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Decrepitation and thermal decomposition of dolomite

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Abstract

A commercially available dolomite was split into six different particle size ranges and thermogravimetric and differential thermal analysis was performed on each of these samples. XRD was performed on each size range before TGA with no differences found. Chemical analysis was performed only on the bulk material. The particle size was found to affect the shape but not necessarily the position of the DTA curve. Decrepitation was found to be most affected by particle size. These data were evaluated in an effort to explain the decrepitation and thermal decomposition of dolomite.

INTRODUCTION

Many of the raw materials that are used for the manufacture of glass come from mined minerals and rocks, which are selected for their long-term purity and stability of composition. The majority of modern glass compositions are based on those of the soda–lime–silica type that contain approximately 8.5 wt.% CaO and approximately 4.0 wt.% MgO. Natural dolomites are used as the source of both MgO and CaO, with the additional CaO content coming from limestone. It is important to understand the thermal decomposition of all the various raw materials of a glass batch to understand the overall decomposition and melting behavior. With this in mind, it is therefore of interest to investigate the thermal analysis of dolomite.

Particle sizing of the various raw materials for glass manufacture is also very important. Particles that are too large are difficult to melt. Particles that are too small cause dusting, which leads to excessive furnace corrosion, regenerator plugging, combustion imbalance, and eventually poor glass quality. An additional factor related to dusting is the phenomenon of decrepitation that exists for materials like dolomite and limestone. Dolomites are normally sized between 12 and 200 mesh to minimize dusting. The size distribution of the material used for this study is given in Table 1.

Most thermal analysts view decrepitation as a nuisance and generally cover their samples to eliminate any problems. Wendlandt [1] mentions decrepitation in his book on thermal analysis in the section on particle size

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TABLE 1

Particle size analysis (cumulative wt.%)

Sieve size		Wt.%
Mesh no.	Opening in mm	
12	1.70	Trace
16	1.18	5.4
30	0.600	24.5
60	0.250	56.9
120	0.150	80.8
140	0.106	93.4
200	0.075	97.9
Pan		100.0

effects; however, he states, without giving any sizes, that it is the larger crystals that decrepitate.

The present study addresses this decrepitation problem as evidenced by TGA and confirms that it is not part of the carbonate decomposition but related to some other thermomechanical phenomenon.

EXPERIMENTAL

The as-received dolomite, which had been sized for the glass industry, was split into the following particle size ranges (see Table 1 for definition of mesh sizes) for thermal analysis: +16 mesh; −16, +30; −30, +60; −60, +120; −120, +140; and −140.

Sample weights of between 26 and 28 mg of each size range were tested by thermogravimetric analysis. The heating rate was varied from 2 to 100°C min^{-1} and all tests were done in triplicate. A stream of nitrogen flowing at 50 ml min^{-1} was used in most cases; however, a few tests were done in carbon dioxide or argon. When samples reached constant weight, they were heated approximately another 100°C. A few studies were done by varying sample weights from 5 to 50 mg. For DTA studies sample weights of approximately 75 mg were tested at a heating rate of 10°C min^{-1} in nitrogen flowing at 50 ml min^{-1}. The reference material was alumina. All thermal analyses were conducted on a Du Pont 2100 thermal analyzer using platinum crucibles or sample pans.

In addition, samples from each size range were heat treated at various temperatures, determined from the TGA, and then examined by X-ray diffraction (XRD) for phase analysis. An automated Siemens D500 diffractometer and Cu Kα radiation was used for these samples.

Chemical analysis of the bulk material was obtained and is reported in Table 2.

TABLE 2

Chemical analysis of dolomite (wt.%)

	Present study [a]	NBS SRM [b]
CaO	30.18	30.12
MgO	21.09	21.03
SiO_2	0.51	1.13
Fe_2O_3	0.11	0.28
Al_2O_3	0.19	0.34
Na_2O	0.04	0.03
K_2O	0.10	0.10
LOI	47.56	46.98
Total	99.78	100.01

[a] 98% between 12 and 200 mesh.

