

# **THERMAL ANALYSIS OF FLUIDISED BED COMBUSTION RESIDUES CONTAINING LIMESTONE SCAVENGER**

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## **Abstract**

A method has been developed using thermoanalytical techniques for the analysis of residues from coal-burning fluidised bed plant where limestone is used as a sulphur scavenger. This completely eliminates the need for lengthy wet chemical analyses and allows the derivation of parameters necessary for efficient plant operation, such as limestone addition rate, calcium utilisation efficiency and calcium to sulphur mole ratio. The method also gives values for the unburned carbon content and the ratio of coal ash to limestone derivatives in the sample.

**Keywords:** fluidisation, thermal analysis

## **Introduction**

The injection of limestone into furnaces is a well-established method for the reduction of SO<sub>2</sub> emissions in stack gases [1, 2]. The optimum temperature for this reaction is in the range 800–1000°C [3], and this is ideally suited to fluidised bed (FB) operation. At higher temperatures the equilibrium is displaced in favour of the formation of calcium and sulphur oxides [4].

For control of FB plant, important criteria are a knowledge of the calcium utilisation or extent to which the available calcium is converted to sulphur compounds, and the limestone addition rate per kg of fuel. It is obviously uneconomic in energy and material costs to use more limestone than is necessary to achieve a target SO<sub>2</sub> emission level.

In order to determine the calcium utilisation and addition rate, it is normal to carry out 'wet' chemical analyses on the solid 'ash' residues from the plant – bed ash, flyash and cyclone (or bag filter) grits. The species determined are: carbonate, sulphide, sulphate, total calcium and unburned carbon. The CO<sub>3</sub>, SO<sub>4</sub>, SO<sub>3</sub> and S are equated to calcium and any excess calcium is reported as calcium oxide.

In view of the fact that most of the species of interest, viz. CaCO<sub>3</sub>, CaSO<sub>4</sub>, Ca(OH)<sub>2</sub> and unburned carbon all give distinguishable thermal responses at dis-

