Thermochimica Acta, 26 (1978) 257–267

LIMESTONE REACTIVITIES WITH SO_2 AS DETERMINED BY THERMOGRAVIMETRIC ANALYSIS AND AS MEASURED IN PILOT SCALE FLUIDIZED-BED COAL COMBUSTORS*

ROBERT SNYDER, W. IRA WILSON AND IRVING JOHNSON
Chemical Engineering Division, Argonne National Laboratory, Argonne, Ill. 60439 (U.S.A.)

ABSTRACT

A thermogravimetric analyzer was used to measure the reactivity of several limestones with SO_2. The laboratory results can be directly used to predict coal combustion results for pilot-plant atmospheric pressure fluidized beds. Also, the TGA information was fitted to two different straight-line least-squares fits. These equations allowed prediction (by two different methods) of calcium utilization in atmospheric-pressure pilot plant fluidized-bed combustors (FBCs) from knowledge of only the $CaCO_3$ content of the limestone. When the predictions based on laboratory work for seven limestones were compared with the pilot-plant experimental results of Pope, Evans and Robbins, Argonne National Laboratory, Consolidation Coal Co.; and Morgantown Energy Research Center, agreement was good for all three methods.

INTRODUCTION

Fluidized-bed combustion of coal is receiving considerable attention due to its potentially higher efficiency and lower capital costs[1] than conventional methods. In this process, coal is burned in a fluidized bed of a partially sulfated solid SO_2-sorbent (such as limestone or dolomite) at 850–950°C and 101–1010 kPa pressure. The heat of combustion is utilized by generating steam in boiler tubes immersed in the bed with the rest of the heat recovered in a downstream steam generator. The bed material not only helps to transfer heat to the boiler tubes but also captures SO_2. The $CaCO_3$ in the limestone (or dolomite) bed material reacts with SO_2 and O_2 at these operating conditions to form stable $CaSO_4$.

Naturally occurring limestones have been intensively studied[1–7] as bed material because of their high calcium content (for SO_2 removal) and their low cost.

Harvey et al.[8] made an extensive study of the Petrographic characteristics of limestones and attempted to correlate their findings with limestone desulfurization data. O'Neil et al.[9] studied the reaction of specific limestones under a variety of

---

* Presented at the 7th North American Thermal Analysis Society Conference, St. Louis, Missouri, September 25–28, 1977.

conditions (101–1010 kPa and 750–1050°C). The rate of calcination of the limestone was found to have a large effect on the SO_2 capacity of the limestones. Coutant et al.[10] studied 25 limestones; however, he used short residence times and small particles (~100 μm). Potter[11] studied 86 limestones and found that the surface area of pores larger than 0.3 μm in limestone particles was important in the capture of SO_2 but that smaller pores were ineffective. Investigators[12, 13] have attempted to model the limestone–SO_2 reaction process. Most models assume that two diffusional processes occur; the diffusion of SO_2 through pores and the diffusion of SO_2 through a solid reaction product which forms on the pore surfaces or grain surfaces.

Lacking from all of these studies is a method of predicting the limestone reactivity with SO_2 at fluidized-bed coal combustion conditions. When a high-sulfur coal (4% S) is used, approximately 85% of the SO_2 must be retained in the bed material in order to meet EPA SO_2 emission standards. Therefore, process R&D engineers, in reporting results from experimental tests, usually give SO_2 reduction or retention as a function of the molar ratio of calcium (in the limestone)/sulfur (in the coal) in the feed. The calcium utilization of the limestone can then be obtained as follows.

$$U = \frac{R}{\mathrm{Ca/S}} \tag{1}$$

where U = the fraction of the calcium converted to calcium sulfate, R = fraction of sulfur dioxide reduction or retained in bed, and Ca/S = molar Ca/S feed ratio.

