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by Arizona Instrument LLC

Loss-On-Drying vs. Thermogravimetric Analysis

Determining the Composition of Flue Gas Desulfurization By-Products by Gravimetric Analysis

Flue Gas Desulfurization Demystified

Flue gas desulfurization (FGD) is a process designed to remove sulfur dioxide (SO_2) from the exhaust gasses of coal burning power plants. The process uses a base, normally calcium hydroxide ($Ca(OH)_2$), to convert the SO_2 into calcium sulfite:

$$\mathrm{Ca(OH)_2} + \mathrm{SO_2} \;{-}{>}\; CaSO_3 + \mathrm{CO_2}$$

The resulting $CaSO_3$ can then oxidized to form a commercially viable product, calcium sulfate dihydrate, known in the industry as synthetic gypsum.

$$+ \,2\mathrm{H_2O} + \mathrm{O_2} {-}{>} CaSO_4 + \mathrm{H_2O}$$

The 'synthetic' moniker serves to differentiate it from natural mined gypsum. The oxidation from $CaSO_3$ to $CaSO_4$ should be monitored to ensure that a product of sufficient purity to be commercially viable is formed. The commercial viability of the resulting gypsum is important because it helps to offset the cost to the power industry of installing FGD equipment, and it prevents literally tons of material annually from ending up in landfills worldwide.

Testing for Gypsum Purity

The gypsum synthesized is used in a variety of applications. The construction industry uses it as the primary ingredient in drywall, and as a setting inhibitor in portland cement. The property of gypsum that makes it valuable as a fire retardant in construction materials is also what makes it a good candidate for thermogravimetric analysis. Namely, in gypsum each molecule of calcium sulfate has two molecules of water chemically bound to it. These waters of hydration can be removed by heating the material above 150°C.

$$\mathrm{CaSO_4} * 2\mathrm{H_2O} {-}{>} CaSO_4 + 2\mathrm{H_2O}$$

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Pure gypsum will lose 20.93 percent of its weight upon heating. This convenient chemical composition makes it relatively simple to test the purity of gypsum thermogravimetrically. First the material is dried by heating to a temperature low enough to drive off free moisture while retaining the chemically bound water, typically 40 to 80°C. Then the dried material is heated to 240°C to completely dehydrate it. Multiply the moisture loss in percent by 4.778 to determine the purity of the starting material. This process can be completely automated by the use of a modern moisture analyzer like the MAX® 5000XL by Arizona Instrument LLC. The instrument can be programmed to do all the calculations in the software, the end user simply has to start the test, load the sample, and record the final result.

Calcium Sulfite Hemihydrate

Things get a bit trickier if the material under test is not pure gypsum. For instance if the oxidation of the $CaSO_3$ is incomplete and not all of the material is converted to gypsum. A moisture analyzer, coupled with the chemistry of the $CaSO_3$ can help in these instances also. The calcium sulfite also exists as a hydrated salt, calcium sulfite hemihydrate. For every two molecules of $CaSO_3$, there is one molecule of chemically bound water. Like gypsum, these waters can be liberated thermally, but at much higher temperatures, typically 390 to 500°C.

$$\mathrm{CaSO_3} * \tfrac{1}{2}\mathrm{H_2O} \mathrel{-}> CaSO_3 + \tfrac{1}{2}\mathrm{H_2O}$$

Pure calcium sulfite hemihydrate will lose 6.97 percent of its weight upon heating to 500°C. Like gypsum, we can exploit this to determine the purity of the initial material. Multiplying moisture loss at 500°C in percent by 14.65 will yield the initial concentration of calcium sulfite hemihydrate in the sample. Again, this process can be automated in the moisture analyzer. The user simply adds the sample and allows the instrument to do the appropriate calculations.

Calcium Hydroxide

The calculations get trickier still if there is unreacted calcium hydroxide to account for. At temperatures sufficient to dehydrate calcium sulfate hemihydrate, $Ca(OH)_2$ decomposes:

$$\mathrm{Ca(OH)_2} \;--> \; CaO + \mathrm{H_2O}$$

The degradation of calcium hydroxide and the dehydration of calcium sulfate hemihydrate begin to occur at almost the exact same temperature. It is difficult, if not impossible, to control the temperature so that the two phenomena can be observed independently. However, since the theoretical weight loss of the two materials is different, the composition of the two constituents can be determined using the observed weight loss and some mathematical tricks. The theoretical loss due to the decomposition of pure CaOH is 24.3%. This corresponds to a factor of 4.111.

Putting it all Together

Using all these factors, a system of equations can be obtained that estimates the initial concentrations of calcium sulfate dihydrate, calcium sulfite hemihydrate, and calcium hydroxide in a sample.

Given:
A = raw result from calcium sulfate dihydrate portion of the test
B = raw result from the combined calcium sulfite hemihydrate and calcium hydroxide portion of the test

J = Calcium sulfate dihydrate constant = 4.778
K = Calcium sulfite hemihydrate constant = 14.655
L = Calcium hydroxide constant = 4.111

X = percent calcium sulfite hemihydrate
Y = percent calcium hydroxide
The result is a system of 2 equations:

$$X + Y + JA = 100 \qquad (1)$$

$$(X / K) + (Y / L) = B \qquad (2)$$

Solving for (2) in terms of (1) yields:

$$X = K(100 - LB - JA) / (K - L) \quad (3)$$

Plugging the constants above for J, K, and L into (3) yields:

$$X = [(14.655)*(100 - 4.111B - 4.778A)] / 10.544$$

Now while this may look somewhat intimidating, what it boils down to is a simple analysis that can be performed using a thermogravimetric analyzer to provide valuable information about the composition of a producer's FGD byproducts. The key components are an instrument that has the capability to reach temperatures sufficient to drive the reactions of interest, and the ability to separate the tests so that meaningful numbers are yielded at each stage. The Computrac® MAX® 5000XL is the ideal instrument for the analysis of not just gypsum, but all FGD by-products.

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