

A TG method for evaluation of limestone sorbents used in circulating fluidized bed combustors ^a

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Abstract

A thermogravimetric (TG) technique has been developed to study the sulphation of limestone sorbents destined for use in circulating fluidized bed (CFB) combustors. This technique accommodates larger sample sizes (1–5 g) than the established TG method and hence more representative samples in terms of particle size distribution. The sample is dispersed in a quartz wool matrix to simulate the typical CFB void fractions encountered by the limestone particles and to minimize the bulk phase diffusion resistance. Gas mixtures of typical CFB composition (0.5% SO₂, 2–5% O₂, 10–15% CO₂, balance N₂) are passed through the calcined limestone sample.

The sulphation rates of six Canadian limestones were studied using this technique. The results indicate that the sulphation of the limestones is well described by a power law dependence on the fraction of unconverted material available. Results obtained for overall sulphation capacities compare favourably with the results from the fluidized bed reactor (FBR) method, indicating that the technique is an effective and simple method for screening sorbents.

INTRODUCTION

Several methods for evaluating limestone sorbents for fluidized bed combustion use have been developed by past investigators [1,2]. The aim of these methods is to allow the prediction, from bench scale test data, of the sulphur removal performances of limestones during combustion. Thermogravimetric (TG) analysis and the fluidized bed reactor (FBR) are the two most widely used techniques.

The established TG method [3,4] generally uses very small samples (15–100 mg) owing to the limitations of bulk gas phase mass transfer to the centre of a larger, heaped sample in a sample pan. This necessitates the use of a particle size which is small enough for the sample to be representative. In general, this method can yield good intrinsic kinetic data, but the

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prediction of actual limestone performance is often unsatisfactory. This is caused by the complications of the pore plugging effect, which is less pronounced in smaller particles ($d_p < 10 \mu\text{m}$), and by the inability of the TG method to take into account the physical phenomena, such as attrition and elutriation, observed in fluidized beds.

The FBR method [5] generally uses an inert bubbling bed (e.g. sand), synthetic flue gas and significantly larger samples (5–10 g). The limestone sample is dropped batchwise into the bed and the exit gas is continuously monitored for SO_2 concentration. This method produces a physical environment which better approximates the actual combustor. It offers satisfactory predictions of limestone performance in bubbling fluidized bed combustors when the data are combined with a fluidized bed combustor (FBC) model [5]. However, there are some limitations to this method. A narrow particle size fraction (around 1 mm) has been adopted as part of the standard technique in order to avoid elutriation losses. Moreover, there is generally no provision for recycling in the reactor configuration. These two factors are likely to lead to the over-prediction of the limestone requirement since there are usually fines in limestone feeds, as well as provision for ash recycle in actual combustors, both of which tend to increase the average limestone utilization. In addition, the FBR method cannot be easily extended to include limestone samples destined for use in circulating fluidized bed (CFB) combustors. The average particle size used in a CFB is about 150–300 μm , which will cause significant elutriation losses in the FBR method.

These considerations led to the development of the present technique, which is an attempt to fill the need for a simple and effective method for predicting limestone requirements in CFB combustors. It is based on a large sample TG analyzer (up to 5 g) with improved reactor configuration and a unique sample loading technique. The TG system offers the possibility of the direct measurement of the reaction rate as well as the easy control of experimental parameters such as gas concentration and reaction temperature. The present report describes the technique in detail and explores how the data may be used to predict limestone requirements for CFB combustors.

