Thermochimica Acta, 38 (1980) 125—137
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APPLICATION OF THERMOGRAVIMETRIC ANALYSIS TO THE CALCINATION OF DOLOMITE AT HIGH PRESSURES *

F.H. ROGAN and KUN LI

Department of Chemical Engineering, Carnegie-Mellon University, Pittsburgh, PA 15213 (U.S.A.)

(Received 19 March 1979)

ABSTRACT

A high-pressure TG system in which sample heat-up to an isothermal steady-state condition is reduced to less than 20 sec has been designed and constructed. The system has been used successfully to obtain conversion-time data for the half-calcination of several dolomites of different geographic origins in 7.8—34.0 atm of CO_2/N_2 mixtures at 750—1000°C.

The conversion-time data show a strong dependence of the rate on temperature, but a lack of total or CO_2 partial pressure effect. Except for low conversions at 760°C, all the data can be fitted to the Avrami equation with a value of n equal to 2.

INTRODUCTION

An investigation of the kinetics of the half-calcination reaction of dolomite at high temperatures and pressures, in order to determine the effects of the conditions of half-calcination on subsequent reaction with hydrogen sulfide, was initiated during 1978 in a high pressure TG system described in detail in a previous publication [1]. Two dolomites, Guelph dolomite (Gibsonburg, OH) and Stockbridge limestone (Canaan, CT), supplied by Pfizer Chemicals, were used in the initial experiments [2,3]. Due to the nature of the system, reasonably isothermal conversion-time data were obtained only within the limited temperature range of 700—800°C.

The rate of calcination was found to be nearly independent of the pressure, the CO_2 partial pressure, and the pellet diameter, but to increase rapidly with increasing temperature. At a given temperature, the rate for Guelph dolomite was greater than that for Stockbridge limestone.

Examination of partially reacted specimens by optical microscopy showed that the reaction products first appeared in patches or colonies along the grain boundaries, which grew toward the center of a grain as the reaction proceeded. The internal structure of these colonies could not be fully resolved by optical microscopy, but a general similarity to pearlite colonies growing in austenite could be noted. Furthermore, a conversion-time relation

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* Presented at the 8th North American Thermal Analysis Society Conference, Atlanta, October 15—18, 1978.

of the form for the pearlite reaction, namely the Avrami equation, was also found to fit the data for the half-calcination of dolomite.

In view of these results, it was decided to conduct a new series of experiments with dolomites of different grain sizes in order to determine the influence of grain size on reaction rate. Plans were made at the same time to modify the experimental system to allow isothermal rate data collection over a broader range of temperatures.

MODIFIED EXPERIMENTAL SYSTEM

Design criteria

In the original system, shown in Fig. 1, the sample had to be charged into the reactor before the furnace could be brought up to temperature. Consequently, the sample was exposed to a thermal transient during the heat-up period of the furnace. Considerable reaction could occur during this heat-up transient, especially at steady-state reaction temperatures above about 750°C. The equilibrium CO_2 pressure for dolomite decomposition [4] is very large, even at moderate temperatures (70 atm at 650°C, for example), so that decomposition could not be suppressed during furnace heat-up by the use of high CO_2 partial pressures. Data collection was therefore limited practically to between 700°C (where complete conversion required several hours) and 800°C (at which temperature a sample might be completely reacted before isothermal conditions were established in the reactor). Within even this narrow temperature range, moreover, the data collected were often strongly affected by significant sample decomposition during the initial temperature transient.

To obtain truly isothermal data over a wide temperature range, a means was sought to reduce drastically the sample heat-up time. It was felt that this could best be achieved by arranging to introduce a very small sample rapidly into a preheated reactor. A successful mechanism for this purpose, however, would also necessarily be compatible with the use of a baffle, essential in concurrent studies of the hydrogen sulfide—dolomite reaction, between the balance housing and reaction zone.

In view of the above constraints, a hydraulic piston was chosen for transmitting motion to the sample. Although apparently simpler, construction of an electrically operated winch similar to that used for this purpose by others [5,6] but capable of continuously keeping the suspension wire properly aligned with the small holes in the baffle and balance arm while transporting lightweight samples at high velocity was felt to be not feasible.

Description

The modified experimental system is shown in Fig. 2. Figures 3 and 4 are schematics of the experimental system and the associated gas feeding system, respectively. The major parts of the system are (1) a hydraulic sample transport column containing the piston, (2) a flanged access port through which

