

# Low-Emission Sulfur Plant Startups and Shutdowns – Part 2

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## ABSTRACT

Many refiners, both in the U.S. and around the world, are facing increasing pressure from regulatory agencies to reduce the sulfur dioxide (SO<sub>2</sub>) emissions that occur when starting up and shutting down their sulfur recovery plants. In fact, many must stay below their permitted SO<sub>2</sub> emissions limits during these periods of transient operation.

This paper is a follow-up to a paper<sup>1</sup> presented in 2016 that attempted to address the question "Is there a better way to achieve low-emission startups and shutdowns in new and existing sulfur recovery plants?" The previous paper (i.e., "Part 1") discusses the options considered, the changes implemented, and the results achieved by two U.S. refineries in their efforts to reduce their sulfur plant startup and shutdown emissions while preserving the mechanical integrity and useful life of their equipment.

This paper presents a similar story with a significantly different outcome. The same modifications were made to a much older sulfur recovery plant in a U.S. refinery and the results were less than ideal. This paper briefly reviews the potential causes of high SO<sub>2</sub> emissions during startups and shutdowns, options for reducing these SO<sub>2</sub> emissions, and the modifications made to this sulfur recovery plant. However, the majority of this paper focuses on the experience gained and the lessons learned during and after the initial restart of this facility following the low-emissions modifications.

## **INTRODUCTION**

In the past, refiners have been allowed to vent higher-than-permitted levels of sulfur dioxide (SO<sub>2</sub>) to the atmosphere while starting up and shutting down their sulfur recovery plants. However, many refiners, both in the U.S. and around the world, are facing increasing pressure from regulatory agencies to reduce the SO<sub>2</sub> emissions that occur during these transient operations.

In the U.S., the Environmental Protection Agency (EPA) has negotiated 37 consent decrees with U.S. companies since March 2000 which cover over 95% of the nation's petroleum refining capacity.<sup>2</sup> As part of these settlements, companies have agreed to significant reductions in NO<sub>x</sub> and SO<sub>2</sub> emissions, resulting in investing more than \$7 billion in control technologies, paying civil penalties of more than \$116 million, and performing additional environmental projects with a total cost of over \$116 million.<sup>2</sup> This has caused a number of U.S. refineries to seek alternative modes of operation to reduce SO<sub>2</sub> emissions and avoid paying substantial penalties.

In 2013/2014, two U.S. refiners – Refiner A and Refiner B – contacted Ortloff (the designer and licensor for their sulfur plants) to study reducing the amount of SO<sub>2</sub> emissions and/or the duration of high SO<sub>2</sub> emissions when starting up and shutting down their sulfur plants. Ortloff studied the potential causes of high SO<sub>2</sub> emissions during startups and shutdowns and examined some of the issues created when refineries attempt low-emission startups and shutdowns without the proper procedures, equipment, or controls. Ortloff presented options for avoiding these issues while also reducing SO<sub>2</sub> emissions, including the cost impact and benefits of each option. The results of the two studies and the changes implemented at each of the refineries were the subject of the cited paper presented in 2016.

In 2016/2017 Refiner X, working with Ortloff, implemented similar changes to one of their sulfur recovery plants. They too were facing pressure to remain below their normal operating SO<sub>2</sub> emissions limit of 250 PPMV on a dry, 0% excess air basis during startup and shutdown. Unfortunately, the results they achieved were not as positive as those achieved by Refiner A and Refiner B. Following implementation of the recommended modifications, Refiner X still exceeded their permitted SO<sub>2</sub> emissions limit when re-starting their facility.

This paper discusses what happened during that startup, why Refiner X exceeded their SO<sub>2</sub> emissions limit, and what can be done in the future to enable them to remain below their normal operating SO<sub>2</sub> emissions limit during startup and shutdown.

The paper is presented in four sections:

1. Section 1 provides background information on the Refinery X sulfur plant, and discusses the typical sources of high SO<sub>2</sub> emissions during startup and shutdown.
2. Section 2 describes the modifications that were implemented by Refiner X.
3. Section 3 describes what went wrong during the restart of each unit in the Refinery X sulfur plant.
4. Section 4 presents conclusions, recommendations, and lessons learned from this startup experience.

# 1 BACKGROUND

## 1.1 SRU Complex at Refinery X

The Refinery X SRU complex consists of two parallel Claus sulfur recovery units (SRUs) with a common tailgas cleanup unit (TGCU) and tailgas thermal oxidation unit (TTO, or incinerator). Sulfur Recovery Unit 1 (SRU 1) was designed for a sulfur production of about 100 LT/D from amine acid gas and sour water stripper (SWS) gas produced elsewhere in the refinery. Sulfur Recovery Unit 2 (SRU 2) was designed for a sulfur production of about 160 LT/D. SRU 1 was designed and installed by The Ortloff Corporation in 1982-1983, along with the TGCU and TTO. SRU 2 was designed by Ortloff Engineers, Ltd. and installed by others in 1992-1993. Each unit was subsequently revamped for low-level oxygen enrichment

The following flow diagram illustrates the general arrangement and key features of the Refinery X sulfur recovery complex.

