

Sulfuric Acid in Gas Samples for CEMS

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Sulfuric acid is commonly found in gas samples for CEMS. This note will discuss the problems created by sulfuric acid in gas samples, sources of the acid in gas samples, and ways to remove while minimizing losses of the other compounds of the sample.

Problems Created by Sulfuric Acid

Pure sulfuric acid (H_2SO_4) is a clear, colorless, oily liquid at room temperature. It is a very strong acid and is highly corrosive. It has a great affinity for water, and will absorb it from surrounding air. It boils at about $290^\circ C$. At $340^\circ C$ it decomposes into sulfur trioxide (SO_3) and water, so at the high temperatures present during combustion processes, sulfuric acid is not present, only sulfur trioxide. When gases are cooled, however, sulfur trioxide will react very readily with any available water to form sulfuric acid. At low concentrations and elevated temperatures this sulfuric acid is present as vapor only, but as the gases cool mists (tiny droplets) of sulfuric acid form. These will coalesce on components of an analysis system, causing damage due to corrosion or clogging.

Since sulfuric acid only forms at lower temperatures, the acid is not removed by filters in stack probes where the gases are still quite hot. It often forms too slowly even to be removed adequately by chiller/condenser systems when they are used to remove water from the sample. When this happens, sulfuric acid corrosion occurs downstream of the chiller, damaging analyzers or other components of the sampling system.

Dew points of complex gas mixtures are not dependent purely upon the water concentration; the final dew point actually depends upon not only on the water content but also upon the content of other compounds that condense into liquids at ambient temperature. The higher the boiling point of the other compound, the more effect it has on the dew point. Because sulfuric has a very high boiling point ($290^\circ C$) it can have a significant effect on the final sample dew point. Other acids such as hydrochloric or nitric acid have much less effect because they have much lower boiling points. Because of its extremely corrosive nature, its tendency to form acid mists at temperatures above the dew point predicted by merely the water content of the sample, and the difficulty in removing it, sulfuric acid is a common source of problems with stack gas sample analysis.

Sources of Sulfuric Acid

Sulfuric acid is produced commercially primarily by two methods:

1. Contact Process
2. Cascade Process

In the Contact Process of sulfuric acid synthesis sulfur dioxide forms sulfuric acid in the presence of oxygen and water by a two-step reaction:



The first reaction in this process has a reaction constant such that the sulfur trioxide level is normally about 10% of the sulfur dioxide level, given the oxygen levels present in stack gas samples. The second reaction proceeds very rapidly to form sulfuric acid whenever the temperature is below 340°C. Consequently when the sulfur dioxide level in a gas sample is high, sulfuric acid problems develop.

In the Chamber Process of sulfuric acid synthesis sulfur dioxide forms sulfuric acid in the presence of nitrogen oxides, oxygen, and water by a somewhat different two-step reaction:



These second reactions imply that if the NO_x levels are high and sufficient sulfur dioxide is present, sulfuric acid problems develop.

When fuels containing sulfur are burned, sulfur dioxide is produced. The Chamber Process and the Cascade Process are two examples of ways in which sulfur dioxide in turn can react with other components in the combustion gases (oxygen, water, nitrogen oxides) to form sulfuric acid.

Elimination of Sulfuric Acid Problems

Even if sulfuric acid forms in a gas sample, as long as it remains in the vapor phase it generally causes little or no problem. When the concentrations of water and sulfuric acid are sufficiently high to form acid mists at ambient temperature, corrosion problems will likely occur.

The dew point of a stream which takes into account the acid concentration may be calculated using the formula located. As a practical matter, most samples of gases from combustion processes where coal or oil is the fuel, contain about 10%-12% water. Gases from combustion processes where natural gas is the fuel contain about 22% water because the fuel has more hydrogen to form water. Gases from wet scrubber

systems have much higher water contents, typically 40-60%. Note that it was assumed that 2%, by weight, of SO₂ will react to form SO₃.

When sulfur dioxide is present in gas samples at concentrations of a few hundred ppm or less, formation of acid mist is not normally a problem unless the ambient temperature is quite low. If the sulfur dioxide concentration in a gas sample is more than 1000 ppm, acid mist problems are more likely, especially if the nitrogen oxides level is also high. One answer to this problem is simply to lower the water content. Since the acid dew point depends upon the water content as well as the acid, lowering the water content sufficiently will prevent the formation of acid mists unless the acid content is quite high. Nafion™ tubing gas dryers from Perma Pure can reduce the water content of a sample down to a water dew point as low as -45°C (about 75ppm of water), although -10°C to -25°C is typical. Several models of GASS™ Gas Analysis Sampling Systems are available from Perma Pure that incorporate these dryers into complete sample conditioning systems to prepare a gas sample for analysis.

The GASS-2040 Gas Analysis Sampling System is designed specifically to address this problem. In this system, a coalescing filter is installed upstream of the gas dryer. The temperature of this filter and an accompanying Hastelloy heat exchanger is controlled separately from the rest of the system. By lowering the temperature of the gas sample sufficiently (typically down to 60°-75°C) while it still contains significant amounts of water, sulfuric acid can be forced to condense. The coalescing filter will then remove the acid from the gas stream. An accompanying automatic drain will periodically remove the condensed acid. This process will remove very little of other gases, even water-soluble ones such as sulfur dioxide or nitrogen oxides, because only sulfuric acid is being condensed not water. The presence of the heat exchanger gives the sample sufficient time to cool down so that sulfuric acid mist droplets will reach a size where they can be efficiently removed by the filter.

After sufficient sulfuric acid has been removed, the sample is reheated and passed to a Nafion™ tubing gas dryer to selectively remove the water. After exiting the GASS system, the sample has a much lower concentration of both sulfuric acid and of water, so acid mists do not form again downstream. Unfortunately, sometimes the sulfuric acid content of a sample is so high that merely removing more water is not enough. From the equation above one can see that even if the water content is zero sulfuric acid alone contributes its own dew point. If the sulfuric acid concentration is quite high it is necessary to reduce both the sulfuric acid concentration and the water concentration to prevent the formation of acid mists. Chiller/condenser systems on the other hand often fail to remove the very fine acid mist formed in the short time the sample is within the cool zone of these systems.

Other related topics can be found at:

“Solving the problem of low level NO_x measurements in hot, wet, sample streams“, a customer testimonial.

“Comparison of SO₂ losses in Continuous Emission Monitoring Systems“, SO₂ solubility in water as a function of temperature.

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