Monitoring of FGD Solids with a Macro TGA System

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Introduction

Wet-limestone scrubbing has been, and will continue to be, a popular method for many flue gas desulfurization (FGD) systems. Limestone is predominantly $CaCO_3$, which is only very slightly soluble in water, but will slowly hydrolyze to produce a basic solution. When hot flue gases introduce SO_2 into a scrubber slurry, sulfurous acid is formed (Eq. 1), which lowers the pH of the mix. $CaCO_3$ then reacts with the acid mixture to eventually form calcium sulfite, $CaSO_3$ (Eqs. 2 and 3). $CaSO_3$ is only slightly soluble in water and precipitates.

$$SO_2 + H_2O \leftrightarrow H_2SO_3 \leftrightarrow H^+ + HSO_3^- \quad (1)$$

$$CaCO_3 + 2H^+ \leftrightarrow Ca^{2+} + H_2CO_3 \leftrightarrow Ca^{2+} + H_2O + CO_{2(g)} \quad (2)$$

$$Ca^{2+} + HSO_3^- \leftrightarrow H^+ + CaSO_{3(s)} \quad (3)$$

$CaSO_3$ is an unwanted product in FGD solids. As a result, lime or limestone scrubbing processes use oxygen in the flue gas or use extra oxidation gas to convert sulfite to sulfate (Eq. 4). $CaSO_4$ is only slightly soluble in water and precipitates (Eq. 5).

$$2HSO_3^- + O_2 \leftrightarrow 2SO_4^{2-} + 2H^+ \quad (4)$$

$$Ca^{2+} + SO_4^{2-} \leftrightarrow CaSO_{4(s)} \quad (5)$$

The initial precipitates in FGD slurries are coprecipitates of the hemihydrates $CaSO_3 \bullet ½H_2O$ and $CaSO_4 \bullet ½H_2O$. After the formation of a few mole percent of these two compounds, the predominant product is $CaSO_4 \bullet 2H_2O$, which is the desired product.

Calcium sulfite-sulfate hemihydrate is an unwanted soft material that sticks to surfaces and leads to build-ups of the solids and subsequent reduction of slurry flows. Most wet-limestone scrubber systems use forced-air oxidation to introduce extra oxidation to minimize the production of sulfites. The main product is then gypsum ($CaSO_4 \bullet 2H_2O$), which precipitates and forms a cakelike material that is easily dewatered. Gypsum is the primary ingredient of wallboard, and many FGD systems produce a wallboard-grade byproduct.

Thermogravimetric analysis (TGA) is an analytical technique in which changes in physical and chemical properties of materials are measured as a function of temperature and/or time. TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss, or gain, due to decomposition, oxidation, or loss of volatile materials such as moisture. Common applications of TGA include:

- *Materials characterization through analysis of characteristic decomposition patterns*
- *Determination of combustible materials and combustion residues from a sample*

Macro TGA systems using gram-size samples have been available for three decades. The larger sample sizes allow more accurate mass measurements for characterization of materials. FGD solids are industrial byproducts that have been monitored using macro TGA systems. Compounds reported to have been successfully determined include free moisture, moisture in hydrates, $CaSO_4 \bullet 2H_2O$, $CaSO_3 \bullet ½H_2O$, and $CaCO_3$.

TGA701 Thermogravimetric Analyzer

A LECO TGA701 macro TGA system was used in a study to characterize the components in various FGD solids. Pure materials, including those listed above, were first analyzed with the TGA701, followed by the analysis of various mixtures of the pure materials. Pure $CaSO_3 \bullet ½H_2O$ is not available and was not used in the study. The study of pure materials and mixtures demonstrated the accuracy of the TGA701 in characterizing the compounds. In most of the previously reported macro TGA studies of FGD solids, $Ca(OH)_2$ is not reported as one of the components in FGD solids. The TGA reaction profiles for $Ca(OH)_2$ and $CaSO_3 \bullet ½H_2O$ decomposition occur in the same temperature range. This study sheds new light on this subject.

Samples and Pure Materials

Pure samples of calcium carbonate were provided by LECO Corporation. The anhydrous $CaSO_3$ sample was ACS reagent grade. The lime, $Ca(OH)_2$, was a Walmart pickling lime. The solid FGD samples were obtained from wet-limestone-forced oxidation (lsfo) scrubber systems from Louisville Gas and Electric (LG&E) and Tennessee Valley Authority (TVA) power plants.

DTG Runs to Find Regions of Mass Loss

To determine the conditions to be used to quantify the compounds discussed above, a macro TGA program using a ramp rate of 10°C/minute and a nitrogen atmosphere was run on each of the pure compounds used in the study. After matching mass losses with a specific compound, a program to isolate and quantify the mass loss was developed. Figure 1 shows the mass loss rates and temperatures for reactions that occur during the heating for three of the pure compounds. Data gathered using the program was used to check the percentages of various components in the compounds and calcium oxalate. Table 1 lists the results of these determinations. These data show excellent agreement between the true and experimentally determined compositions of the compounds. This agreement is an indication of the accuracy of the choice of analysis conditions. The data also illustrate the accuracy of the LECO TGA701 mass measurements.