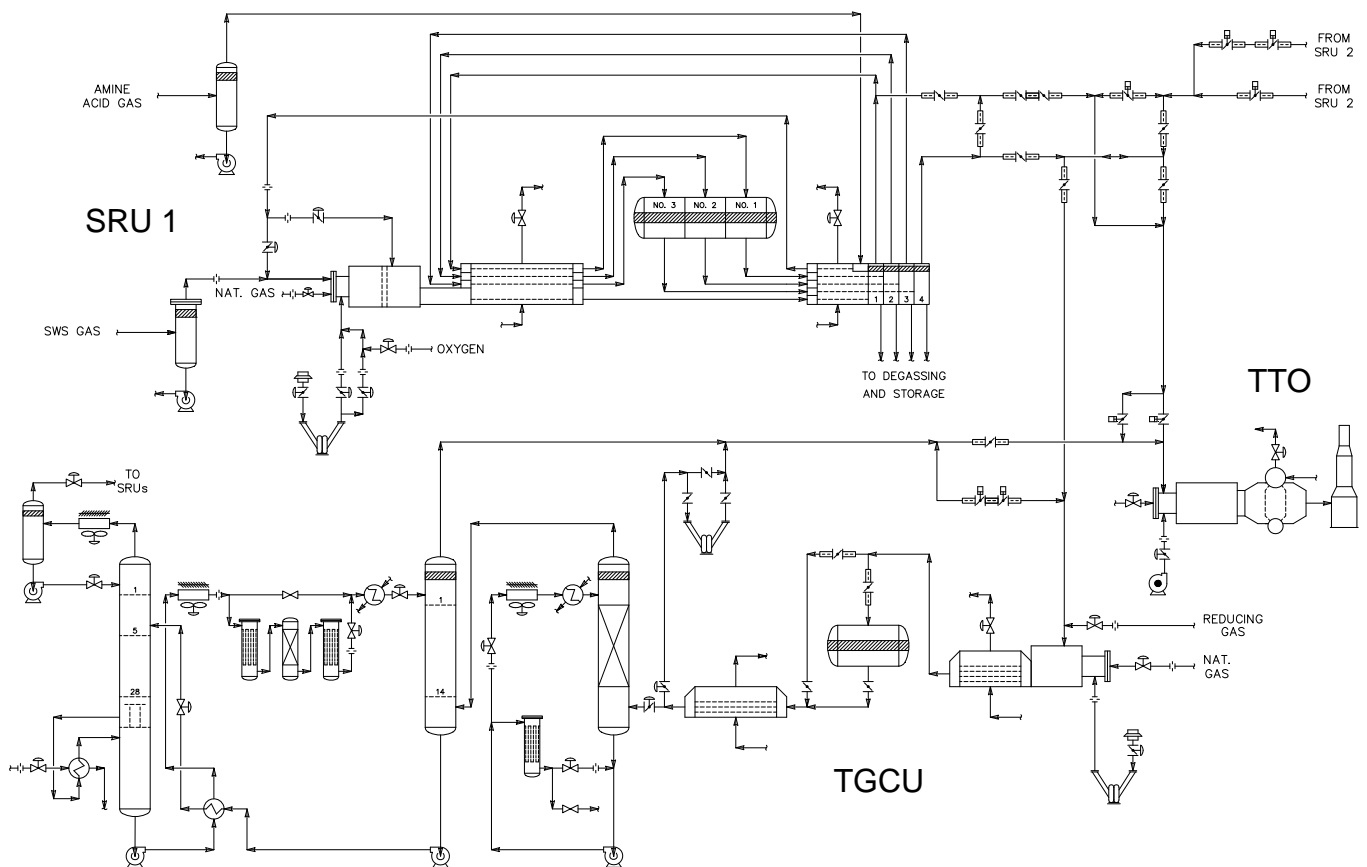


Figure 1 – Flow Diagram of the Refinery X SRU Complex

### **1.1.1 Requirement for Low SO<sub>2</sub> Emission Startups and Shutdowns**

This sulfur recovery complex was designed to recover 99.8+% of the contained sulfur as elemental sulfur product under normal operating conditions, and produce an incinerated vent stream that complies with the New Source Performance Standards (NSPS) for petroleum refineries, i.e., containing no more than 250 PPMV SO<sub>2</sub> on a dry, 0% excess air basis. The SRUs were originally designed to start up directly to the TTO, with the downstream TGCU bypassed. The design intention was to route tailgas from each SRU to the TGCU only after that SRU had been warmed up on fuel gas, had been switched over to acid gas firing, and was operating stably on acid gas. This startup concept minimizes the chances of damaging equipment or solvent in the TGCU, but also results in relatively high SO<sub>2</sub> emissions from the TTO during startup and shutdown since any sulfur compounds not recovered by the SRUs are oxidized to SO<sub>2</sub> in the TTO and then vented.

Unfortunately, Refiner X (like many other refiners) is now facing increasing pressure from regulatory agencies to reduce the SO<sub>2</sub> emissions that occur when starting up and shutting down their sulfur plant. They must reduce the amount of SO<sub>2</sub> emissions and/or the duration of high SO<sub>2</sub> emissions when starting up and shutting down so that:

- The 12-hour rolling average SO<sub>2</sub> concentration in the TTO vent gas does not exceed 250 PPMV  
and
- The excess SO<sub>2</sub> above 250 PPMV in the TTO vent gas does not exceed 500 Lbs (7.8 lbmols) in a 24-hour rolling average period.

### **1.1.2 Constraints on Modifications**

Sulfur plant operators know startup and shutdown operations provide plenty of opportunities to damage refractory, catalyst, equipment, and the quench water and solvent solutions. This is why this facility was designed to bypass the TGCU during these periods of instability. Any modifications to Refiner X's operating procedures, piping, equipment, or controls had to achieve the same goals, which include avoiding the following undesirable conditions:

- High temperatures in the TGCU reducing gas generator (RGG)
- High temperatures or fouling in the catalyst beds
- Excessive refractory temperature or heating rate in the SRU furnace
- Corrosion and/or degradation in the quench and solvent systems
- Overheating and/or damage to the SRU burners

### **1.1.3 Original Design Features**

Like many Orloff-designed sulfur recovery complexes, this sulfur plant includes several design features that make it difficult to start up with the SRUs "coupled" to the TGCU. These design features and operating philosophies minimize the chances of damaging catalyst, equipment, or solvent, but also contribute to high SO<sub>2</sub> emissions during startup and shutdown.

### 1.1.3.1 SRU Warmup with Excess Air

Most SRUs warm up by firing the burner with fuel gas and stoichiometric air and routing the combustion products through the catalyst beds. This requires very close operator attention during the warmup procedure to keep the air:fuel gas ratio from getting too high (which would allow free oxygen to reach the catalyst) or too low (which will cause the burner to form soot and foul the catalyst with carbon). However, the Refinery X SRUs were originally designed for cold reactor bed startup. Instead of firing the SRU burners at stoichiometric air:fuel ratio, they use excess air to control the furnace temperatures, and route the combustion products through the SRU warmup bypass lines directly to the TTO as shown in Figure 2.

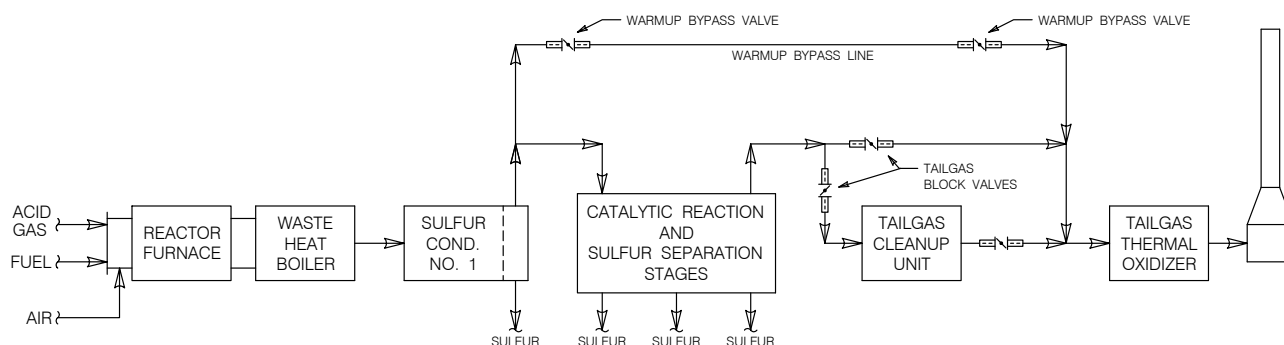


Figure 2 – SRU Cold Reactor Bed Startup Design

This startup procedure has been shown to extend the catalyst life in an SRU and minimize the chances of overheating the catalyst beds during warmup. However, the oxygen in the combustion products can react with iron sulfide or residual elemental sulfur in the equipment and piping in the warmup path to form  $\text{SO}_2$  that is then emitted from the TTO.

Note that it is the excess air in the combustion products, not bypassing the catalyst beds, that causes the high  $\text{SO}_2$  emissions while warming up. The cold reactor bed startup procedure can extend catalyst life regardless of the oxygen content in the warmup combustion products. However, compared to stoichiometric firing, warming up the SRUs using excess air generates much more  $\text{SO}_2$ . Therefore, in order to achieve low-emission startups and shutdowns, these SRUs needed the ability to warm up with near stoichiometric air and route SRU tailgas through the TGCU during these phases of operation.

### 1.1.3.2 TGCU Reducing Gas Generator / In-line Heater

This TGCU uses a direct-fired reducing gas generator (RGG) to heat the SRU tailgas feeding the TGCU reactor. Since the refinery has a reliable source of good-quality hydrogen, the RGG can fire fuel gas at about 95% of stoichiometric air to generate heating gas. The burner has a minimum firing rate to avoid soot formation, so a minimum amount of gas (approximately 20-25% of normal) is required to quench the temperature in the RGG and keep it below the high temperature shutdown point. This is a significant limitation during SRU startups and shutdowns when the flow rate of gas leaving the SRUs is much lower than the minimum required to quench the temperature in the RGG.

The original TGCU startup blower piping arrangement was designed to re-circulate the RGG combustion products through the TGCU front-end (i.e., furnace and reactor) to maintain the minimum flow requirement