[b] 100% minus 60 mesh; SRM 886.

The individual particles were examined by optical and scanning electron microscopy for texture and impurities.

RESULTS AND DISCUSSION

The data for the study of the effects of heating rate (constant particle size of +30 mesh) are given in Table 3. The average of the three separate runs is plotted in Fig. 1.

As one would expect, the temperature for completion of the decomposition, T_f, increased with increasing heating rate. However, this relationship was not apparent for the temperature of decrepitation, T_d. This particular reaction exhibited essentially no change with heating rate, ranging from 349 to 387°C. It appears that decrepitation is a phenomenon related to particle size rather than a normal decomposition reaction. This can be seen clearly by examination of Fig. 2. The mid-sized range of particles clearly exhibited a greater effect due to decrepitation. Each sample reported in Table 3 was taken from the +30 mesh size range that contained individual particles ranging in size from 0.600 to 1.18 mm. Since the phenomenon of jumping out of the sample pan is related to the mass of the sample particle, it follows that different size particles would jump out at different temperatures, most likely due to thermal conductivity and specific heat effects. Therefore a sample containing a small range of particle sizes will exhibit a variation in temperature for the reaction.

The other temperature given in Table 3, T_i, is the temperature of the initial reaction, if one ignored decrepitation. This temperature also exhibited the expected increase with increase in heating rate.

The total weight loss, also shown in Table 3, did not exhibit any significant trends with heating rate. The total average loss for all runs was

TABLE 3

Reaction temperature for various heating rates (+30 mesh)

Rate (°C $\min^{-1}$)	T_d (°C)	T_i (°C)	T_f (°C)	Wt. loss (%)
2	385	666	738	59.1
2	382	671	738	52.4
2	386	668	734	61.7
Avg.	384	668	737	57.7
Dev.	1.7	2.5	1.9	4.8
5	350	705	777	54.2
5	356	701	773	59.6
5	363	704	770	64.1
Avg.	356	703	773	59.3
Dev.	6.5	2.1	3.5	5.0
10	375	705	786	68.8
10	371	719	797	63.6
10	325	722	797	60.1
Avg.	357	715	793	64.2
Dev.	22.7	9.1	5.2	4.4
20	400	754	834	62.1
20	367	752	841	62.7
20	395	760	843	52.1
Avg.	387	755	839	59.0
Dev.	14.5	4.2	3.9	6.0
50	407	782	886	56.6
50	354	783	886	65.3
50	372	789	883	62.4
Avg.	378	785	885	61.4
Dev.	22.0	3.8	1.4	4.4
100	336	807	920	68.9
100	347	808	933	61.6
100	365	810	918	59.6
Avg.	349	808	924	63.4
Dev.	12.0	1.5	6.6	4.9
Average weight loss by TGA (LOI)				61.3 (48.0)

61.3%, which is slightly more than the 48% expected from the loss on ignition (LOI) data shown in Table 2. The difference between these two values is the amount of decrepitation for this particle size sample (approximately 12%).

The shapes of the individual curves shown in Fig. 2 and the percent residue are very interesting. The +16 mesh and the +140 mesh samples exhibited smooth curves representative of a single weight loss reaction,

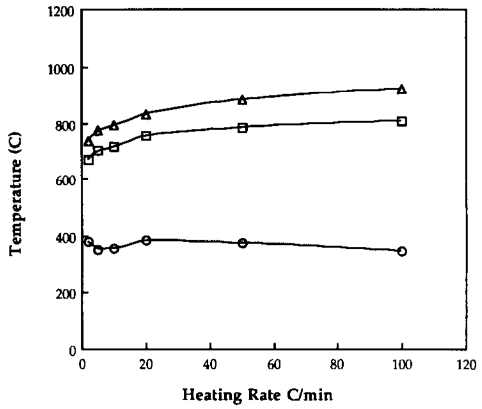

Fig. 1. Effect of heating rate on reaction temperatures for +30 mesh dolomite; ○, decrepitation temperature; □, initial decomposition temperature; and △, final decomposition temperature.

yielding a total weight loss very close to that expected for this dolomite (LOI from Table 2 of 47.56% compared to 48.5 and 52.40%, respectively). There was a very slight weight loss that can be attributed to decrepitation in the +16 mesh sample but not in the +140 mesh sample.

