

# Minimize Sulfur Pit Vent Contribution to Stack Emissions

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## Abstract

SO<sub>2</sub> 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 SO<sub>2</sub> on 12 hour rolling average corrected at zero percent excess air or a mass limit in pounds SO<sub>2</sub> 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 H<sub>2</sub>S 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 H<sub>2</sub>S 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% H<sub>2</sub>S in the vapor space. Both sources contain sulfur compounds and contribute to SO<sub>2</sub> emissions in the stack.

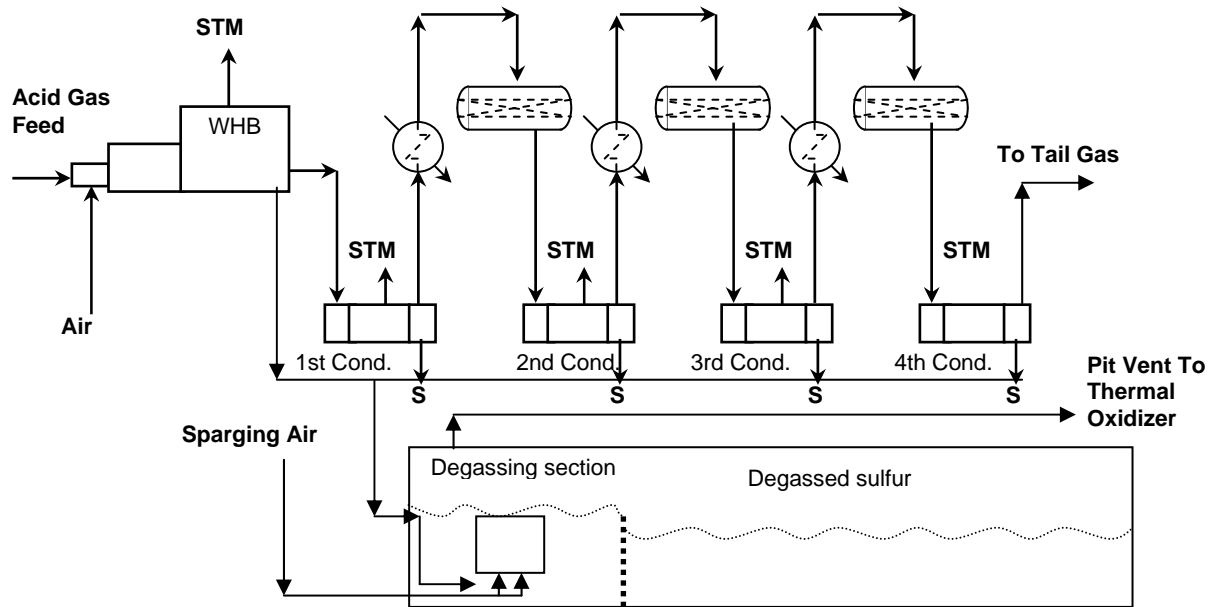
When SO<sub>2</sub> emissions in the stack are near the maximum limit, the operators typically cut back the flow of pit vent gas. However, this may lead to blocking in the pit vent gas inadvertently, allowing H<sub>2</sub>S containing gases to emit to the atmosphere, resulting in personal H<sub>2</sub>S exposure and possible sulfur pit fire/explosion. This article is a summary of the effort to quantify the relative SO<sub>2</sub> 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 SO<sub>2</sub> emissions.

In the sulfur pit, the dissolved H<sub>2</sub>S and H<sub>2</sub>S<sub>x</sub> in liquid sulfur from waste heat boiler and sulfur condensers are stripped with sparging air and oxidized to form elemental sulfur and SO<sub>2</sub>. Sulfur vapor, SO<sub>2</sub> and unconverted H<sub>2</sub>S are swept to the thermal oxidizer.