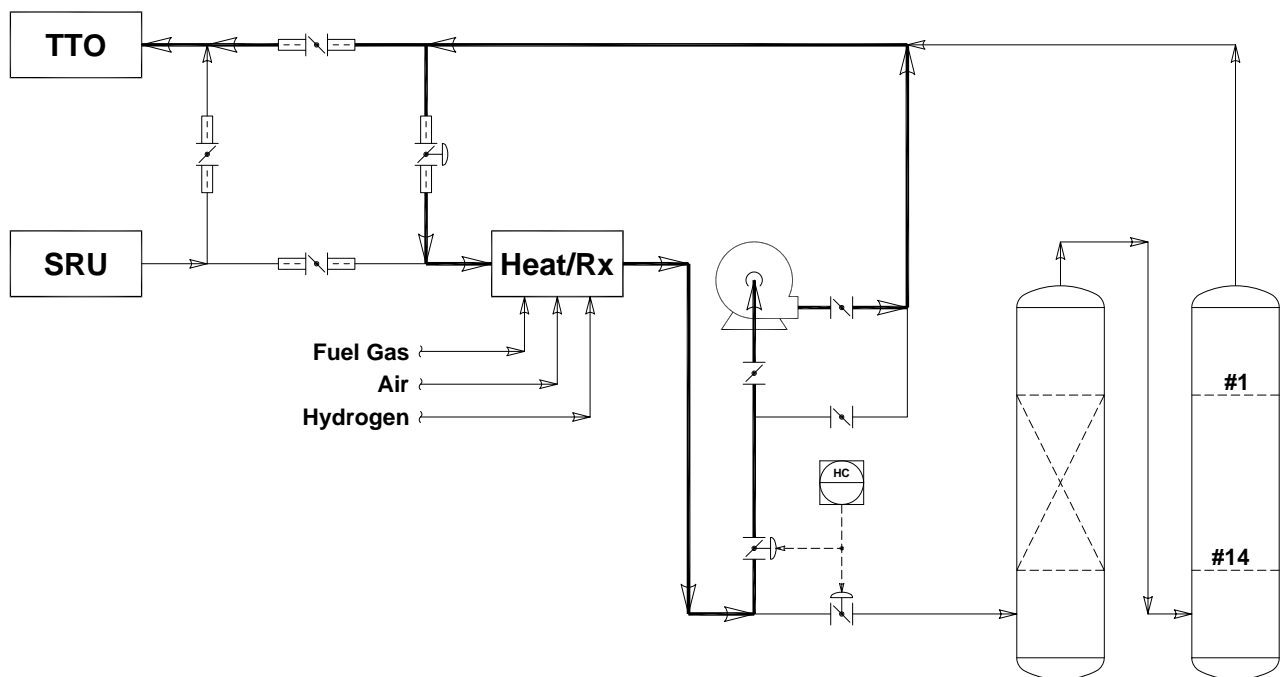
for the RGG. However, the original piping arrangement did not provide a means to re-circulate tailgas through the TGCU back-end (i.e., the quench and absorber columns).

**1.1.3.3 TGCU Absorber Column Internals**

In most TGCUs, random or structured packing is used in both the quench column and the absorber to minimize pressure drop and decrease the diameter of these columns. However, Refiner X's absorber column contains 14 two-pass valve trays with 2½" [64 mm] weirs. Using trays rather than packing in the absorber column was common practice when this TGCU was built in the early 1980s. However, the static head due to the liquid level on the trays creates significant pressure drop through the absorber regardless of the gas flow rate.

**1.1.3.4 TGCU Startup Blower Location**

In many designs, the TGCU startup blower (or eductor) takes its suction between the quench column and the absorber column. However, the Refinery X TGCU startup blower takes its suction upstream of the quench column as shown in Figure 3. This provides operating flexibility and prevents corrosion and fouling of the quench water system; however, as described above, this piping arrangement does not allow the re-circulating gas to be routed through the quench or absorber columns.



**Figure 3 – TGCU Startup Blower Original Piping**

## **1.2 Sources of High SO<sub>2</sub> Emissions during Startup and Shutdown**

The 2016 paper discussed the various sources of the high SO<sub>2</sub> emissions observed by Refiner A and B during recent startups and shutdowns. While the magnitude of the emissions from various sources will differ from plant to plant, nearly all sulfur plants will be prone to these same sources of emissions.

### **1.2.1 High SO<sub>2</sub> Emissions during Startup**

#### **1.2.1.1 Warming Up the SRU / Hot Stand-by**

Excess Air – When warming up an SRU with excess air, or firing fuel gas with excess air during hot stand-by, SO<sub>2</sub> emissions may increase for multiple reasons. First, the residual oxygen in the combustion products can oxidize the iron sulfide normally found in the equipment and piping and generate SO<sub>2</sub>. Second, the residual oxygen can oxidize any sulfur that has accumulated in the piping or equipment (usually in the sulfur condensers) and generate SO<sub>2</sub>.

Sulfur Accumulation – High SO<sub>2</sub> emissions during warmup may also be a result of accumulated sulfur being vaporized (or carried-over) by the warmup combustion products and then oxidized in the TTO. It is not uncommon to accumulate sulfur in the outlet channels of the sulfur condensers, in the mist eliminators, or in the Claus catalyst beds if they have not been adequately "stripped" of sulfur prior to shut down. Regardless of the cause, an accumulation of sulfur anywhere in a sulfur plant can result in high SO<sub>2</sub> emissions while warming up the SRU.

#### **1.2.1.2 Switching the SRU to Acid Gas**

In a perfect world, the switch from firing fuel gas while warming up an SRU to processing acid gas is made with the SRU tailgas directed to the TTO rather than the TGCU. This gives the operators time to stabilize the operation of the SRU and confirm that the tailgas analyzer is working correctly, without the risk of causing an upset in the TGCU or damaging the quench or solvent systems. However, this means that, once the SRU begins firing acid gas, any residual sulfur in the SRU tailgas goes directly to the TTO until the SRU tailgas is switched into the TGCU (which may take 30 minutes or more). The magnitude of the SO<sub>2</sub> emissions during this period will depend on the sulfur recovery efficiency in the SRU. Likewise, the magnitude of the SO<sub>2</sub> emissions exceedances will depend on how quickly SRU tailgas can be switched into the TGCU.

#### **1.2.1.3 Pre-Sulfiding / Activating TGCU Catalyst**

Typically, new catalyst in a TGCU reactor must be pre-sulfided (i.e., activated) before the TGCU can be placed in service. However, the catalyst may not always consume all of the sulfur entering the reactor throughout this procedure. If the piping configuration for the TGCU startup blower (or ejector) does not allow circulation through the TGCU columns, then any residual sulfur will not be removed by the TGCU solvent and will go straight to the TTO where it may cause the SO<sub>2</sub> emissions to be high.

## **1.2.2 High SO<sub>2</sub> Emissions during Shutdown**

### **1.2.2.1 Cooling the SRU**

In most sulfur plants, when cooling the Claus catalyst beds with nitrogen, the SRU tailgas is routed directly to the TTO because the flow rate is not high enough to quench the temperature in the TGCU RGG and

prevent it from shutting down due to high temperature. Consequently, any sulfur compounds that are carried away by the cool-down nitrogen enter the TTO and cause high SO<sub>2</sub> emissions.

Likewise, when cooling an SRU with air from the SRU air blower, the flow rate is not high enough to quench the temperature in the RGG, and the excess oxygen can damage the TGCU catalyst and solvent. Consequently, the cooling air must be routed directly to the TTO and any SO<sub>2</sub> that is generated (or sulfur compounds that are carried-over) contribute to high SO<sub>2</sub> emissions.

### **1.2.2.2 Passivating TGCU Catalyst for Reactor Entry and Catalyst Replacement**

Many refiners elect to passivate their TGCU catalyst during shutdown to allow entry into the TGCU reactor or removal of the catalyst without the need for an inert atmosphere. Passivation is accomplished by exposing the catalyst to small concentrations of oxygen in order to slowly oxidize the metal sulfides in the catalyst bed. The excess oxygen, as well as the SO<sub>2</sub> generated during the passivation procedure, cannot be routed to TGCU columns because both will damage or degrade the quench water and solvent solutions. Instead, the gas leaving the TGCU reactor must be routed directly to the TTO, which can result in high SO<sub>2</sub> emissions during this procedure.

## **2 MODIFICATIONS**

As discussed in the 2016 paper, Refiner A and Refiner B made a number of modifications to their sulfur plants to minimize their SO<sub>2</sub> emissions during startup and shut down operations. As a result of the positive outcomes achieved by Refiner A and B, Refiner X elected to make similar changes to their sulfur recovery plant. These changes can be organized into three categories or levels of modification:

- Level 1 – Changes to operating procedures
- Level 2 – Minor changes to equipment, piping, and controls
- Level 3 – Extensive changes to equipment, piping, and controls to accomplish near-zero exceedances

### **2.1.1 Level 1 — Changes to Procedures**

The first level of modifications included changes to Refiner X's startup and shutdown procedures.

#### **2.1.1.1 Changes to the Startup Procedures**

The first change recommended by Ortloff was to coordinate the startup of the TGCU so that the TGCU would be ready to process sulfur-bearing gases at the same time that the SRUs begin producing sulfur-bearing gases. This requires starting up the units in the sulfur plant in reverse order – beginning with the TTO, then the TGCU, and finally the SRUs – rather than starting them up in parallel or starting up the TGCU after the SRUs are up and running.

#### **2.1.1.2 Changes to the Shutdown Procedures**

Ortloff also recommended keeping the SRUs and TGCU "coupled" for as long as possible when shutting down the units. Refiner X commonly shut down their TGCU prior to shutting down the associated SRUs.



However, SO<sub>2</sub> emissions may be reduced by shutting down the SRUs and TGPU at the same time, and then shutting down the TTO.