The next range (−16, +30) exhibited a weight loss curve representative of decrepitation as evidenced by the rapid weight loss as particles jumped from the pan. This sample lost a total of 68.8% of its weight. The −120, +140 mesh size sample exhibited a curve indicative of two reactions, but

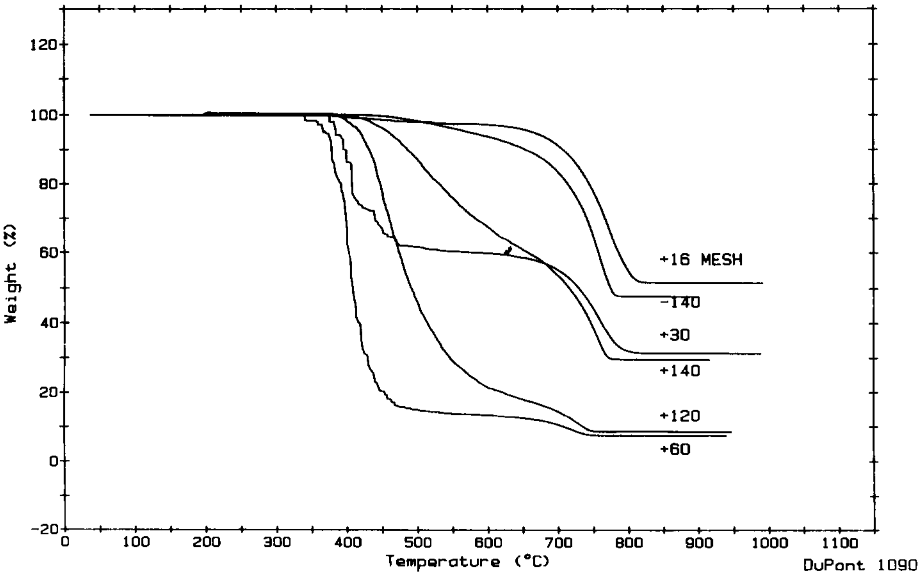

Fig. 2. Effect of particle size on TGA of dolomite.

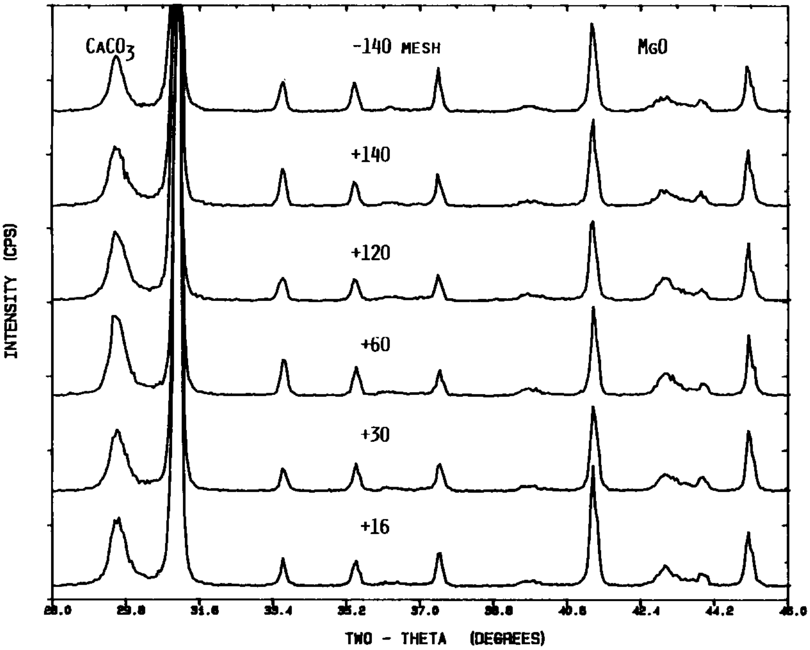

Fig. 3. X-ray diffraction of various particle sizes of dolomite heated to 700°C.

not necessarily of decrepitation. Total weight loss in this case was 70.60%.

