

CHLORIDE SALT EFFECTS ON THE DECOMPOSITION OF DOLOMITE

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ABSTRACT

A great deal of variability in decomposition temperature(s), activation energy and rate of decomposition exists in the literature on the decomposition of dolomite. Although differences may be due to experimental factors such as sample size, grain size, heating rate and atmospheric conditions, it has been found that the presence of small concentrations of alkali or alkaline earth salts in the naturally occurring minerals has a strong effect on their decomposition. From DTA and isothermal studies, it is illustrated that the temperature of decomposition of dolomite is reduced and that the rate of decomposition is enhanced relative to pure dolomite when small amounts of chloride salts such as LiCl, NaCl, MgCl₂ and CaCl₂ are added. From X-ray analysis, pure dolomite is seen to decompose directly into CaO and MgO, but when chlorides are present it initially decomposes into MgO and CaCO₃. The decomposition reaction for both pure dolomite and dolomite containing chlorides follows the contracting-area model

$$1 - (1 - \alpha)^{1/2} = kt$$

Activation energies for pure and doped dolomites have been evaluated and are similar to those reported in literature.

INTRODUCTION

The decomposition of carbonates has been widely studied and reported throughout the literature. A general review of this literature indicates that a great deal of variability exists in the reported values for decomposition temperature(s), activation energies and rates of decomposition. The differences may be due to experimental factors such as sample size, grain size, heating rate or atmospheric conditions, to name a few. It is suggested though that many of the reported differences may also be a result of the presence of a small concentration of alkali or alkaline earth salts in the naturally occurring minerals that have been used for study. Although the effect of sodium chloride on the decomposition of dolomite (MgCO₃ · CaCO₃) has been reported [1–6], there have been no systematic studies of other chloride

salts or their effect on the kinetics of decomposition. In this paper, the effect of four different chloride salts on the decomposition kinetics of dolomite at various temperatures as studied by differential thermal analysis, isothermal thermogravimetric analysis and X-ray diffraction will be reported.

EXPERIMENTAL PROCEDURE

For all studies, a dolomite from California was used exclusively because of its high purity as detected by emission spectroscopy (Table 1), large crystal size (1.65 mm) and its high grain density with no internal porosity. The dolomite was crushed, screened into a $-100 + 270$ mesh-size powder ($-149 + 53$ micrometers), and washed in deionized water to remove any soluble impurities that may not have been detected. Four different reagent-grade chloride salts were added to the dolomite powder via solution at a molar ratio of 0.02 moles anhydrous salt per 0.98 moles dolomite powder. The salts used were LiCl, NaCl, $MgCl_2$ and $CaCl_2$ which will be designated as LC, NC, MC and CC, respectively. Isothermal thermogravimetry (TG) was performed in air in order to obtain activation energies for the decomposition reactions. The isothermal analysis involved lowering powder samples of 300 ± 2 mg on a platinum pan into the furnace which was at a fixed temperature (Fig. 1) and continuously monitoring the weight loss. Decomposition was also studied using differential thermal analysis (DTA) in flowing air (29 ml min^{-1}) with sample sizes of 31 ± 1.5 mg. Flowing air was used in the DTA experiments to more closely simulate the convective air flow that occurs in the TG experiment. Several portions were taken from the TG sample after 15% weight loss in order to determine the phase composition at this stage of decomposition by X-ray diffraction analysis.

RESULTS AND DISCUSSION

The results of the DTA analyses for the pure and salt-doped samples are given in Fig. 2. The decomposition occurs by either a single or a two-step process. A single peak indicates that the dolomite dissociates simultaneously

TABLE 1

Chemical composition of the dolomite used

	Constituent					
	MgO	CaO	Fe_2O_3	SiO_2	Al_2O_3	Cl^{-1}
Weight (%)	20.6	31.7	0.12	0.5	0.07	< 0.01

