

# **Low-Emission Sulfur Plant Startups and Shutdowns – Options and Pitfalls**

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## **ABSTRACT**

This paper attempts to address the question "Is there a better way to achieve low-emission startups and shutdowns in new and existing sulfur recovery plants?"

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. Unfortunately, as an industry we have begun to see the mechanical and operational issues created by these enforced limitations as simply the cost of doing business.

This paper discusses the potential causes of high SO<sub>2</sub> emissions during startups and shutdowns. Options for reducing these SO<sub>2</sub> emissions are examined, and the cost impact and benefits of each option are presented.

Finally, this paper 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 still preserving the mechanical integrity and useful life of their equipment. For both refineries, three levels of modification were evaluated. Each level includes changing the refinery's current operating procedures; the differences were varying levels of physical changes (minimal or none, minor, or extensive) to the existing facility equipment, piping, and controls.

Each refinery concluded that relatively little could be accomplished to reduce the SO<sub>2</sub> emissions with only minimal or minor modifications. Instead, attention was focused on three different options for more extensive modifications needed to accomplish near-zero exceedances. The option selection for each refinery was driven by a number of different factors, including timing and budgetary constraints.

## **INTRODUCTION**

In years past, short-term operations such as starting up and shutting down sulfur plants were allowed an exemption for venting higher levels of SO<sub>2</sub> to the atmosphere than allowed during normal operations. However, 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 plants.

In the U.S., the Petroleum Refinery Initiative of the Environmental Protection Agency (EPA) sought to address air emissions from the nation's petroleum refineries and negotiated consent decrees that have led to 32 settlements since March 2000 with U.S. companies that comprise over 90% of the nation's petroleum refining capacity. These settlements cover 109 refineries in 32 states and territories and are aimed to reduce annual emissions by more than 93,000 tons of nitrogen oxides (NO<sub>x</sub>) and more than 256,000 tons of SO<sub>2</sub>. These companies have agreed to significant reductions in NO<sub>x</sub> and SO<sub>2</sub> emissions, resulting in investing more than \$6.5 billion in control technologies, paying civil penalties of more than \$93 million, and performing additional environmental projects with a total cost of over \$80 million.<sup>1</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.

As an industry, we often view the mechanical and operational issues created by these enforced limitations as simply the cost of doing business, but there are options for limiting them. In 2013/2014, two U.S. refineries 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. Ortloff studied the potential causes of high SO<sub>2</sub> emissions during startups and shutdowns and examined some of the issues created when these refineries attempted 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. This paper presents the results of the two studies and the changes implemented at each of the refineries.

In this paper, we present the experiences and perspectives of the three parties involved in the studies: the process licensor – Ortloff, and the two refiners – Refiner A and Refiner B. The common goal was to reduce SO<sub>2</sub> emissions during startup and shutdown to remain below the normal operating SO<sub>2</sub> emissions limit of 250 PPMV on a dry, 0% excess air basis.

The paper is presented in four sections:

1. Section 1 provides background information on the refinery sulfur plant designs and discusses the issues faced at both refineries.
2. Section 2 provides a discussion of the likely sources of high SO<sub>2</sub> emissions during startup and shutdown and presents the modification options.
3. Section 3 includes an economic evaluation of the modification options and the results of the changes that were implemented.
4. Section 4 presents conclusions and further questions that arose during these evaluations.

# 1 BACKGROUND

## 1.1 The Refiners' SRU Complexes

### 1.1.1 SRU Complexes at Refinery A

The SRU A1 complex at Refinery A was designed by Ortloff and installed in 1999-2000. It consists of two parallel 50% Claus sulfur recovery units (SRUs) with a common tailgas cleanup unit (TGCU) and tailgas thermal oxidation unit (TTO, or incinerator). It was designed for a sulfur production of about 400 LT/D from amine acid gas and sour water stripper (SWS) gas produced elsewhere in the refinery. The SRU A2 complex was also designed by Ortloff and installed in 2005-2006. Other than some differences in plant layout, SRU A2 is essentially a duplicate of SRU A1. Both complexes were revamped in 2011-2012 for low-level oxygen enrichment to raise the sulfur production capacity to about 500 LT/D each.

### 1.1.2 SRU Complexes at Refinery B

Refinery B has four Ortloff-designed sulfur recovery complexes, including SRU B1 and SRU B2 installed in the 1980s and 1990s. This paper focuses on the newer sulfur recovery complexes, SRU B3 and SRU B4, which were designed by Ortloff and installed in 2008-2010. The SRU B3 and B4 trains each include an SRU, TGCU, and TTO. The total nominal capacity of each train is about 180 LT/D when operating with air and about 225 LT/D when operating with low-level oxygen enrichment. Other than some differences in plant layout, SRU B4 is essentially a duplicate of SRU B3.

The following composite flow diagram illustrates the general arrangement and key features of both the Refinery A and Refinery B sulfur recovery complexes.