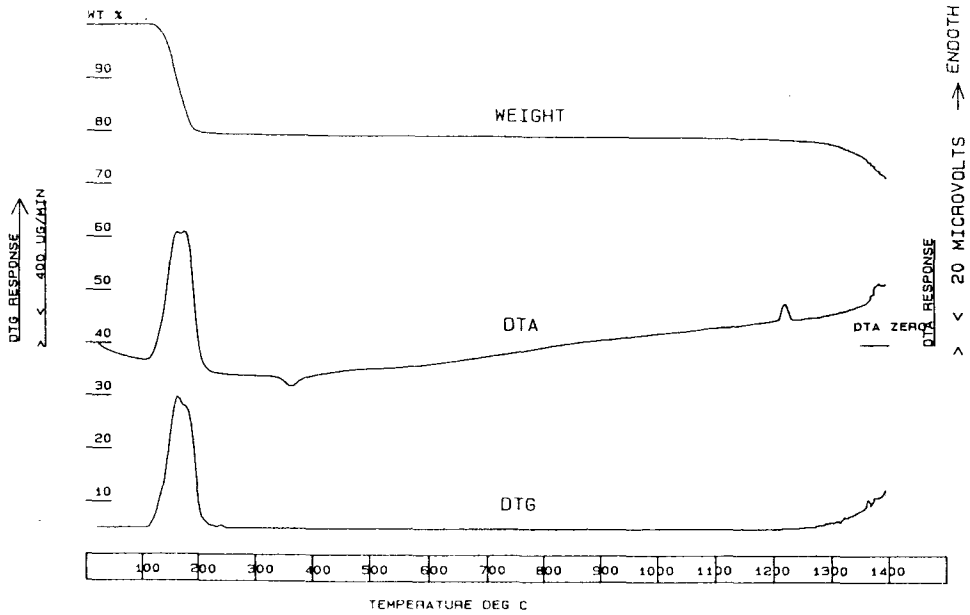


Fig. 1 Calcium sulphate dihydrate in nitrogen

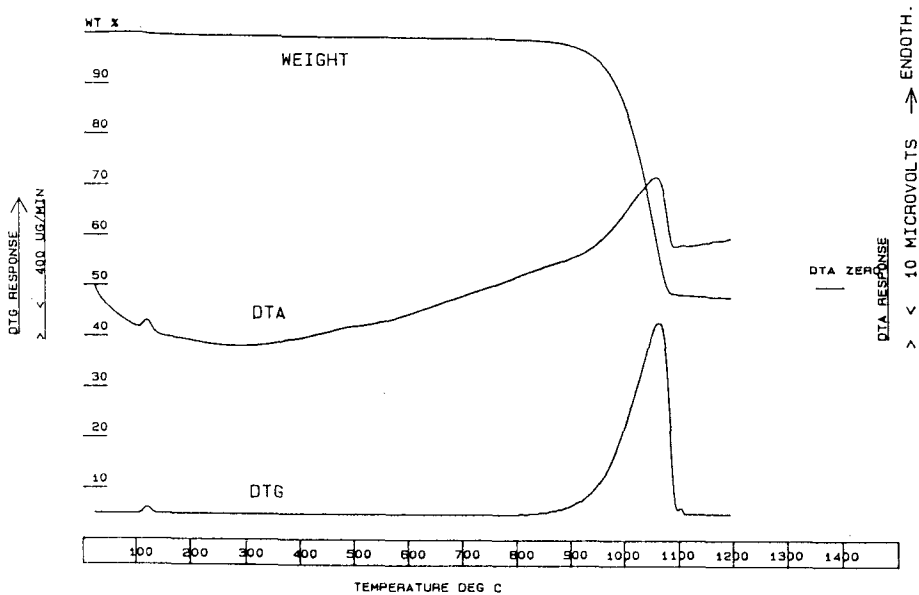


Fig. 2 Mixture of anhydrite ( $\text{CaSO}_4$ ) and carbon showing weight loss due to evolution of  $\text{CO}_2$

tinct temperatures, it was decided to investigate the potential of thermal analysis as an alternative to the established time-consuming procedure.

## Experimental

### *Equipment*

The Stanton-Redcroft STA 780 instrument was used in its simultaneous TG/DTG/DTA configuration. Sample masses were 25 mg, and the gas flow was 50 ml·min<sup>-1</sup> of air or nitrogen as required. The heating rate was 20 deg·min<sup>-1</sup> for all experiments, and the DTA reference was 25 mg of pure calcined alumina. All samples were ground to pass a 75 micron sieve.

### *Synthetic mixtures*

The three major compounds under consideration, CaSO<sub>4</sub>·2H<sub>2</sub>O, Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> all give weight losses very close to the theoretical values due to the loss of water in the case of the first two and CO<sub>2</sub> in the latter. Figure 1 shows a typical curve obtained for gypsum (calcium sulphate dihydrate – CaSO<sub>4</sub>·2H<sub>2</sub>O). This could not, however be used for real FB ashes since at the combustion temperature, a modified crystalline structure, anhydrite, (CaSO<sub>4</sub>) is formed and this will not re-absorb water to form gypsum.

Fortunately, there is another reaction which can be used; at temperatures between 800 and 1000°C calcium sulphate is reduced by carbon to calcium sulphide with a weight loss due to the liberation of CO<sub>2</sub>:



Figure 2 is the thermal curve for a mixture of carbon and CaSO<sub>4</sub>. The weight loss over the reaction peak (800–1000°C) is 50.8% and this is equivalent to 78.5% as CaSO<sub>4</sub> which compares very well with the 78.3% actually present in the mixture. Thus a viable strategy for the analysis of FB residues is to add a known quantity of carbon prior to the thermoanalytical assay in order to reduce the sulphate and render it 'visible'.

Before addressing the problem of unreactive species such as CaS and CaO, let us look at a synthetic mixture of the three major species, with additional carbon. Figure 3 shows the thermal curve for a mixture of the composition given in Table 1. Note that after completion of the sulphate – carbon reaction at 1100°C, the atmosphere was changed from nitrogen to air in order to burn off the residual carbon, giving rise to a sharp weight loss and DTA exotherm.