Figure 1: Claus Process and Sulfur Rundown:

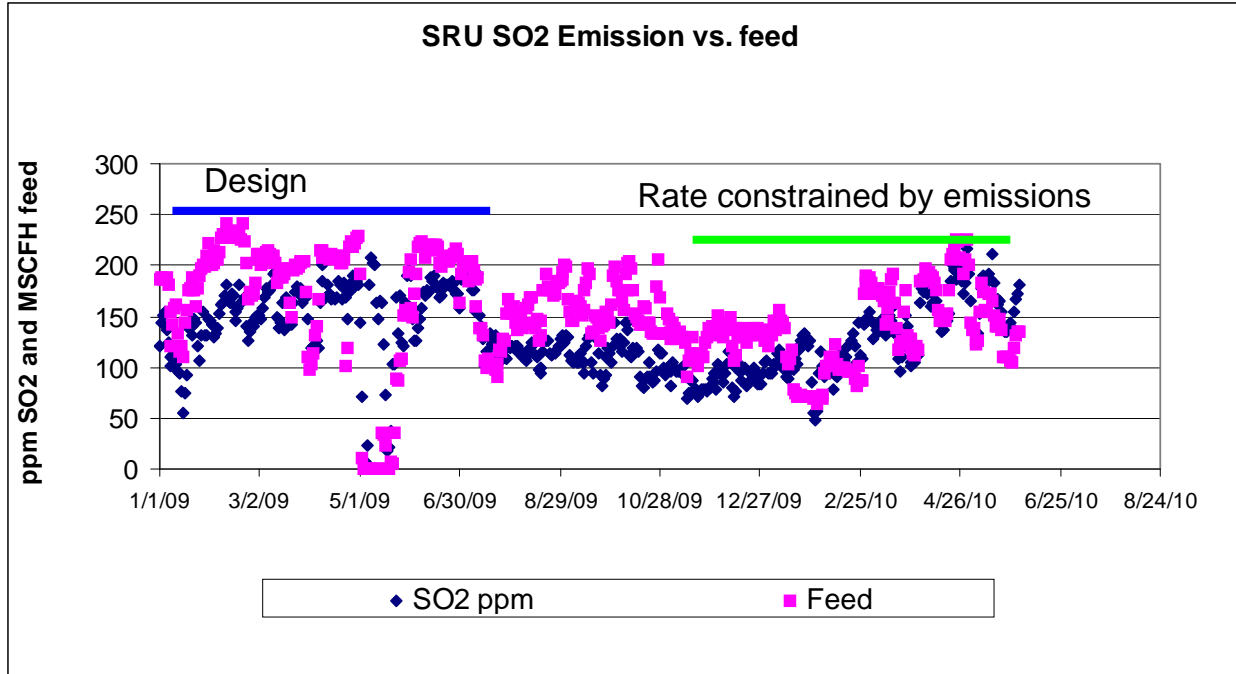


### The problem

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 SO<sub>2</sub> 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 SO<sub>2</sub> emissions vs. feed rate.



The troubleshooting effort started with determining the SO<sub>2</sub> sources to the stack. This led to a number of optimization adjustments in operating temperatures from Claus and hydrogenation bed inlet temperatures. The most significant reduction of stack SO<sub>2</sub> emission came from reducing liquid sulfur temperature and lowering the pit sweep gas flow rate.

### SO<sub>2</sub> 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.

Sulfur Rundown Sample Source	Dissolved, ppm		
	H <sub>2</sub> S	H <sub>2</sub> S <sub>x</sub>	Total
SRU WHB Rundown	440	196	636
SRU Cond 1 Rundown	263	285	548
SRU Cond 2 Rundown	58	53	111
SRU Cond 3 Rundown	12	10	22
SRU Cond 4 Rundown	2	1	3
SRU Degassed (pit)	42	41	83

Process Gas and Pit Vent Gas Analysis

Sample Source	H <sub>2</sub> S, ppm	COS, ppm	SO <sub>2</sub> , ppm
SRU Absorber OVHD	30~50	100~130	-
SRU Sulfur Pit Gas	200 ~900	<80	200~600

To determine the SO<sub>2</sub> mass balance, the pit vent gas was blocked away from thermal oxidizer temporary. 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).