The designer of a plant knows the value of R required to meet the EPA SO_2 emission standards for a designated coal and needs to know the Ca/S ratio required, for designated limestone(s), to meet this EPA standard. Therefore, if the calcium utilization, U, for a given limestone can be predicted, then the Ca/S ratio required to meet the EPA SO_2 emission standard, R, can be determined from eqn. (1). However, the limestone calcium utilization, U, is a function of the Ca/S ratio. Obviously, when a Ca/S ratio of 4 is used, the maximum calcium utilization is 0.25. Therefore, for a highly reactive limestone, the calcium utilization will be limited by the availability of SO_2 or the Ca/S ratio, whereas for a limestone which has a low reactivity with SO_2, the calcium utilization will be limited by the reactivity of the limestone. When the value of R is just large enough to meet the EPA SO_2 standard, the minimum required Ca/S ratio is known. The predictions presented below are only for atmospheric fluidized-bed combustion and cannot be directly used to predict pressurized fluidized-bed operating conditions.

EXPERIMENTAL

A thermogravimetric analyzer (TGA), Fig. 1, was used for all kinetic studies. A sample (100–200 mg) was placed in a wire mesh platinum basket and was suspended from one arm of a recording microbalance in a quartz reactor tube. The reactor tube was heated by a platinum-wound furnace which was controlled to ±5°C at tempera-

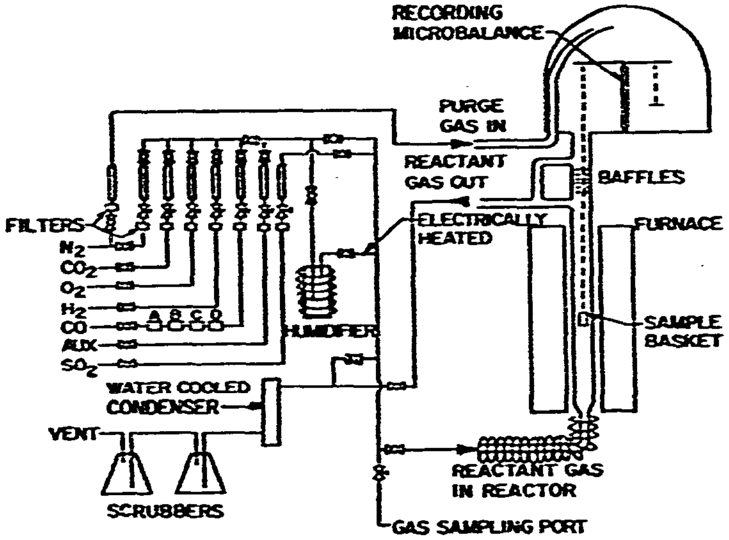

Fig. 1. Schematic diagram of the TGA apparatus.

tures up to 1200°C. Two Pt/Pt–10% Rh thermocouples were used for temperature monitoring and controlling.

The gas mixtures were prepared by blending streams of the individual constituents. Mass spectrometric analyses were made on samples of the final gas mixture to verify its composition; the measured values of the SO_2 and O_2 concentrations were within 5% of the values computed from the flow rates.

The gas mixtures, which reacted with the samples, passed upward through the heated reaction tube and exited through a condenser and a series of scrubbers. A nitrogen purge gas that flowed through the microbalance bell jar kept it free of the corrosive reactant gases.

The TGA unit continuously recorded the weight change of the sample during its reaction with the gas mixture. Therefore, chemical analyses of the sample at the completion of a TGA run were utilized to help determine and quantify the chemical changes which had occurred. The accuracy of the TGA was approximately ±1 mg or approximately ±3% of the total weight change.

RESULTS

Seven limestones which had previously been tested in pilot-scale FBC's were tested for reactivity with SO_2 and O_2 in the TGA. All reactions were performed at 900°C with a 0.3% SO_2–5% O_2 in N_2 synthetic combustion gas. All limestones, sized to −18 +20 mesh (1000 μm), were precalcined in either 20% CO_2 or 100% CO_2 prior to reaction with the synthetic combustion gas.