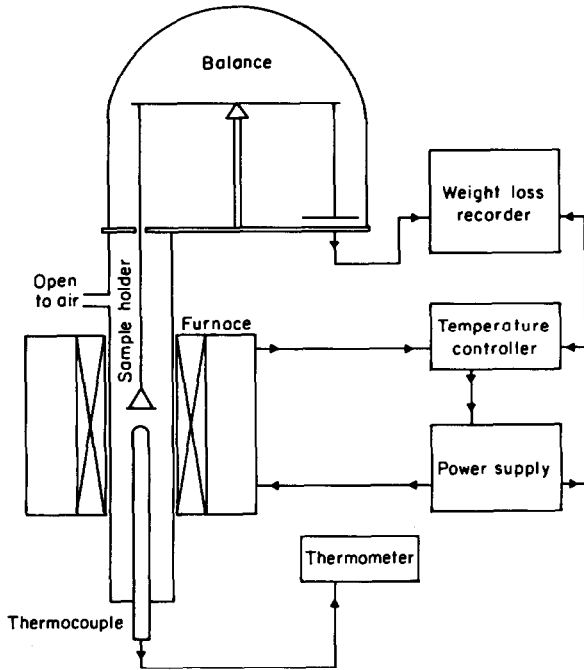


Fig. 1. A schematic representation of the experimental apparatus for isothermal decomposition studies.

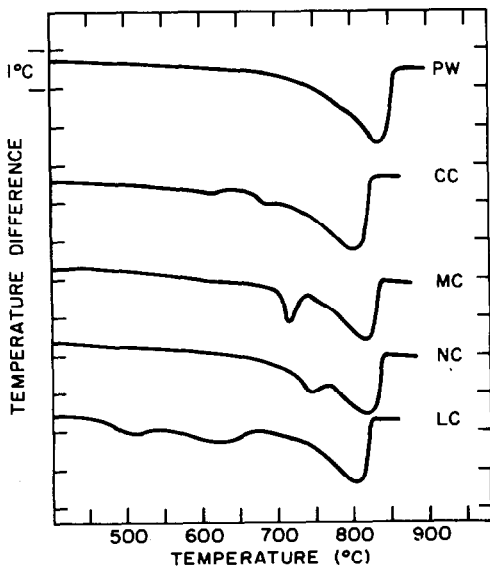


Fig. 2. Differential thermal analysis curves of pure and salt-doped dolomite obtained in flowing air.

into MgO and CaO whereas two peaks indicate that the dolomite decomposes by a two-stage process. This result suggests that the presence of the salt enhances the decomposition of the dolomite. In fact, the decomposition process is initiated at lower temperatures than observed for the pure dolomite. However, each salt affects the process to a different degree with the LiCl lowering the first decomposition peak the most and the CaCl₂ the least (as measured at the peak midpoint). Furthermore, in all cases the second decomposition peak is lowered relative to pure dolomite although the variation in the temperatures is significantly less than that observed for the first peak. This suggests that the salts promote the formation of MgO and CaCO₃ during the early stage of decomposition.

To determine if the activation energies for the decomposition process are influenced by the presence of the salt, a series of isothermal TG experiments were carried out at 635, 710 and 800°C. The decomposition kinetics are presented in Fig. 3 for the pure and doped dolomites. At 635°C, in the presence of the salt, decomposition occurs as much as 4 times faster up to 20% weight loss and then decreases to a rate which is similar to that observed for pure dolomite. The inflection point is seen to occur for all salt-doped samples but not for pure dolomite, further indicating that the decomposition process is significantly altered by the salts. Each salt yields a somewhat different rate of decomposition at the lower temperature as shown in Table 2 but the differences are considerably reduced for calcination at 800°C and are almost non-existent above the inflection point. As a result of the rapid initial decomposition, the process is completed in much shorter times for all salt-doped samples than for pure dolomite.

To determine whether there is a difference in the energetics for decomposition between the pure and doped material, the isothermal calcination data was fitted to four models (Table 3) that are commonly used to describe decomposition reactions. From a regression analysis of the best line fit, the TGA data for both the doped and undoped dolomite at all temperatures was found to best fit the contracting-area model for a cylindrical geometry. The correlation coefficient obtained from linear regression analysis was at least 0.97 and > 0.99 for most cases. The same model has been reported by Gallagher and Johnson [8] to best fit the decomposition of calcite.