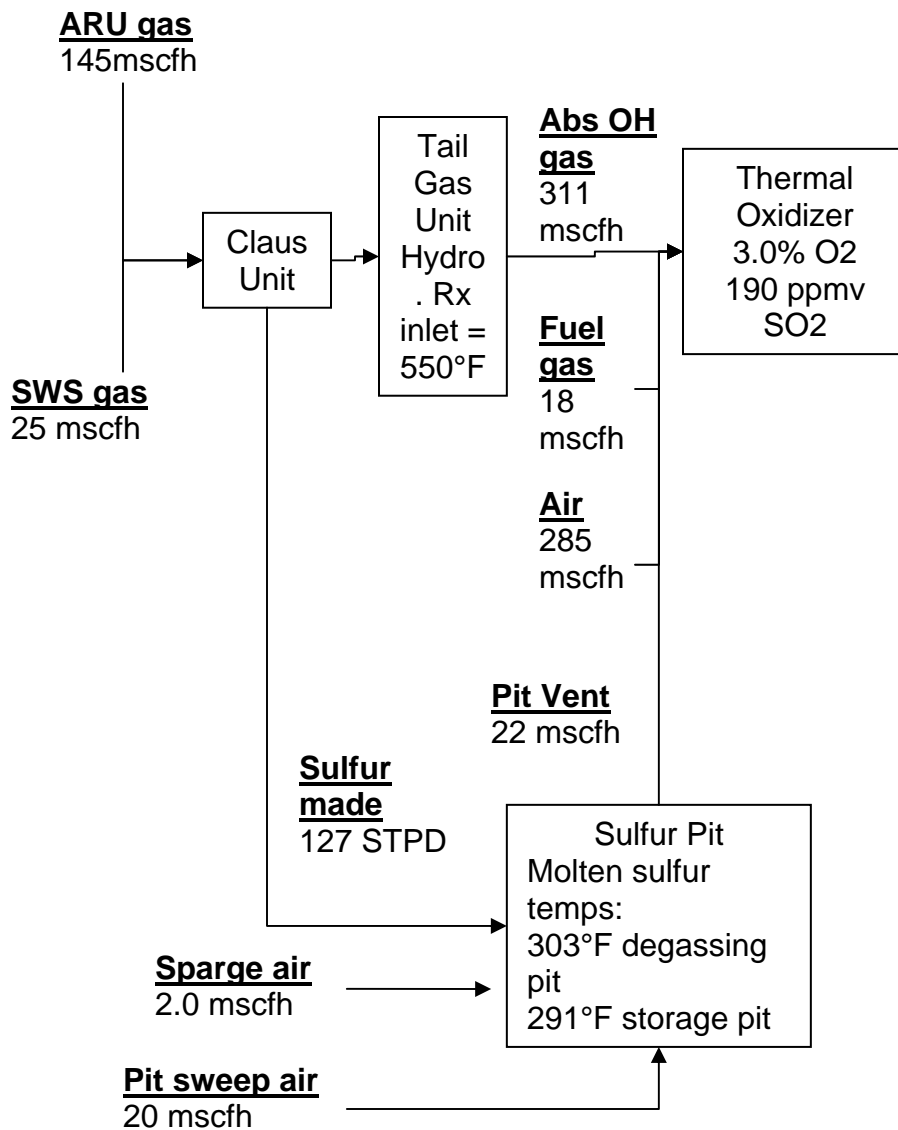


Figure 3: Process conditions with pit vent gas

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
- SO<sub>2</sub> at T.O.: 190 ppmv.
- SO<sub>2</sub> 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.
- SO<sub>2</sub> at T.O.: 110 ppmv.
- SO<sub>2</sub> volume = 591 MSCFH \* 110 ppmv = **65 SCFH** or /379 \* 64 = 11 lbs/hr

3. Equivalent SO<sub>2</sub> concentration in process gas:

$$= 65 \text{ scfh} / 311 \text{ MSCFH} = 209 \text{ ppmv}$$

The equivalent SO<sub>2</sub> concentration (209 ppm) was higher than the normal expected level and the analytical test results in the past (30 ppm H<sub>2</sub>S 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 H<sub>2</sub>S to form COS and H<sub>2</sub> 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 SO<sub>2</sub> concentration in pit vent:

The SO<sub>2</sub> contribution from pit vent was calculated with the results from step 1 and 2.

