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FLUORIDE SALT EFFECTS ON THE DECOMPOSITION OF DOLOMITE

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ABSTRACT

From DTA and isothermal studies, it is evident 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 fluoride salts, e.g., LiF, NaF, MgF_2 and CaF_2 are mixed with the dolomite powder. From X-ray analysis pure dolomite is seen to decompose directly into CaO and MgO but when the fluoride salts are present at 800 °C it initially decomposes into MgO and $CaCO_3$. The contracting area was used for describing the decomposition kinetics for each case. The reaction rate constants are much higher when LiF and NaF are present at 635–800 °C whereas only at 800 °C do MgF_2 and CaF_2 enhance the decomposition process. These differences were attributed to the higher vapor pressures and ease of transport for LiF and NaF. It is further suggested that lower temperature eutectics are formed between dolomite and its decomposition products and the fluoride salts which then affect the decomposition process.

INTRODUCTION

The decomposition characteristics of many carbonates have been reported. When comparing these data, decomposition temperatures, activation energies and rates of decomposition are found to vary significantly. These differences can often be attributed to differences in sample size, grain size, heating rate and atmosphere during thermal analysis. Recently, it has been shown that the presence of impurity amounts of various halide salts can significantly lower the decomposition temperatures and enhance the rate of decomposition of dolomite, $MgCa(CO_3)_2$ [1] and calcite, $CaCO_3$ [2–4]. It was reasoned that if the chloride salts affect decomposition then the fluoride salts would have a similar effect. The obvious practical advantage of lowered decomposition temperatures and enhanced decomposition kinetics is one of reduced energy consumption during calcination. In this communication the effect of four different fluoride salts on the decomposition of dolomite at various temperatures as studied by differential thermal analysis, isothermal thermogravimetric analysis and X-ray diffraction is reported.

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EXPERIMENTAL

For all studies, a high purity (Table 1), chloride-free dolomite was used. After crushing the large crystal size (~ 1.76 mm) dolomite to −100, +270-mesh powder (−149, +53 μm) it was mixed in deionized water with the fluoride salts. The composition of the dry mixture was 0.02 mol anhydrous fluoride salt and 0.98 mol dolomite powder. The salts studied were LiF, NaF, MgF_2 and CaF_2 and are designated throughout this paper as LF, NF, MF and CF, respectively, and PW represents the pure dolomite.

The thermal analysis experiments included differential thermal analysis (DTA), isothermal gravimetric analysis (TG) and X-ray diffraction performed in the same manner as described in the earlier study [1] and under the same conditions. To determine how the fluoride salts affect the decomposition reactions, several special TGA investigations were performed and are described later.

RESULTS AND DISCUSSION

The results of the DTA analyses at 10 °C min^{-1} and in flowing air (29 ml min^{-1}) for pure and fluoride-added dolomite are shown in Fig. 1. Pure dolomite decomposition gives a single endothermal peak indicating that decomposition occurs by a single-step process

$$MgCa(CO_3)_2 = MgO + CaO + 2\,CO_2 \tag{1}$$

The decomposition of all fluoride-added dolomites shows two separate endothermal peaks indicating that decomposition occurs by a two-step reaction [5–7]

$$MgCa(CO_3)_2 = MgO + CaCO_3 + CO_2 \tag{2a}$$

$$CaCO_3 = CaO + CO_2 \tag{2b}$$

Relative to pure dolomite decomposition, the decomposition temperature (temperature determined by the endothermal peak position) for fluoride-added samples shifts to lower temperatures, the amount of the shift is dependent on the specific fluoride additive. These results are similar to those presented for the decomposition of chloride-added dolomite samples [1]. It appears that NF reduces the temperature at which decomposition is first