THEORY

The reaction between calcined limestone and sulphur dioxide has been studied extensively and many reaction models have been proposed [1,6]. It is generally accepted that the principal route of the reaction under fluidized bed combustion conditions is



It has been found that the rate dependence on the O_2 concentration is

almost negligible at the oxygen levels normally employed, and that the limiting step is the adsorption of sulphur dioxide with a first order dependence on SO_2 concentration [7,8]. If the adsorption of the SO_2 molecule onto the unreacted CaO sites is assumed to be the rate controlling step, then a plausible reaction rate expression is

$$\frac{d\alpha}{dt} = kC_g [D - \alpha]^n \quad (2)$$

where k is the rate constant, C_g is the local SO_2 concentration, D is the maximum achievable conversion of the calcium oxide, α is average conversion of the bed material and n is the reaction order to be determined. Thus, the rate is dependent upon the extent of conversion and will decline as the reaction progresses. This is perhaps a rather simplistic way of accounting for the very complex phenomena arising from pore closing but, as shown below, it can offer explicit predictions of limestone performance in CFBs by using, in an appropriate CFB model, parameters which are determined from simple TG experiments.

In CFB combustors the gas is essentially plugflow and the solids are generally assumed to be well mixed. A time averaged mass balance of the SO_2 gives

$$U \frac{dC_g}{dx} = g - r \quad (3)$$

where U is the superficial gas velocity, x is the axial position, g is the SO_2 generation rate and r is the SO_2 depletion rate (which equals the sorbent reaction rate). If we further assume that the SO_2 is generated uniformly across the base of the combustor only and nowhere else, i.e. $g = 0$ for all $x > 0$, then substitution of eqn. (2) into eqn. (3), followed by rearrangement and integration, gives

$$C_{gx} = C_{g0} \exp \left[- \frac{k}{U} (D - \alpha)^n x \right] \quad (4)$$

where k and n must be evaluated for each limestone feed. The present TG technique offers the possibility of using the limestone feed as is, rather than using an effective particle diameter as called for by the established TG method and the FBR method. It is worthwhile to examine whether the sulphation of such a sample can be represented by eqn. (2). If so, the parameters k and n could then be used in a CFB model under development to yield better predictions of limestone performance.

EXPERIMENTAL

The present technique uses a Cahn 1000 Electrobalance, which can accommodate a maximum weight change of 10 g. In practice, a sample of 1–5 g can be used in the test. This sample size is large enough to provide

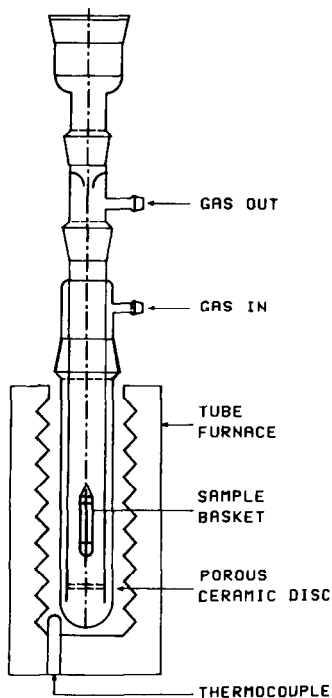


Fig. 1. Schematic diagram of the TG reactor assembly.

representative samples of most CFB combustor limestone feeds as received. The major problem associated with a large sample in a static environment such as this is the increased diffusional resistance to mass transfer between the bulk phase reactant and the particles. This problem is resolved by using a unique method for loading the samples, as described below.

The sample holder is a cylindrical basket made entirely from 1 mm quartz rods to provide the maximum number of openings for the gas flow. It has an inside diameter of 12 mm and is about 35 mm long. The limestone sample is pre-weighed and carefully loaded into the basket interlaced with thin layers of quartz wool. This procedure produces loaded samples that are dispersed in a loosely packed quartz wool matrix, thus minimizing the bulk phase diffusional resistance to mass transfer. The calculated minimum void fraction of the loaded sample basket is $\sim 90\%$ with the typical value being $> 95\%$. These void fractions approximate those encountered by the solid particles in actual CFB environments.