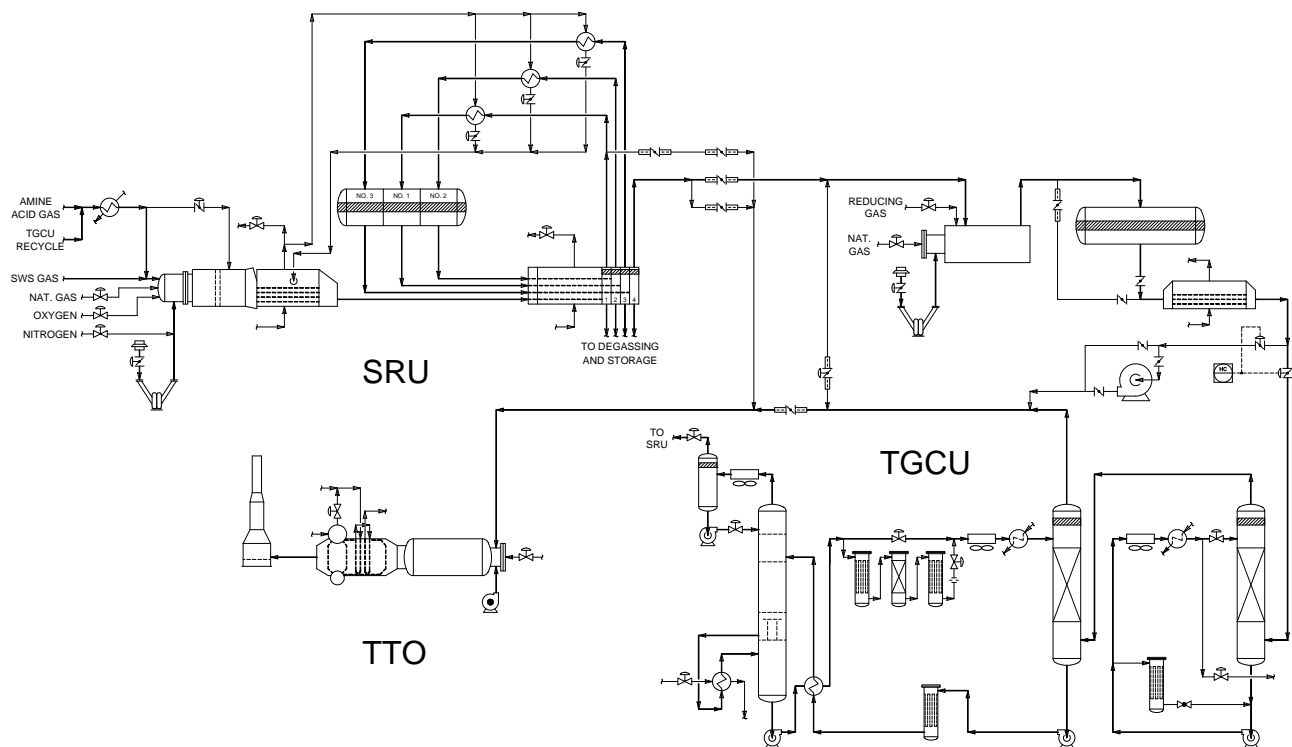


Figure 1 – Composite Flow Diagram for the Refiner's SRU Complexes

### **1.1.3 Refiner's Requirements for Low SO<sub>2</sub> Emission Startups and Shutdowns**

Each of these sulfur recovery complexes 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<sup>(1)</sup>, i.e., containing no more than 250 PPMV SO<sub>2</sub> on a dry, 0% excess air basis. These SRUs were originally designed to start up directly to the TTOs, with the downstream TGCUs bypassed. The design intention for each complex was to route tailgas from the SRU to the TGPU only after the 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 TGPU, 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 SRU are oxidized to SO<sub>2</sub> in the TTO and then vented.

Unfortunately, Refiner A and Refiner B (like many other refiners) are now facing increasing pressure from regulatory agencies to reduce the SO<sub>2</sub> emissions that occur when starting up and shutting down their SRU complexes. Both refiners asked Ortloff to investigate changes that would 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> emission above 250 PPMV in the TTO vent gas does not exceed 500 Lbs (7.8 lbmols) in a 24-hour rolling average period.

### **1.1.4 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 the reason that the original design intent for these units was to bypass the TGPU during these periods of instability. Any modifications to the Refiner's operating procedures, piping, equipment, or controls had to achieve the same goals, which include avoiding the following undesirable conditions:

- High temperatures in the TGPU 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

### **1.1.5 Original Design Features**

These sulfur recovery complexes include several design features that make it harder to start them up with the SRU "coupled" to the TGPU. 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.

1.1.5.1 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 A and Refinery B SRUs were originally designed for cold reactor bed startup. Instead of firing the SRU burner at stoichiometric air:fuel ratio, they use excess air to control the furnace temperature, and route the combustion products through the SRU warmup bypass line directly to the TTO as shown in Figure 2.

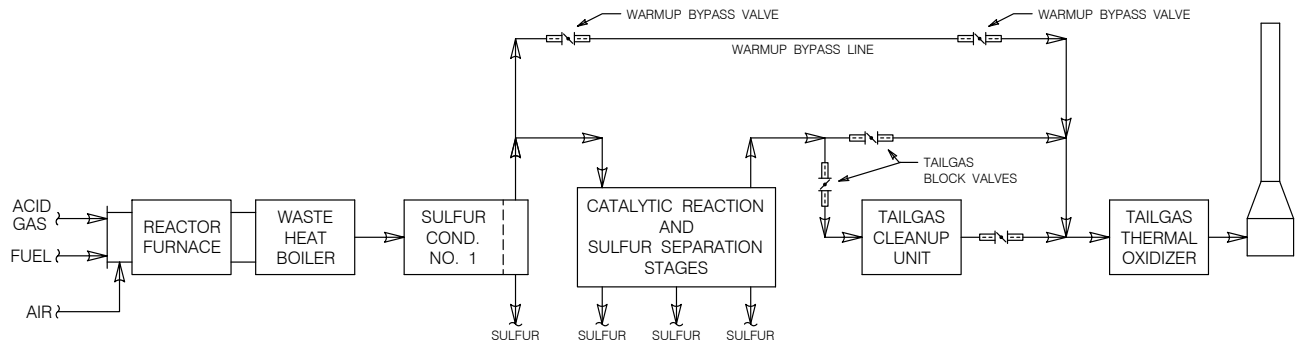


Figure 2 – SRU Cold Reactor Bed Startup Design

This startup procedure has been shown to extend the catalyst life in the 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 SO<sub>2</sub> 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 SO<sub>2</sub> 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 SO<sub>2</sub>. Therefore, in order to achieve low-emission startups and shutdowns, Refiners A and B needed the ability to warmup with close to stoichiometric air and route SRU tailgas through the TGCU during these phases of operation.