TABLE 1

Chemical composition of dolomite

Constituent	MgO	CaO	Fe_2O_3	SiO_2	Al_2O_3	Cl
Wt%	20.6	31.7	0.12	0.5	0.07	< 0.01

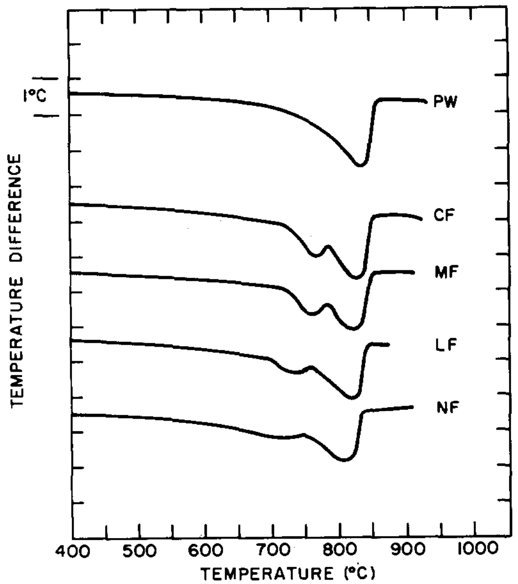


Fig. 1. Differential thermal analysis curves of pure and fluoride salt-added dolomite at 10 °C min^{-1} and in flowing air.

initiated by more than any of the other salts.

The isothermal TG results of fluoride-added dolomite can be interpreted by using a contracting area model (Fig. 2) and the weight loss kinetics can be expressed as

$$1-(1-\alpha)^{1/2}=kt \tag{3}$$

where α = weight loss fraction, k = rate constant, and t = time. Based on the k values derived from Fig. 2 and the temperature, the activation energy (or energies for two-step decomposition) were calculated from the slope of ln K vs. $1/T$ (Fig. 3) and are listed in Table 2.

The phase compositions of pure dolomite and dolomite containing MgF_2 or LiF were examined by X-ray diffraction after a weight loss of 15% at 710 °C. For dolomite containing LiF a 15% weight loss is located below the inflexion point (Fig. 4), in other words, it is during the first stage of decomposition. For comparison, the composition of sample LF after a weight loss of 38% at the same temperature was also examined. The results, shown in Fig. 5, indicate that the decomposition of pure dolomite and dolomite containing MgF_2, both of which give a smooth curve in the diagram of weight loss vs. time, follow reaction (1). However, for the decomposition of sample LF, since there is no CaO in the phase composition during decomposition below the inflexion point, the decomposition reaction during the first stage should follow eqn. (2a).

It is seen from the plots of weight loss vs. time (Fig. 4) that the weight-loss

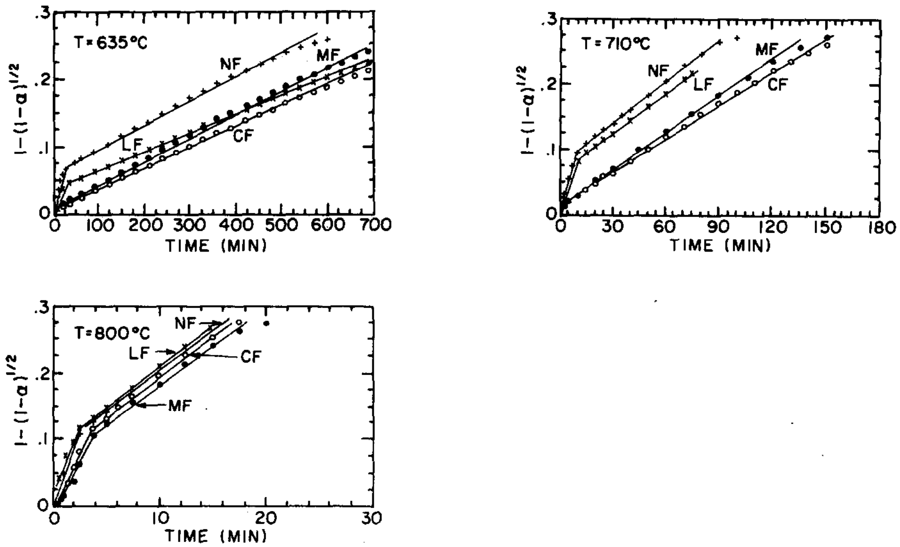


Fig. 2. Isothermal TG data fit to the contracting area model.

