on the tray is taken as the index of decrepitation. In general, decrepitation indices of <5 are highly desirable, whereas values >20 are not normally recommended for use.

Results obtained from the test for the limestone and dolomite fractions studied in this work are presented in Fig. 1. It is evident that both

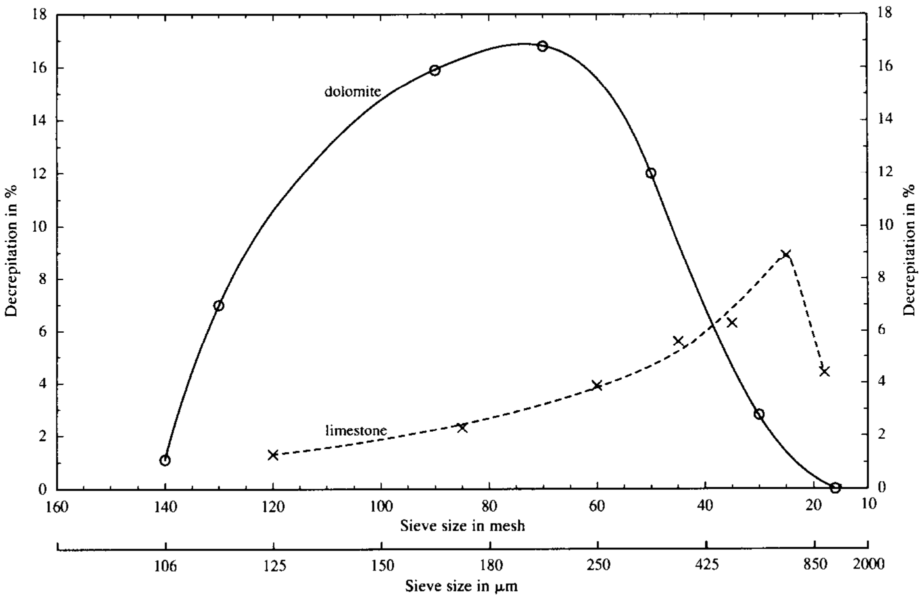

Fig. 1. Decrepitation of limestone and dolomite plotted as a function of particle size measured by the Pilkington test.

carbonates exhibit significant decrepitation although both fall below the 20% value recommended as the allowed maximum. However the behaviour of the two materials was found to be different. The limestone showed a low decrepitation for the finest fractions and the extent of decrepitation increased steadily as the mesh size decreased and the particle size increased, reaching a maximum value at 640–850 μm (20–30 mesh). The largest particle size of 850–1180 μm (16–20 mesh) had a lower degree of decrepitation. In contrast, the rate of increase of decrepitation for dolomite was much more rapid, and had reached the maximum value of 16.8% by 180–250 μm (60–80 mesh). The decrease in the degree of decrepitation fell just as rapidly and was zero by 850 μm (20 mesh).

TG tests

A typical TG–DTG curve for a sample of non-decrepitating limestone exhibits a single smooth decomposition step (see Fig. 2). In contrast, the TG–DTG curve for decrepitating limestone (Fig. 3) has two major mass losses. Similar thermograms are obtained for non-decrepitating and decrepitating forms of dolomite. The lower temperature mass loss, which commences at 390°C for limestone and 500°C for dolomite, is not smooth but consists of many small mass losses. This is indicative of the ejection of particles from the sample pan as they decrepitate. As the

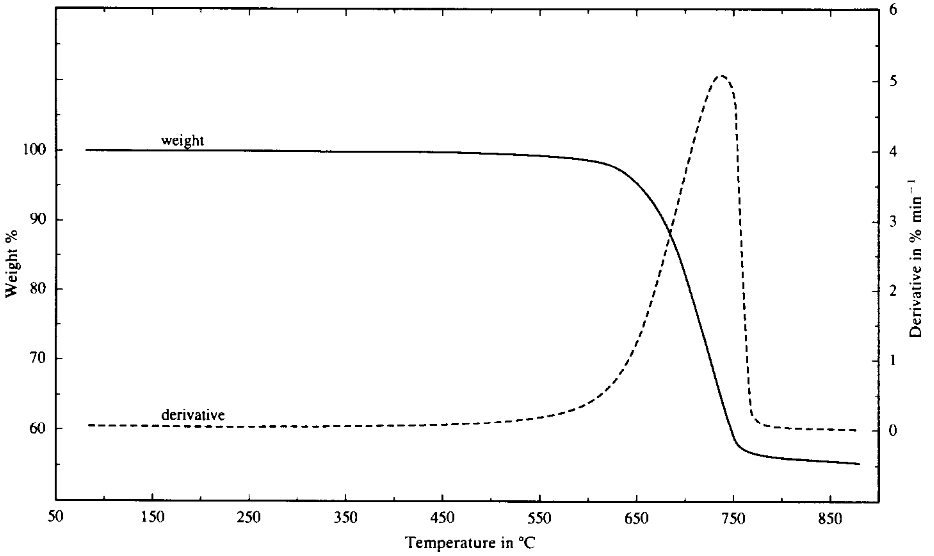

Fig. 2. TG–DTG curve for non-decrepitating limestone. Sample mass ≈ 40 mg; heating rate, 10°C min^{-1}; air atmosphere.

particle size decreases the mass loss becomes smoother, as the ejected individual particles are obviously of smaller mass. The mass loss in this temperature region is taken as the degree of decrepitation. The higher temperature mass loss is the decomposition of the limestone or dolomite remaining in the pan.

