Minimize Sulfur Pit Vent Contribution to Stack Emissions

Grant Qui, P.E.  
Excel Paralubes - ConocoPhillips 
2800 Old Spanish Trail 
Westlake, LA 70609 
337-491-5464 
Grant.Q.Qui@conocophillips.com

Al Keller  
Refining Technical Services - ConocoPhillips 
3008 MO 
Houston, TX 77079 
281-293-3168 
Al.E.Keller@conocoPhillips.com

Abstract

SO₂ stack emissions approaching the EPA rolling 12 hour average of 250 ppmv limited the capacity of two parallel 90 LTPD SRU/TGU trains at the ConocoPhillips Lake Charles Manufacturing complex. Using data from a performance test by Brimstone STS on the SRU/TGU and sulfur storage pit, a plan was developed to reduce TRS and sulfur pit vapor emissions allowing increased acid gas throughput. Individual plan steps and subsequent positive results are discussed.

Introduction

Sulfur recovery units have environmental limits on emissions from the sulfur plant stack. These limits include a concentration limit such as 250 ppmv SO₂ on 12 hour rolling average corrected at zero percent excess air or a mass limit in pounds SO₂ emission per hour. There are two sulfur containing gas streams normally going to the sulfur plant stack. The first one is the process gas from the tail gas amine absorber overhead, which is then routed to the incinerator (thermal oxidizer) for H₂S destruction and enters the stack. The other sulfur containing gas stream going to the incinerator is the pit vent gas. The pit vent gas carries H₂S released from liquid sulfur by natural degassing or forced degassing in the sulfur pit (or storage tank) to keep the sulfur storage safely below the lower explosion limit (LEL) of 3.7% H₂S in the vapor space. Both sources contain sulfur compounds and contribute to SO₂ emissions in the stack.

When SO₂ emissions in the stack are near the maximum limit, the operators typically cut back the flow of pit vent gas. However, this may lead to blocking in the pit vent gas inadvertently, allowing H₂S containing gases to emit to the atmosphere, resulting in personal H₂S exposure and possible sulfur pit fire/explosion. This article is a summary of the effort to quantify the relative SO₂ contribution to the stack from process gas and pit vent gas. It also describes an effort to minimize the pit vent gas contribution while maintaining a safe and reliable sulfur plant operation.

Figure 1 shows a typical Claus process and sulfur rundown diagram using an underground storage pit. The process gas from tail gas amine absorber overhead and
the pit vent from sulfur storage pit are the two sources that contribute to stack SO₂ emissions.

In the sulfur pit, the dissolved H₂S and H₂Sₓ in liquid sulfur from waste heat boiler and sulfur condensers are stripped with sparging air and oxidized to form elemental sulfur and SO₂. Sulfur vapor, SO₂ and unconverted H₂S are swept to the thermal oxidizer.

*Figure 1: Claus Process and Sulfur Rundown:*

The problem

The Lake Charles Refinery Manufacturing Complex has sulfur processing capacity including 4 Claus/TGU trains, a sulfuric acid plant, and an off-site NaHS plant. The loss of a significant amount of capacity in any one of these units can impact the overall sulfur balance in the refinery which may require adjustments in upstream unit rates including crude units, hydrodesulfurization units, FCC, Coker units or sometimes to shut down wash water to HDS units or sour water processing units (sour water strippers) temporarily. Crude slate changes and higher severity of hydrotreating for cleaner diesel and gasoline can also add more acid gas feed to the SRUs. Any constraints in sulfur processing units such as SRU stack emission constraints are not desirable. Sulfur plant stack emission will naturally go up over time as the Claus catalyst or the tail gas hydrogenation bed catalyst ages slowly losing its activity. When a sulfur plant can not run the rate it used to run, there will be an intensified effort to review sulfur plant operation and troubleshoot for sulfur plant emission problems. A lower sulfur stack emissions also supports our core value of reducing pollution!
Figure 2 shows the stack SO₂ was trending higher near the maximum 250 ppm in April / May 2010 and the unit could not run the rate demonstrated in the first half of 2009.