curves for the CaF_2- and MgF_2-added dolomites are very similar to the pure dolomite curve (PW) at temperatures of 635 and 710 °C. However, at 800 °C these decomposition kinetics are similar to those shown for LF- and NF-added samples. This indicates that only at a high temperature (i.e., 800 °C) do MgF_2 and CaF_2 affect the dolomite decomposition, and that at a lower temperature the decomposition reaction is unaffected. It should be noted here that the lowest melting salts are LiF (845 °C) and NaF (993°C), MgF_2 and CaF_2 have melting temperatures of 1261 and 1423°C, respectively.

To determine how the fluorides change the decomposition reaction, TG tests using "unmixed" samples of LF, MF and CF were conducted. An "unmixed sample" means that instead of thoroughly mixing the fluoride salts with the dolomite powder as described earlier [1], the fluorides were put directly on the bottom of the platinum pan then covered by dolomite powder

TABLE 2

Activation energy of decomposition (kcal mol^{-1})

Sample	Single step	Two step	
		First	Second
LF	–	42.0	43.5
NF	–	33.2	41.2
MF	–	–	41.9
CF	–	–	42.9
PW	41.4	–	–

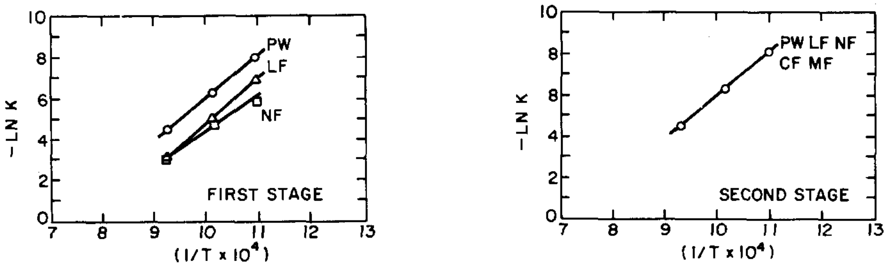


Fig. 3. Reaction rate as a function of temperature for the first and second stages of decomposition.

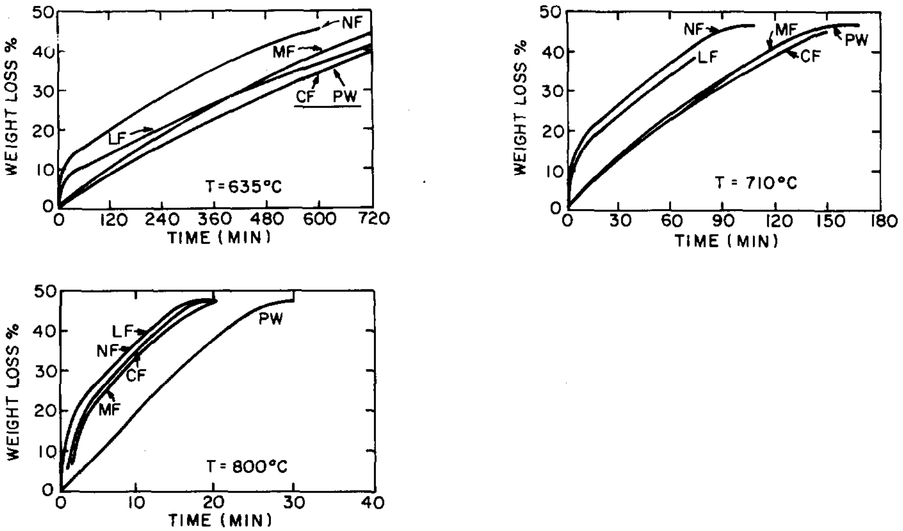


Fig. 4. Isothermal TG results for pure and salt-added dolomite at 635, 710 and 800 °C.

with the total mole fraction of the fluoride salt still being 0.02 (Fig. 6). The results for the three additives are shown in Figs. 7–9. For comparison, the weight-loss curves of pure dolomite and dolomite containing well mixed fluoride are also plotted.