From the foregoing analysis it is possible to derive the reaction rate constants that are recorded in Table 2 for the three temperatures studied. Knowing that decomposition is a thermally activated process, a plot of $-\ln K$ vs. $1/T$ (Fig. 4) can be used to determine the activation energy for the decomposition process. This analysis is somewhat complicated by the differences in the decomposition paths for the pure sample and the salt-doped samples. That is, the pure sample decomposes by a single-stage process and the salt-doped dolomite in a two-stage process. Therefore, an activation energy was determined for each linear portion of the plot. The activation energies determined from this analysis are presented in Table 4. It is

TABLE 2

Rate constants of decomposition as determined from isothermal TG for pure and salt-doped dolomite

Sample	Stage	Calcination temperature (°C)		
		635	710	800
LC	1	1.37×10^{-3}	9.82×10^{-3}	4.22×10^{-2}
	2	4.06×10^{-4}	2.48×10^{-3}	1.43×10^{-2}
NC	1	6.58×10^{-4}	4.18×10^{-3}	4.28×10^{-2}
	2	2.89×10^{-4}	2.49×10^{-3}	1.35×10^{-2}
MC	1	7.82×10^{-4}	4.34×10^{-3}	2.31×10^{-2}
	2	3.27×10^{-4}	2.46×10^{-3}	1.49×10^{-2}
CC	1	1.18×10^{-3}	4.75×10^{-3}	2.41×10^{-2}
	2	4.31×10^{-4}	3.01×10^{-3}	1.47×10^{-2}
PW		3.17×10^{-4}	1.88×10^{-3}	1.01×10^{-2}

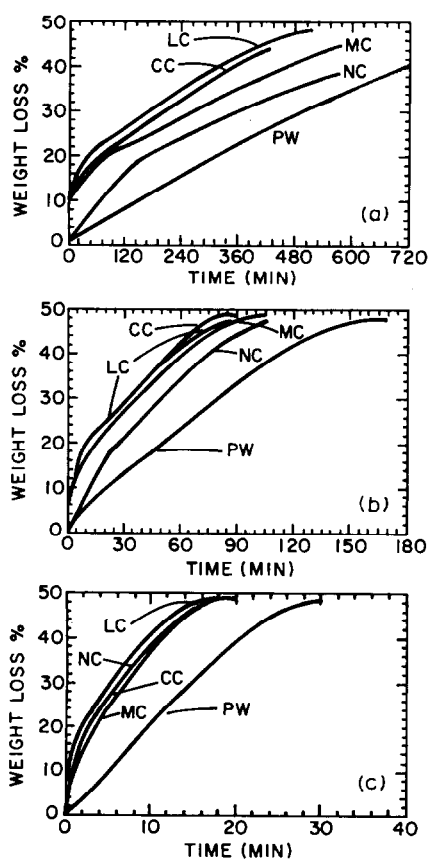


Fig. 3. Isothermal TG results for pure and salt-doped dolomite at (a) 635°C, (b) 710°C and (c) 800°C.

TABLE 3

The models used for activation energy analysis

Model	Equation
Contracting area (cylindrical geometry)	$1 - (1 - \alpha)^{1/2} = kt$
Contracting area (sphere)	$1 - (1 - \alpha)^{1/3} = kt$
Erofeev ($n = 2$)	$[-\ln(1 - \alpha)]^{1/n} = kt$
Two-dimensional diffusion	$(1 - \alpha) \ln(1 - \alpha) + \alpha = kt$

apparent that there isn't a large difference in the activation energies for decomposition, indicating that the salts do not "activate" the process by lowering the thermal requirements for decomposition. This conclusion is supported by the similarity in the activation energies obtained here and by other investigators [10] for various dolomites as shown in Table 4.