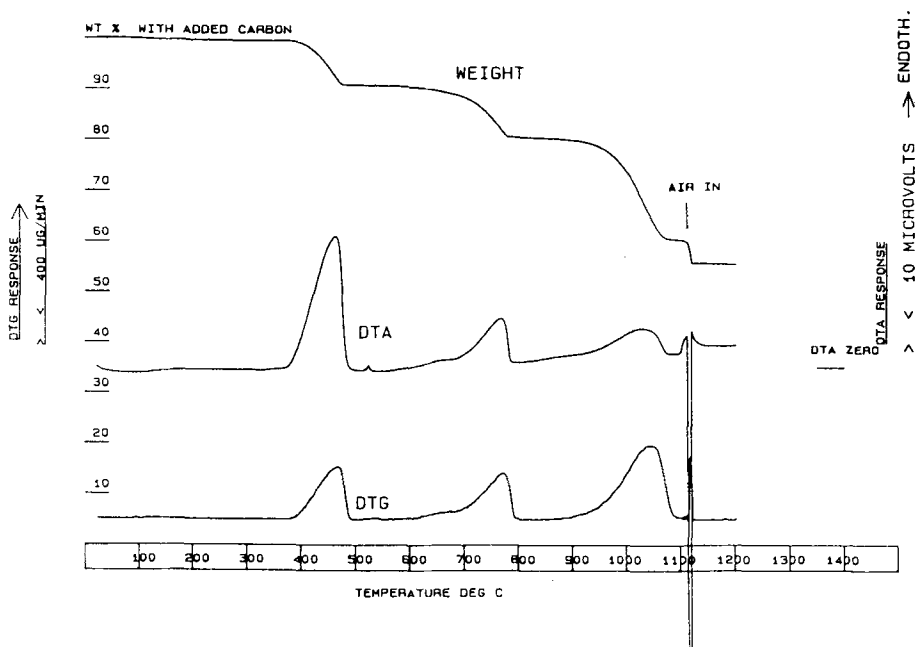


Fig. 3 Synthetic mixture of anhydrite, calcium hydroxide and calcium carbonate with additional carbon. Note burn-off of excess carbon on admitting air

Table 1

	As prepared	TG result
	%	
CaSO <sub>4</sub>	30.7	30.9
Ca(OH) <sub>2</sub>	37.4	36.2
CaCO <sub>3</sub>	22.2	22.7
Carbon	9.7	10.0

The proportion of each component in the mixture is obtained by multiplying the weight loss over its decomposition step by the ratio of the molecular weight of the evolved gaseous species to that of the parent compound. Thus for Ca(OH)<sub>2</sub>;

$$\text{Weight loss (350–500°C)} = 8.8\%$$

$$\text{Ca(OH)}_2 = 8.8 \times 74/18 = 36.2\%$$

And similarly for CaSO<sub>4</sub> and CaCO<sub>3</sub>.

In the case of the residual carbon the weight loss on burning in air must be added to the carbon used in reducing the sulphate:

$$\text{Thus } C = (59.5 - 54.8) + 12/44(79.5 - 59.5) = 10.0\%$$

In a fluidised bed residue, there may also be small but significant proportions of calcium compounds which give no definite TA response. In the 'reacted' category, these are calcium sulphide ( $\text{CaS}$ ), and calcium sulphite ( $\text{CaSO}_3$ ), and in the 'unreacted' category, calcium oxide ( $\text{CaO}$ ). It has been found that boiling with 5 volume hydrogen peroxide, followed by careful drying converts these to species amenable to thermal analysis. Thus  $\text{CaS}$  and  $\text{CaSO}_3$  are oxidised to calcium sulphate in the dihydrate form ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), while calcium oxide is slaked to calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) and while the true analysis of the original material cannot be precisely determined, the distinction between reacted and unreacted calcium is maintained. In practice the quantities of these minor species are normally so small that their presence makes little difference to the results.