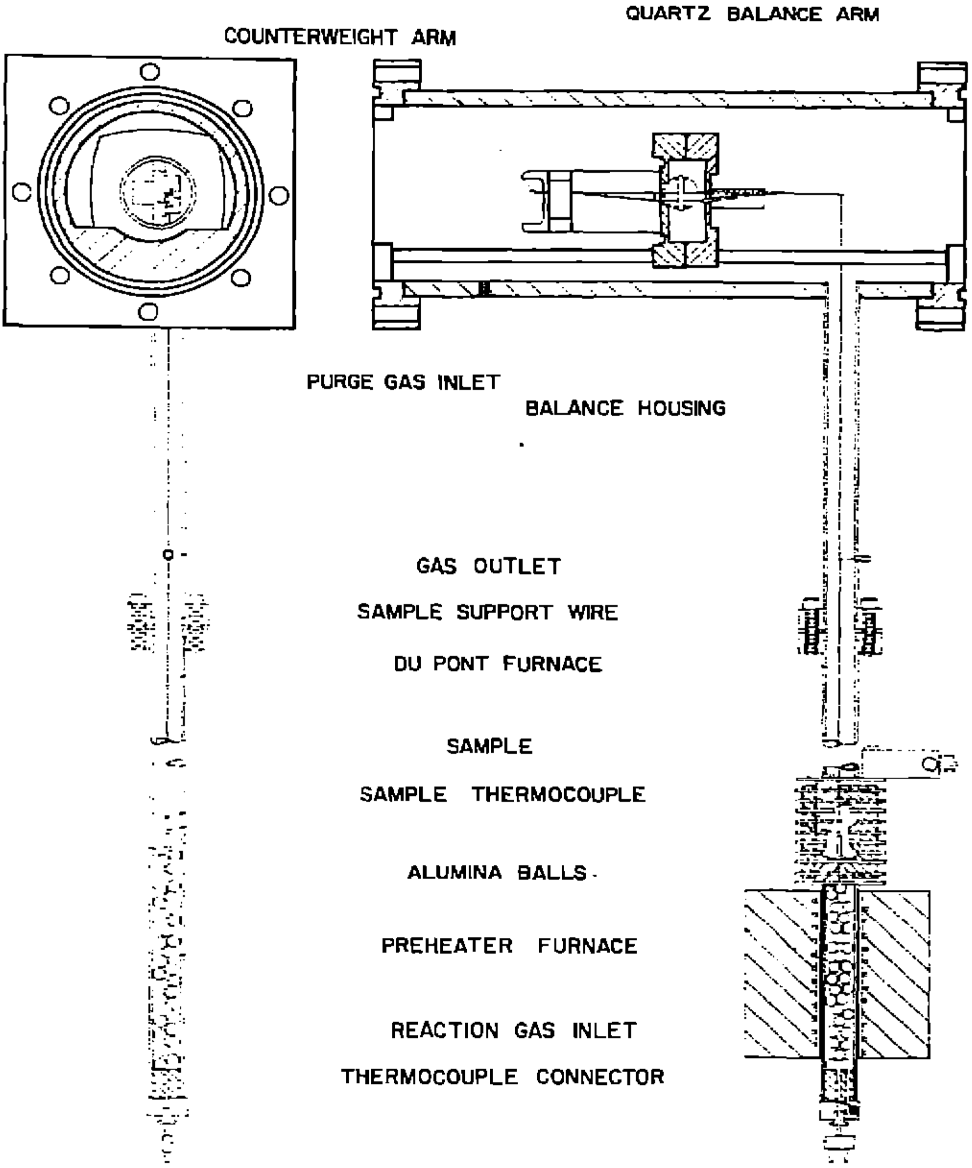

Fig. 1. Cross-section of the earlier experimental system.

one arm of a duPont balance movement can be introduced into the system, (3) a high pressure housing for the duPont balance movement, (4) an access port for introducing samples into the system, (5) a ball valve for isolating the reactor from the remainder of the system, and (6) a 2 ft. long alonized Inconel 617 reactor tube (not shown in Fig. 2).

Figure 5 shows the duPont 951 microbalance movement installed in its high pressure enclosure. In order to reduce overall system volume to a minimum, the large aluminum housing provided for the balance movement by duPont has been removed. A nitrogen purge inlet is provided, positioned so as to minimize the effect of the purge flow on the operation of the balance.