### **2.1.2 Level 2 — Minor Changes to Equipment, Piping, and Controls**

The second level of modifications included minor changes to the piping, and controls that would allow Refiner X to warm up the SRUs without excess air:

1. Add LP quench steam to the SRU burner/furnace – As noted previously, these SRUs were designed to warm up by firing fuel gas with excess air. The air:fuel ratio could be adjusted to stoichiometric, but without the excess air moderating the flame temperature, the temperature of the resulting combustion products would exceed the temperature rating of the refractory in the furnaces.

Ortloff recommended that Refiner X install LP (50 PSIG [3.5bar(g)]) steam piping, instrumentation, and controls and tie it in to the acid gas piping upstream of each SRU burner. This would enable them to operate the SRU burners at stoichiometric air:fuel and inject LP steam to control the furnace temperature. With sufficient steam available for quench, Refiner X could warm up the SRU furnaces with the SRU burners firing at stoichiometric, thereby eliminating the excess oxygen that causes high SO<sub>2</sub> emissions during warmup.

2. Incorporate the fuel gas into the air flow control loop – When firing supplemental fuel gas in an SRU, it is convenient to have the air flow control scheme add the air required to burn the fuel gas automatically rather than requiring an operator to adjust the air flow manually. Since these SRUs did not have this feature, Ortloff recommended that it be added. Ortloff also recommended that the manual globe valve used to control the fuel gas flow in SRU 1 be replaced with an automated flow control valve.

### **2.1.3 Level 3 — Modifications to the TGPU Startup Blower Piping**

Finally, Ortloff recommended that Refiner X reconfigure the startup blower piping in the TGPU. This third level of modifications, in addition to the Level 1 and Level 2 modifications, could effectively reduce the occurrence of SO<sub>2</sub> emission exceedances to nearly zero.

As stated previously, this TGPU uses a reducing gas generator (in-line heater or RGG) to heat the SRU tailgas to the proper reaction temperature before it enters the TGPU reactor. The TGPU burner operates with slightly less than stoichiometric air to prevent oxygen from escaping and damaging the reactor catalyst. Because of this substoichiometric operation, the burner has a limited turndown range to avoid forming soot, which will also damage the reactor catalyst.

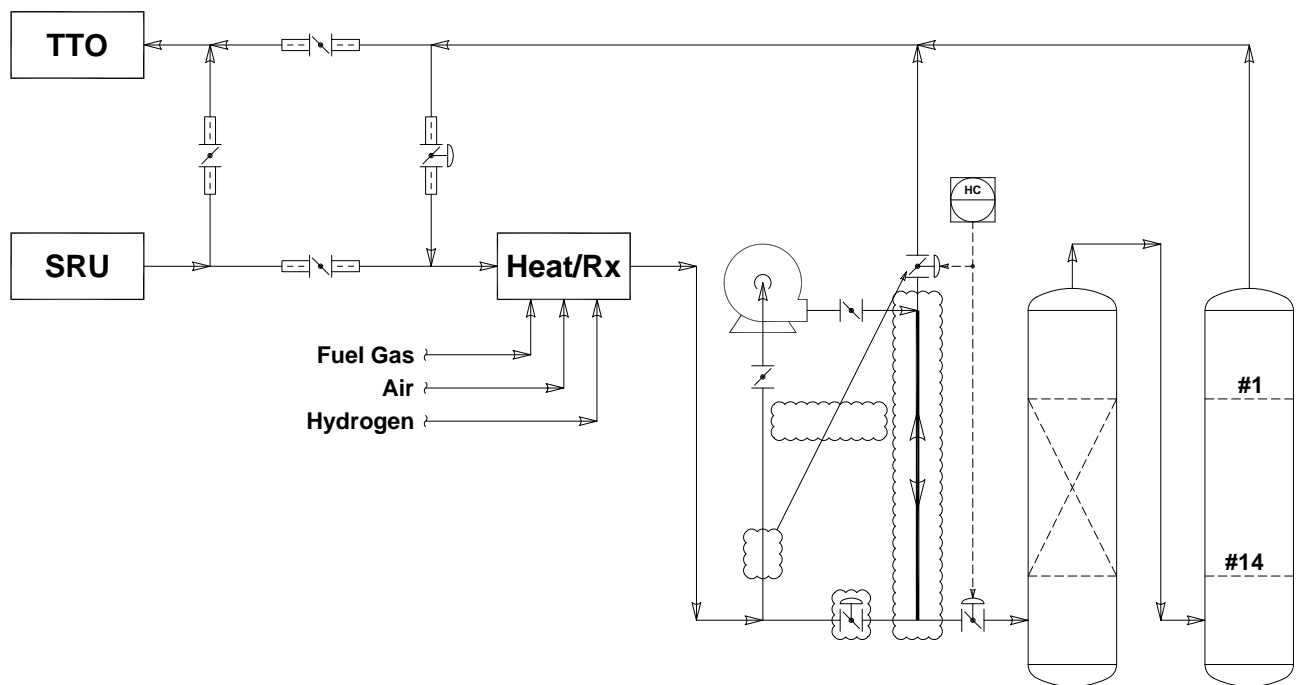
During the course of starting up the TGPU, it is necessary to adjust the in-line burner to the proper substoichiometric air:fuel ratio. In order to do this without overheating the furnace and reactor (since this occurs before SRU tailgas is introduced), there must be gas flowing through the system to control the extreme temperature (3000+°F [1650+°C]) of the burner effluent. The TGPU startup blower accomplishes this by re-circulating a portion of the process gas leaving the TGPU waste heat boiler (WHB) back to the furnace (see Figure 3). This process gas must continue to circulate through the system until a sufficient amount of SRU tailgas is routed to the furnace, at which time the startup blower can be shut down.

One of the limitations with Refiner X's TGCU was that process gas could not be directed into the TGCU columns (quench column and absorber) while the startup blower was being used to re-circulate gas to the TGCU burner/furnace. As a result, there were phases during SRU startup and shutdown when the SRU effluent could not be processed in the TGCU columns because the flow rate was not high enough to keep the TGCU furnace from overheating.

Ortloff recommended that Refiner X make the following modifications to the piping around the startup blower to remove this limitation. These modifications are shown in Figure 4:

- Relocate the quench column bypass valve to the blower discharge piping
- Install a new blower bypass valve in the quench column inlet piping
- Take the existing blower bypass valve and piping out of service
- Install a new bi-directional bypass line

With these changes, the startup blower could be used to re-circulate gas through just the TGCU front-end when starting up the TGCU burner as shown in Figure 5, or to re-circulate gas through the TGCU front-end and the back-end columns when processing effluent from the SRUs (tailgas, combustion products, etc.) as shown in Figure 6.