The phase composition was determined (Fig. 5) by X-ray diffraction for a pure dolomite sample which had been partially decomposed to 15% weight loss at 710°C and for a dolomite sample containing magnesium chloride which had been partially decomposed to 15% weight loss at two different temperatures. The phase composition indicates that in the presence of the

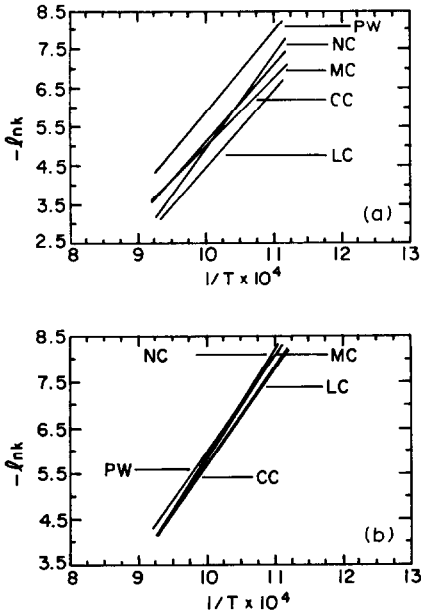


Fig. 4. Reaction rate as a function of temperature for (a) the 1st and (b) the 2nd stages of decomposition. (PW is the same line on each plot).

TABLE 4

Activation energies determined from isothermal TG for pure and doped dolomite

Sample	Activation energies (kcal mole ⁻¹)		
	1st stage	2nd stage	Single stage
PW			41.4
LC	40.0	41.7	
NC	48.6	44.7	
MC	39.4	44.4	
CC	35.6	41.6	
Bischoff [10]			44.2
Young [9]			45.0, 40.0
Powell and Searcy			46.5

salt, MgO and CaCO₃ are formed, whereas, in the pure sample both MgO and CaO are formed. This is consistent with the relative change observed earlier in the DTA experiment. That is, the first decomposition peak is shifted to a lower temperature when the salt is present indicating the preferential decomposition into MgO and CaCO₃.

The foregoing analysis suggests that the chloride salts interact in some manner to enhance the decomposition of dolomite. The melting temperatures of the salts (i.e. LC, 605°C; NC, 800°C; MC, 711°C and CC, 765°C) is

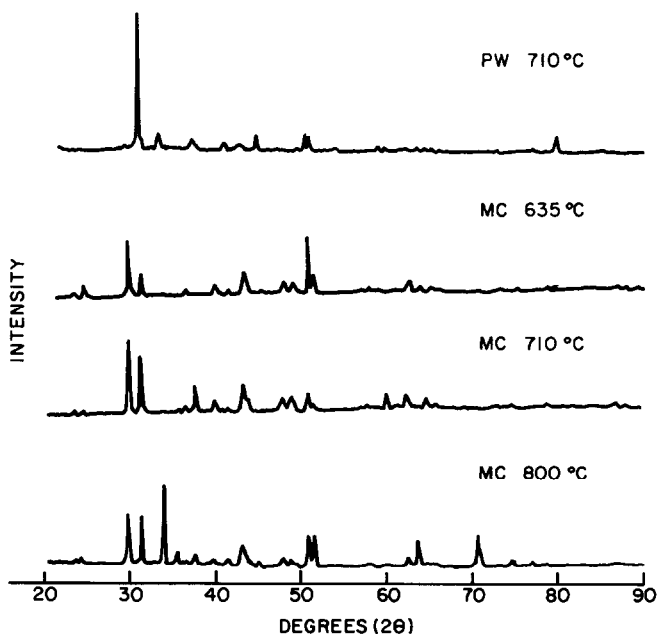


Fig. 5. X-Ray diffraction patterns after 15% weight loss for MC-doped dolomite decomposed at 635, 710 and 800°C.

such that they exist in the liquid state at some stage of the decomposition process. However, as shown in Table 2, the reaction rate is accelerated by all salts at 635°C even though only the LiCl melts by this temperature. Thus, it is hypothesized that the salts form a liquid with dolomite before or during decomposition and the formation of the liquid would result in the disruption of the local crystal lattice and accelerate the decomposition of the dolomite. Preliminary experiments support this hypothesis and the results will be reported in another paper.

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