A custom-made annular quartz reactor assembly (Fig. 1) fits inside a 70 mm diameter tubular furnace which is controlled by an RKC PS-962 programmable temperature controller. A loaded sample is suspended from a quartz wire in the centre of the reactor chamber. The synthetic flue gas flows through a porous ceramic disc and into the chamber. This ceramic disc serves two important functions: it imposes a back pressure, thus ensuring

TG DESIGN CALCULATIONS: CANMET/CAHN 1000

BASIC INPUT PARAMETERS

Operating temperature(=T1), deg C	850
Operating pressure(=P1), mm Hg	760
Room temperature(=Tr), deg C	25
Molecular wt. of the gas, g/mol	29
True density of sample, kg/cu m	2000
Max gas flowrate @ STP, cc/min	550
Total sample weight, g	1
Delta(expected max weight change), g	0.5
Hangdown tube inside diameter, mm	30
Sample pan diameter, mm	15

CALCULATED PARAMETERS

Gas density @ T1 & P1, kg/cu m	0.314726
Kinematic viscosity of gas, sq m/s	0.00013
Area of tube, sq cm	7.068583
Area of pan, sq cm	1.767145
Pan/tube area ratio (must be <0.33)	0.25
Max gas velocity at Tr, cm/s	4.887002

DETERMINATION OF THE DRAG FORCE

Flow direction(+1 if down, -1 if up, and "0" if flow is horizontal)	-1
Operating pan Reynold's no.	10.57692
Operating tube Reynold's no.	21.15384
Drag formulation for $2 < Re < 500$:	4.493203
Drag formulation for $Re < 2.0$	2.269090
Drag coefficient, Cd	4.493203
Total Drag force, N (x1000)	-0.00186
Drag/Delta ratio, %	0.038068

SPECIAL NOTE: The buoyancy results from the volume of the sample, suspension wire & pan. It becomes significant when the net sample weight is small. The cells below calculate the buoyancy based on the total volume, including sample pan and suspension wire.

VOLUME DUE TO SAMPLE

Void in packed sample	0
Sample volume, cc	0.5

VOLUME DUE TO SUSPENSION WIRE

Wire diameter, mm	0.3
Wire length, mm	550
Volume of the wire, cc	0.038877

VOLUME DUE TO SAMPLE PAN/BASKET

Note: Basket volume is estimated as a length of wire; pan volume must be calculated with the appropriate formula.

Quartz basket wire diameter, mm	1
Total wire length used in basket, mm	400
Total volume of the basket, cc	0.314159

DETERMINATION OF THE BUOYANT FORCE

Total Volume, cc	0.853036
Buoyant force, N (x1000)	-0.00263
Buoyancy/Drag ratio	1.410459
Buoyancy/Delta ratio, %	0.053694
NET CORRECTION NECESSARY, g	-0.00045

Fig. 2. Spreadsheet of TG reactor design calculations.

that the gases are well mixed and evenly distributed by the time they reach the sample, and it also serves as an excellent heat transfer medium. The reactor was designed as a hangdown tube for the Cahn 1000 Electrobalance. The balance mechanism is protected from the corrosive reaction gas by a small counter-flow of N_2 through a flow constriction funnel located just above the exit sidearm. Design calculations were performed using a spreadsheet which determines the drag and buoyant forces for combinations of the variable experimental parameters (maximum gas flow rate, sample holder size, reactor diameter, sample weight). As shown in Fig. 2, the design was thus optimized to provide a negligible net correction for buoyancy and drag.

At the beginning of each run the furnace is quickly brought to the operating temperature, 850°C , and is then raised over the reactor tube with

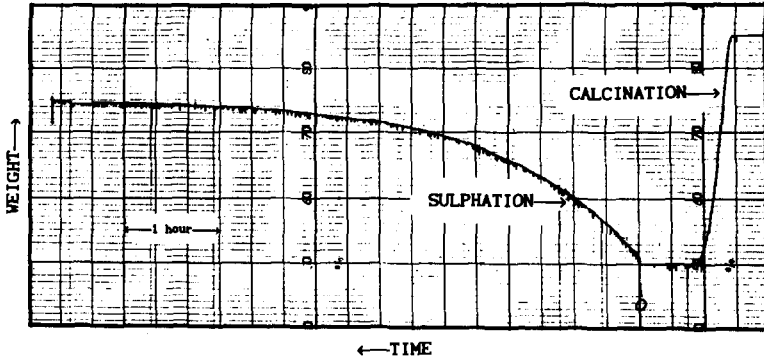


Fig. 3. Typical weight versus time trace (Havelock, 850–1000 μm).