**Figure 2: SRU SO₂ emissions vs. feed rate.**

The troubleshooting effort started with determining the SO₂ sources to the stack. This lead to a number of optimization adjustments in operating temperatures from Claus and hydrogenation bed inlet temperatures. The most significant reduction of stack SO₂ emission came from reducing liquid sulfur temperature and lowering the pit sweep gas flow rate.

**SO₂ Mass Balance**

Brimstone STS were brought in to conduct sample analysis in 2007. Data was used to establish optimum operating conditions and benchmark the sulfur plant process gas and pit vent emission contributions.

Summary data are listed below for the sulfur rundown and gas streams.

<table>
<thead>
<tr>
<th>Sulfur Rundown</th>
<th>Dissolved, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Source</td>
<td>H₂S</td>
</tr>
<tr>
<td>SRU WHB Rundown</td>
<td>440</td>
</tr>
<tr>
<td>SRU Cond 1 Rundown</td>
<td>263</td>
</tr>
<tr>
<td>SRU Cond 2 Rundown</td>
<td>58</td>
</tr>
<tr>
<td>SRU Cond 3 Rundown</td>
<td>12</td>
</tr>
<tr>
<td>SRU Cond 4 Rundown</td>
<td>2</td>
</tr>
<tr>
<td>SRU Degassed (pit)</td>
<td>42</td>
</tr>
</tbody>
</table>
Process Gas and Pit Vent Gas Analysis

<table>
<thead>
<tr>
<th>Sample Source</th>
<th>H₂S, ppm</th>
<th>COS, ppm</th>
<th>SO₂, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRU Absorber OVHD</td>
<td>30~50</td>
<td>100~130</td>
<td>-</td>
</tr>
<tr>
<td>SRU Sulfur Pit Gas</td>
<td>200~900</td>
<td>&lt;80</td>
<td>200~600</td>
</tr>
</tbody>
</table>

To determine the SO₂ mass balance, the pit vent gas was blocked away from thermal oxidizer temporarily. The process gas contribution to stack was measured with the thermal oxidizer analyzer. Process flows with and without pit sweep were generated (see Figure 3 for the block diagram and flow conditions).

Figure 3: Process conditions with pit vent gas
1. With pit vent to thermal oxidizer, T.O., with flows in MSCFH in ()
   - Estimated flow to T.O.: = Abs ovhd gas (311) + fuel gas (18) + air (285) + pit vent (22) = 636 MSCFH
   - SO₂ at T.O.: 190 ppmv.
   - SO₂ volume = 636 MSCFH * 190 ppmv = 120.8 SCFH or /379 * 64 = 20.4 lbs/hr

2. Without pit vent to thermal oxidizer
   - Estimated flow to T.O.: = Abs ovhd gas (311) + fuel gas (16) + air (264) + pit vent (0) = 591 MSCFH.
   - SO₂ at T.O.: 110 ppmv.
   - SO₂ volume = 591 MSCFH * 110 ppmv = 65 SCFH or /379 * 64 = 11 lbs/hr

3. Equivalent SO₂ concentration in process gas:
   = 65 scfh/311 MSCFH = 209 ppmv

The equivalent SO₂ concentration (209 ppm) was higher than the normal expected level and the analytical test results in the past (30 ppm H₂S and 100 ppm COS). COS was believed to be formed in the hydrogenation reactor where unconverted CO from the water gas shift reaction participated with H₂S to form COS and H₂ in the “sour gas” shift reaction. Adjustment was made to increase hydrogenation bed temperature to increase COS destruction in the hydrogenation bed. The Claus bed temperatures were also optimized based on the above calculation.

4. Equivalent SO₂ concentration in pit vent:

The SO₂ contribution from pit vent was calculated with the results from step 1 and 2.