1.1.5.2 TGCU Reducing Gas Generator / In-line Heater

Each of the Refinery A and B TGCUs use a direct-fired reducing gas generator (RGG) to heat the SRU tailgas feeding the TGCU reactor. Since each refinery has a reliable source of good-quality hydrogen, the RGGs fire fuel gas at about 95% of stoichiometric air to generate heating gas. These burners have a minimum firing rate to avoid soot formation, so a minimum amount of inlet 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 SRU is significantly 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 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).

### 1.1.5.3 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 A and B TGCU startup blowers take their 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, the original piping arrangement did not allow the re-circulating gas to be routed through the quench or absorber columns.

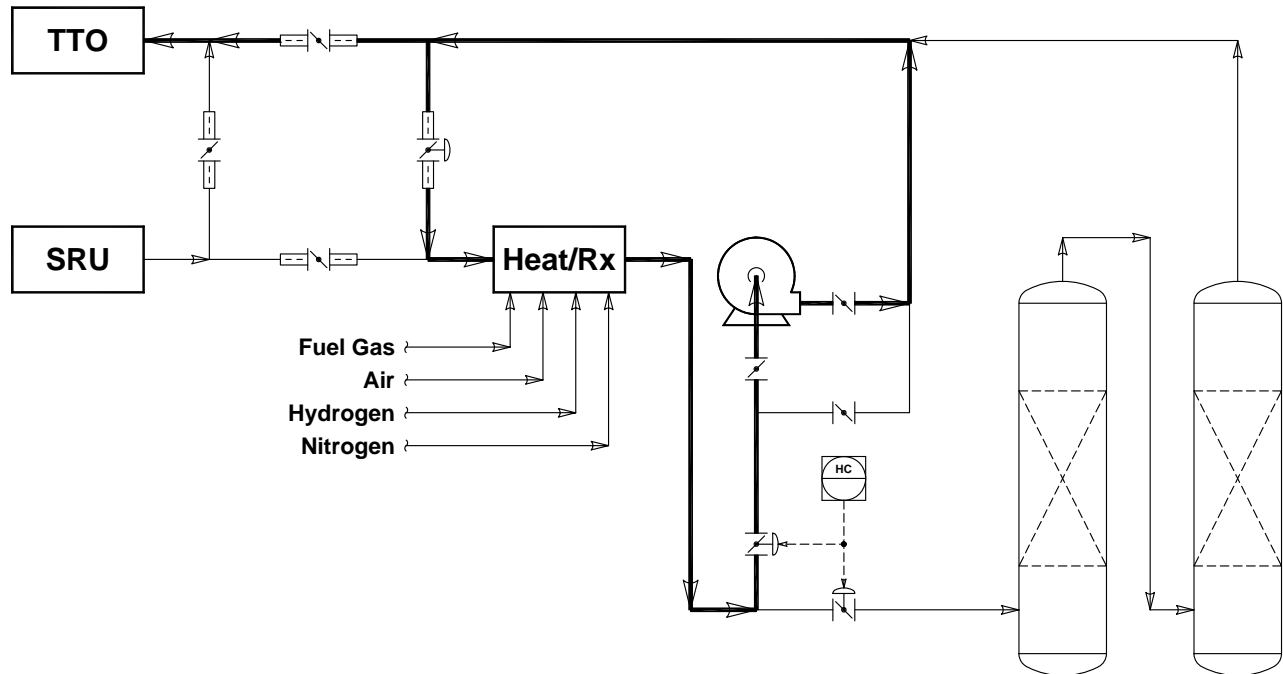


Figure 3 – TGCU Startup Blower Original Piping

## 2 LICENSOR'S PERSPECTIVE

### 2.1 Likely Sources of High SO<sub>2</sub> Emissions during Startup and Shutdown

In 2013/2014, Refiner A and Refiner B retained Ortloff to study options for reducing SO<sub>2</sub> emissions during startup and shutdown of their sulfur recovery complexes. Each refiner had observed high SO<sub>2</sub> concentrations during the following phases for one or more of their recent startups and shutdowns.

- The SO<sub>2</sub> concentration increased significantly when firing fuel gas to warm up the SRU.
- The SO<sub>2</sub> concentration increased significantly when the SRU was firing fuel gas with excess air during hot stand-by.
- A relatively minor increase in SO<sub>2</sub> concentration occurred when the SRU was switched from firing fuel gas to firing acid gas (before the SRU tailgas was routed to the TGCU).
- The SO<sub>2</sub> concentration increased when pre-sulfiding the TGCU catalyst. (The catalyst does not always consume all of the sulfur entering the reactor throughout the procedure.)
- The SO<sub>2</sub> concentration increased when the SRU reactors were cooled with nitrogen.
- The SO<sub>2</sub> concentration increased when the SRU reactors were cooled with air from the SRU air blowers.
- The SO<sub>2</sub> concentration increased when the TGCU catalyst was passivated. Passivation is accomplished by exposing the catalyst to small concentrations of oxygen in order to slowly oxidize the metal sulfides in the catalyst bed.