The −30, +60 mesh size range exhibited a weight loss curve similar to the +30 size range; however, a much larger total weight loss was experienced. This sample exhibited the largest weight loss of all tested, at 92.63%.

The curve for the −60, +120 mesh size particles did not show rapid weight-loss jumps as the particles jumped from the pan, but exhibited a smooth curve with an indication of two reactions. This indication of a double reaction could be due to decrepitation at the lower temperatures and then decomposition. The total weight loss of 91.63% indicated that a considerable amount of material exhibited decrepitation but it was on a very fine and continuous scale.

To determine the nature of the two reactions indicated by the shape of the TG curves, samples of each size range were heated to 500, 600 and 700°C at 10°C min^{-1}, held for 10 min and examined by X-ray diffraction (XRD). It was found that this dolomite did not decompose uniformly but, instead, first decomposed to a mixture of MgO, calcite, and dolomite, as reported by Chesters [2] and explained in more detail by Goldin and Kulikova [3]. From an examination of Fig. 3, one can see that particle size had essentially no effect on the phases present after heat treatment.

Temperatures of reactions normally decrease as the particle size becomes finer. As shown in Fig. 2, this seems to be the case for both the initial and final temperatures for the sizes +16, +30, and +60. From the +120

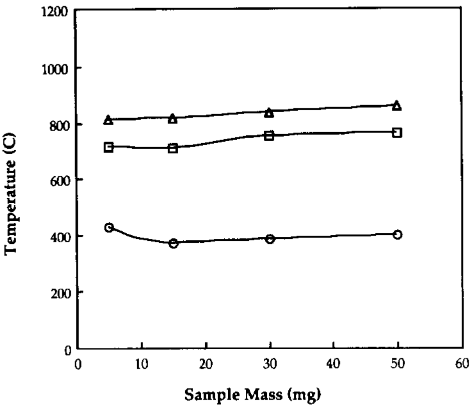

Fig. 4. TGA mass effect for +30 mesh dolomite: ○, decrepitation temperature; □, initial decomposition temperature; and △, final decomposition temperature.

fraction down to the −140 fraction, this trend is reversed. If one considered only the mass effect, it would be expected that the +60 and +120 size range would exhibit the lowest T_f, which was the case. Thus the effects on T_f as shown in Fig. 2 appeared to be more of a mass effect due to decrepitation than one of particle size. The true sample mass effect is shown in Fig. 4, where sample masses of approximately 5, 10, 15 and 50 mg were tested. As expected, a slight increase in T_f and T_i were found for the larger sample masses; however, no mass effect was apparent for decrepitation, T_d.

The double reaction exhibited by the +140 and +120 TG curves appears to be the result of decrepitation on a very fine scale and then decomposition, rather than a two-step decomposition, even though the two-step decomposition was confirmed by XRD. The double-decomposition was also confirmed by and is more apparent in the DTA curves as shown by Fig. 5. Only at the heating rate of 100°C min^{-1} was the double-decomposition apparent in the TG curve.

The four temperatures designated in Fig. 5 are given in Table 4 for the various particle sizes. Only the mid-range particle size samples of +60 and +120 exhibited a slight bend in the DTA curve designated as T_1. These two particle size ranges were the ones that also exhibited the most decrepitation as evidenced by TGA. The other temperatures exhibited no obvious trends, only random variations. The variations appear to be close to within the limitations of precision of the experiment, and thus one would conclude that particle size had no effect on these reactions. However this is in conflict with the TGA results.