The conversion of the calcium in the limestone to calcium sulfate is given in Fig. 2 for the seven limestones calcined in 100% CO_2. (For limestones precalcined in 20% CO_2, for which data are omitted, initial reaction rates were the same but total

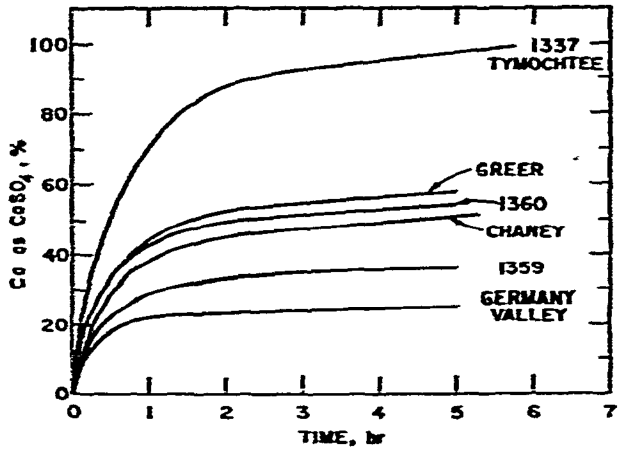

Fig. 2. Conversion of calcium to $CaSO_4$ for several limestones precalcined in 100% CO_2 at 900°C.

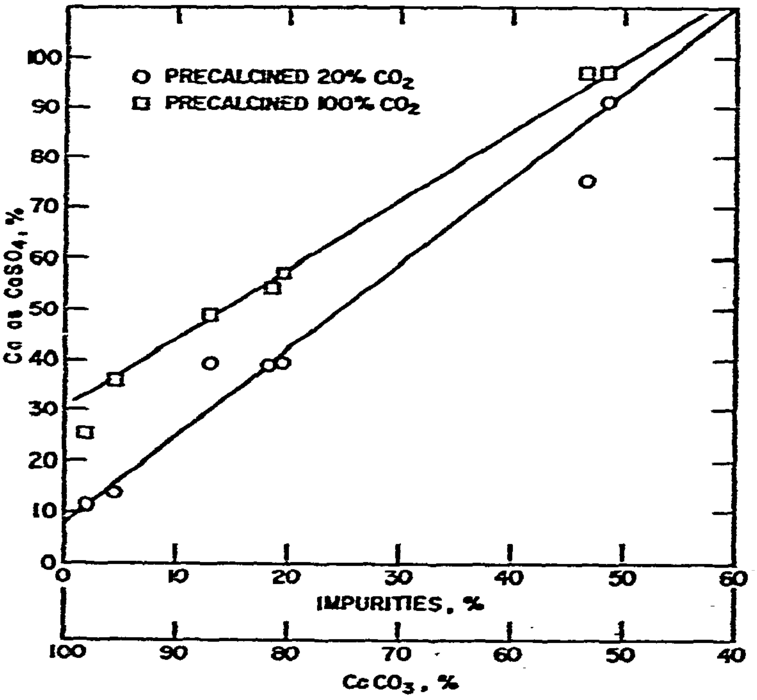

Fig. 3. Calcium utilization in 5 h for various limestones precalcined in 20% or 100% CO_2.

calcium utilizations were lower than when calcined in 100% CO_2.) Reaction is rapid in the first hour and then becomes limited either by the gas–$CaSO_4$ solid diffusion process or by the decrease in the pore diffusion coefficient of SO_2 due to a reduction in pore size[13].

In Fig. 3, the calcium utilization after 5 h is given as a function of $CaCO_3$ content. Increasing the CO_2 concentration of the calcination gas from 20% to 100% increases the time for calcination (from 10–15 min to 1–1½ h), which increases the