The nitrogen purge, in conjunction with the baffle located at the bottom

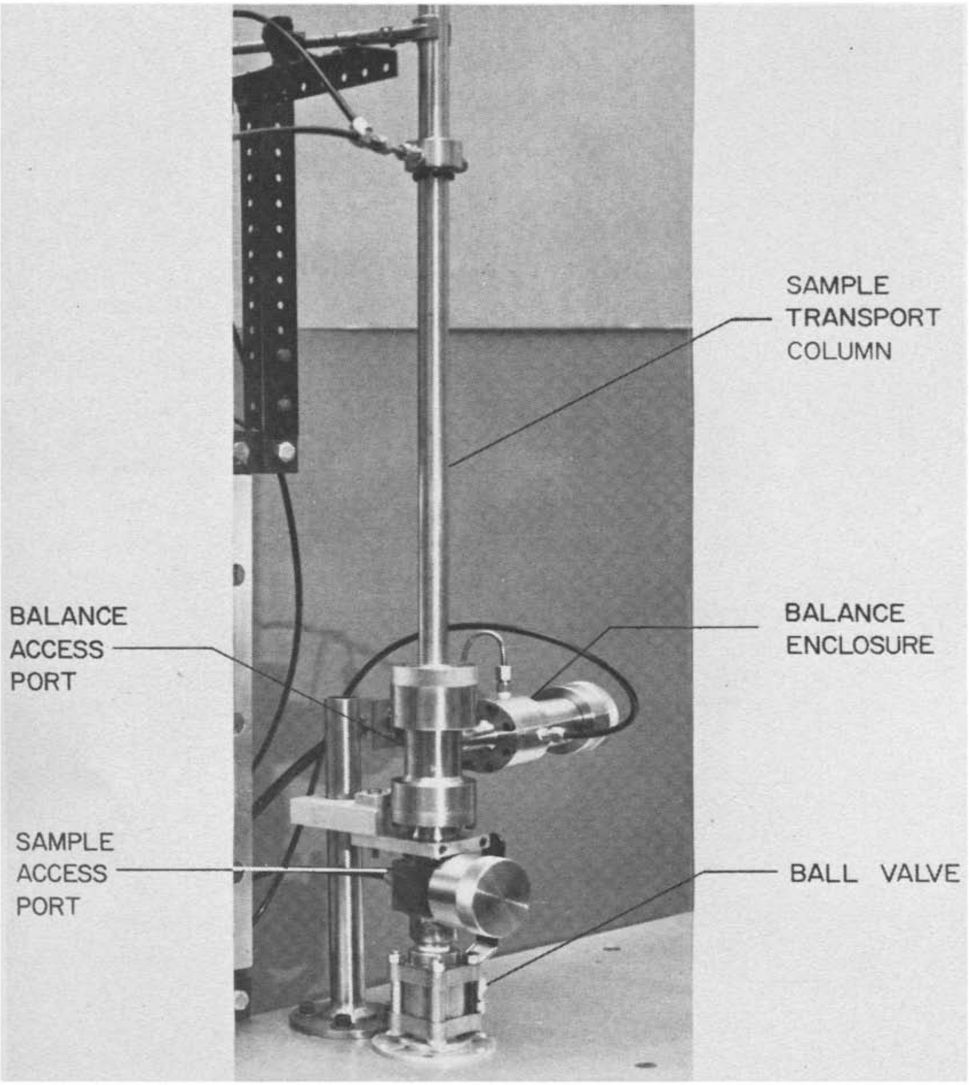

Fig. 2. Photograph of the upper section of the new experimental system showing sample transport column, balance access port, balance high pressure housing, sample access port, and ball valve.

of the balance access port, serves to protect the balance mechanism from the reactant gas, if corrosive. In the present system, the volume contained above the baffle is less than 200 cm^3, while that below the baffle is more than 1 l. Consequently, increasing the setting of the back pressure regulator will tend to cause flow from the balance housing into the reactor. In the former system, the balance housing volume greatly exceeded that of the reactor, so that increases in system pressure tended to force corrosive gases into the balance housing. This problem may have contributed to the several balance mechanism failures which occurred in the former system.

To start a run, the threaded cap just below the balance housing is removed, giving access to the sample basket. A sample is placed in the basket and, if necessary, the balance can be tared by adjusting the weights on the

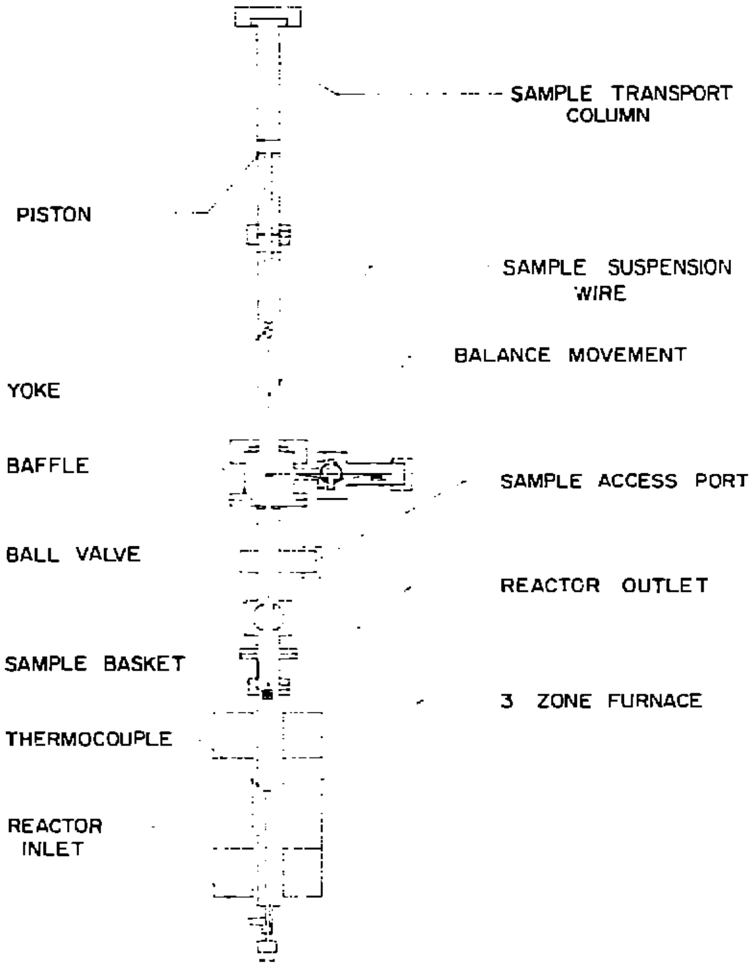

Fig. 3. Schematics of the new experimental system.

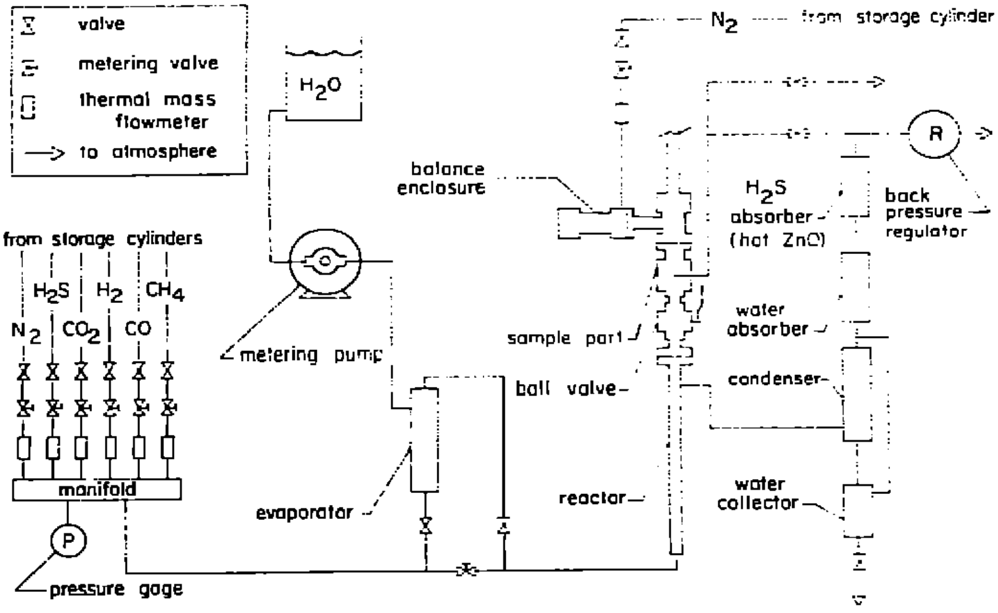

Fig. 4. Schematics of the gas feeding system.