nitrogen flowing through the reactor at $\approx 450 \text{ ml min}^{-1}$. The weight loss begins almost immediately, owing to calcination, and is recorded on a pen plotter. The calcination proceeds quickly, and is usually complete after about 20 minutes, when there is no further weight change. The total content of CaO (or CaCO_3 , and thus the purity of the limestone) is calculated assuming that the weight loss during calcination is due only to the evolution of CO_2 from CaCO_3 . The sulphation step is then initiated by admitting a gas mixture ($\approx 550 \text{ ml min}^{-1}$) consisting of SO_2 (0.5%), O_2 (2.5%), CO_2 (15%), and the balance N_2 through the reactor. The flow of each gas is controlled by a Matheson mass flow controller. The reaction rate was found to be independent of gas flow rate over the range 550–1100 ml min^{-1} . The sulphation step is carried out until the weight change is no longer appreciable, which may take up to 8 h, depending on the limestone. A typical weight versus time trace is shown in Fig. 3. The weight versus time plot is used to extract the reaction rate data and the maximum conversion to sulphate.

The sulphation reactions of two Canadian limestones, Havelock and Athabasca, were studied using this technique in order to assess the validity of the power law representation (eqn. (2)). The analyses of these two limestones are given in Table 1. Four additional limestones from Nova Scotia were also tested in order to compare this technique with the FBR method. The analyses of these samples are given by Richards et al. [9].

RESULTS AND DISCUSSION

Athabasca and Havelock

In order to determine whether the sulphation of these limestones can be represented by eqn. (2), the maximum conversion (D) for each sample was calculated, and then the log–log plot of the reaction rate ($d\alpha/dt$) versus fraction unconverted ($D - \alpha$) for each of the runs was made. The maximum

TABLE 1

Analysis of limestone samples (wt%)

	Havelock	Athabasca
LOI ^a	42.6	35.2
Ash	57.4	64.8
CO ₂	—	33.8
CaO	55.3	41.2
MgO	0.68	1.2
SiO ₂	0.94	13.6
Al ₂ O ₃	0.94	3.3
Fe ₂ O ₃	0.53	1.4
SO ₃	—	1.4

^a Loss on ignition.

conversion and the slope and intercept of the regression fitted lines from the log-log plots (Figs. 4 and 5) are given in Table 2.

The results for the Havelock samples (Fig. 4) show that the slopes for the runs agree well, but the intercept values are quite different. This is not the case for the Athabasca runs (Fig. 5) where all the data seems to fall together in one line with the slope being very close to 1.0. Since the only other variable studied here is the particle size, this would suggest that the Athabasca limestone might be more homogeneous than the Havelock. The physical properties which govern the sulphation, such as porosity and pore