The weight-loss curves for the decomposition of unmixed MF and unmixed CF at 800 °C (Figs. 8 and 9) as well as that of unmixed LF at 710 °C (Fig. 7a) are very close to the weight-loss curve for pure dolomite decomposition. It is clear that if dolomite does not have direct contact with the fluoride powders at these temperatures then the fluorides do not affect the decomposition reaction. The weight-loss curve for unmixed LF at 800 °C is parallel to that of the normal LF sample at the same temperature (Fig. 7b). This demonstrates that the decomposition reaction is affected by LiF, even

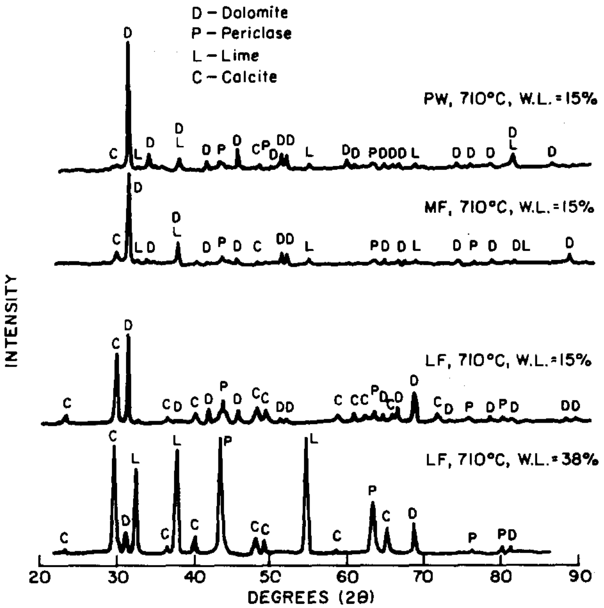


Fig. 5. X-ray diffraction patterns after 15% weight loss for PW, MF and LF samples at 710 °C and for LF after 38% weight loss at 710 °C.

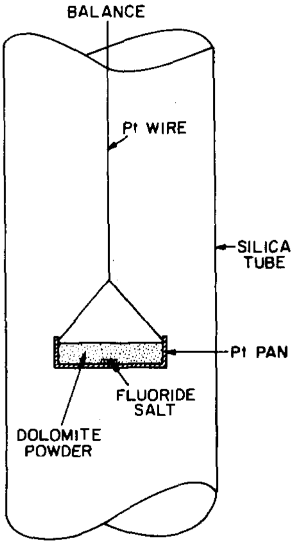


Fig. 6. Schematic diagram of TG apparatus for isothermal decomposition studies of unmixed samples.

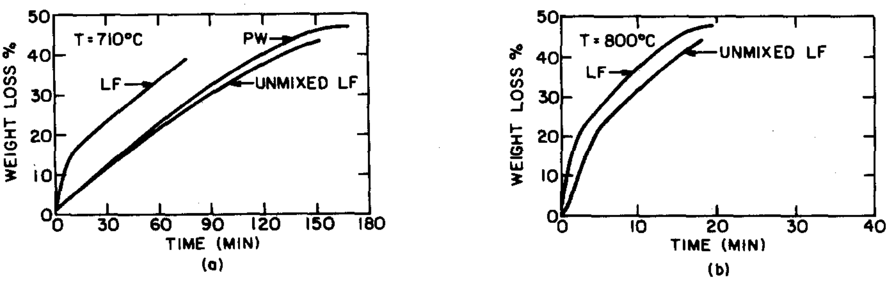
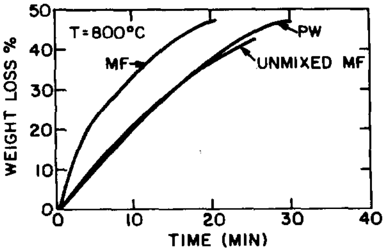


Fig. 7. Isothermal TG results for dolomite samples with uniformly mixed and unmixed LF at (a) 710 °C, and (b) 800 °C.