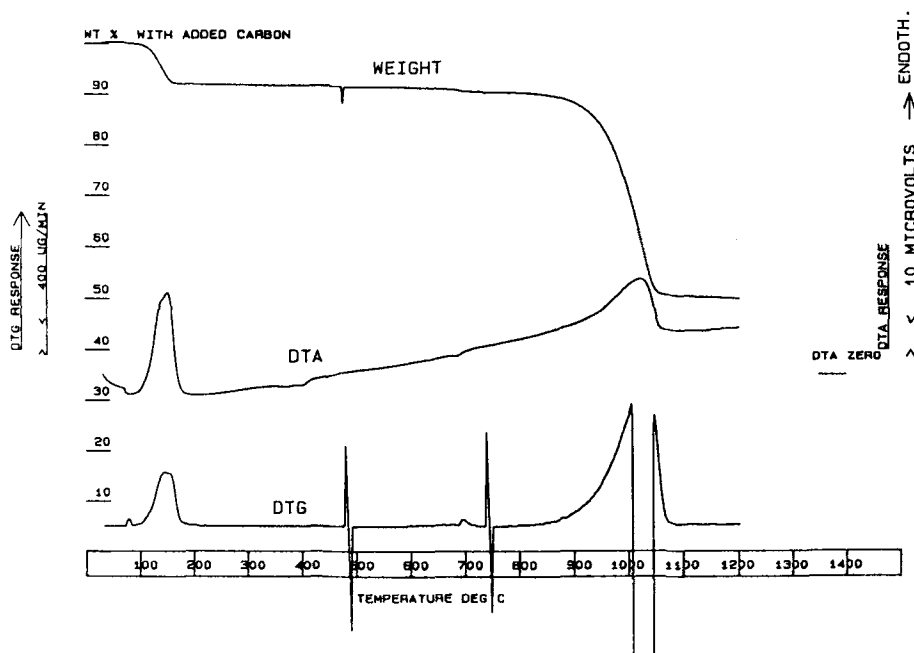


Fig. 4 Calcium sulphate dihydrate formed by oxidising calcium sulphide in hydrogen peroxide. Contains added carbon to effect reduction of  $\text{CaSO}_4$

Figure 4 demonstrates the oxidation of calcium sulphide to gypsum by hydrogen peroxide. 0.5 g of  $\text{CaS}$  were treated with a few ml of 5-vol  $\text{H}_2\text{O}_2$ , and then dried below  $50^\circ\text{C}$ . The resulting material was ground with carbon so that

the mixture contained 25% by weight of the latter. The TG curve shows a large endotherm and weight loss at 100–160°C corresponding to the dehydration of the gypsum formed, and a second weight loss from 800 to 1100°C due to the reaction of the sulphate with the carbon. The latter step is 38.8% of the starting weight, equivalent to 75.5%  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and this is consistent with the material being pure gypsum.