#### 2.1.1 High SO<sub>2</sub> Emissions during Startup

Based on these observations, and other anecdotal information from both Refiners, Ortloff concluded that the likely sources of the observed high emissions were as follows:

##### 2.1.1.1 Warming Up the SRU / Hot Stand-by

Excess Air - When warming up the 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>. The observation of high SO<sub>2</sub> emissions during warmup and hot stand-by operations indicated that the operating philosophy of warming the SRU with excess air (instead of stoichiometric air) was likely a major contributing factor to high SO<sub>2</sub> emissions.

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. Both Refiner A and Refiner B had observed significant sulfur accumulation in their sulfur condenser separator chambers due to "cold spots" during recent turnarounds. The design intent for these sulfur condensers is to prevent any sulfur accumulation in the outlet channels by sloping the condensers, steam jacketing the outlet



nozzles, and sloping the sulfur rundown lines. However, both Refiners reported finding large quantities of solid sulfur in their condensers, indicating that their condensers were not draining completely.

Both Refiners confirmed there was no plugging in the steam-heated rundown lines or drains seals, so it is likely that "cold" spots developed at or near the sulfur outlet nozzles, which allowed sulfur to freeze and "stack-up" into the condenser chambers. We concluded that the likely causes for these "cold" spots were:

- Failure of the steam heating on the sulfur outlet nozzles
- Excessive heat losses to the surroundings – Although relatively hot gas is flowing through the separator chambers, at low flow rates the heat losses to the surroundings may be significant enough to cause freezing of sulfur in the separator chambers even if the sulfur outlet nozzles are not plugged.

Regardless of the cause, an accumulation of sulfur in the outlet chamber(s) of the sulfur condenser can result in high SO<sub>2</sub> emissions from the TTO while firing fuel gas to warm up the SRU.

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

With the original plant configuration, the switch from firing fuel gas while warming up the SRU to processing acid gas in the SRU is made with the SRU tailgas directed to the TTO rather than the TGPU. This means that once the SRU begins firing acid gas, the residual sulfur in the SRU tailgas goes directly to the TTO until the SRU tailgas is switched into the TGPU, 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.

#### **2.1.1.3 Pre-Sulfiding / Activating TGPU Catalyst**

Whenever the catalyst in the TGPU reactor is replaced, it must generally be pre-sulfided or activated before the TGPU can be placed in service. However, the catalyst may not always consume all of the sulfur entering the reactor throughout this procedure. The original piping configuration for the TGPU startup blower in these units only allowed circulation through the front-end of the TGPU, so any residual sulfur bypassed the TGPU columns and went straight to the TTO, where it caused the SO<sub>2</sub> emissions to be high at times.

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

#### **2.1.2.1 Cooling the SRU**

With the original plant configuration, the SRU tailgas is routed directly to the TTO when cooling with nitrogen because the flow rate is not high enough to quench the temperature in the TGPU 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.

During the final cooling of the SRU using air from the SRU air blower, the flow rate is also not high enough to quench the temperature in the RGG, and the excess oxygen can damage TGPU 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 higher SO<sub>2</sub> emissions.

### 2.1.2.2 Passivating TGCU Catalyst for Reactor Entry and Catalyst Replacement

Many refiners (including Refiner A and Refiner B) 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.

## 2.2 Solutions and Impact on SO<sub>2</sub> Emissions

Ortloff organized the potential changes for reducing Refinery A and Refinery B's SO<sub>2</sub> emissions into three categories or levels of modification:

- Level 1 (Low / No Cost) — Changes to current operating procedures with few or no changes to the equipment, piping, and controls
- Level 2 (Moderate Cost) — Changes to current operating procedures and minor changes to the equipment, piping, and controls
- Level 3 (High Cost) — Changes to current operating procedures and more extensive changes to the equipment, piping, and controls to accomplish near-zero exceedances

### 2.2.1 Level 1 — Changes to Procedures

The first level of modification for reducing SO<sub>2</sub> emissions during startup and shutdown was to make changes to the current operating procedures. This is obviously the lowest cost option, since it requires essentially no changes to the current equipment, piping, or controls.

As discussed below, some slight improvements to the current startup, operating, and shutdown procedures were possible. However, the expected overall impact on the SO<sub>2</sub> emissions during startup and shutdown was minimal.

#### 2.2.1.1 Changes to the Startup Procedures

Coordinate startup better – With the existing configuration of equipment and piping in the sulfur recovery complexes, little could be done to improve the current procedures used for startup of the SRUs. Ortloff's suggestion to both Refiners was to coordinate startup of the TGCU so that the TGCU is ready for SRU tailgas by the time the associated SRU is ready for acid gas introduction. This would minimize the duration of high emissions after switching the SRU from fuel gas to acid gas.

Maximize TTO air flow during startup – Both Refiners adjusted the air flow to the TTO as the plant load changed. This is contrary to the design intent for the units, and actually causes the SO<sub>2</sub> concentration in the TTO vent gas (which is corrected to 0% excess air) to increase when the air flow is reduced. Maintaining the TTO air flow rate at the design value regardless of plant load has multiple benefits:

1. The corrected SO<sub>2</sub> concentration in the TTO vent gas is lower when the air flow rate is high because higher air flow requires combustion of more fuel gas to maintain the same TTO operating temperature. Combustion of the additional fuel gas produces more CO<sub>2</sub> in the burner, which then dilutes the SO<sub>2</sub> in the vent gas.
2. Keeping the air flow rate high prevents the "bogging" that can occur if the SRU gets off-ratio and sends large amounts of H<sub>2</sub>S to the TTO. This H<sub>2</sub>S causes the TTO temperature to increase, forcing its temperature controller to "back out" fuel gas to reduce the temperature. If the air flow rate is too low, there will not be sufficient air to combust all of the H<sub>2</sub>S and fuel gas when the TTO begins to recover, resulting in the TTO temperature going down as the controller sends more and more fuel gas to the burner. If the air flow is always kept high, this phenomenon cannot occur.

