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## Thermogravimetry: A Great Tool for Flue Gas Desulfurization Solids Analysis

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### INTRODUCTION

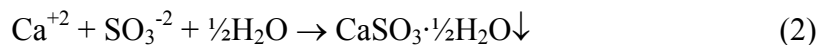
Over 50 percent of the electricity generated in the United States comes from coal-fired power plants. Perhaps a hundred or so utility boilers are already equipped with flue gas scrubbers. Anticipated tightening of sulfur dioxide (SO<sub>2</sub>) emissions regulations will require other existing and new plants to also install scrubbers. A popular design has been and will be the wet-limestone type, where finely ground, slurried limestone is sprayed onto the flue gas to remove SO<sub>2</sub>. Reliable monitoring of scrubber solids chemistry is critical for proper operation of scrubbing systems. Thermogravimetry is an excellent tool for these analyses.

### A Brief Overview of Scrubber Chemistry

Flue-gas scrubbing is a step-wise chemistry process, where the overall reaction is a classic example of aqueous acid-base chemistry applied on an industrial scale. Alkaline limestone slurry (composed primarily of calcium carbonate, CaCO<sub>3</sub>) reacts with acidic sulfur dioxide, as represented in Equation 1.



In the absence of any other reactants, calcium and sulfite ions will precipitate as a hemihydrate, where water is actually included in the crystal lattice of the scrubber byproduct.



Proper operation of a scrubber is dependent upon the efficiency of the above-listed reactions. Control of pH via reagent feed is very important. Many wet-limestone scrubbers operate at a solution pH of around 5.6 to 5.8. A very acidic scrubbing solution

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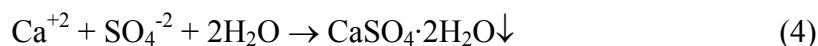
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inhibits SO<sub>2</sub> transfer from gas to liquid, while an excessively basic slurry (pH > 6.0) indicates overfeed of limestone.

Oxygen in the flue gas greatly influences chemistry. Aqueous bisulfite and sulfite ions react with oxygen to produce sulfate ions (SO<sub>4</sub><sup>-2</sup>).



Approximately the first 15 mole percent of sulfate ions co-precipitates with sulfite to form calcium sulfite-sulfate hemihydrate [(0.85CaSO<sub>3</sub>·0.15CaSO<sub>4</sub>) ·½H<sub>2</sub>O]. Any sulfate above the 15 percent mole ratio precipitates with calcium as gypsum.



Control of byproduct chemistry offers interesting challenges. Experience shows that operating in either a completely oxidized state (no calcium sulfite-sulfate hemihydrate in the scrubbing slurry) or a completely un-oxidized state (no gypsum in the slurry) minimizes scaling of internal scrubber components. Deposit formation on scrubber internals and subsequent gas flow restrictions may cause unit de-rates and even forced outages if gas flow is severely restricted. (Note: Modern scrubber towers are often of the open spray type easing the difficulties related to deposit formation (1).) A typical deciding factor on the choice of oxidized or non-oxidized byproduct involves the handling characteristics and commercial value of the solid. Calcium sulfite hemihydrate is a soft material that tends to retain water. It has little value as a chemical commodity. For this reason, many scrubbers are equipped with forced-air oxidation systems to introduce additional oxygen to the scrubber slurry. A properly designed oxidation system will convert all of the liquid sulfite ions to sulfate ions. Sulfate of course precipitates with calcium as gypsum, which forms a cake-like material when subjected to vacuum filtration. In many cases, this relatively simple mechanical process can extract 85 to 90 percent of the free moisture in gypsum. High-purity, dried synthetic gypsum has become a favorite material of wallboard manufacturers.

Limestone utilization is also an important issue. If the limestone reacts poorly in the system, overfeed is required for adequate SO<sub>2</sub> removal. This of course results in excess reagent usage. Limestone costs for large scrubbers may reach or exceed a million dollars per year, so loss of reagent due to poor utilization can be rather expensive. Each percentage increase of unused limestone that exits with the scrubber byproduct at Kansas City Power and Light's La Cygne facility costs approximately \$10,000 annually. Factors that influence utilization include limestone quality and reactivity, limestone grind size, residence time of the reagent within the scrubbing system, and performance of slurry separation devices.

Efficient scrubber operation is dependent upon proper chemistry. Accurate analyses of scrubber slurry solids and limestone reagents are important for monitoring and optimizing process chemistry. This issue leads to the heart of this paper, which discusses thermogravimetric analytical techniques for scrubber solids.

## **TGA Analysis of Scrubber Byproduct**

A thermogravimetric analyzer is a quantitative not a qualitative instrument, so the operator needs to have a good idea of the primary constituents in the sample before analysis. If the individual compounds decompose at distinct and separate temperatures, it becomes easy to calculate the concentration of the original materials. Wet-limestone

scrubber byproducts lend themselves well to this technique. The following equations illustrate the decomposition chemistry of wet-limestone flue gas desulfurization (FGD) solids. The typical decomposition temperature ranges are also shown.