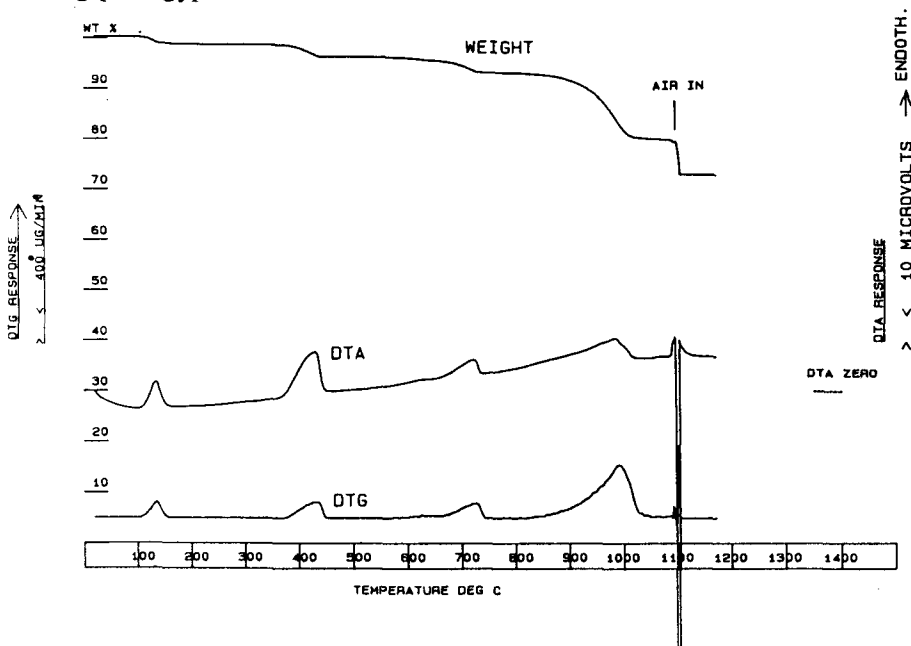


Fig. 5 Simulated fluidised bed residue containing anhydrite, calcium sulphate dihydrate, calcium hydroxide, calcium carbonate and with added carbon

The method was then applied to a synthetic mixture representing a FB ash which had been treated in the manner described, i.e. oxidised with hydrogen peroxide, dried, and mixed with carbon. Alumina was added to simulate inert coal ash, and the thermal curve is shown in Fig. 5. The proportions of the various components can be calculated as follows:

$$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \text{ (100–160}^\circ\text{C)} = (100 - 98.9) \times 172 / 36 = 5.2\%$$

$$\text{Ca(OH)}_2 \text{ (350–450}^\circ\text{C)} = (98.5 - 95.9) \times 74 / 18 = 10.7\%$$

$$\text{CaCO}_3 \text{ (650–750}^\circ\text{C)} = (95 - 92.8) \times 100 / 44 = 5.0\%$$

$$\text{Total SO}_4 \text{ (800–1100}^\circ\text{C)} = (92.5 - 79.5) \times 96 / 88 = 14.2\%$$

Therefore  $\text{CaSO}_4 = (14.2 - (5.2 \times 96 / 172)) \times 136 / 96 = 16.0\%$

Carbon (1100°C) =  $(78.8 - 72) + (92.5 - 79.5) \times 12 / 44 = 10.3\%$

The comparison between the mixture 'as prepared' and the TG results is given in the following table:

Table 2

	As prepared	From TG
	%	
Al <sub>2</sub> O <sub>3</sub>	52.2 (Diff.)	52.8 (Diff.)
CaSO <sub>4</sub>	15.1	16.0
CaSO <sub>4</sub> ·2H <sub>2</sub> O	6.0	5.2
Ca(OH) <sub>2</sub>	11.0	10.7
CaCO <sub>3</sub>	4.9	5.0
Carbon	10.8	10.3

Although there are minor discrepancies between the CaSO<sub>4</sub> and CaSO<sub>4</sub>·2H<sub>2</sub>O values, the comparison on the basis of total sulphate ion (i.e. calcium utilised) is good; 14.0 as prepared and 14.2 by TA.

