Formation of Ammonium Bisulfate

Attn: HRSG End Users
Re: Formation of Ammonium Bisulfate

Observation: Why is it that some plants experience severe fouling from Ammonium Bisulfate and others do not?

Those HRSG’s that have Selective Catalyst Reduction systems (SCR’s) or NOx catalysts experience a whitish, yellowish and sometimes black substance on the finning of the tubes and in the basement areas of the HRSG. The substance is typically ammonium sulfate/bisulfate, ammonium hydrogen sulphate, or worse ammonium bisulfate (black and tar like). The latter being the most corrosive.

The basic formula for a traditional ammonia type NOx catalyst is as follows:

\[ 4 \text{NO} + 4 \text{NH}_3 + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} \]
\[ 6 \text{NO}_2 + 8 \text{NH}_3 \rightarrow 7 \text{N}_2 + 12 \text{H}_2\text{O} \]

The NOx contained in normal flue gas is generally composed of Nitrogen (~95%), and Nitrous Oxides (~5%). Sulfur is present in most fuels even in Natural Gas; in the winter the sulfur content in natural gas has been known to be as high as 50 ppm. As a result of this sulfur, ammonium sulfates can form, as illustrated by the following equation:

\[ 2\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{HSO}_4 \]
\[ \text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{HSO}_4 \]

Ammonium sulfates are also formed when the NH3 content of the flue gas exceeds that of the sulfur (SO3); the amount of ammonium bisulfate then can increase as the ammonia slip increases. Ammonia slip can be decreased with the better controls and improved Ammonia Injection Grids (AIG’s), but insufficient slip can create ammonium bisulfite which is acidic (sulfates are not, they are a neutral salt). Other variables are velocity/temperature profiles, oxygen levels, water content, cycling, presence of a CO or Burner, NH3/SO3 ratios, etc.

These formations or salts typically form in the cooler sections of the HRSG and are a real problem in those areas where the temperatures are below the water dew point. Once the sulfates form, there are three choices to clean the heating surfaces:

1. Water Washing
2. Bead Blasting
3. CO2 Cleaning

CO2 cleaning offers the advantage of not requiring as many hazardous material waste containers because it evaporates, thus only the ABS is disposed of.

Besides the sulfates forming that will degrade performance, sulfuric acid can also form which will corrode those areas where the temperatures are below the acid and water dew point. Areas to be concerned with are Low Pressure Economizers, Feed Water Pre-Heaters that have Carbon Steel fins, and basement areas where there are casing penetrations. The formula for this reaction is as follows:

\[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \]

Want to know more or view some JPEG files of actual formations, give us a call at 502.899.4500 and ask for the Aftermarket Department.

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