The SO₂ volume from pit vent = SO₂ volume with pit vent (120.8) - SO₂ volume without pit vent (65) = 55.8 SCFH.

The equivalent SO₂ concentration in the process gas:
= SO₂ volume (55.8 scfh) /pit vent volume (22 mscfh) = 2536 ppmv

The equivalent SO₂ concentration of 2536 ppm in the pit vent was very high comparing to the design concentration of 350 to 900 ppm H₂S and 350 to 550 ppm sulfur mist (The analytical test in 2007 showed 200 to 900 ppm H₂S, 200 to 600 ppm sulfur mist was not included). **Amount of sulfur mist and sulfur vapor in the pit vent exceeded the design by about 1000 to 1500 ppm.**

Higher liquid sulfur temperature and higher pit sweep flow can carry excess sulfur mist and sulfur vapor to the pit vent and thermal oxidizer. A step test was conducted to lower the degassing pit liquid sulfur temperature and reduce the abnormal high pit vent flow to a comfortably safe level.
**Step Test**

There are two ways to reduce the temperature of liquid sulfur from the sulfur condensers: a sulfur cooler if it is available and/or reduce the steam pressure of the sulfur condensers (typically 50 psig steam pressure). For a sulfur pit degassing operation, a sulfur cooler is provided to cool the liquid sulfur from the sulfur condensers to about 275 °F in order to achieve the optimum degasification. For our case, the sulfur cooler is no longer available due to plugging problems. The steam pressure from the sulfur condensers is the handle we chose. The steam pressure was reduced from 57 psig to 53 psig. The sulfur pit temperature dropped about 5 °F as a result.

What is the proper volume of pit vent gas? Criteria for proper volume of pit vent should include: 1) Achieve vacuum condition in pit at all time (no H2S exposure in the pit area), 2) maintain less than 3.7% LEL of H2S in pit vapor space (no pit fire and/or explosion) and 3) minimize elemental sulfur carrying over to thermal oxidizer (no excess stack emissions).

The pit vapor sample analysis in 2007 showed 200 to 900 ppm H2S in the pit vent with pit vent flow at 24 MSCFH. The concentration was far less than the 3.7% H2S LEL. An operating envelope can be defined from LEL and safety margin consideration (25% of LEL considered acceptable). For a 180 LTPD design capacity of sulfur unit with sulfur degassed from 400 ppm to 10 ppm H2S, the minimum pit vent flow at LEL can be defined: Sulfur production 180 LTPD *2240 /24 hr *390 ppm /34 MW *379 /3.7% = 2 MSCFH. The safe operating window can be ~8 MSCFH based on 25% of LEL. A modification on pit flow control was done to lower the pit vent flow.

Below are the test steps and observed responses:

<table>
<thead>
<tr>
<th></th>
<th>Dissolved H2S + H2Sx in liquid sulfur</th>
<th>Degassing efficiency</th>
<th>Unconverted H2S + H2Sx to pit vent</th>
<th>Sulfur vapor</th>
<th>Sulfur mist</th>
<th>Stack SO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid Sulfur Temperature from 300 °F to 295 °F</td>
<td>↓</td>
<td>↓</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
<td>15 ppm</td>
</tr>
<tr>
<td>Sulfur Pit Vent Flow from 22 mscfh to 15 mscfh</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>30 ppm</td>
</tr>
</tbody>
</table>

With a lower sulfur temperature and lower sulfur pit vent flow, the overall stack SO2 emission was reduced by about 50 ppm. Unit rate was regained back to the design rate.
Conclusion

Excess sulfur plant stack emissions can be caused by different reasons. We often focus on catalyst activities and amine absorption efficiency during troubleshooting and forget about the sulfur mist and vapor carrying over to the thermal oxidizer. The SO$_2$ contribution from the pit vent was found to be about 50% from mass balance. With a lower sulfur temperature and defining better operating window for the pit vent flow, we can achieve a lower SO$_2$ emission and improve unit rate.

References