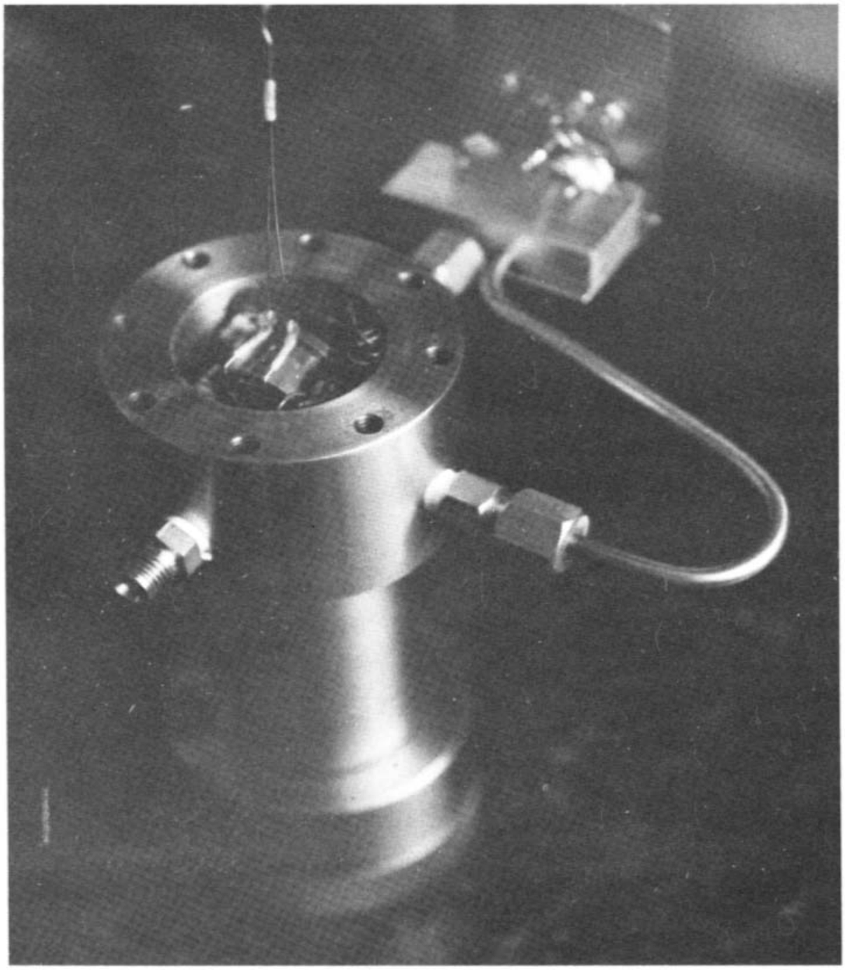

Fig. 5. Photograph of the duPont 951 TGA balance mechanism mounted in the high-pressure enclosure.

counterweight arm of the balance, which is accessible by removing another threaded cap. The threaded caps are leak-tight up to 170 atm when tightened by hand. After taring the balance and closing the access ports, desired steady-state conditions are established in the reactor. Vacuum pump oil at high pressure is then forced through a metering valve into the space above the piston in the sample transport column, causing it to descend. The piston motion is transmitted through a sliding seal in the bottom of the cylinder to a yoke in the lower half of the column by a connecting rod. The sample basket is suspendend by a fine platinum wire from a hook which rests on the yoke while the piston is in transit. As the piston approaches the end of its stroke, the yoke travels beyond the end of the balance arm, causing the hook to be left behind, suspended from the balance arm. Total sample travel during the transfer operation is about 60 cm, and the transit time can be varied from as little as 2 sec up to several minutes by adjusting the metering valve.

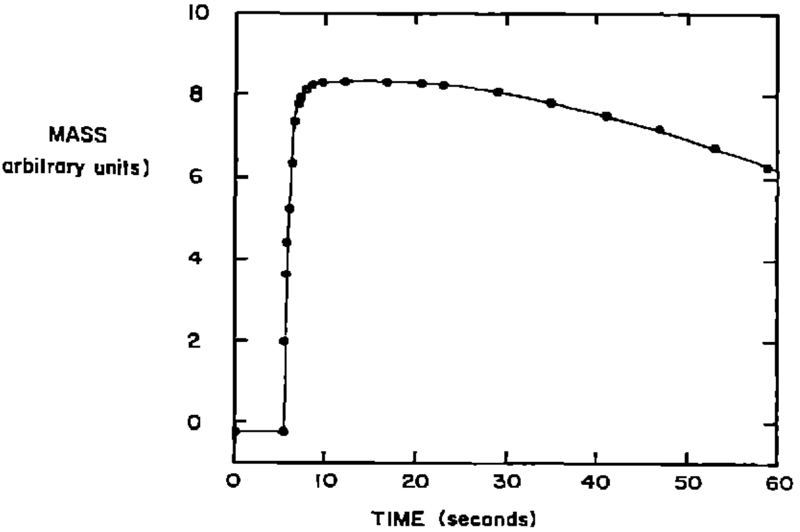

Fig. 6. Typical data obtained with the new experimental system. Half-calcination of a 3.6 mm pellet of Guelph dolomite at 825°C in 15.7 atm of 40% CO_2 in N_2. Flow rate: 1.0 l(STP) min^{-1}.