Since the mid-range particle size samples exhibited the most decrepitation as evidenced by TGA, one might conclude that the initial reaction of these same particle sizes in DTA is due to decrepitation; however, it occurred at a much higher temperature than in TGA. If this is not the case, then

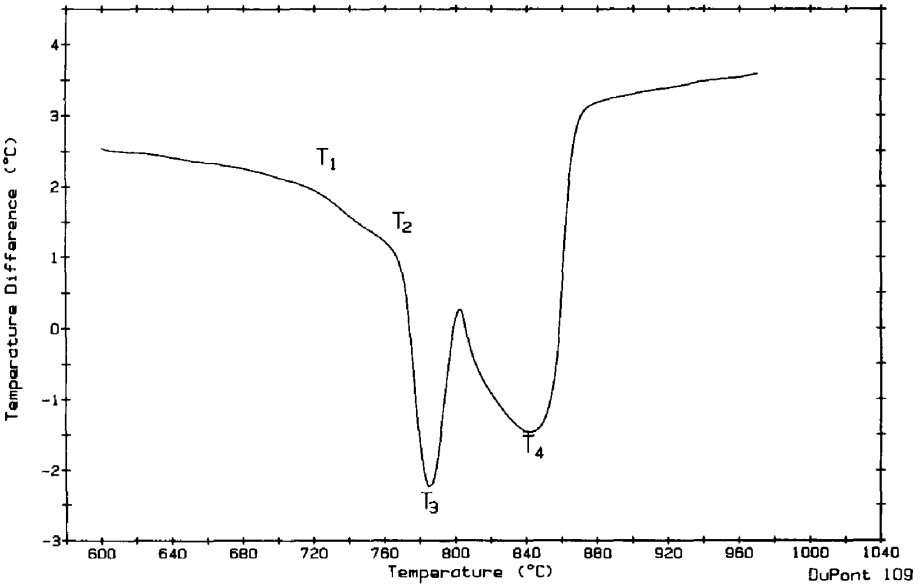

Fig. 5. Typical DTA dolomite decomposition.

decrepitation had essentially no effect on the DTA data. Decrepitation would also be minimized in DTA due to the cylindrical sample-holder geometry as compared to the flat basket of the TGA. Thus the cause of the change in slope at T_1 is unclear.

The largest and smallest size range exhibited the least amount of decrepitation, with the mid-size range exhibiting the largest amount. This most likely relates to the mass of the particles and the internal pressure build-up within the dolomite structure. Larger particles have too much mass to be moved by the released pressure and the smaller particles do not have sufficient strength to allow the pressure to build up. As pressure is released from the mid-size particles there is sufficient energy to carry these particles a rather large distance.

TABLE 4

DTA reaction temperatures (10°C min^{-1}; 50 ml min^{-1} N_2)

Size (mesh)	T_1	T_2	T_3	T_4
+16	–	770	790	845
+30	–	763	788	840
+60	692	779	795	833
+120	711	771	788	843
+140	–	793	801	838
−140	–	776	798	838