TABLE 1

COMPARISON OF PREDICTED AND PILOT PLANT CALCIUM UTILIZATION

Organization	Limestone	Pilot plant results			Predictions (%)			
		Ca/S	Particle residence time (hr)	Calcium utilization (%)	Method 1 TGA data and fluid-bed eqn.		Method 2 [$CaCO_3$], calcined in 100% CO_2	Method 3 [$CaCO_3$] + fluid bed eqn., calcined in 100% CO_2
					Calcined in 20% CO_2	Calcined in 100% CO_2		
PER	Germany Valley	4.9	2.6	16.0	5.2	14.3	17.2	16.5
PER	Germany Valley	2.8	2.6	25.0	6.7	18.7	30.1	24.0
PER	Chaney	3.7	2.6	21.6	17.7	20.4	22.8	22.3
PER	Greer	3.4	3	26.3	21.4	24.4	24.7	24.7
PER	Greer	3.1	2.6	26.6	22.6	26.3	27.2	26.7
PER	Greer	2.9	2.6	27.9	23.6	27.6	29.0	28.1
PER	Greer	2.4	2.6	28.0	25.8	31.5	35.1	31.8
MERC	Greer	5.76		13.6	16.8	17.1	14.6	17.1
MERC	Greer	2.17		40.6	32.6	43.9	38.8	39.5
ANL	1359	2.6	15	20	10.7	28	30.8	30.0
ANL	1359	2.4	15	22	10.8	29	30.8	30.8
ANL	1359	2.6	15	20	10.7	28	30.8	30.0
ANL	1359	2.3	15	36	11.0	29.3	30.8	31.2
ANL	1359	2.5	15	32	10.7	28.3	30.8	30.4
ANL	1359	2.5	15	34	10.7	28.3	30.8	30.4
ANL	1360	2.3	15	32	30.9	38.5	36.6	37.1
ANL	1337	2.2	15	37	42.7	42.4	38.3	43.2
ANL	Tymochtee	1.6	15	54	55.5	56.4	52.6	55.5
ANL	Tymochtee	1.5	15	53	58.5	59.5	56.1	57.3
CCC	Tymochtee	8.0	2.5	12.3	12	12	10.5	12.3
CCC	Tymochtee	4.0	5	23.3	24	24	21.1	24.5
CCC	Tymochtee	1.9	11	47.4	49.5	49.5	44.3	49.7
CCC	Tymochtee	1.5	13	62	59.5	60.3	56.1	58.2
CCC	Tymochtee	0.95	21	82	74	81.5	82.1	62.7
Standard variation						±4.2	±4.3	±5.5

average pore diameter of the calcined limestone, and thus increases limestone reactivity and calcium utilization. There is less effect on dolomitic limestones due to their favorable pore structure created by the conversion of $MgCO_3$ to MgO during precalcination.

Three methods were investigated as possible means of predicting calcium utilization in atmospheric-pressure FBCs using the kinetic information obtained with the TGA. These predictions are shown in Table 1 and are compared with pilot plant experimental results. Pope, Evans and Robbins[2] (PER) determined the desulfurization behavior of Greer, Germany Valley, and Chaney limestones; Argonne National Laboratory (ANL) studied limestones 1359, 1360, 1337, and Tymochtee dolomite. Consolidation Coal Co. (CCC) tested Tymochtee dolomite, and Morgantown Energy Research Center (MERC) tested Greer limestone.

It should be noted that pilot-plant results in Table 1 were for a wide range of operating conditions. The PER combustion runs were done at 815–832°C. The ANL and MERC pilot-plant runs were all performed at 871 °C. The Consolidation Coal Co. runs with Tymochtee dolomite were performed at 982°C. In contrast, all TGA runs were performed at 900°C.

The superficial gas velocities ranged from 0.61 m/sec in the MERC runs to 4.51 m/sec used by PER. Pope, Evans and Robbins used −1/4 in. limestone; 50% by weight of the material was smaller than 30 mesh (600 μm diam.). It would be expected that very little of the material smaller than 30 mesh stayed in the bed for an appreciable time. In the ANL experimental runs, an average particle size of 540–630 μm was used while Consolidation Coal Co. used −16 +28 mesh (1190–1000 μm) material. All TGA laboratory kinetic data was taken using −18 +20 mesh (1000–841 μm) limestone.

The most involved calculation method (method 1 in Table 1) requires the use of the kinetic information (Fig. 2) along with a fluid-bed desulfurization equation developed by Keairns et al.[6], viz.

$$U = \frac{1}{\mathrm{Ca/S}} \left[1 - \frac{V}{kH\varepsilon} \left(1 - e^{-kH\varepsilon/V} \right) \right] \tag{2}$$

where U = calcium utilization, fraction, Ca/S = calcium to sulfur mole ratio, V = superficial gas velocity (m/sec), H = fluidized-bed height (m), ε = bed voidage, assumed to be 0.5, and k = average particle reaction rate constant (sec^{-1}). This fluid-bed desulfurization equation gives the calcium utilization as a function of the "average" reaction rate constant of the particles in the bed (provided the superficial gas velocity and bed height are known). Thus, in order to determine U, the "average" rate constant, k, must be known.

