Severe Corrosion in the Incinerator of an SRU

The case study that is the subject of this month’s issue of The Contactor™ arose from stack tests on an SRU. High SO₂ levels were found together with a high concentration of acid mist. Acid mist seemed to be related to the operation of the sour water stripper (SWS) but in a way whose chemistry was not understood. However, ammonia was suspected to be a contributor.

Most of the ammonia produced in a refinery is collected in sour water. Sometimes it can be prevented from entering the SRU from the SWS by employing a two-stage stripping process which produces concentrated streams of H₂S and NH₃. ProTreat® is an excellent tool for accurate design and simulation of two-stage SWSs. Either this ammonia stream can be further concentrated into a marketable anhydrous form, or it can be directly incinerated. In both cases though, two-stage stripping keeps most of the ammonia out of the SRU. However, when ammonia is incinerated, its combustion products include NOₓ. If the ammonia stream is combined with tail gas from an SRU and incinerated, produced SO₂ and NOₓ are present together in an oxidizing atmosphere, and we have all the ingredients for making sulfuric acid (mist) via the lead chamber process!

This process was once a large industrial scale route to sulfuric acid. Sulfuric acid was first produced this way in 1746, and even in 1946 about a quarter of all sulfuric acid was still produced using this method. First, sulfur dioxide is produced either from elemental sulfur or by roasting pyritic ores:

\[ S₈ + 8O₂ → 8SO₂ \]

\[ 4FeS₂ + 11O₂ → 2Fe₂O₃ + 8SO₂ \]

In an SRU, SO₂ will always be produced by burning the H₂S contained in the tail gas. There is even more present during an SO₂ breakthrough.

In the lead chamber process, oxides of nitrogen are formed either by the action of sulfuric acid on sodium nitrate:

\[ 2NaNO₃ + H₂SO₄ → Na₂SO₄ + H₂O + NO + NO₂ + O₂ \]

or by hydrolysis of nitrosylsulfuric acid:

\[ 2NOHSO₄ + H₂O → 2H₂SO₄ + NO + NO₂ \]

In the incinerator of an SRU,combusting ammonia also produces NOₓ components because the main fuel is actually hydrocarbon. For example, it has been reported in a very interesting paper that the degree of conversion of ammonia to NOₓ is a strong function of excess air, ammonia content in the hydrocarbon fuel, and the degree of mixing in the flame. So the chemical species necessary for generating sulfuric acid by the chemistry of the lead chamber process are present because (1) there is always SO₂, and (2) ammonia enters the incinerator either directly from a 2-stage SWS, or from incomplete destruction of NH₃ in the reaction furnace.

Note: ProTreat includes a real kinetic model for NH₃ destruction in the reaction furnace.

Nitric oxide, NO, acts as a homogeneous catalyst for SO₂ oxidation to SO₃:

\[ NO + \frac{1}{2}O₂ → NO₂ \]

\[ NO₂ + SO₂ → NO + SO₃ \]

The first reaction is the rate determining step. Of course, water is a combustion product, too, and it reacts with SO₃ to form sulfuric acid:

\[ SO₃ + H₂O → H₂SO₄ \]

Thus, there is the possibility that highly corrosive sulfuric acid mist can be generated in the incinerator and stack from an SRU if ammonia is present.

To learn more about this and other aspects of gas treating, plan to attend one of our training seminars. Visit www.protreat.com/seminars for details.

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