#### **2.2.1.2 Changes to the Shutdown Procedures**

Another recommendation was to keep the SRU and TGCU "coupled" for as long as possible when shutting down the units. Both Refiners commonly shut down their TGCU prior to shutting down the associated SRU. However, the SO<sub>2</sub> emissions may be reduced by shutting down the SRU and TGCU at the same time, and then shutting down the associated TTO.

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

The second level of modifications included the Level 1 modifications to the operating procedures plus minor changes to the current equipment, piping, and/or controls. Three such changes were identified:

1. Add LP quench steam to the SRU burner/furnace – As noted previously, the SRUs were designed to warm up by firing fuel gas with excess air. The air:gas ratio could be adjusted to stoichiometric, but without another means of 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 both Refiners install LP (50 PSIG [3.5bar(g)]) steam piping, instrumentation, and controls and connect it to the acid gas piping upstream of each SRU burner. This would enable them to operate the SRU burner at stoichiometric air:fuel ratio and inject LP steam to control the furnace temperature. With sufficient steam available for quench, the unit operators could warm up the SRU furnace with the SRU burner firing at stoichiometric, thereby eliminating the excess oxygen that caused the high SO<sub>2</sub> emissions during warmup.

2. Add heating to the sulfur condenser outlet channels – To prevent sulfur from accumulating in the sulfur condenser separator chambers, Ortloff also recommended more reliable heating of the outlet channels. This included two modifications:
  - Add steam heating panels to the lower quadrants of the condenser outlet channels.
  - Remove the existing steam jackets on the liquid sulfur outlet nozzles (which were prone to failure and steam leakage) and install bolt-on steam jackets on each nozzle. The bolt-on jackets would be less prone to failure than the existing steam jackets, but would still ensure maximum heat transfer surface in contact with the nozzle, thus ensuring that there are no "cold" spots.

3. Incorporate fuel gas into the air flow control loop where applicable – 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. The older SRUs at Refinery B, SRU B1 and SRU B2, did not have this feature.

Summary of Improvements for Level 1 plus Level 2

Supplying LP quench steam to the SRU burners and incorporating fuel gas into the air flow control loops (where not already provided) gives the Refiners the means to warm up the SRU with stoichiometric air and with good air flow control. With careful operator attention, this reduces the free oxygen in the warmup tailgas to 1-2% or less and greatly reduces SO<sub>2</sub> emissions caused by the oxidation of iron sulfide and/or residual sulfur normally present in the plant.

Installing more reliable heating for the sulfur condenser outlet channels reduces sulfur vaporization/carry-over by eliminating "cold spots" and sulfur accumulation in the condenser separator sections. Ortloff suspects sulfur vaporization/carry-over was likely a contributing factor to high SO<sub>2</sub> emissions at both Refineries during SRU warmup and cool-down procedures.

These modifications would likely reduce the high SO<sub>2</sub> emissions observed during warmup of the SRU and cool-down of the SRU with nitrogen, but were not expected to reduce the emissions associated with switching from fuel to acid gas, pre-sulfiding, or passivating the TGCU catalyst. Table 1 summarizes the expected improvements from the proposed Level 1 and Level 2 modifications.

**Table 1** – Summary of Improvements for Level 1 plus Level 2 Changes

<b>Operating Mode</b>	<b>SO<sub>2</sub> Emissions</b>
Warming up the SRU	Reduced
Switching the SRU to acid gas	No change
Pre-sulfiding TGCU catalyst	No change
Normal operation	No change
Upsets during normal operation	No change
Cooling the SRU with nitrogen	Reduced
Final SRU cooling with air	No change
Passivating TGCU catalyst	No change

### **2.2.3 Level 3 — Major Changes to Equipment, Piping, and Controls**

The third level of modification for reducing SO<sub>2</sub> emissions during startup and shutdown is changes to the current equipment, piping, and/or controls that could reduce the occurrence of SO<sub>2</sub> emission exceedances to nearly zero. For this level, much more extensive changes, modifications, and additions were considered in light of trying to reduce or eliminate SO<sub>2</sub> exceedances as much as possible under all operating scenarios. This level also has the highest cost impact. Three options were studied for Level 3: Option A, Option B, and Option C.

### 2.2.3.1 Option A —Modifications to the TGCU Startup Blower Piping

The TGCUs in both refineries use a reducing gas generator (in-line heater or RGG) to heat the SRU tailgas to the proper reaction temperature before it enters the TGCU reactor. The TGCU burner operates with slightly less than stoichiometric air to prevent oxygen from escaping and damaging the reactor catalyst. Because of this sub-stoichiometric 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 a TGCU, it is necessary to adjust its in-line burner to the proper sub-stoichiometric air:gas 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 TGCU startup blower accomplishes this by re-circulating a portion of the process gas leaving the TGCU waste heat boiler (WHB) back to the furnace as shown previously in Figure 3. This process gas must continue to circulate through the system until the SRU tailgas is routed to the furnace, at which time the startup blower can be shut down.

One of the limitations with the current TGCUs is that process gas cannot be directed into the TGCU columns (quench column and absorber) while the startup blower is being used to re-circulate gas to the TGCU burner/furnace. As a result, there are phases during SRU startup and shutdown when the SRU effluent cannot be processed in the TGCU columns because the effluent flow rate is not high enough to keep the TGCU furnace from overheating without the additional recycle gas from the TGCU startup blower.