The TGA kinetic information [the slopes of curves in eqn. (2)] gives the instantaneous rate constant, k', as a function of calcium utilization. Therefore, the average limestone calcium utilization, U, is that value at which k and k' are equal (see Kearin et al.[6] for calculation details). The predictions using method 1, shown in Table 1, are also plotted in Figs. 4 and 5 for limestones precalcined in 20% CO_2

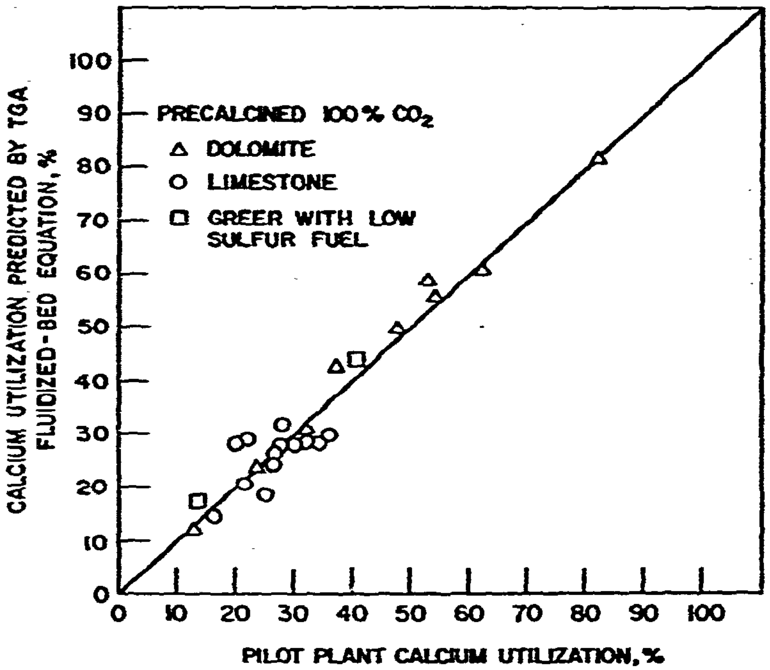

Fig. 4. Predicted calcium utilization via method 1. Limestones precalcined in 20% CO_2.

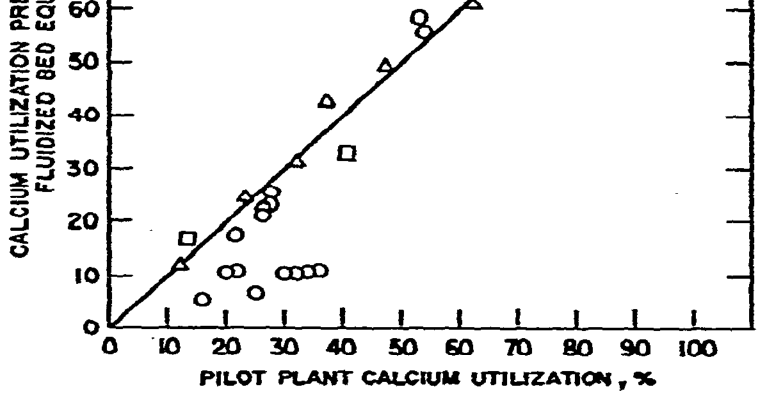

Fig. 5. Predicted calcium utilization via method 1. Limestones precalcined in 100% CO_2.

and 100% CO_2, respectively. For limestones precalcined in 20% CO_2, the agreement between TGA and pilot plant results is excellent for the dolomitic limestones; however, the predicted calcium utilizations for calcitic limestones (1359, Germany Valley, Greer, and Chaney) are low (overall standard deviation of 11). However, for the slowly calcined limestones (Fig. 5), the agreement for all limestones is excellent; the standard deviation is 4.2.