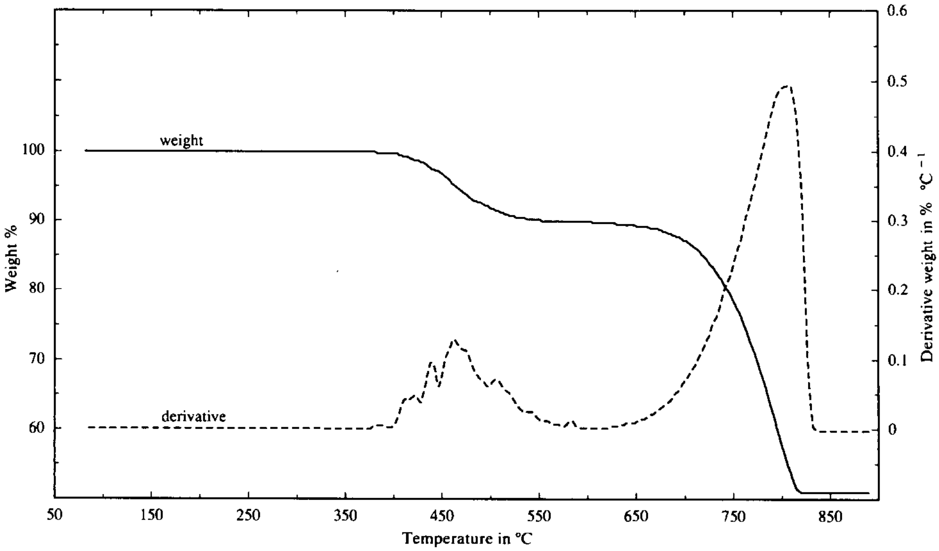

Fig. 3. TG–DTG curve for decrepitating limestone. Same conditions as Fig. 2.

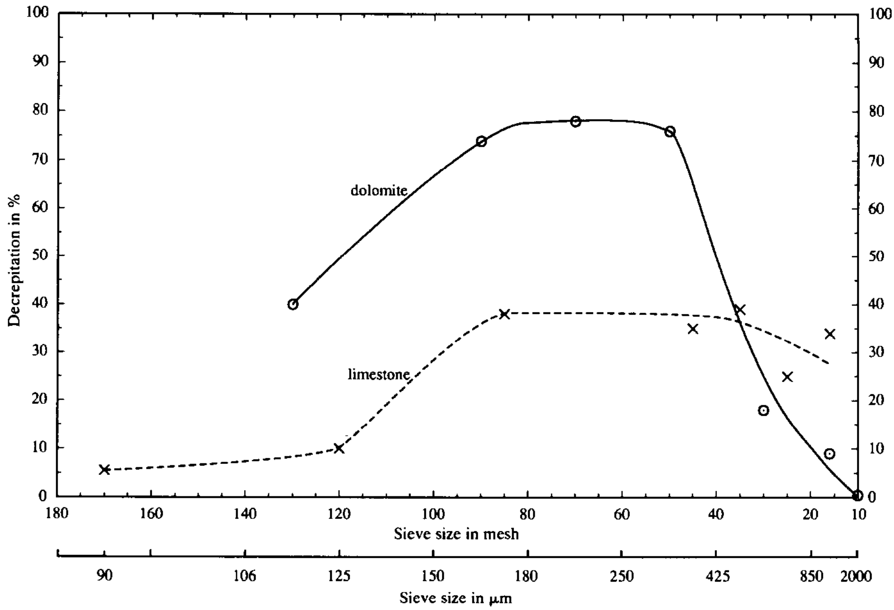

Fig. 4. Decrepitation of limestone and dolomite plotted as a function of particle size measured by the TG test.

Plots of the degree of decrepitation against particle size for limestone and dolomite are given in Fig. 4. The limestone sample had a steady increase in decrepitation with increase in particle size, reaching a maximum of 40% at 180 μm (80 mesh). There was some drop off beyond that, although for large particles the reproducibility is low and so it is difficult to be certain that the result for the 600–850 μm (20–30 mesh) fraction is genuine. Time did not permit reproducibility studies and this will need to be established in future work. The dolomite again exhibited a more regular trend reaching 78% decrepitation at 180–250 μm (60–80 mesh), falling to zero by 2 mm (10 mesh).

DISCUSSION

The two different tests, the Pilkington test and the TG test, showed similar trends in the behaviour of dolomite but not for limestone. Thus, using the Pilkington test, limestone had low decrepitation for the finest fractions with a gradual increase as the particle size increased, with a maximum value of 40% for the 640–850 μm (20–30 mesh) fraction. In the TG test, the maximum value was achieved at a much finer sieve size of 180 μm (80 mesh). Dolomite, however, showed a rapid rise in decrepitation with a maximum at 180–250 μm (60–80 mesh) followed by an equally rapid fall-off to zero at around 850 μm (20 mesh). The TG technique was more sensitive, giving decrepitation indices 4–5 times greater than the

Pilkington test. This effect may vary with heating rate, so that the sensitivity of the TG method may be capable of being adjusted to suit a particular application. The small sample sizes of about 40 mg, the most that can be placed on the pan of the TG apparatus, made representative sampling difficult in the larger particle size range, and also had an effect on the reproducibility of the result.

The results obtained for dolomite by the TG method are similar to those obtained by McCauley and Johnson [8], who found a similar dependency between the degree of decrepitation and particle size, with the maximum values being in the range of 150–250 μm (60–100 mesh). However this is the first time that the two different tests have been compared and extended to include results for limestone samples. More studies are in progress to ascertain if the differences in behaviour of the limestone and dolomite found in this study are common, or vary with the source of the material.

CONCLUSIONS

The limestone and dolomite studied in this work showed different decrepitation behaviour as a function of particle size. The two test methods used gave good correlation of results for the dolomite sample but not such good correlation for the limestone sample. Further work is required with limestones and carbonates of different properties to establish (a) the general behaviour of such materials, and (b) the correlation between the Pilkington and TG tests.

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