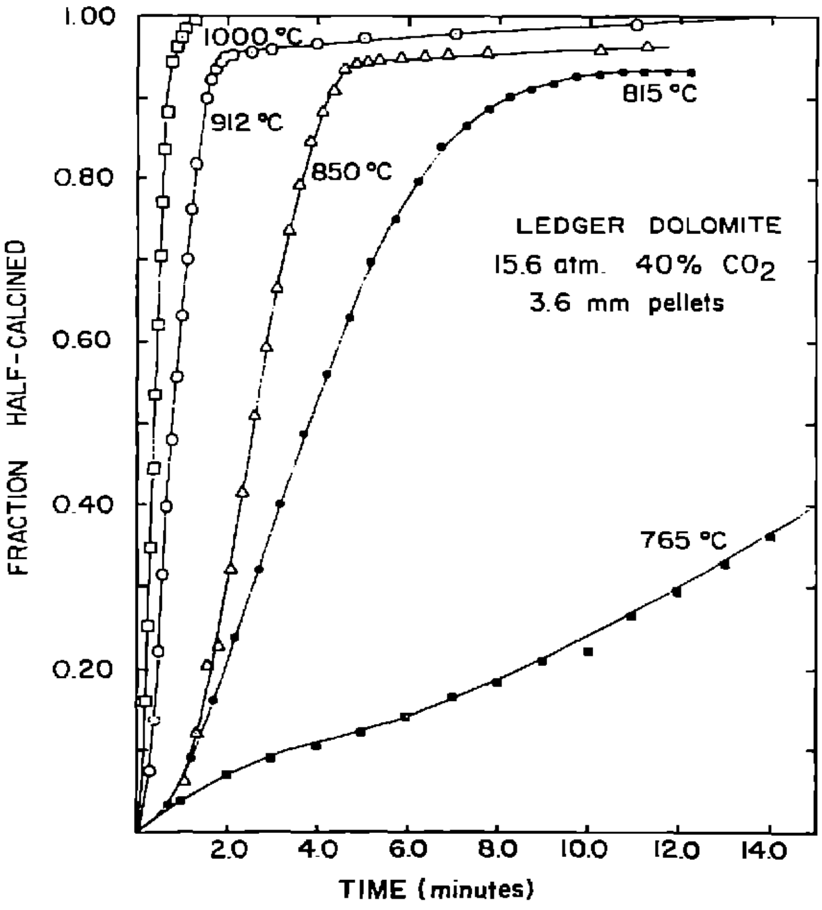

Fig. 7. Progress of the half-calcination of 3.6 mm pellets of Ledger dolomite, in 15.7 atm of 40% CO_2 in nitrogen and different temperatures. Fraction half-calcined = fraction of Mg atoms converted to MgO. Flow rate: 1.0 l(STP) min^{-1}.

EXPERIMENTAL RESULTS

Figure 6 is an example of data obtained with the modified experimental system. The initial minute of the half-calcination of a 3.6 mm sphere of Guelph dolomite at 825°C is shown. The sweep of an X - - Y recorder was begun at the moment the piston was actuated. During the piston travel, in this case requiring just over 5 sec, the balance indicates a negative mass. When the piston leaves the sample suspended from the balance arm, the recording pen rises rapidly to a position corresponding to the initial mass of the sample. The major part of the mechanical and electrical transient resulting in the balance mechanism when the sample is suddenly dropped onto the balance arm is damped out within 2.5 sec, although a small transient signal, in amplitude equal to about 1/4% of the initial sample mass, persists for about 10 sec. For this sample, heat-up to within 1% of the final steady-state temperature required about 38 sec. Sample heat-up is thus the longest of all transient phenomena in the new system, but appreciably shorter than in the former system. The data for the reaction shown are, for