The better agreement for the stone precalcined in 100% CO_2 implies that the limestones when used in a pilot-plant fluidized bed undergo slow calcinations. It is difficult to imagine a high CO_2 concentration in the combustor or a slow rise in particle temperature when it is injected into the bed. Thus, the good agreement between slow-calcination TGA results and pilot-plant results has not been explained. These results also imply that precalcination may provide no enhancement of reactivity. However, the effect of precalcination must still be determined in pilot-plant operation.

The results in Figs. 4 and 5 were obtained from the reaction rate curve for each designated limestone on a TGA and by use of eqn. (2). However, the calcium utilization can be predicted by "method 2" by knowing only the calcium carbonate content of a limestone. The maximum calcium utilization of the limestone (only the slow calcination condition with 100% CO_2 is considered in the remainder of the paper) is shown as a function of $CaCO_3$ content in Fig. 3. If it is assumed that particle residence time in the bed is long (on the order of hours), then there will be maximum utilization of the calcium in the particle, provided that the reaction is not limited by too little sulfur (high Ca/S ratio). For example, for Greer limestone, this method would predict a calcium utilization of 57% (80.4% $CaCO_3$, see Fig. 2) for a Ca/S ratio smaller than 1/0.57 and would predict a calcium utilization of 1/(Ca/S) for a Ca/S ratio larger than 1/0.57. This method, for the seven limestones, predicts values of *U* which are higher than the pilot plant results by approximately 19% (data not included). Since the TGA calcium utilization in Fig. 3 can be predicted from the calcium

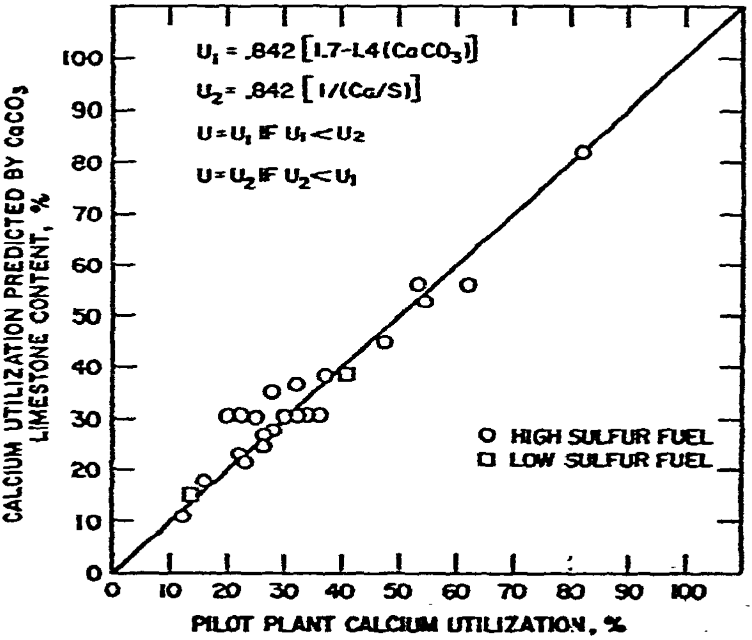

Fig. 6. Predicted calcium utilization via method 2. Limestones precalcined in 100% CO_2.

carbonate limestone content by the use of a straight line fit to the data, the pilot-plant calcium utilization can be estimated by adjusting the results lower by a factor of 0.842 to take into account the high predictions. The equations for method 2 are given below.

$$U_1 = 0.842\ (1.7 - 1.4\ [\mathrm{CaCO_3}]) \tag{3}$$

$$U_2 = 0.842\ [1/(\mathrm{Ca/S})] \tag{4}$$

$$U = U_1 \text{ if } U_1 < U_2 \tag{5}$$

$$U = U_2 \text{ if } U_2 < U_1 \tag{6}$$

where, U U_1, U_2 = calcium utilization, $[\mathrm{CaCO_3}]$ = $\mathrm{CaCO_3}$ content, fraction. Figure 6 (predictions obtained by method 2, also listed in Table 2) shows the good agreement between the pilot-plant experimental results and the calcium utilizations predicted by eqns. (3)–(6) using method 2. The standard deviation is ± 4.3.