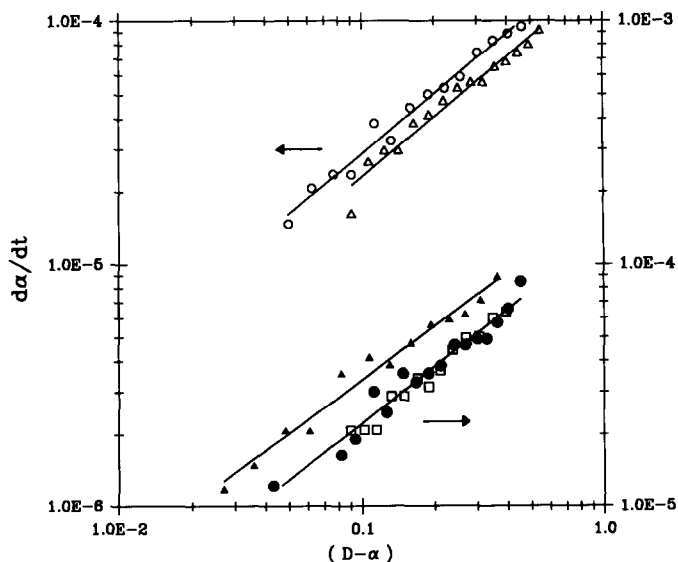


Fig. 4. Plot of reaction rate ($d\alpha/dt$) versus fraction unconverted ($D - \alpha$) for Havelock samples: (□) 850–1000 μm ; (○) 600–850 μm ; (▲) 300–500 μm ; (●) 212–300 μm ; (▲) < 850 μm .

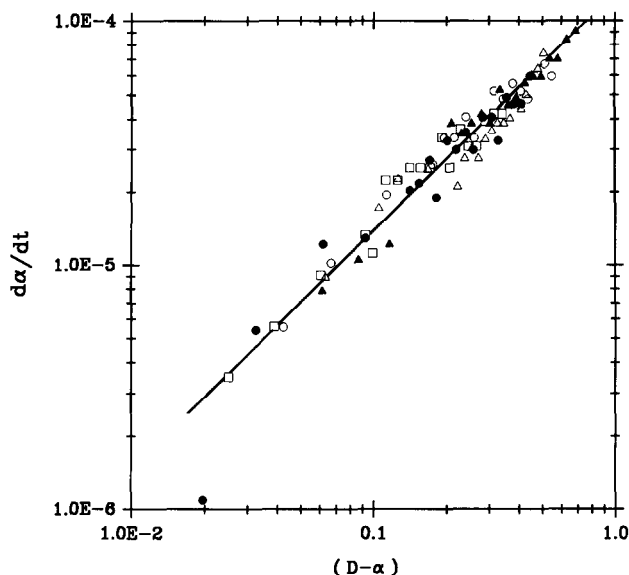


Fig. 5. Plot of reaction rate ($d\alpha/dt$) versus fraction unconverted ($D - \alpha$) for Athabasca samples: (\square) 1000–1700 μm ; (\bullet) 850–1000 μm ; (\circ) 600–850 μm ; (Δ) < 600 μm ; (\blacktriangle) < 425 μm .

size distribution, would thus tend to remain constant for the Athabasca stone within the sizes studied here.

As shown in Figs. 4 and 5, the data are well fitted by the power law representation for the sulphation reaction (eqn. (2)). The scatter is more pronounced in the late time regime, where only the smallest pores are still

TABLE 2

TG limestone characterization results ^a

Sorbent type	Particle size (μm)	Sample weight (g)	Calc. ^b purity (%)	Maximum conversion D	Slope n	Intercept at $(D - \alpha) = 1$
Havelock	850–1000	0.8169	97.2	0.3927	0.806	1.38E–04
	600– 850	0.7317	96.2	0.4647	0.818	1.18E–04
	300– 500	0.7153	97.7	0.4337	0.753	1.40E–04
	212– 300	0.8140	93.4	0.4513	0.777	1.33E–04
	< 850	0.9825	95.8	0.5462	0.816	1.82E–04
Athabasca	1000–1700	0.8320	89.2	0.3396	1.11	1.56E–04
	850–1000	0.8809	87.1	0.4473	1.05	1.42E–04
	600– 850	0.8798	85.1	0.5081	1.02	1.19E–04
	< 600	0.6859	81.7	0.6120	0.94	1.31E–04
	< 425	0.8127	72.6	0.6872	1.01	1.36E–04

^a All runs were carried out at 850°C using the synthetic flue gas: 0.5% SO_2 , 2.5% O_2 , 15% CO_2 , balance N_2 .