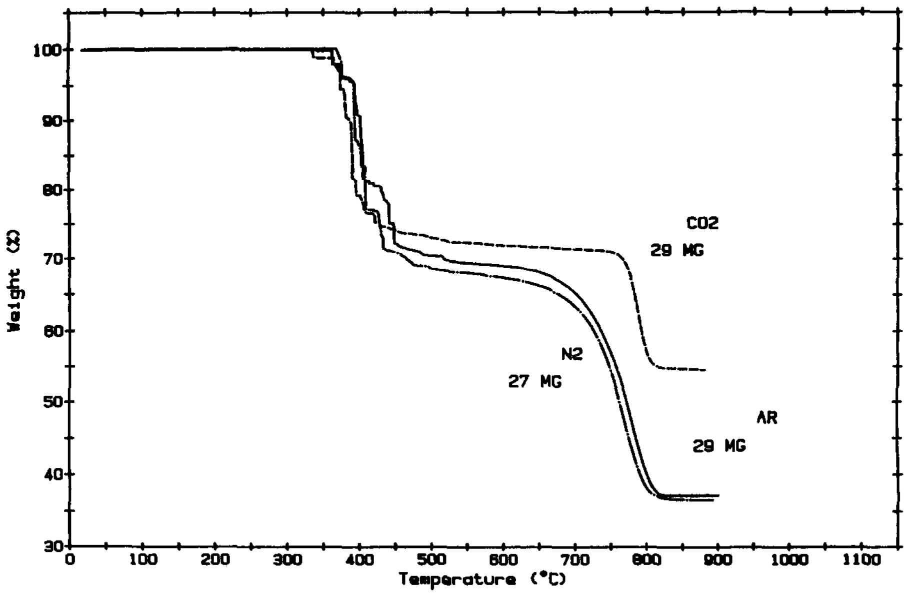

Fig. 6. TGA atmosphere effect for +30 mesh dolomite: heating rate, 10°C $\min^{-1}$; gas flow rate, 50 ml $\min^{-1}$.

To examine the possible effect of atmosphere on the decrepitation reaction temperature, tests were conducted in flowing carbon dioxide and in argon for comparison with those done in nitrogen. As can be seen from Fig. 6, atmosphere had no effect on the decrepitation temperature, confirming the idea that decrepitation is not a form of decomposition. The expected increase in T_i for the carbonate decomposition in a carbon dioxide atmosphere did occur, as compared to nitrogen or argon atmospheres.

In an effort to determine if impurities were present that may cause decrepitation, polished section samples were examined by optical and scanning electron microscopy. Although an exhaustive search was not conducted, a sulfur-containing compound was found. Its chemistry by EDS is shown in Fig. 7. A back-scattered SEM image in Fig. 8 shows the presence of calcite embedded within the dolomite. The presence of a trace of calcite was also confirmed by XRD. The amounts of these impurities did not appear to be sufficient to cause the amount of decrepitation found.

It is known from the current study that decrepitation is affected by particle size and that it is not affected by heating rates, furnace atmosphere, or total sample mass. The fact that no decomposition takes place during decrepitation was confirmed by collecting particles that jumped from the TGA pan and comparing them by XRD with particles remaining in the pan. The current belief is that decrepitation is a result of the pressure build-up of the water within the lattice until it exceeds the mechanical strength of the particle resulting in a mini-explosion. An unsuccessful attempt to confirm

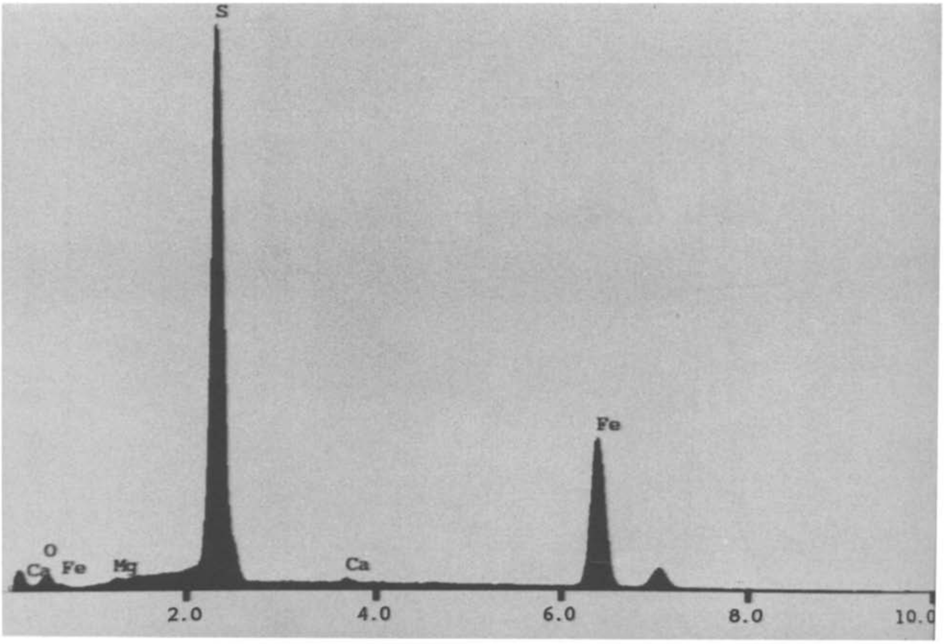

Fig. 7. EDS of impurity contained in dolomite.

the release of water caused by decrepitation was conducted on a TG/FTIR heated to 500°C. Apparently the amount of water released for the small sample size (25 mg) was below the detection limits of the instrumentation.