The third method also requires only knowledge of the $\mathrm{CaCO_3}$ content of the limestone. The equation for the third method was developed from data used in the first method, which requires plotting of the instantaneous reaction rate constant, k', as a function of calcium utilization, U, for each limestone. This curve is a straight line except at the beginning and end. Except for very high or low Ca/S ratios, the fluid-bed desulfurization curve (k vs. U) and the instantaneous reaction rate curve (k' vs. U) intercept on the straight-line portion of the k' vs. U curve.

It was also found that the straight lines for the various limestones were parallel. A linear equation was obtained for the intercept as a function of calcium carbonate content. With this and the slope of the curves known, an equation was developed

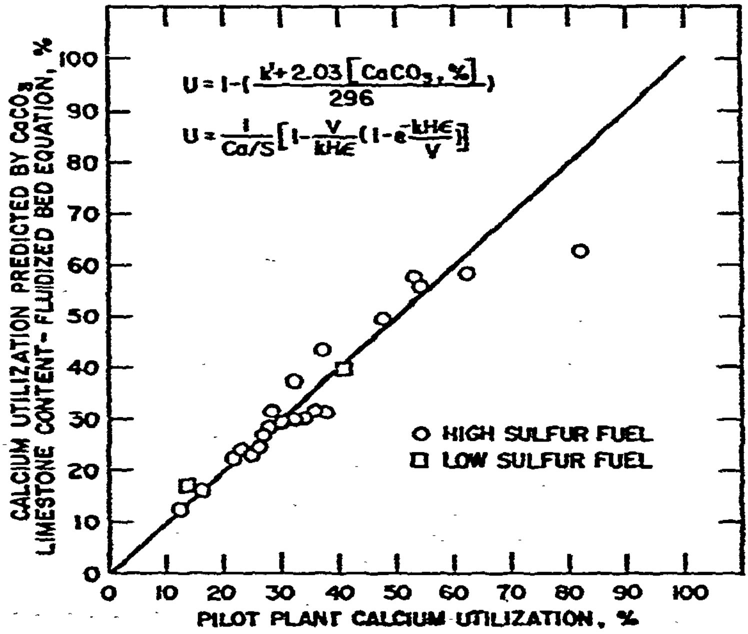

Fig. 7. Predicted calcium utilization via method 3. Limestones precalcined in 100% $\mathrm{CO_2}$.

which predicts calcium utilization as a function of (1) $CaCO_3$ content and (2) the instantaneous rate constant. Using this equation in conjunction with the fluid-bed desulfurization equation, eqn. (2), allows the pilot-plant calcium utilization to be predicted from only the limestone calcium carbonate content, Ca/S ratio, superficial gas velocity, and bed height:

$$U = 1 - \left(\frac{k + 2.03\,[\mathrm{CaCO_3}]}{296}\right) \tag{7}$$

$$U = \frac{1}{\mathrm{Ca/S}}\left[1 - \frac{V}{kH\varepsilon}\left(1 - \mathrm{e}^{-kH\varepsilon/V}\right)\right] \tag{2}$$

U is then the predicted calcium utilization when $k' = k$.

The comparison between predicted and experimental results is shown in Fig. 7 (also in Table 1 under method 3). Except for one point for Tymochtee dolomite for which a low Ca/S ratio of 0.95 was used, the correlation is excellent (a standard deviation of ±3.9 with one point excluded; for all points, a standard deviation of 5.5).

Predicted results are in good agreement with pilot plant results using all three methods. However, the predictions are more reliable using method 1 which requires kinetic TGA information and the fluid-bed desulfurization equation.

CONCLUSIONS

A number of methods can be used to predict desulfurization performance of a specific limestone in fluidized-bed combustors for a specified Ca/S ratio. One method requires only knowledge of the $CaCO_3$ content of the limestone. Another requires knowledge of the $CaCO_3$ limestone content, the superficial gas velocity, and the fluidized-bed height. Both methods give good predictions of FBC limestone performance. Method 1, which is even more reliable, requires determination of the conversion of Ca to $CaSO_4$ as a function of time for the particular limestone, using a thermogravimetric analyzer. The standard deviation between predicted and experimental results was ±4.2. In all of these methods, kinetic data was obtained on slowly calcined limestones (1–1½ h in 100% CO_2). Limestones calcined in 20% CO_2 (in 15 min) did not correlate with FBC desulfurization results.