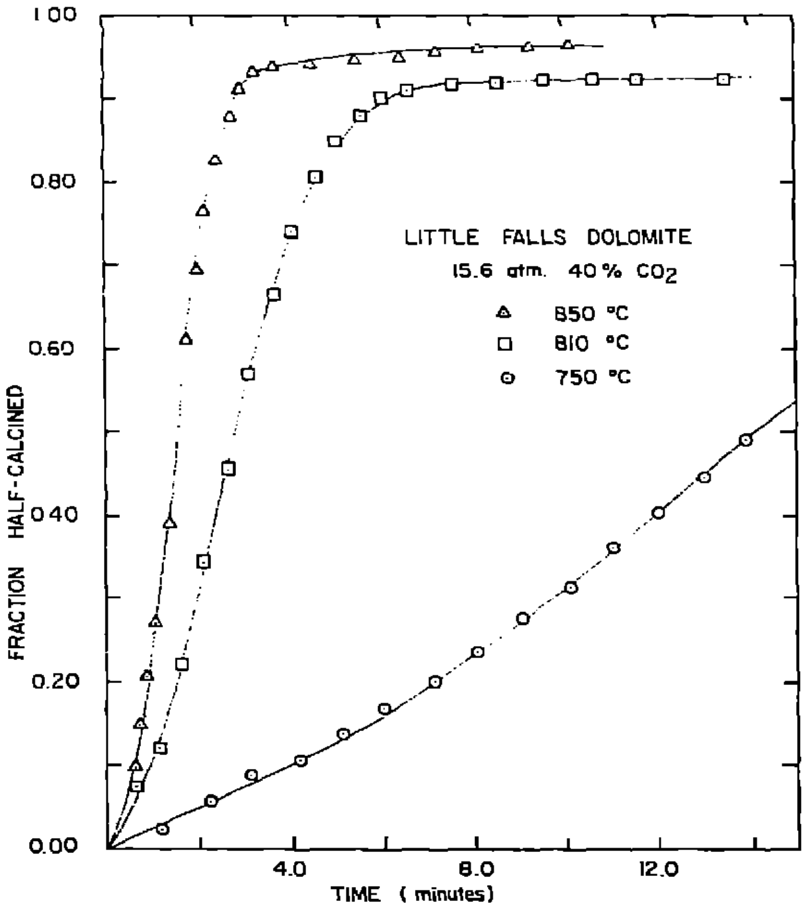

Fig. 8. Progress of the half-calcination reaction of 3.6 mm pellets of Little Falls dolomite in 15.7 atm of 40% CO_2 in N_2 and different temperatures. Fraction half-calcined = fraction of Mg atoms converted to MgO. Flow rate: 1.0 l(STP) min^{-1}.

example, obtained under truly isothermal conditions after 5% conversion. In the former system, the sample could not have been heated to 825° C before decomposition was complete. More rapid heat-up can be achieved by using yet smaller samples. At present, the mininum sample size is 8—10 mg; samples of this size can be heated from room temperature to 800—1000° C in approximately 18 sec. Heat-up time appears not very sensitive to final temperature within the above range.

Conversion-time data are shown in Fig. 7 for Ledger dolomite (from near Norristown, PA) and in Fig. 8 for Little Falls dolomite (from central New York State) at various temperatures between 760 and 1000° C. Data obtained for Tomstown dolomite (from Millville, WV), not shown, are nearly identical to those for Little Falls dolomite. The reaction rate can be seen to be quite sensitive to the temperature, roughly doubling for every 40° C temperature rise above 760° C.

Figure 9 shows the pressure and CO_2 concentration dependence of the half-calcination rate of Guelph dolomite at 1000°C. Increasing the CO_2 partial pressure from 6.25 to 15.66 atm has no apparent effect on the con-

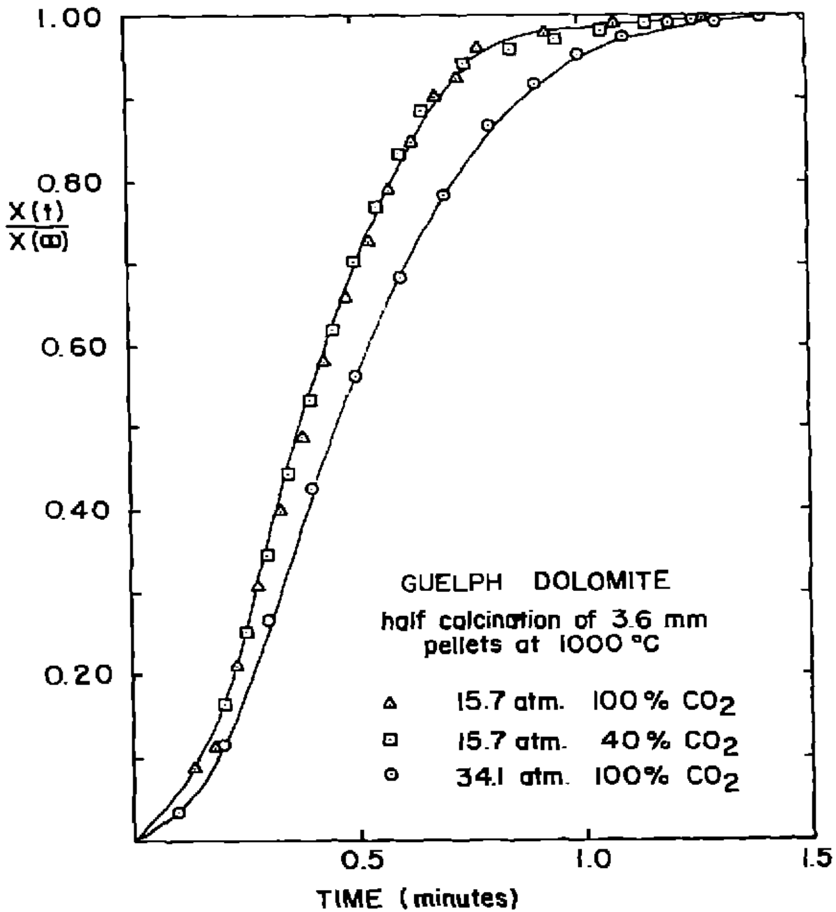

Fig. 9. Progress of the half-calcination reaction of 3.6 mm pellets of Guelph dolomite at 1000°C, illustrating the dependence of reaction rate on pressure and concentration of CO_2. $X(t)$ = fraction of Mg atoms converted to MgO at time t. Flow rate: 1.0 l(STP) min^{-1}.

version-time data, while increasing the pressure by more than a factor of two, from 15.66 to 34.08 atm, slows the reaction only slightly.