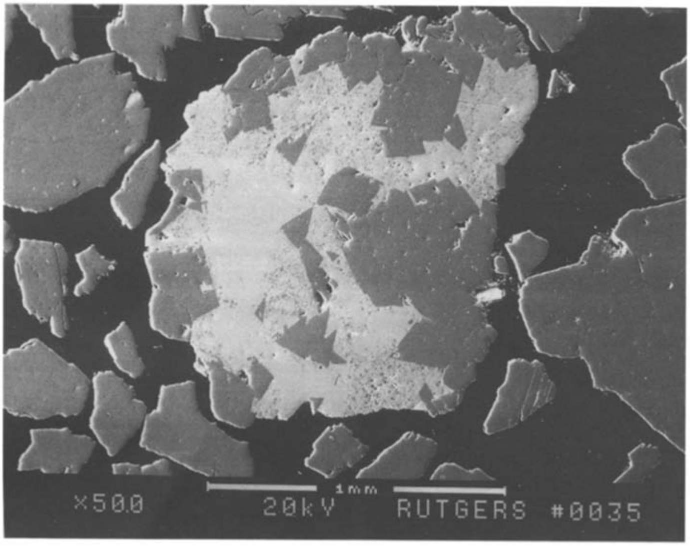

Fig. 8. SEM back-scattered image: lightest area, calcite; darker area, dolomite; and darkest area, epoxy. Original magnification × 500.

TABLE 5

Dolomite strength data [a]

Sample no.	Width (mm)	Height (mm)	MOR (psi)
1	5.04	3.46	3748
2	5.00	3.59	3814
3	5.06	3.76	3848
4	5.02	3.44	3600
5	5.07	3.42	3523
6	4.87	3.99	3773
7	5.06	3.52	4117
8	5.07	4.00	3606
9	5.04	3.74	4149
10	5.00	3.66	3743
11	5.03	3.80	3621
Average MOR			3777
Deviation			203

[a] Three-point bend; 1.0 in span and 0.1 in/min^{-1} crosshead speed.

Knowing that the water vapor pressure at 374°C is 3200 psi [4], a study of the mechanical strength was performed for comparison, assuming that if the water vapor pressure exceeds the strength of the material, decrepitation will occur. Table 5 shows the results of a three-point bend test on eleven bars approximately 5 by 3.5 mm in cross section by 7 mm long. Care was taken in preparing and breaking the bars to obtain the highest possible bend strength. The bars were cut from a large ten-pound boulder of dolomite to minimize internal cracks. The three-point bend test was used that yields a strength slightly higher (about 10%) than a four-point bend test. The average room temperature strength of these samples was 3777 psi. Since decrepitation occurs at temperatures (Table 3) ranging from 349 to 387°C (average for each heating rate of +30 mesh particles) with corresponding water vapor pressures from 2367 to 3642 psi (estimated), respectively, it is believed that these data confirm the assumption that decrepitation is caused by water trapped within the lattice of the dolomite.

CONCLUSIONS

It was determined that furnace atmosphere, total sample mass, and heating rate do not affect the temperature of decrepitation. The particle size of the sample, however, does affect that temperature. In an effort to determine the actual cause of decrepitation, it was found that water trapped within the dolomite lattice was the most likely cause, since the vapor pressure of water at the temperature of decrepitation was very nearly the same as the mechanical strength of the material. The differences found between the vapor pressure and the strength were most likely due to the fact that the strengths were determined at room temperature and that the mechanical strength samples were cut from a large dolomite boulder that most likely had less internal cracks and, therefore, a higher strength than the individual particles that decrepitate.

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