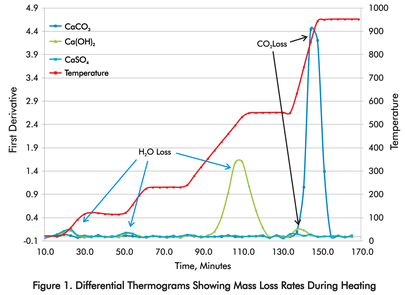

Figure 1. Differential Thermograms Showing Mass Loss Rates During Heating

Table 1. Composition of Pure Materials Used.

Compound	Component	Calculated Percent	Experimental Percent
$CaCO_3$	CaO	56.03	56.05
	CO_2	43.97	43.91
CaC_2O_4	CaO	38.38	38.33
	H_2O	19.17	19.19
	CO	30.12	29.86
	CO_2	12.33	12.02
$Ca(OH)_2$	CaO	75.68	75.16
	H_2O	24.32	23.61
$CaSO_4$	$CaSO_4$	100.0	99.6

The macro TGA program used for the runs with the pure compounds was adjusted and used to measure the mass losses of materials in various FGD solids. Table 2 lists the parameters measured, the temperature ramps, atmospheres, and other conditions used in the six-step macro-TGA program developed for the analysis of FGD solids.

Table 2. Parameters Measured, Temperature Ramps, and other Conditions for the Analysis of FGD Solids.

Parameter	Thermal Ramp	Ramp Rate	Hold Time	Atmosphere	Final Weight
Free moisture	Ambient to 50°C	1°C	—	Nitrogen	At constancy
$CaSO_4 \bullet 2H_2O$	50-240°C	17°C	15 Minutes	Nitrogen	End of step
$CaSO_3 \bullet ½H_2O$	240-400°C	17°C	5 Minutes	Nitrogen	End of step
$CaSO_3 \bullet ½H_2O$	400°C	0	15 Minutes	Oxygen	End of step
$Ca(OH)_2$	400-550°C	10°C	25 Minutes	Nitrogen	End of step
$CaCO_3$	550-950°C	25°C	15 Minutes	Nitrogen	End of step

Figure 2 is a thermogram of an FGD solid. The mass loss rate peaks corresponding to the evolution of various compounds used to quantify the compounds in the FGD solid are identified on the thermogram. Using these assignments, the macro TGA analysis of a large group of FGD solids was carried out. Data from a representative group of these samples is shown in Table 3. A measure of the accuracy of the analysis is how close the sum of the measured individual components come to 100%. The last column in Table 3 shows that all values are within 0.26% of the expected 100% total mass balance result, and is typical of the mass balance totals for the other samples used in the study.

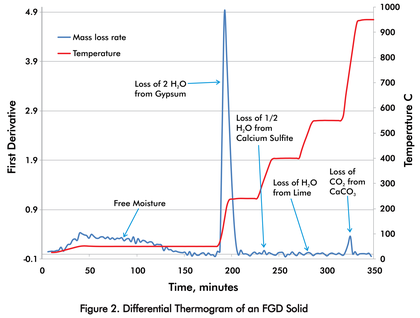

Figure 2. Differential Thermogram of an FGD Solid

Table 3. Examples of Results from Six-Step TGA Runs. (All values are percent mass fractions and are reported on a dry basis.)

	Compounds				Determined Ash	Calculated Ash	Calculated Fly Ash	Total Mass Balance
Sample	$CaSO_4 \bullet 2H_2O$	$CaSO_3 \bullet ½H_2O$	$Ca(OH)_2$	$CaCO_3$				
TVA 120	70.98	1.72	1.15	10.59	80.19	64.75	15.44	99.88
TVA 130	70.83	2.58	1.03	11.47	79.77	65.94	13.83	99.74
TVA 140	70.71	1.58	1.19	11.54	79.84	64.95	14.89	99.91
TVA 220	66.38	2.01	1.48	14.36	79.42	63.78	15.64	99.87
TVA 230	67.28	2.01	1.19	12.35	80.17	63.14	17.02	99.85
TVA 240	64.16	0.86	1.4	18.39	78.12	63.01	15.12	99.93
TVA 250	67.95	1.29	1.32	13.06	79.88	63.41	16.47	100.09
MC1	96.56	1.83	0.33	1.87	78.83	79.59	-0.76	99.84
MC2	95.98	2.32	0.33	1.74	79.18	79.58	-0.60	99.77

The MC1 and MC2 samples listed in Table 3 are from an LG&E plant that produces an FGD solid product that is wallboard-grade with $CaSO_4 \bullet 2H_2O$ values around 96%. As a side note some labs may choose to use just the first two steps of the program to determine the amount of $CaSO_4 \bullet 2H_2O$ in the FGD solid. As long as the $CaSO_4 \bullet 2H_2O$ content equals or exceeds the amount needed for wallboard-grade, the determination of the quantities of other materials in the FGD solid is not always necessary. The TVA samples contain a considerable amount of fly ash, as shown in the Table 3. Even with this variation in component concentrations, the macro TGA analysis yields results with excellent mass balance summaries for different types of samples.