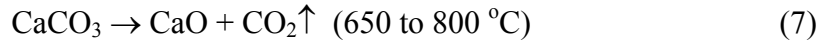
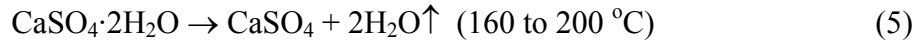


Figure 1 illustrates a TGA analysis of a pre-dried (we use a step-wise drying procedure in a simple microwave oven) scrubber solids sample containing all three of the major constituents (2). For the moment we will ignore the decomposition shown at 600 °C. This will be addressed shortly.

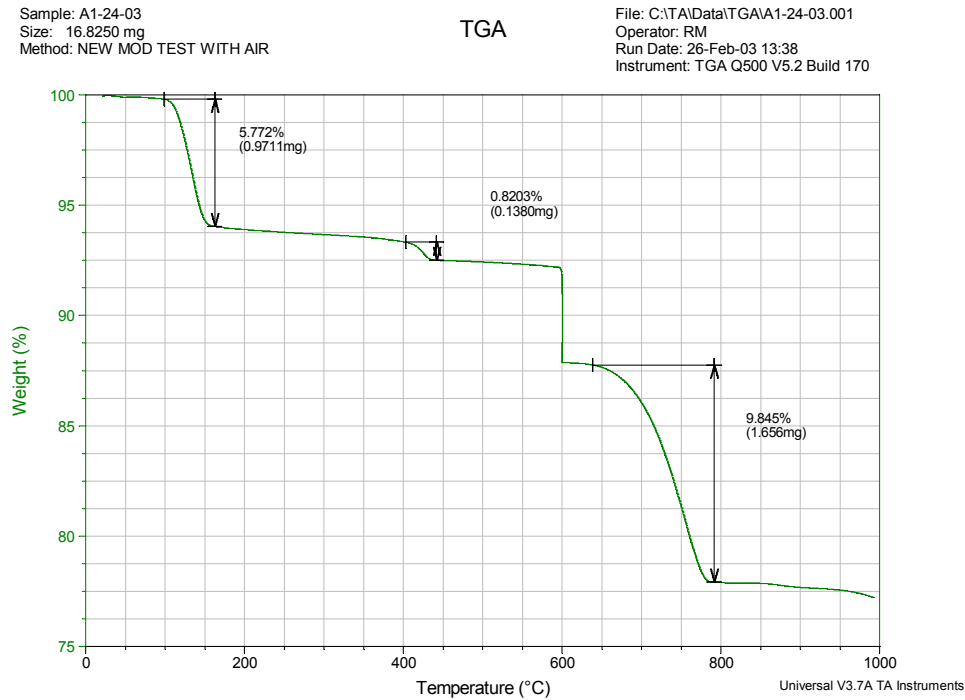


Figure 1 - TGA Plot of a Solids Sample from the La Cygne Scrubber.

The calculations to determine original constituent concentrations are straightforward. The molecular weight of gypsum is 172 g/mol and that of the water forced out is 36 g/mol, so the initial gypsum content is determined by multiplying the weight loss (5.772 %) times a factor of  $172 \div 36$  (4.78). For calcium sulfite-sulfate hemihydrate, the weight-change factor is  $131.9 \div 9$  (14.6), where the mole ratio of calcium sulfite to calcium sulfate is assumed to be 85:15. For the calcium carbonate decomposition, the factor is  $100.1 \div 44$  (2.27). Thus, for the analysis shown in Figure 1, the gypsum content is 27.6 percent, the calcium sulfite-sulfate hemihydrate content is 12.0 %, and the calcium carbonate content is 22.3 %.

This sample comes from a wet-limestone scrubber that serves the dual purpose of removing SO<sub>2</sub> and fly ash from the gas stream. Initially the scrubber solids were analyzed in a nitrogen atmosphere, but it was found that volatile discharge from the unburned coal that carried over with the fly ash blended in with the calcium carbonate decomposition. So, the analysis process was modified to introduce air to the furnace at 600 °C. (The air-injection stage has subsequently been lowered to 500 °C). The step is isothermal with a 25-minute hold time that allows all volatile matter and carbon to burn away. The procedure is clearly illustrated by the vertical slope at 600 °C in Figure 2. Following the isothermal step, the initial heating rate resumes and the furnace ramps up to 1000°C. The calcium carbonate decomposition proceeds unmasked. A side benefit of the unburned carbon analysis is that Operations personnel may be expediently informed of upsets in the boiler. High carbon residuals in the scrubber solids indicate combustion difficulties.