**Figure 4 – Startup Blower Piping Modifications**

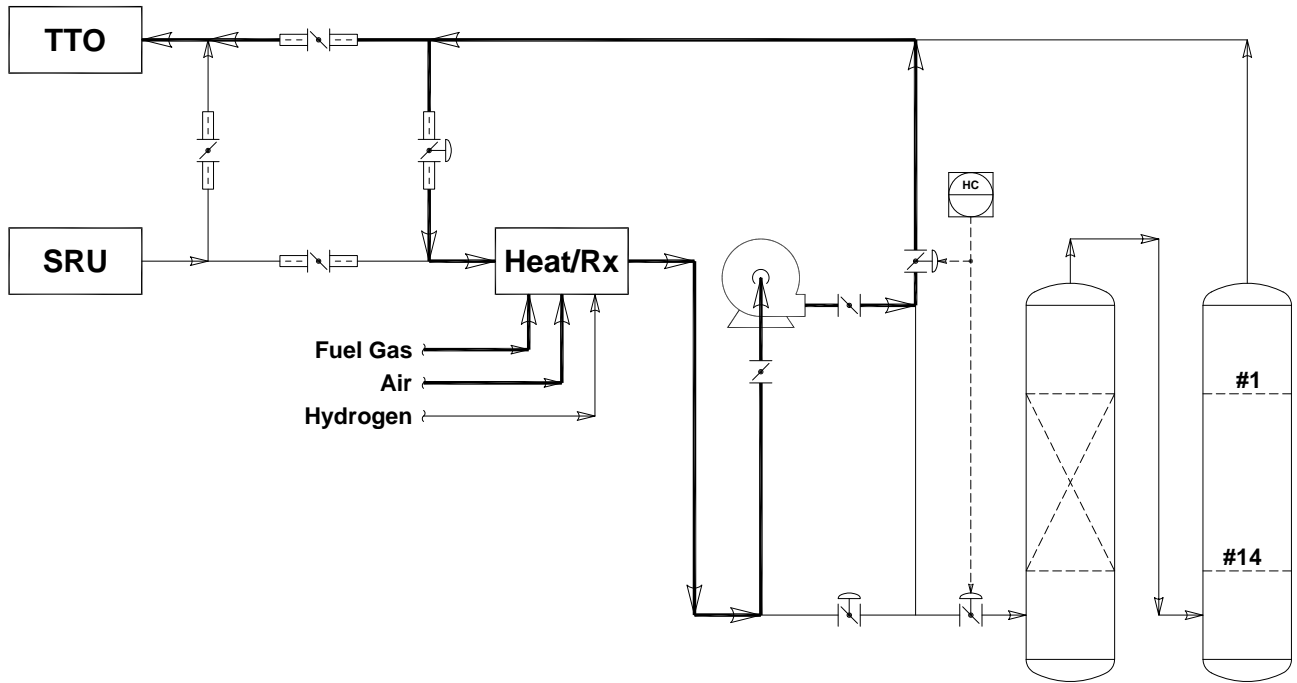


Figure 5 – Re-circulation of the TGCU Front-End ("Short" Loop)

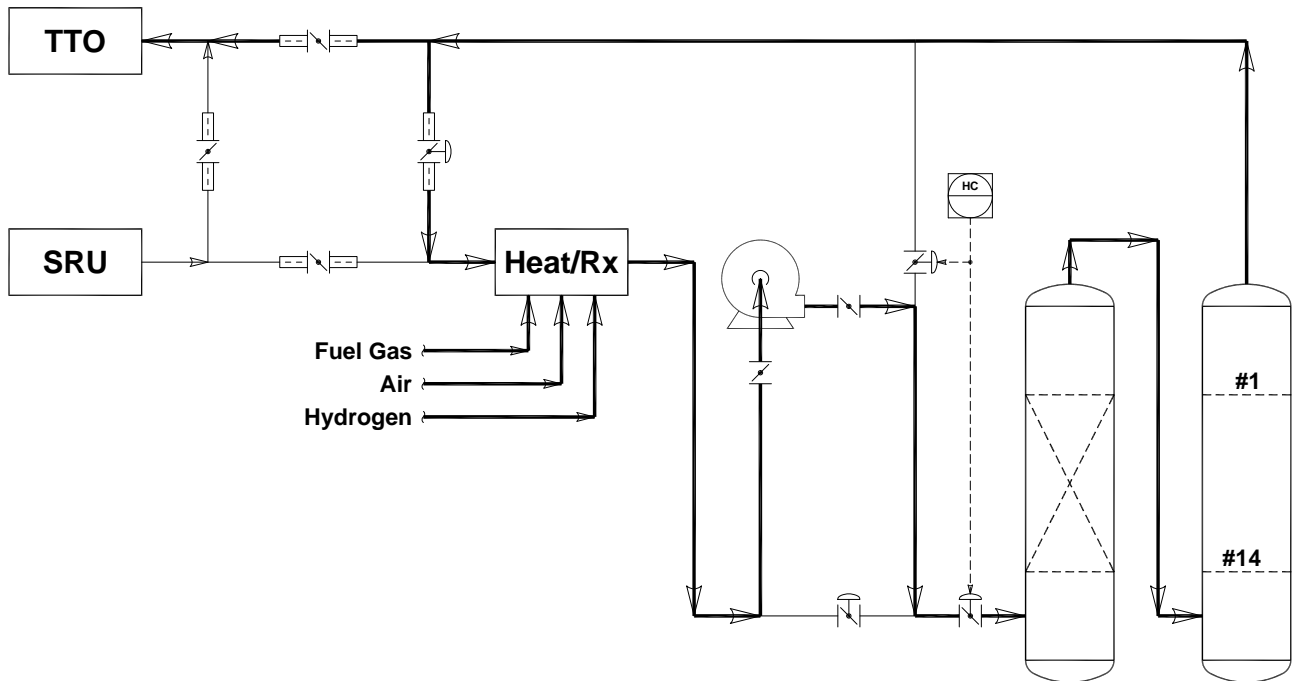


Figure 6 – Re-circulation of the TGCU Front-End and Back-End ("Long" Loop)

### **2.1.4 New Capabilities Added by these Modifications**

The goal of these modifications was to give Refiner X's sulfur plant the following capabilities:

1. The SRUs could be "coupled" to the TGCU during startup as soon as the SRUs are firing fuel gas with stoichiometric air. The SRUs and TGCU could remain coupled until the final air cooling of the catalyst beds in the SRUs when shutting down the SRU for entry. During all the time in between these two phases, whatever sulfur species that are in the effluent from the SRUs could be processed in the TGCU, with the TGCU reactor converting them to H<sub>2</sub>S and the TGCU solvent then removing this H<sub>2</sub>S, so that there are no SO<sub>2</sub> emission exceedances at the TTO.
2. The catalyst bed in the TGCU reactor could be cooled more quickly. With the "long" recycle loop from the absorber overhead, the gas re-circulating to the TGCU furnace will be much cooler than it is with the suction of the startup blower coming from the outlet of the TGCU WHB. Since the re-circulating gas is cooler, the TGCU reactor will cool down more rapidly.
3. The SO<sub>2</sub> emissions from the TTO could be minimized while pre-sulfiding the catalyst in the TGCU reactor by re-circulating through the TGCU columns. Any residual H<sub>2</sub>S leaving the reactor would be removed in the TGCU absorber (following cooling in the TGCU WHB and quench column), so that hardly any H<sub>2</sub>S escapes to the TTO.

## **3 STARTUP EXPERIENCE**

The modifications described in sections 2.1.1, 2.1.2, and 2.1.3 above were made by Refiner X during their spring 2017 turnaround. In addition, the refractory in the SRU 2 furnace and the catalysts in both SRUs and the TGCU were replaced. The units were restarted in May 2017 and Ortloff personnel were onsite to provide startup support.

Prior to making these modifications, Refiner X regularly exceeded their SO<sub>2</sub> emissions limit (250 PPMV SO<sub>2</sub> on a dry, 0% excess air basis) during startup and shutdown of the sulfur recovery plant. During the startup in May 2017, following completion of the recommended modifications, Refiner X once again exceeded both their SO<sub>2</sub> concentration limit and their total pounds of SO<sub>2</sub> limit. In addition, due to the various issues that arose during the startup, the length of the startup (from lighting burners to introducing acid gas) was 1-2 days longer than normal.

### **3.1.1 SRU 1 Startup**

When Ortloff personnel arrived onsite, the SRU 1 furnace was operating at 1000-1300°F firing fuel gas with excess air. Our first objective was to transition to stoichiometric firing with quench steam. As Refiner X began reducing the air flow rate to the burner and adding LP steam, we saw that the observed furnace temperature did not correspond with the fuel gas flow rate. Likewise, the flow meter on the LP steam line did not appear to be accurate. The refinery's I&E technicians investigated both meters and determined that the fuel rate was not being calculated correctly and that there was water in the sensing lines for the LP steam meter. Both issues were addressed and we continued to transition in a step-wise fashion from firing with excess air to firing at stoichiometric air:fuel with quench steam.

In order to avoid heating up the refractory too quickly, we initially targeted a steam rate that would result in a calculated gas temperature of 1300-1600°F. However, injecting this quantity of steam caused the flame to become unstable and the refractory temperature to drop. We then reduced the steam rate gradually, while monitoring the flame stability, until we reached a steam:fuel ratio of about 6:1, which corresponds to a calculated gas temperature of 2400-2600°F. At this ratio, we were confident that we would not overheat the burner tips, and the refractory began warming up at a rate of about 200°F [93°C] per hour, which is generally considered acceptable for a normal warmup.

### Conclusion

When firing an SRU burner with stoichiometric air, steam (or other quench gas) is added for three reasons: (1) to avoid overheating the refractory, (2) to control the rate of heating, and (3) to protect the burner components. Contrary to expectation, targeting a steam:fuel ratio that was sufficient to protect the burner tips also resulted in acceptable refractory temperatures and rates of heating. However, these parameters should always be monitored closely since all SRU furnaces and burners are unique and may warm up at different rates.