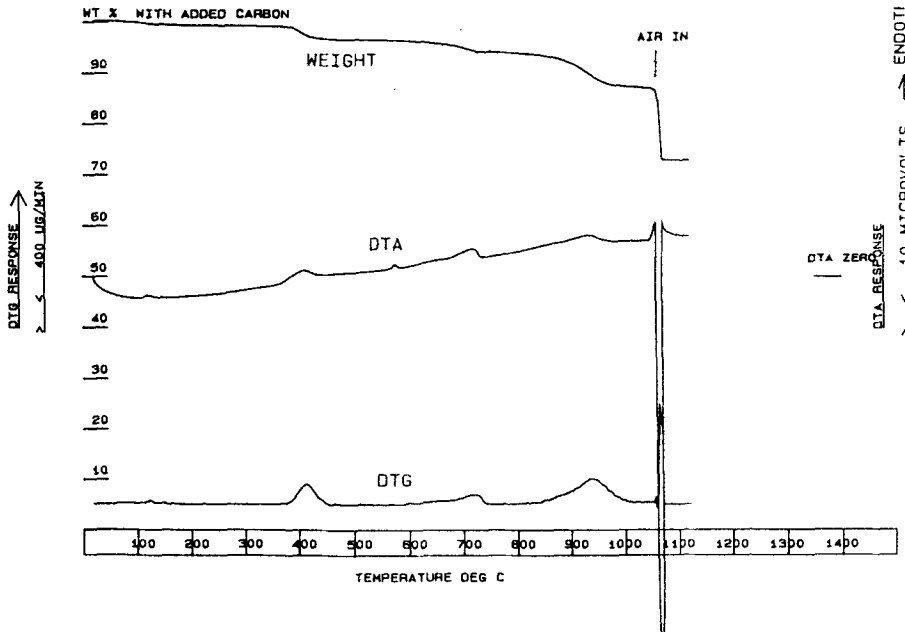


Fig. 6 'Real' bed ash oxidised in hydrogen peroxide and containing added carbon

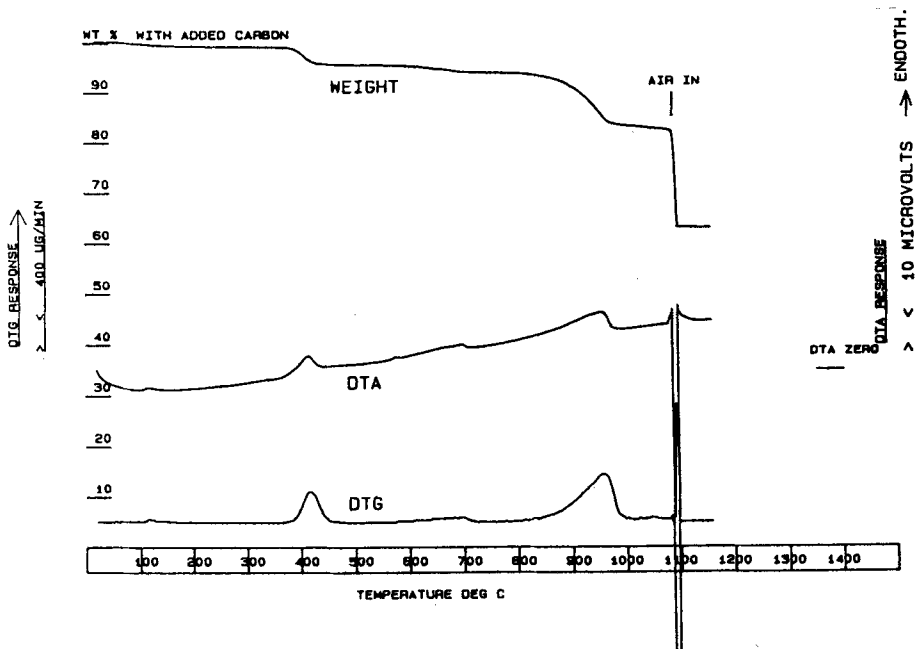


Fig. 7 'Real' cyclone grit oxidised in hydrogen peroxide and containing added carbon

### Real ashes

A bed ash and a cyclone grit were chosen from stock, collected during operation of a FB test rig. These were subjected to the analytical regime described above, and the thermal curves are shown in Figs 6 and 7. The compositions of the two materials as analysed are, using the above method:

Table 3 Real ashes (as analysed)

	Bed ash	Cyclone grit
	%	
Ash	58.4(Diff.)	38.2(Diff.)
CaSO <sub>4</sub> ·2H <sub>2</sub> O	2.4	2.4
CaSO <sub>4</sub>	8.9	18.3
Ca(OH) <sub>2</sub>	10.3	13.6
CaCO <sub>3</sub>	4.1	3.6
Carbon	15.9	23.9

From a knowledge of the amount of carbon added, the results in Table 3 can be corrected back to the original values before the addition of carbon:



**Table 4** Real ashes—original compositions

	Bed ash	Cyclone grit
	%	
Ash	68.4	49.8
CaSO <sub>4</sub> ·2H <sub>2</sub> O	2.8	3.1
CaSO <sub>4</sub>	10.4	23.9
Ca(OH) <sub>2</sub>	12.1	17.7
CaCO <sub>3</sub>	4.8	4.7
Carbon	1.5	0.8