The designer of an atmospheric pressure FBC plant may wish to screen potential limestones near a plant site location by using methods 2 or 3. Potentially attractive limestones could then be tested in a TGA for more reliable estimates of their desulfurization potentials.

ACKNOWLEDGMENTS

This work was performed under the auspices of the U.S. Energy Research and Development Administration. We would like to thank A. A. Jonke, D. Webster, and L. Burris for their support and guidance. We would also like to thank K. Jensen for his analytical assistance and J. Simmons the Technical Editor.

REFERENCES

1 G. J. Vogel, L. Johnson, P. Cunningham, B. Hubble, S. Lee, J. Lene, J. Montagna, F. Nunes, S. Siegel, G. Smith, R. Snyder, S. Saxena, W. Swift, G. Teats, C. Turner, I. Wilson and A. Jonke, *A Development Program on Pressurized Fluidized-Bed Combustion*, ERDA Report No. ANL/ES-CEN-1016, Argonne, Illinois, July 1976.

2 J. E. Mesko, *Multicell Fluidized-Bed Boiler Design, Construction, and Test Program*, ERDA Report No. FE-1237-Q76-3, March 1976.

3 S. S. Strom, T. E. Dowdy, W. C. Lapple, J. B. Kitto, T. P. Stanoch, R. H. Boll and W. L. Sage, *Preliminary Evaluation of Atmospheric Pressure Fluidized-Bed Combustion Applied to Electric Utility Large Steam Generators*, EPRI No. RP 412-1 interim report, Alliance, Ohio, February 1976.

4 R. L. Gall, J. S. Mei and J. S. Wilson, *Fluidized-Bed Combustion Test of Low-Quality Fuels. I. Anthracite Refuse*, Morgantown Energy Research Center, Morgantown West Virginia, May 1977.

5 R. C. Hoke, R. R. Bertrand, M. S. Nutkis, D. D. Kinzler, L. A. Ruth and M. W. Gregory, *Studies of the Pressurized Fluidized-Bed Coal Combustion Process*, EPA-600/7-76-011, Exxon Research and Engineering Company, Linden, New Jersey, September 1976.

6 D. L. Keairns, D. H. Archer, J. R. Hamm, S. A. Jansson, B. W. Lancaster, E. P. O'Neill, C. H. Peterson, C. C. Sun, E. F. Sverdrup, E. J. Vidt and W. C. Yang, *Fluidized-Bed Combustion Process Evaluation, Phase II, Pressurized Fluidized-Bed Coal Combustion Development*, EPA-650/2-75-027-C Westinghouse Research Laboratory, Pittsburgh, Pennsylvania, September 1975.

7 N. H. Coates (Editor), *Fluidized-Bed Combustion*, Mclean Virginia, 1975, Mitre Corporation, 1976.

8 R. D. Harvey, R. R. Frost and J. Thomas, Jr., *Petrographic Characteristics and Physical Properties of Marls, Chalks, Shells, and their Calcines Related to Desulfurization of Flue Gases*, EPA-650/2-73-044, Illinois State Geological Survey, Champaign, Illinois, September 1973.

9 E. P. O'Neil, D. L. Keairns and W. F. Kittle, *Thermochim. Acta*, 14 (1976) 209.

10 R. W. Coutant, J. S. McNulby, R. E. Barrett, J. J. Carson, R. Fischer and E. H. Longher, *Investigation of the Reactivity of Limestone and Dolomite for Capturing SO$_2$ from Flue Gas*, Battelle Memorial Institute Columbus, Ohio, August 1968.

11 A. Potter, *Am. Ceram. Soc. Bull.*, 48 (1969) 855.

12 R. L. Pigford and G. Sliger, *Ind. Eng. Chem. Process Des. Dev.*, 12 (1973) 85.

13 M. Hartman and R. Coughlin, *A.I.Ch.E. J.*, 22 (1976) 490.