Figure 10 is a comparison of conversion-time data obtained for five different dolomites at 760°C in 15.7 atm of 40% CO_2 in N_2. The average grain size was determined by optical microscopy for each of the dolomites. It can be seen that, with the possible exception of Little Falls dolomite, the rate decreases with increasing grain size. In the figure, 100% conversion corresponds to conversion of all of the Mg in the samples to MgO; the Mg content of a sample is based on the Mg content of a representative sample for each dolomite, obtained by wet chemical analysis. The results of the chemical analysis were most uncertain for Little Falls dolomite; generally lower final conversions obtained for this dolomite suggest that the Mg content by chemical analysis may be 2% too high. If an adjustment is made to the data shown in Fig. 10, the conversion-time curves shown for Little Falls and Tomstown dolomites would be virtually identical up to about 55% conver-

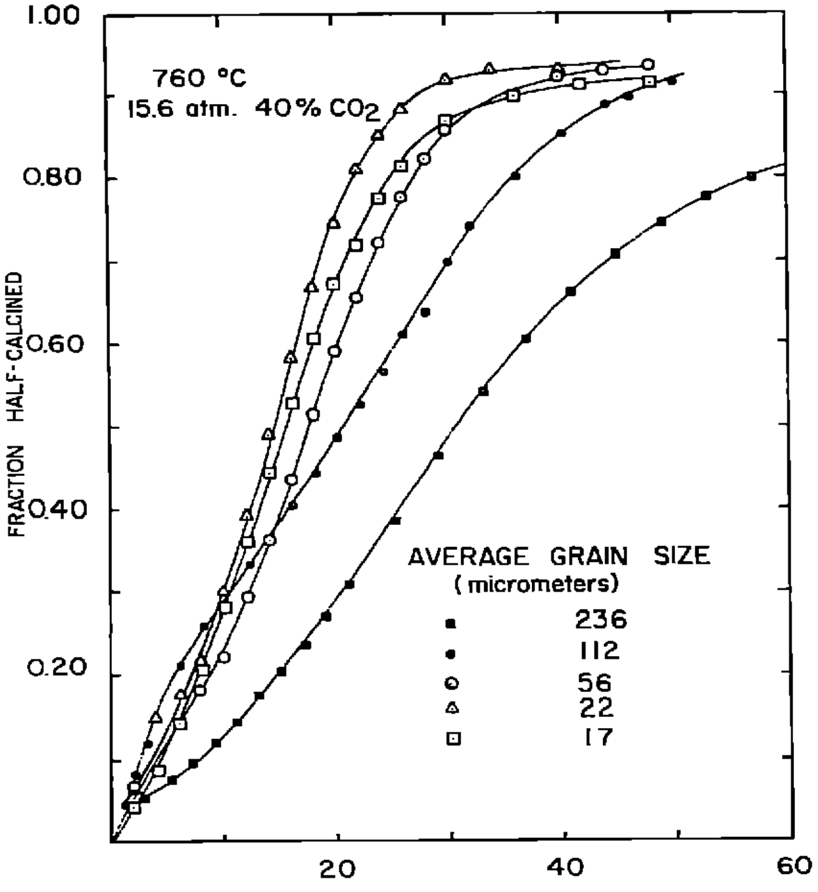

Fig. 10. Effect of grain size on the progress of the half-calcination reaction of dolomite. Dolomites of five geographic origins half-calcined at 760°C in 15.7 atm of 40% CO_2 in N_2. Pellet size: 3.6 mm. Flow rate: 1.0 l(STP) min^{-1}. Fraction half-calcined = fraction of Mg atoms converted to MgO. The correspondence between dolomite and average grain size is: Stockbridge 236 μm; Guelph 112 μm; Ledger 56 μm; Tomstown 22 μm; Little Falls 17 μm.

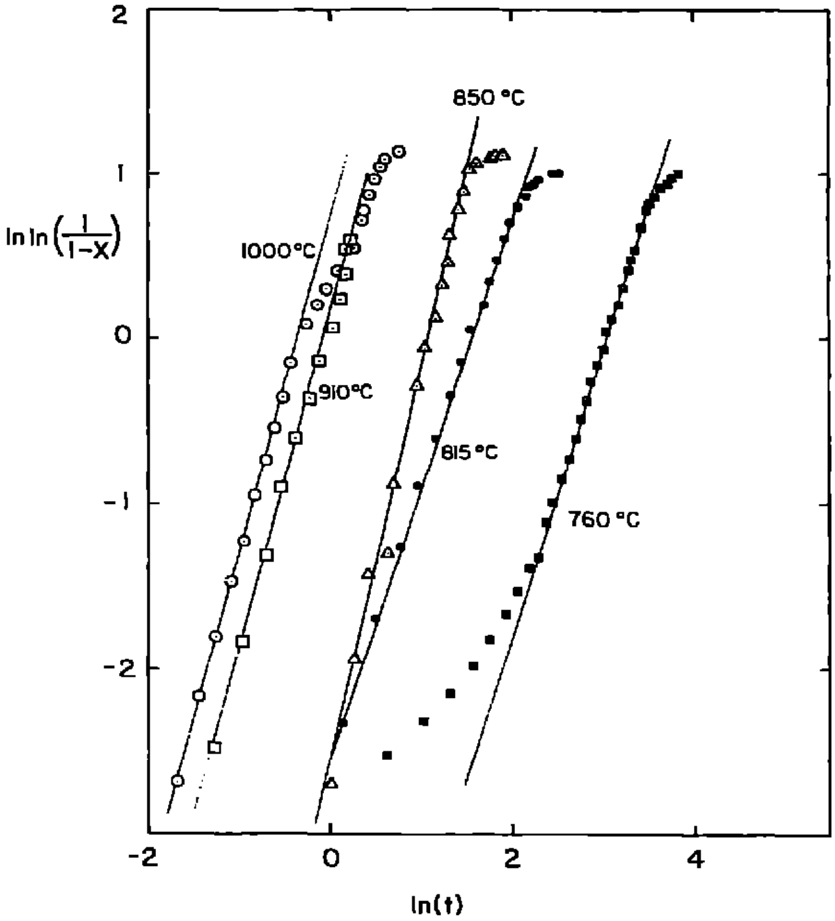

Fig. 11. Data of Fig. 7 plotted as ln ln[1/(1 − x)] vs. ln t.