#### **3.1.1.1 Pressure Compensation of SRU 1 Air Flow**

As stated previously, we experienced several issues with flow measurement during warmup of the SRU 1 furnace, but the issue that caused the most difficulty was the absence of pressure compensation for the air flow meter. When warming up an SRU furnace with excess air, the actual air:fuel gas ratio (and therefore the actual air flow rate) is not important. The air flow is simply adjusted to reach the desired furnace temperature. However, when attempting to fire an SRU burner with stoichiometric air, the difference between compensated and un-compensated flow calculations becomes much more important.

To understand the issue this created, it is helpful to first review the equations used to calculate flow through an orifice meter. The calculated mass flow of a gas through an orifice plate ( $Q_m$ ) is a function of the gas density ( $\rho$ ),

$$(1) \quad Q_m = \frac{\pi}{4} d^2 C_d Y_1 \sqrt{\frac{2\Delta P \rho}{1 - \frac{d^4}{D^4}}}$$

and, from the ideal gas law, the gas density is a function of absolute pressure (P) and temperature (T).

$$(2) \quad \rho = \frac{P * MW}{R * T}$$

Uncompensated flow calculations are based on an assumed density (the density at design conditions). However, at pressures and temperatures significantly different from design, the difference in the gas density can result in substantial errors in the calculated flow rate. Substituting Equation 2 into Equation 1 and combining all the constants into a single constant (K) yields the following equation for mass flow:

$$(3) \quad Q_m = K \sqrt{\frac{\Delta P * P}{T}}$$

From this we can derive the relationship between the actual mass flow ( $Q_A$ ) and the mass flow at design conditions ( $Q_D$ ).

$$(4) \quad Q_A = Q_D \sqrt{\frac{P_A * T_D}{P_D * T_A}}$$

Typically, in a sulfur plant, differences in temperature are minimal and do not result in significant errors in calculated flow. However, the errors due to differences in pressure can be substantial because of the low operating pressures in an SRU.

When these SRUs were designed and built, it was not common to pressure or temperature compensate the flow meters. Since the primary controlled variable in an SRU is the air to acid gas ratio (and not the individual flow rates) using uncompensated flows is acceptable. At any time, the pressure of the air and acid gases at their respective flow meters is roughly equal to the burner pressure. Thus, any error resulting from differences between the actual pressure and the design pressure is effectively canceled out in the ratio (i.e., the individual flow readings are not accurate, but the ratio is).

Unfortunately, the same is not true when firing fuel gas and injecting quench steam. In SRU 1, the flow meters for both fuel gas and steam are located upstream of their respective control valves, so they operate at a relatively constant pressure. Conversely, the air meters (main and trim) are located downstream of their control valves, so the pressure at these meters is approximately equal to the burner pressure. At design rates, the burner pressure is typically 8.5-10 PSIG. However, during warmup when the flow rate through an SRU is much lower, the pressure at the burner is much lower (0.2-3.0 PSIG). For illustration, Table 1 shows the compensated and un-compensated air rate at different burner pressures and the corresponding air:fuel gas ratios.

	Design	Warmup				
Air Pressure, PSIG	9.8	0.5	1.0	1.5	2.0	3
N.G. Pressure, PSIG	25	25	25	25	25	25
N.G. Flow, SCFM	10	10	10	10	10	10
Uncompensated Air Flow, SCFM	100	100	100	100	100	100
Compensated Air Flow, SCFM	100	78.8	80.1	81.3	82.6	85.0
<b>Actual Air: Fuel gas Ratio</b>	<b>10</b>	<b>7.9</b>	<b>8.0</b>	<b>8.1</b>	<b>8.3</b>	<b>8.5</b>

**Table 1** – Compensated versus un-compensated air flows

Had the SRU 1 operators relied on the uncompensated air rates displayed in the DCS, they would have been operating at an actual air:fuel ratio significantly less than stoichiometric. Since SRU 1 does not have a burner designed for substoichiometric combustion of fuel gas, this likely would have resulted in soot formation and plugging/fouling of the downstream catalyst beds.

To avoid this issue, each time the operators made a change to the fuel gas flow, they had to (1) determine the stoichiometric air flow rate, (2) back-calculate the target air flow rate (the rate displayed in the DCS) from the

stoichiometric air flow rate and the actual furnace pressure, and then (3) adjust the main and trim air valve positions to hit that target air flow rate. This pressure compensation "on the fly" added a layer of complexity (and uncertainty) to an already abnormal procedure.

### Conclusion

The air flow control scheme in SRU 1 was modified during the turnaround to include the air required for fuel gas (i.e., stoichiometric air), but pressure compensation of the air flow was not considered. As a result, the operators had to keep the air control in manual and use an external calculation to determine the target air rate. In short, the procedure required more operator attention than intended and it was difficult, at times, to know when we were truly firing at stoichiometric.

### **3.1.2 TGCU Startup**

Once SRU 1 was firing stably with stoichiometric air and quench steam, we turned our attention to starting up the TGCU. The plan for starting up the TGCU was as follows:

1. Light the TGCU burner.
2. Warm up the refractory in the RGG with excess air.
3. Start the TGCU startup blower and establish circulation through the "short" loop.
4. Adjust the burner to a substoichiometric air:fuel ratio and introduce supplemental hydrogen.
5. Close the TGCU reactor bypass valves and route gas through the TGCU reactor to bring it up to operating temperature.
6. Open the quench tower inlet valve, route gas through the TGCU columns, and establish circulation through the "long" loop.
7. Route the tailgas from SRU 1 to the TGCU so that any sulfur compounds could be converted in the TGCU reactor and removed by the TGCU solvent.

#### **3.1.2.1 TGCU Reactor High Temperature**

The first issue arose when we began routing gas through the TGCU reactor. Prior to this, the TGCU burner was operating stably at an indicated air:fuel ratio of about 8:1. As expected, the bed temperatures began to increase as soon as flow was established into the reactor. However, the bed temperatures continued to increase, surpassing the inlet temperature, until they reached about 700°F [370°C] in the upper section of the bed. At that point, the decision was made to bypass the TGCU reactor until the cause of the high temperatures could be determined.

During the turnaround, the catalyst in the TGCU reactor was replaced with pre-sulfided (activated) catalyst. Since the gas from both SRUs was still being routed directly to the TTO, we concluded that there were only two possible explanations for the rapid temperature increase in the catalyst bed: oxygen ingress or additional activation of the catalyst.

Since the most likely cause of the temperature increase was oxygen ingress, this was investigated first. The refinery's I&E technicians looked at both the TGPU air and fuel gas flow meters and concluded that they were configured and calibrated correctly.

That left the possibility that the temperature increase was due to additional activation of the catalyst. In the past, Refiner X had purchased pre-sulfurized catalyst, which must be activated in situ by adding hydrogen. One concern was that the catalyst installed was not actually pre-sulfided, but pre-sulfurized. However, the catalyst supplier confirmed that the catalyst was indeed pre-sulfided and that, while some residual activation is possible, it would not account for the rapid temperature rise we saw in the bed. They agreed that the most likely cause of the temperature increase was oxygen ingress.

At this point, the TGPU burner was still operating at an indicated substoichiometric ratio and the effluent was circulating via the "short" loop with the TGPU reactor bypassed. So, the decision was made to verify the oxygen level in the circulating gas with a hand-held oxygen meter. The unit operators took multiple readings and discovered that the oxygen concentration in the circulating gas was 1-2 percent. Clearly, the air:fuel gas ratio displayed in the DCS was not accurate. The operators reduced the air:fuel ratio until the hand-held meter indicated that the circulating gas was oxygen-free. This corresponded to an indicated air:fuel ratio of about 6.5:1 in the DCS.

In hindsight, the TGPU air:fuel ratio had likely been higher than indicated for some time. Prior to the turnaround, Refiner X had been experiencing frequent episodes of SO<sub>2</sub> breakthrough from the TGPU reactor that resulted in near constant caustic (NaOH) addition to the quench system in order to maintain pH. Although there were known deficiencies in the air control schemes in both SRUs, these episodes did not correspond to any upsets or periods of off-ratio operation in the SRUs. There was also no indication that they were running out of hydrogen in the TGPU reactor. The conclusion was that the catalyst was losing activity, but there was no reason why it should. However, frequent or continuous oxygen ingress into the catalyst bed due to an inaccurate air:fuel ratio would explain the catalyst deactivation we suspected.