For those contemplating use of a TGA for FGD solids analyses, a special point must be noted. It was learned during previous TGA experiments that calcium sulfite will break down at high temperatures when analyzed in an atmosphere devoid of oxygen (2). An analysis of similar decomposition products at La Cygne revealed both sulfur and oxygen, so there may be two competing reactions.



This phenomenon often appears during routine scrubber solids analysis. Figure 2 illustrates this effect.

The trained analyst can distinguish the end of the calcium carbonate decomposition and the beginning of the calcium sulfite decomposition. This transition is apparent at the shoulder in the decomposition pattern at 750 °C.

With regard to analyses of residual limestone in the La Cygne scrubber byproducts, prior to acquisition of the TGA plant personnel analyzed samples via inaccurate wet-chemistry tests. Once the instrument was up and running, we discovered that residual limestone concentrations in the byproduct ranged from 15 to 25 percent. The FGD operators have subsequently adjusted the limestone grinding mills to produce a finer size of reagent. Recent results indicate that 5 to 10 percent unused limestone in the byproduct is possible with the proper grind size of reagent from the ball mills.

## CONCLUSION

Thermogravimetry is an excellent method for tracking wet-limestone flue gas desulfurization chemistry, especially when quick results are required, when checking for process upsets, and when making process changes. The technique is infinitely better than earlier wet-chemistry tests that were inaccurate and time consuming.

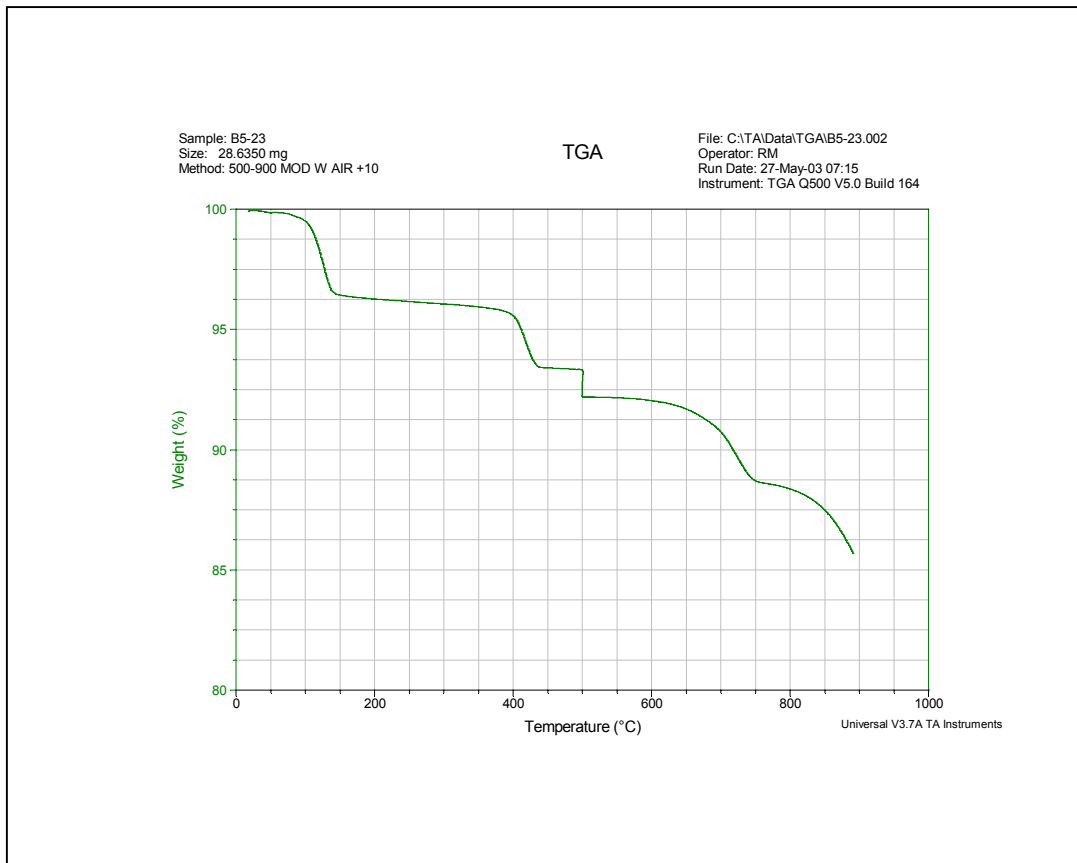


Figure 2 - Extra Weight Loss Due to Decomposition of Calcium Sulfite in a Nitrogen Atmosphere.

**REFERENCES**

1. Buecker, B., and P. Dyer, P.E., “Flue Gas Desulfurization Systems for the Future”; *PowerPlant Chemistry*, **July 2003**, 5 (7), pp. 435-439.
2. Work conducted at City Water, Light & Power, Springfield, Illinois.

**KEYWORDS**

compositional analysis, inorganic, minerals, thermogravimetric analysis

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