sion, above which conversion level the rate for Little Falls dolomite again falls behind that for Tomstown dolomite. In either case, however, $t_{1/2}$, the time for 50% conversion, is found to satisfy

$$t_{1/2} = 7.13(\bar{d})^{1/4}$$

within 10%, where $\bar{d}$ is the average grain size in micrometers, and $t_{1/2}$ is given in minutes.

Figure 11 shows the fit of the data of Fig. 7 to the Avrami equation [7]

$$x = 1 - \exp[-\alpha t^n]$$

Each of the points shown in Fig. 7 is plotted in Fig 11 as ln ln[1/(1 − x)] vs. ln t. It can be seen that, except for the data obtained at the lowest temperature, a straight line fits the data for each sample from about 2 to about 90% conversion. The slopes are all near 2, the greatest deviation occurring at 850°C where the slope is 2.5. In Fig. 12, the points shown in Fig. 11 for each run are fitted to a straight line of slope 2. It can be seen that the fit is good for the runs at 1000, 910 and 815°C, and for the 760°C run except for low conversions (below 20% conversion).

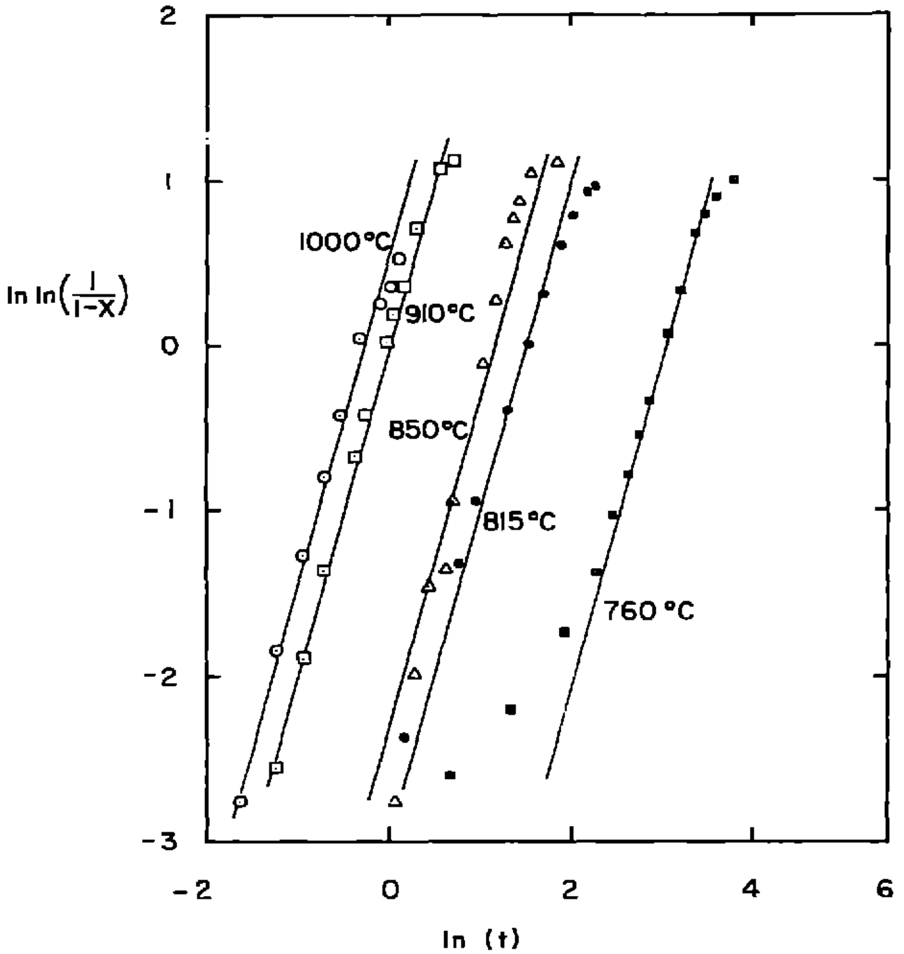

Fig. 12. Data of Fig. 7 fitted to the Avrami equation with the parameter $n = 2$.

CONCLUSIONS

Initial transient effects found in our previous TG system have been drastically reduced by incorporating a hydraulic sample transport mechanism into a modified system recently completed. Performance of the new system has proved highly satisfactory.

Conversion-time data collected in the modified system for the half-calcination of several dolomites show that the rate is independent of total pressure or CO_2 partial pressure, but approximately doubled for a given dolomite for every 40° temperature rise above 760°C. At a given temperature, however, the reaction rate decreased with increasing average grain size. At 760°C, the time for 50% conversion is approximately proportional to the one-fourth power of the average grain size. Except for conversion levels below 20% at 760°C, the conversion-time data for all the dolomites can be fitted to the Avrami equation

$$x = 1 - \exp(-\alpha t^n)$$

with the parameter $n = 2$.

ACKNOWLEDGEMENTS

This work was carried out under Contract No. Ex-76-S-01-2408 from the U.S. Department of Energy. Messrs. J.H. Yen, C.S. Huang, K. Meyer and J. Martin contributed to the construction of the experimental system.

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