### Conclusion

When stoichiometric or substoichiometric operation is critical (as it was for this startup), independently verifying the oxygen content of the burner effluent is good practice. This is especially true when operating at low pressures / low flow rates where dP type flow meters (annubars, orifice meters, etc.) may be less accurate. Although Refiner X was able to reduce the air:fuel ratio and proceed with startup, they will ultimately need to identify and address the root cause of the inaccuracy to avoid future issues with the TGPU catalyst.

### **3.1.2.2 Circulation Through the "Long" Loop**

The second major issue arose when we attempted to circulate gas through the TGPU columns via the "long" loop. After reducing the air:fuel ratio and verifying that the circulating gas was oxygen-free, the burner effluent was again routed through the TGPU reactor. Once the bed was up to operating temperature, the inlet valve to the quench tower was opened and the bypass valve closed to send gas through the TGPU columns.

During our first attempt, the quench tower inlet valve would only open to 50%. This caused the RGG temperature to rise due to insufficient flow through the "long" loop. We did not want to risk shutting down the TGPU on high temperature, so the quench tower bypass valve was re-opened to allow gas to flow through the "short" loop while I&E technicians worked on the valve.



After correcting the issue with the quench tower inlet valve, a second attempt was made to route gas through the columns. This time the valve opened to 100%, but the RGG temperature again started to increase and eventually approached the shutdown point. To avoid a shutdown, the quench tower bypass valve was opened again to allow gas to flow through the "short" loop while we investigated the cause of the temperature increase.

As stated previously, the TGCU burner has a minimum firing rate, so a minimum amount of gas is required to quench the temperature in the RGG and keep it below the high temperature shutdown point. The startup blower was specified to supply 25-30% of normal flow (8,570 ACFM [4.0 m<sup>3</sup>/s]) at a differential pressure of 1.2 PSI [0.083 bar]. However, we were clearly not able to supply this amount of flow to the RGG when routing gas through the columns.

Our first objective was to determine our actual operating point relative to the design point of the startup blower. We ran a simulation of the TGCU using the fuel gas rate indicated in the DCS to determine the flow required to control the RGG at the temperature shown in the DCS. The simulation required a flow rate through the startup blower slightly higher than the design point at about 10,900 ACFM [5.1 m<sup>3</sup>/s]. From the blower curve, this corresponded to a pressure rise across the blower of about 1.15 PSI [0.079 bar], which seemed like a reasonable pressure drop for the "short" loop.

Next we looked at the column internals. The quench tower contains 15 feet of Cascade Mini-Rings. We initially estimated that at 25% of normal flow the pressure drop through this column would be on the order of 0.05 PSI [0.003 bar]. Unless there was significant fouling or plugging in the packing, this column was probably not the source of the problem. That left the TGCU absorber. Unlike the absorbers in Refiner A's and Refiner B's sulfur plants, this absorber contains 14 valve trays with 2½" [64 mm] weirs instead of random or structured packing. So, the static head from the liquid on the trays contributes at least 1.3 PSI [0.09 bar] to the  $\Delta P$  through the column regardless of the gas rate. This alone was more than the maximum  $\Delta P$  for the startup blower. (We later confirmed these estimates by calculating the pressure drop through the columns using a sizing program from a column internals vendor. At the design flow rate for the startup blower, the calculated pressure drop through the quench tower was 0.025 PSI [0.0017 bar] and the calculated pressure drop through the absorber was 1.5 PSI [0.1 bar]).

### Conclusion

As a result of the extra pressure drop imposed by the trays in the TGCU absorber, it was not possible to circulate through the TGCU columns via the "long" loop. Gas from SRU 1 could be routed to the TGCU and any sulfur compounds would be converted in the TGCU reactor, but that gas would still bypass the columns and be sent straight to the TTO where it would cause high SO<sub>2</sub> emissions from the TTO vent stack.

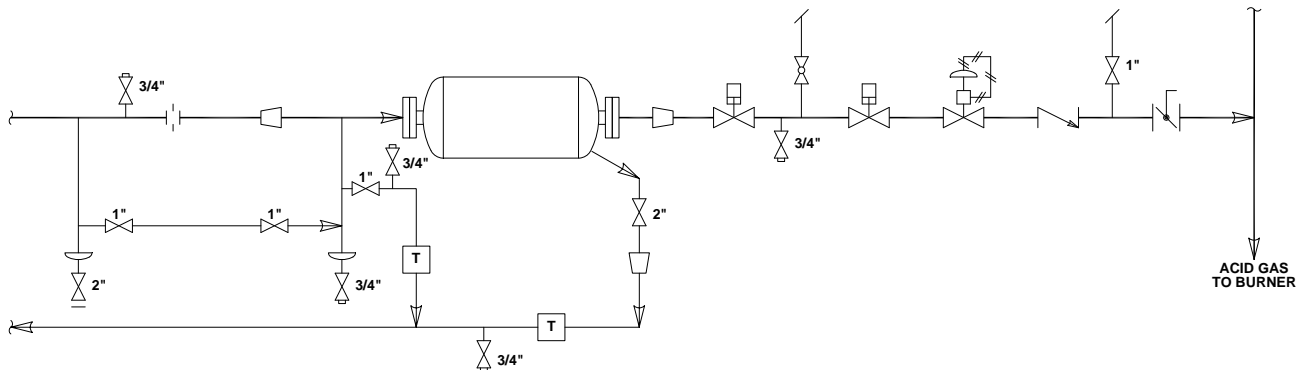
### **3.1.3 SRU 2 Startup**

Since no further progress could be made on the TGCU, our focus shifted to SRU 2. The refractory in the SRU 2 furnace was replaced during the turnaround, which necessitated a prolonged dry-out. Up until this point, SRU 2 had been firing fuel gas with excess air and following the recommended dry-out schedule for new refractory. However, we were now ready to transition to stoichiometric firing with quench steam.

As with SRU 1, our goal was to transition in a step-wise fashion from firing with excess air to firing at stoichiometric with quench steam. Since a fuel gas:steam ratio of about 6:1 was stable and resulted in an acceptable warmup rate in SRU 1, we made this our target. However, unlike SRU 1, as soon as we began introducing steam into SRU 2, the flame became unstable and SRU 2 quickly shut down due to flame failure.

We re-started SRU 2 and made a second attempt to introduce steam, this time with operators located at the burner to observe the flame. Once again, the flame became very unstable as soon as steam was introduced. The operators reported that it looked like the flame was being "pushed off" the burner tips radially, and they said that they could see liquid water flowing from the acid gas tip "like a sprinkler".

In theory, there should not have been any liquid water in the steam supply to the burner. Figure 7 shows the design of the steam supply piping for both SRU 1 and SRU 2. Two dip-legs collect any free water in the LP steam piping before it enters a cyclonic separator. Both dip-legs drain to a common steam trap. Any liquid removed in the cyclonic separator also drains to a steam trap and the outlet of both traps is routed to the LP condensate header. The dry steam flows through two automated block valves, a flow control valve, and a check valve. Where the steam supply ties in to the acid gas piping, near the burner, there is a manual isolation valve and a 1" warmup vent to atmosphere.



**Figure 7** – LP steam piping to SRU 2

When introducing steam to an SRU, the unit operators first open the two automated block valves and the 1" vent valve near the burner. Then, using the control valve, they vent steam through the 1" line in order to warm up the piping between the control valve and the burner. Once dry steam is observed at the vent, the control valve is closed, the 1" vent valve is closed, and the manual isolation valve near the burner is opened.

Prior to introducing steam into SRU 2, the operators had used the 1" vent to warm up the steam supply piping. However, the take-off point for the LP steam supply to SRU 2 is at the end of the LP steam header in this section of the refinery. During the turnaround, this section of the header was taken out of service. Therefore, it was possible that a large quantity of condensate had collected in the header and migrated to the SRU 2 supply line once flow was established.

After discovering liquid water flowing from the acid gas tip, the operators stopped the flow of steam and opened all of the bleed and vent valves to flush out any residual water. Steam was vented until only dry steam was seen flowing from each vent/bleed valve. We attempted to introduce steam for a third time into SRU 2, but the flame again became unstable. The operators also noticed liquid water dripping from the acid

gas tip again, although the quantity of water was much less. At that point, we discontinued steam addition to SRU 2 and completed the warmup with excess air.