A LECO SC832 sulfur and carbon analyzer was used to verify some of the macro TGA results. The system was calibrated with $CaSO_4$ (23.5% S) for sulfur and $CaCO_3$ (12.0% C) for carbon. The promoter COM-CAT™ was used in the analyses of the CaSO4 and all FGD solid samples. Table 4 lists some of the results from the analyses. The Percent Relative Error values for the sulfur comparisons are quite small and average near zero. The Percent Relative Error values for the carbon comparison are much higher and represent a high bias of about 0.7% (absolute) carbon for the measurements of the TVA samples. This "extra" carbon in these samples is attributed to unburned carbon in the original samples. This carbon is combusted and lost during the analysis. The LG&E samples (MC1 and MC2) have negligible carbon and fly ash contents.

Table 4. Comparison of Calculated and Determined Sulfur and Carbon Values.

Sample	Calculated Sulfur (%)	Determined Sulfur (%)	Sulfur Relative Error (%)	Calculated Carbon (%)	Determined Carbon (%)	Carbon Relative Error (%)
TVA 160	10.12	10.20	0.79	3.55	3.89	8.63
TVA 140	12.07	11.90	-1.42	2.31	2.96	22.09
TVA 210	13.72	14.00	1.98	1.18	1.95	39.25
TVA 110	14.19	14.00	-1.32	1.02	1.76	42.32
TVA 120	13.54	13.4	-1.05	1.29	2.11	38.90
TVA 130	13.63	13.6	-0.21	1.38	1.94	28.84
TVA 140	13.40	13.2	-1.54	1.37	2.23	38.47
TVA 160	12.69	12.7	0.06	1.90	2.54	25.33
TVA 210	13.46	13.8	2.46	1.21	2.31	47.68
TVA 220	12.88	12.7	-1.39	1.75	2.79	37.44
MC1	18.58	18.12	-2.53	0.22	0.36	40.12
MC2	18.71	18.24	-2.25	0.2	0.18	-12.73

A series of TGA runs were made with mixtures prepared by adding varying amounts of $CaCO_3$, $CaSO_4$, and $Ca(OH)_2$ (lime) to the MC1 FGD solid. The objective of the study was to evaluate the accuracy of measuring these three materials in the mixtures. The experiments showed that adding $CaCO_3$ had no effect on the other materials in the mixture. However, adding $Ca(OH)_2$ to the mixture produced a reaction in which a significant portion of the $Ca(OH)_2$ decomposed with the release of H_2O. The rate of the reaction of $Ca(OH)_2$ was about 25% for the amounts used. At the same time $CaSO_4$ was converted to the hydrated form $CaSO_4 \bullet 2H_2O$ in the presence of $Ca(OH)_2$. The rate of conversion to $CaSO_4 \bullet 2H_2O$ was about 20% of the amounts used in the experiments. In the absence of $Ca(OH)_2$, the rate of conversion was only 5-10%. Some of these results are shown in Table 5.

The composition of the MC1 FGD solid are given in Table 3. The values listed are given on the dry basis, but the actual sample contains about 14% moisture. The MC1 sample provides a moist and probably an acidic solid medium for reactions to occur. Thus the added lime reacts to release water. The reactive medium also allows some of the added $CaSO_4$ to absorb the water and form $CaSO_4 \bullet 2H_2O$. These experiments indicate $Ca(OH)_2$ readily reacts with FGD mixtures, even solid mixtures. In wet flue gas desulfurization systems, it is not likely any significant amount of $Ca(OH)_2$ will survive the desulfurization process.

Table 5. Results From Macro TGA Experiments with Mixed Solids.

Sample	Predicted $Ca(OH)_2$ Value (%)	Measured $Ca(OH)_2$ Value (%)	Percent Difference	Predicted $CaSO_4 \bullet 2H_2O$ Value (%)	Measured $CaSO_4 \bullet 2H_2O$ Value (%)	Percent Difference
10% $Ca(OH)_2$ + 10% $CaSO_4$ + 10% $CaCO_3$	9.137	5.419	40.70	64.99	77.40	-19.10
20% $Ca(OH)_2$ + 20% $CaSO_4$ + 20% $CaCO_3$	17.498	12.439	28.91	36.13	43.29	-19.81
30% Lime + 0% $CaSO_4$ + 0% $CaCO_3$	26.665	21.792	18.27	65.435	65.81	-0.57

Conclusions

Based on the data presented in this paper the following conclusions and summations can be made.

- The macro TGA analysis program developed during this study can be used to accurately quantify the various materials in flue gas desulfurization (FGD) solids.
- If the objective of a FGD system is to produce a wallboard-grade product, a short program using only the first two steps of the six-step program can be used to monitor $CaSO_4 \bullet 2H_2O$.
- Carbon and sulfur analysis data support the macro TGA results for the FGD solids.
- In wet FGD systems it is not likely that any significant amount of $Ca(OH)_2$ will survive the desulfurization process.
- The data and analytical results in this study demonstrate the accuracy of the LECO TGA701 mass measurements.

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