Figure 4 shows a relatively simple modification to the piping around the startup blower that can eliminate this limitation:

- The quench column bypass valve is relocated to the blower discharge piping
- A new blower bypass valve is installed in the quench column inlet piping
- The existing bypass valve and piping is taken out of service
- A new bi-directional bypass line is installed

With this change, the blower can be used to re-circulate gas through just the TGCU front-end (furnace/reactor) 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 SRU (tailgas, combustion products, etc.) as shown in Figure 6.

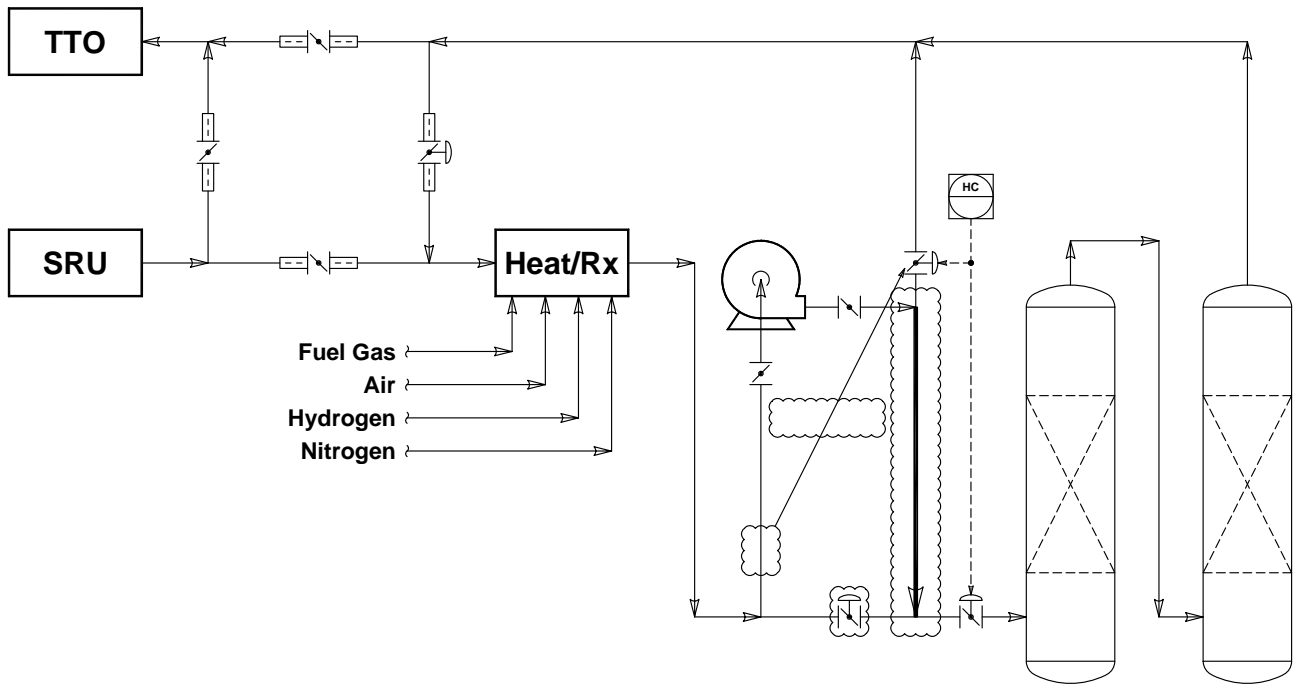


Figure 4 – Option 3A Changes – Startup Blower Piping Modifications

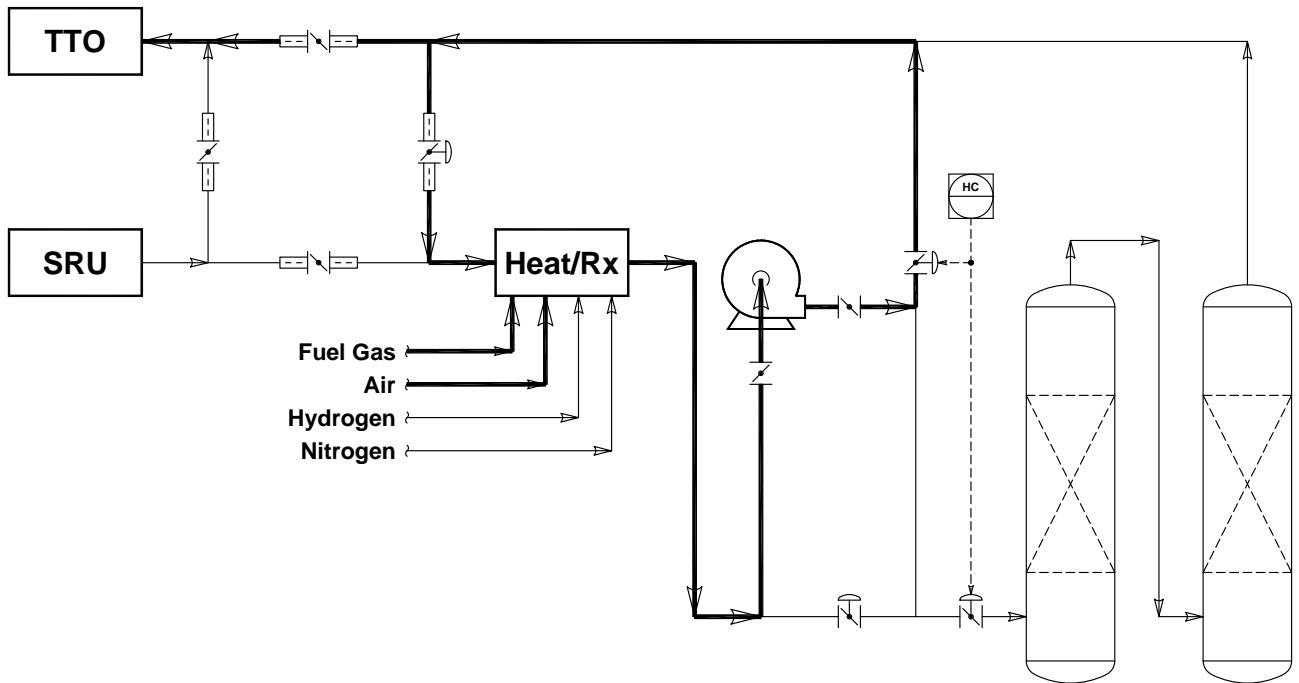


Figure 5 – Option 3A Changes – Re-circulation of the TGCU Front-End ("Short" Loop)

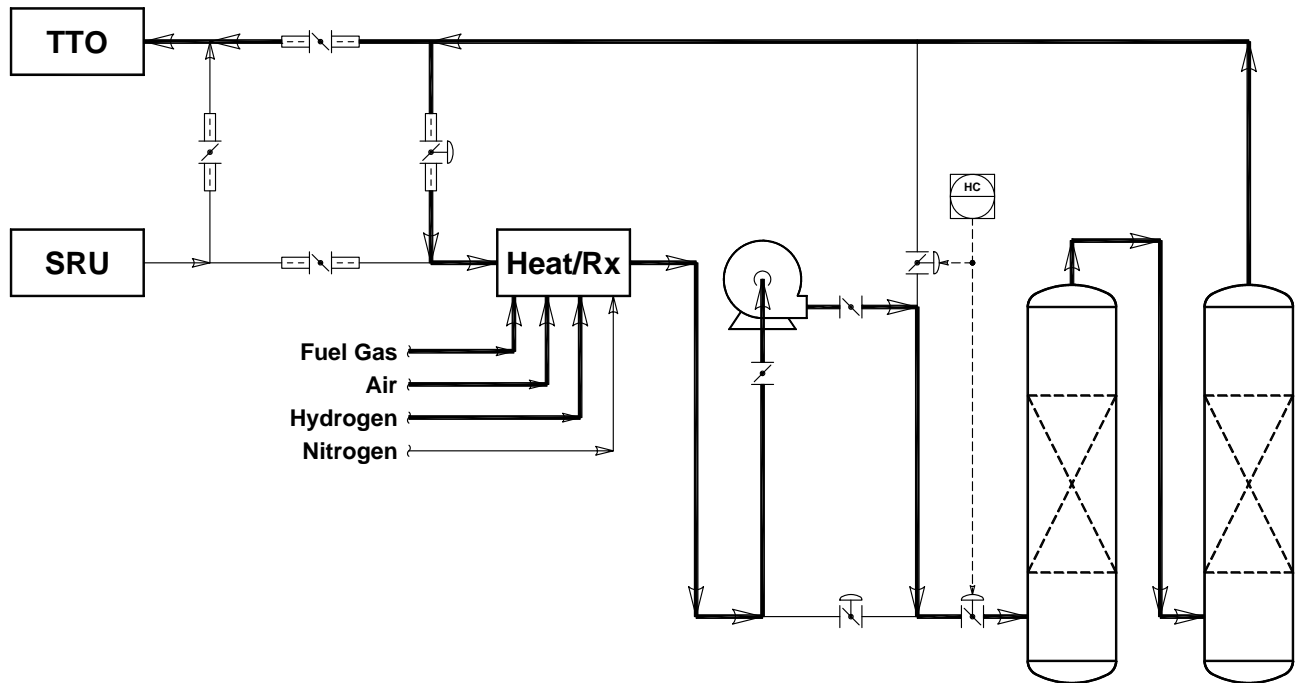


Figure 6 – Option 3A Changes – Re-circulation of the TGCU Front-End and Back-End ("Long" Loop)

### 2.2.3.2 New Capabilities Added by the Option 3A Modifications

With these changes (plus the Level 1 and Level 2 modifications described earlier), the TGCU will have the following capabilities:

1. The SRU can be "coupled" to the TGCU during startup as soon as the SRU is firing fuel gas with stoichiometric air. The SRU and TGCU can remain coupled until the final air cooling of the catalyst beds in the SRU when shutting down the SRU for entry. During all the time in between these two phases, whatever sulfur species are in the effluent from the SRU can be processed in the TGCU, with the TGCU reactor converting them to H<sub>2</sub>S and the TGCU absorber 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 can 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 now 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 cools down more rapidly.
3. The SO<sub>2</sub> emissions from the TTO can 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 will be removed by 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.

### **2.2.3.3 Option B — Convert the TGCU to Steam Heating**

The second option studied for Level 3 was converting the front-end of the TGCU to steam heating. In the time since these SRU complexes were designed, low-temperature hydrogenation/hydrolysis catalysts that have significantly lower reaction initiation temperatures have been developed and demonstrated. These catalyst allow using HP steam as the heating medium, rather than an RGG, thereby eliminating the TGCU burner and burner management system (BMS), the combustion controls, the turndown constraints, and most of the ESD safeguards in the TGCU. Since steam heating eliminates the turndown constraints of the current in-line burner heating system, the TGCU can be "coupled" to the SRU regardless of how much gas (tailgas, combustion products, or nitrogen) is leaving the SRU. The result is simpler and quicker TGCU startups and shutdowns, simpler and easier TGCU operation, and far fewer TGCU outages. All of these advantages mean the TGCU will be off-line for shorter durations.