We suspect that the flame stability issues observed in SRU 2 were primarily due to liquid water in the steam supply to the burner. Any liquid water entering the burner would vaporize when it mixed with the hot burner effluent. This would both cool the flame and generate a large volume of steam which would disturb the flame (similar to blowing out a candle). This would explain the operators' observation that the flame was being "pushed off" the burner tips.

We also learned later that for a period of time while they were "drying out" the steam piping, the manual isolation valve near the burner was open. Since the steam line ties in to the acid gas piping, and the acid gas piping was cold and stagnant at that time, our theory is that some of the steam entered this vertical run of pipe, migrated upward, cooled, condensed, and ran back down and out the acid gas tip. This could explain why we continued to see liquid water dripping from the acid gas tip even after drying out the steam supply.

### Conclusion

Operating the SRUs at stoichiometric air:fuel ratio was a critical component of achieving low emissions during startup. Likewise, having a reliable source of dry quench steam is critical to operating at stoichiometric without damaging the equipment in the SRUs. We were able to add the same ratio of steam to fuel gas, from the same steam supply header, and with the same piping design in SRU 1, and did not see significant flame stability issues. Therefore, we can only conclude that something unique to SRU 2 made this operation unsuccessful.

## 4 CONCLUSIONS

Reducing the SO<sub>2</sub> emissions from Refinery X's sulfur plant during startup and shutdown (while still protecting the equipment and preserving its useful life) required successfully accomplishing two things:

1. Firing the SRU burners with stoichiometric air and controlling the furnace temperatures with quench steam.
2. Using the TGCU startup blower to circulate gas through the back-end of the TGCU so that any sulfur compounds in the gas can be converted into H<sub>2</sub>S in the TGCU reactor and removed by the TGCU solvent regardless of the flow rate of gas from the SRUs.

Unfortunately, we were not able to fully accomplish either of these things during this startup. We were not able to circulate gas through the TGCU columns because of the high pressure drop through the absorber and we were not able to add quench steam to the SRU 2 burner. In addition, there was a temperature excursion in the TGCU reactor and various issues with flow meters, analyzers, flame scanners, pyrometers, and automated valves. Each of these required time and manpower to address and, although not a direct cause of high emissions, troubleshooting these issues caused delays that prolonged the startup and lengthened the time that the SO<sub>2</sub> emissions were high.

In addition, after introducing acid gas into SRU 1 and routing its tailgas to the TGCU, we realized that SRU 1 had likely been contributing more to the total SO<sub>2</sub> emissions than we expected. During all of the time that SRU 1 was firing at stoichiometric air:fuel with quench steam, SRU 2 had been firing with excess air. The

SO<sub>2</sub> emissions had been high (on a concentration basis) throughout the startup but we attributed this to the excess oxygen in the SRU 2 effluent. However, when SRU 1 was brought fully online and its tailgas routed to the TGPU (which could then be brought fully online as well), the SO<sub>2</sub> emissions decreased by almost 50%. That indicates that almost half of the sulfur entering the TTO originated in SRU 1. (We also saw an emissions increase during the temperature excursion in the TGPU reactor, but the emissions returned to their previous levels and stayed there once the air:fuel ratio in the TGPU was reduced.)

Regrettably, the cause of the higher-than-expected emissions from SRU 1 is still unknown. It is possible that SRU 1 was not truly firing at a stoichiometric air:fuel ratio. (We did not verify the oxygen content of the SRU 1 burner effluent.) It is also possible that the burner was firing at stoichiometric air:fuel but the mixing was poor and free oxygen was still present in the burner effluent. Additionally, it is possible that there was more sulfur buildup in SRU 1 than expected.

### 4.1 Recommendations

Refiner X will need to make additional modifications to their sulfur recovery plant in order to achieve their goal of not exceeding their normal emissions limits during startup and shutdown.

#### 4.1.1 SRU 1

In SRU 1, the following modification is recommended to simplify warming up at stoichiometric air:fuel with quench steam:

- Pressure compensate the air and acid gas flow rates in the DCS using the existing pressure transmitter on the air line upstream of the burner.

#### 4.1.2 SRU 2

In SRU 2, the following modifications are recommended to prevent liquid water from entering the SRU 2 burner and to allow Refiner X to successfully fire this burner with stoichiometric air and quench steam:

- Keep the final block valve in the steam supply line closed when warming up the steam piping.
- Install a level gauge/glass on both dip legs.
- Consider replacing the existing cyclonic separator with a condensate pot and level control valve or adding a condensate pot and control valve upstream of the cyclonic separator.
- Consider using higher pressure and/or superheated steam or nitrogen to control the furnace temperature.
- Pressure compensate the air and acid gas flow rates in the DCS using the existing pressure transmitter on the air line upstream of the burner.

#### 4.1.3 TGPU

In the TGPU, the following modifications are recommended to enable circulation through the back-end of the TGPU (the "long" loop) and to prevent future oxygen ingress into the TGPU reactor.

- Replace the trays in the TGCU absorber with structured packing.  
or
- Replace the TGCU startup blower with a higher-head blower.
- Replace the existing TGCU air flow meter (an annubar meter) with a better flow meter.
- Consider modifying the TGCU air blower controls to improve flow control at low rates.
- Consider replacing the existing packing in the quench tower with structured packing to improve performance and reduce pressure drop.

## **4.2 Lessons Learned**

Along with the recommendations listed above, there were a number of important lessons learned during this startup.

1. There is no such thing as a "one-size-fits-all" solution.

Although there are many similarities between Refiner X's sulfur plant and Refiner A's and Refiner B's sulfur plants, the unique features of this sulfur plant resulted in the same modifications being unsuccessful.

2. Always check the hydraulics in the "long" loop.

The project team did not account for the impact of trays in the TGCU absorber on the pressure drop through the "long" loop because the original study, on which these changes were based, focused primarily on other sulfur plants owned by Refiner X which have packed columns. However, regardless of the specific column internals, the hydraulics in the "long" loop should always be checked to verify that the TGCU startup blower has sufficient head to overcome the additional pressure drop imposed by the columns.

3. Use a hand-held oxygen meter to verify that the burner effluent is oxygen-free when operating at stoichiometric / substoichiometric.

Had we verified the oxygen content in the TGCU burner effluent prior to routing gas to the catalyst bed, we could have avoided the temperature excursion we experienced in the TGCU reactor. Likewise, had we verified the oxygen content in the SRU 1 burner effluent we could have known if excess oxygen from SRU 1 was contributing to the SO<sub>2</sub> emissions.

4. Make sure that all analyzers are functional during startup/shutdown.

Analyzers can provide valuable information when troubleshooting issues in a facility. We were able to verify that the TGCU burner was operating below stoichiometric by watching the carbon monoxide reading from the CEMS in the TTO. The TGCU hydrogen analyzer could have provided more direct verification that we were substoichiometric (or not), but it was unavailable for the majority of the TGCU startup.

5. Add sufficient steam to protect the SRU burners from overheating.

Depending on the particular details of the SRU furnace/burner, adding enough steam to protect the burner components will also likely be enough to protect the refractory.

6. The steam supply to an SRU burner must be "dry". If there is not a source of "dry" steam, consider using nitrogen or another inert gas.
7. Concentrate on one unit at a time (especially the first time).

There is always pressure to start up the units in a sulfur plant in parallel to minimize the overall startup schedule. However, after making significant changes to a facility, it is prudent to start up one unit at a time when possible. This allows the unit operators to focus on a single unit and makes it easier to troubleshoot any issues that may arise. Many symptoms of the problems that we experienced during this startup were masked by things that were happening in the other units. As a result, it took longer to troubleshoot issues than it probably would have if we had started up each unit individually.

### 4.3 Final Thoughts

There is clearly more work to do to enable Refinery X to get the full benefit from the modifications they made to reduce their SO<sub>2</sub> emissions during startup and shutdown. Unfortunately, what may be a relatively simple modification to a newer facility can be much more complex when applied to an older facility. There is always risk when modifying a facility to do something that it was not designed to do and that risk increases the further you get from the original design intent.

As an industry, we are continually being pressured to reduce emissions by regulators, corporate policies, and even the general public, and as limits on SO<sub>2</sub> emissions become more stringent, increasingly expensive modifications will be required for existing facilities to stay in compliance. If this trend continues, owners and operators of older facilities will be forced to ask, "When do we reach the point of diminishing returns?", or (more specifically), "When do we reach the point where so many modifications are required to meet current and future requirements that it no longer makes sense to continue operating the facility?" We suspect that none of us are going to like the answer to this question.

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