^b Calculated from the calcination weight loss.

available for reaction. This good fit is significant since eqn. (2) is both a reasonable and a desirable way of describing the sulphation reaction, because it eliminates the time dependence in the rate expression. The time dependence usually arises from accounting for the decay in reactivity due to the pore plugging phenomenon. Therefore, the solids residence time distribution function, which is usually unknown, is avoided in the final integrated expression of the sulphur balance.

The effect of the particle size is seen in the maximum conversion of the samples (Table 2), with the general trend of higher utilization for smaller particle diameters. This is more evident in the Athabasca samples where the conversion increased monotonically with decreasing particle diameter. Interestingly, the purity of the Athabasca samples decreased monotonically with decreasing particle size. One possible explanation for this may be that impurities such as silica or clay became separated and concentrated in the finer fractions during the screening process.

The effect of the limestone type is clearly indicated by the slope or the reaction order n , as in eqn. (2). Havelock samples all have slopes near 0.79, while those of the Athabasca samples are near unity. This implies that the sulphation rate of the Havelock limestone decays more slowly than that of the Athabasca limestone. As shown in Figs. 4 and 5, the sulphation rates at a given $(D - \alpha)$ are higher, in general, for the Havelock samples than for the Athabasca samples. However, the maximum conversion of the Havelock samples is generally lower than that of the Athabasca samples. Interestingly, the intercept values at $(D - \alpha) = 1.0$ for both rocks are scattered about 1.4×10^{-4} , suggesting that if experiments were conducted with much finer sizes the effect of rock type would almost vanish. This is not unreasonable, since full conversion is only possible if pore plugging is absent, and when particle size diminishes to the magnitude ($< 1 \mu\text{m}$) of the pores themselves, pore closing should no longer pose a problem.

Nova Scotia limestones

Samples of the four Nova Scotia limestones (850–1000 μm) were tested in order to compare maximum conversions with results from the FBR method. The results from these samples plus the Havelock test are given in descending order with respect to maximum conversion in Table 3. They show that Calpo and Glen Morrison limestones performed substantially better than the others, a finding supported by the results from test burns conducted at a 22 MW(e) CFB plant [9]. When compared with the FBR method, it is seen that the present method consistently yielded higher conversions. In the case of Glen Morrison limestone, the FBR method under-predicted the limestone utilization by almost 10% in absolute terms and 20% relatively. A difference between these two techniques is anticipated, because both calcination and sulphation occur simultaneously in the FBR, whereas they are sequential in

TABLE 3

Sulphation capacities of Nova Scotia limestones

Sorbent type	Particle size (μm)	Sample weight (g)	Calc. ^a purity (%)	Maximum conversion	
				Present method	FBR ^b
Calpo	850–1000	0.7873	96.6	0.517	0.450
Glen Morrison	850–1000	0.7678	87.2	0.485	0.380
Havelock	850–1000	0.8169	97.2	0.393	0.330
Glendale	850–1000	0.8663	98.3	0.359	0.310
	850–1000	0.8702	97.8	0.330	0.290
Marble Mountain	850–1000	0.7630	94.6	0.334	0.250

^a Calculated from the calcination weight loss.^b Tests performed by C.A. Hamer using FBR technique [5].

the TG reactor. In fact, a slightly lower conversion in the FBR is expected if attrition is a problem. However, the cause of this rather large discrepancy is not known at present. Nonetheless, this tendency by the FBR technique to yield a lower conversion than the present TG method is expected to worsen with finer particle sizes, corresponding to the onset of elutriation.

CONCLUSIONS

The TG technique employed here has been shown to accommodate samples with particle size distributions between 0 and 1.7 mm, and weighing up to 1 g. It has effectively filled the gap created by the established methods, and its potential as a standard technique for evaluating sorbents for CFB use has also been demonstrated.

While the present technique can use representative samples and minimize the bulk phase mass transfer resistance, it cannot simulate the physical environment such as attrition and recirculation of the CFB combustor. However, it is an effective and simple method for quick determinations of the limestone sulphation characteristics and, with a comprehensive CFB model, these data may be used to predict the limestone performance in actual combustors.

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