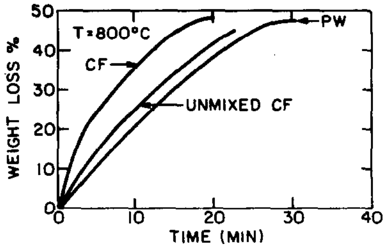


Fig. 8. Isothermal TG results for dolomite samples with uniformly mixed and unmixed MF at 800 °C.

Fig. 9. Isothermal TG results for dolomite with uniformly mixed and unmixed CF at 800 °C.

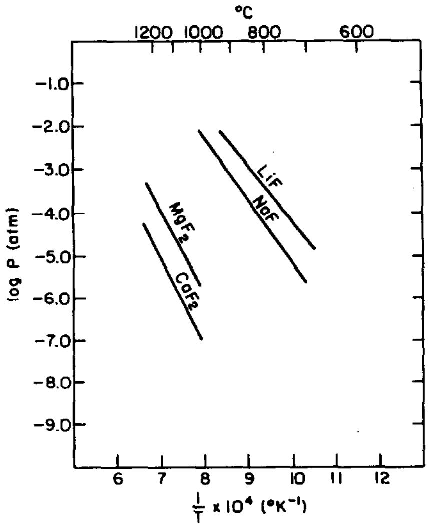


Fig. 10. Vapor pressure of the fluoride salts as a function of temperature.

though most of the dolomite powder is not in direct contact with the fluoride salt.

This can be explained by noting that the vapor pressure of LiF at 800 °C is about 0.417×10^{-4} atm [8] which is high enough to allow LiF to transfer to the whole surface of dolomite powder via a vaporization–condensation mechanism. Since time is required for LiF to vaporize and to penetrate through the voids of the powder bed, it is expected that the weight loss of the unmixed LF would be delayed by a short period relative to that observed for a well-mixed LF sample. Alternatively, an eutectic may be formed which slowly wets the remaining particulate bed.

Figure 10 illustrates the relation between vapor pressure of the fluoride salts and temperature [8–11]. It can be seen from the plot that the vapor pressures of MgF_2 and CaF_2 are much lower than those of LiF and NaF. Therefore, MgF_2 and CaF_2 cannot be transferred to the surface of the dolomite powder by a vaporization process. The requirement of direct contact with the dolomite particles for MgF_2 and CaF_2 to affect decomposition suggests that a liquid phase is formed which acts to enhance the decomposition process.

REFERENCES

1 M. Li and G.L. Messing, Thermochim. Acta, 68 (1983) 1.

2 J.A. Shearer, I. Johnson and C.B. Turner, Bull. Am. Ceram. Soc., 59 (1980) 521.

3 G.F. Knutsen, A.V. Searcy and D. Beruto, J. Am. Ceram. Soc., 65 (1982) 219.

4 D. Beruto, G. Belleri, L. Barco and V. Longo, Ceram. Int., 9 (1983) 53.

5 O.A. Esin, P.V. Geld and S.I. Popel, Zh. Prikl. Khim. (Leningrad), 22 (1949) 354.

6 W.R. Bandi and G. Krapf, Thermochim. Acta, 14 (1976) 221.

7 E.K. Powell and A.W. Searcy, J. Am. Ceram. Soc., 61 (1978) 216.

8 A.M. Evseev, G.V. Pozharskay, An.N. Nesmeynov and Ya.I. Gerasinov, Zh. Neorg. Khim., 4 (1959) 2189.

9 E.E. Lukashenko, V.S. Shapovalov and V.E. Kislov, Zh. Fiz. Khim., 48 (1974) 497.

10 R.R. Hammar and J.A. Pask, J. Am. Ceram. Soc., 47 (1964) 264.

11 D.A. Schulz and A.W. Searcy, J. Phys. Chem., 67 (1963) 103.