The SO<sub>2</sub> volume from pit vent = SO<sub>2</sub> volume with pit vent (120.8) - SO<sub>2</sub> volume without pit vent (65) = **55.8 SCFH**.

The equivalent SO<sub>2</sub> concentration in the process gas:

$$= \text{SO}_2 \text{ volume (55.8 scfh) } / \text{pit vent volume (22 mscfh)} = 2536 \text{ ppmv}$$

The equivalent SO<sub>2</sub> concentration of 2536 ppm in the pit vent was very high comparing to the design concentration of 350 to 900 ppm H<sub>2</sub>S and 350 to 550 ppm sulfur mist (The analytical test in 2007 showed 200 to 900 ppm H<sub>2</sub>S, 200 to 600 ppm SO<sub>2</sub>. 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.

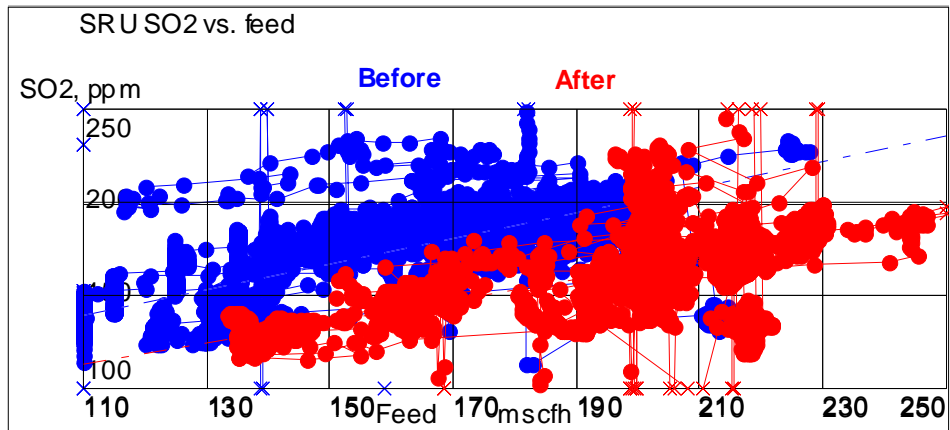
What is the proper volume of pit vent gas? Criteria for proper volume of pit vent should include: 1) Achieve vacuum condition in pit at all time (no H<sub>2</sub>S exposure in the pit area), 2) maintain less than 3.7% LEL of H<sub>2</sub>S in pit vapor space (no pit fire and/or explosion) and 3) minimize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

The pit vapor sample analysis in 2007 showed 200 to 900 ppm H<sub>2</sub>S in the pit vent with pit vent flow at 24 MSCFH. The concentration was far less than the 3.7% H<sub>2</sub>S 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 H<sub>2</sub>S, 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:

	Dissolved H <sub>2</sub> S + H <sub>2</sub> S <sub>x</sub> in liquid sulfur	Degassing efficiency	Unconverted H <sub>2</sub> S + H <sub>2</sub> S <sub>x</sub> to pit vent	Sulfur vapor	Sulfur mist	Stack SO <sub>2</sub>
Liquid Sulfur Temperature from 300 °F to 295 °F ↓	↓	↑	↓	↓	↓	15 ppm ↓
Sulfur Pit Vent Flow from 22 mscfh to 15 mscfh ↓	—	—	—	↓	↓	30 ppm ↓

With a lower sulfur temperature and lower sulfur pit vent flow, the overall stack SO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> emission and improve unit rate.

### References

1. "Sulfur Recovery Unit Test Run Report", by Brimstone STS, February 2007.
2. "Shell Sulfur Degasification Units for Sulfur Recovery Unit" Goar, Allison & Associates, Inc. September 1994.