## Derived parameters

### Calcium utilisation

The calcium utilisation can be calculated from the ratio of the calcium associated with sulphur to the total calcium. Thus:

$$= \frac{[\text{CaSO}_4] + [\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]}{[\text{CaSO}_4] + [\text{CaSO}_4 \cdot 2\text{H}_2\text{O}] + [\text{Ca}(\text{OH})_2] + [\text{CaCO}_3]} \times 100$$

From the analyses in Table 4, the calcium utilisation values are 30.6% for the bed ash and 40.5% for the cyclone grit.

### Limestone addition rate

The limestone addition rate can also be estimated from the above analyses by calculating the total moles of calcium in the ash, converting to calcium carbonate, and expressing the result in terms of kg of limestone to kg of ash. From a knowledge of the ash and sulphur content of the coal this can be processed to give the addition rate in kg of limestone per kg of coal or the calcium: sulphur mole ratio. Assume the ash content of the coal used in the test run which produced the above samples was 15.0% and the sulphur 0.11%. Then for the bed ash sample:

Total moles calcium in 1 kg residue,

$$= (2.8/172) + (10.4/136) + (12.1/74) + (4.8/100) = 0.304 \times 10 = 3.04$$

This is equivalent to  $3.04 \times 100 = 304$  g CaCO<sub>3</sub> in 1 kg residue, i.e. for every 696 g of ash, 304 g of CaCO<sub>3</sub> were added. But 696 g of ash are equivalent to  $696/0.15 = 4640$  g coal.

Therefore addition rate = 304 g limestone per 4640 g coal,

or 0.066 kg/kg

### *Ca:S mole ratio*

No. of moles Ca in 0.066 kg limestone =  $66/100 = 0.66$

No. of moles S in 1 kg coal =  $1000 \times 0.011/32 = 0.343$

Therefore Ca:S mole ratio =  $0.66/0.343 = 1.92:1$

### *Sulphur removal efficiency*

The percentage of the sulphur in the coal removed by the limestone can also be estimated:

From the above it was seen that 1 kg of residue contains 684 g of ash. Therefore 1 kg of residue represents  $684/0.15 = 4560$  g or 4.56 kg coal and 4.56 kg coal contain  $4.56 \times 0.011 = 0.05$  kg of sulphur. 1 kg of residue contains  $(0.028 \times 32/172) + (.104 \times 32/136) = 0.0297$  kg S. Therefore removal efficiency =  $100 \times (0.0297/0.05) = 59.4\%$ .

## **Conclusions**

The thermogravimetric method outlined above appears to be a viable alternative to the conventional chemical method, and is much quicker. Another advantage is that it probably gives a more accurate estimate of unburned carbon. The conventional method relies on a total carbon determination which involves subtraction of the CO<sub>2</sub> evolved from the calcium carbonate, determined separately. The present work has shown that at temperatures above 800°C the carbon reacts with calcium sulphate, releasing CO<sub>2</sub>, which will give an erroneously high result. The TG method circumvents this source of error.

## **References**

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**Zusammenfassung** — Unter Verwendung thermoanalytischer Techniken wurde eine Methode zur Analyse von Rückständen aus Kohleverbrennungsanlagen mit Fluidbett entwickelt, in denen Kalkstein als Entschwefelungsmittel verwendet wird. Dies beseitigt vollkommen die Notwendigkeit von langwierigen chemischen Naßanalysen und erlaubt die Ableitung von Parametern, die für einen effizienten Anlagenbetrieb erforderlich sind, wie z.B. die Zugabegeschwindigkeit von Kalkstein, die Calciumverwertungseffizienz und das Calcium: Schwefel Molverhältnis. Diese Methode liefert weiterhin Werte für den Gehalt an unverbranntem Kohlenstoff und des Verhältnisses Kohlenasche:Kalksteinderivaten innerhalb der Probe.