The modifications required to replace the existing RGG with steam heating are shown in Figure 7. The SRU tailgas is re-piped to enter a new feed heater, which uses saturated HP steam to heat the tailgas to 465-475°F (240-246°C). The reducing gas that is currently supplied to the RGG is combined with the hot tailgas leaving the heater and thoroughly mixed by a new static mixer before entering the reactor. The conventional catalyst in the reactor is replaced with one of the new low-temperature catalysts. The converted tailgas leaving the reactor proceeds to the WHB and quench column as before. The existing air blowers, burner, and RGG can be removed or abandoned in-place, and the startup bypass for the reactor can be removed or blinded off.

Startup of the TGCU front-end is very quick and easy with steam heating. All that is required is to fill the front-end filled with nitrogen, re-circulate the nitrogen with the startup blower, and use the feed heater to heat the nitrogen and bring the front-end up to temperature.

Shutdown is equally simple. Take the SRU tailgas out of the TGCU, purge the residual process gas to the TTO with nitrogen, and then re-circulate the nitrogen through the front-end using the startup blower. The large flow of nitrogen quickly brings the reactor temperature down. If reactor entry is necessary, a small amount of plant air can be added to the circulating nitrogen to passivate the reactor catalyst.



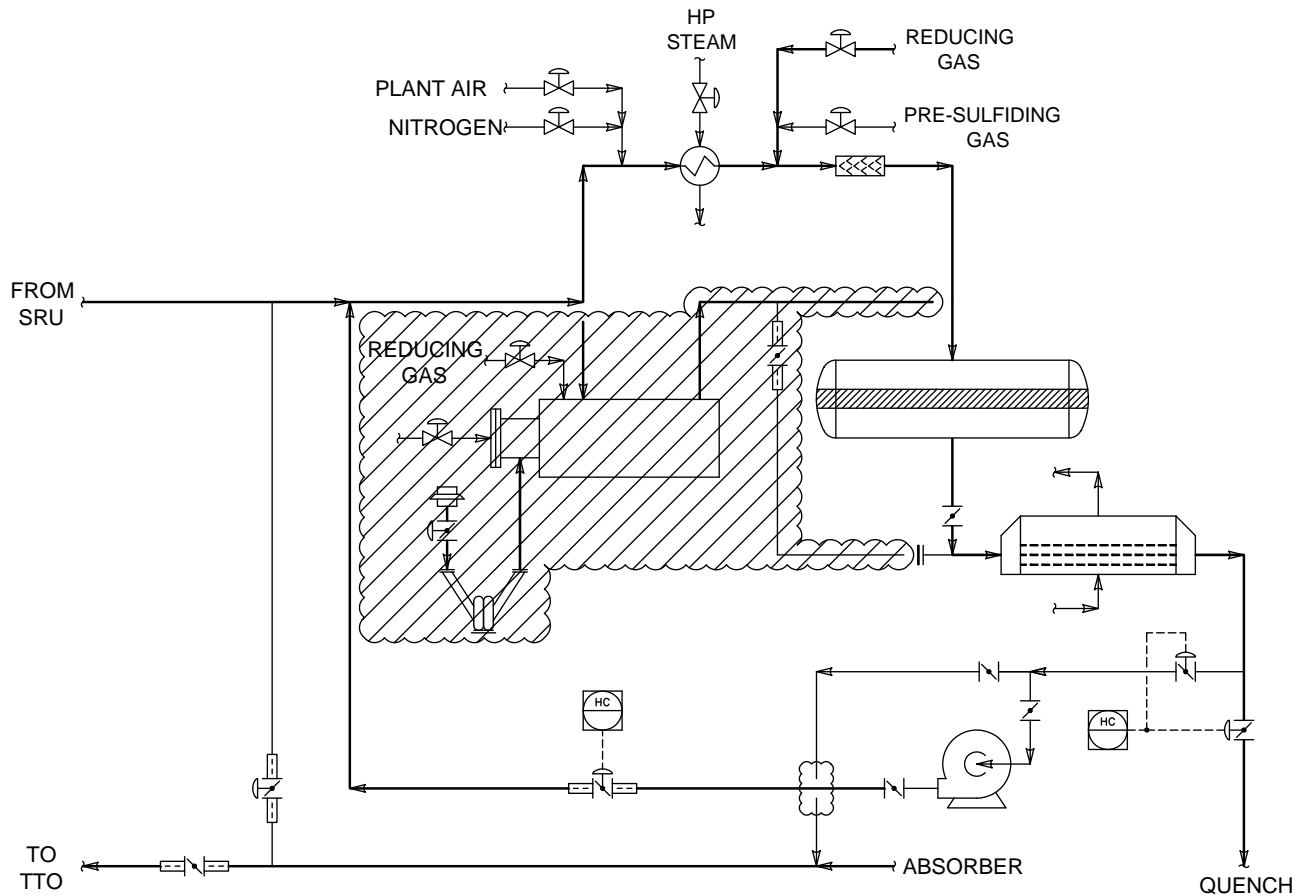


Figure 7 – Option 3B Changes – Converting the TGCU Front-End to Steam Heating

#### 2.2.3.4 New Capabilities Added by the Option 3B Modifications

With the Option 3B changes (plus the Level 1 and Level 2 modifications described earlier), the TGCU will have the following capabilities:

1. The SRU can be "coupled" to the TGCU during startup as soon as the SRU is firing fuel gas with stoichiometric air, and remain coupled until the final air cooling of the catalyst beds in the SRU when shutting down the SRU.
2. There are no longer any turndown limitations in the TGCU.
3. Startup and shutdown of the TGCU is quicker and easier.
4. Operation of the TGCU is simpler and requires less operator attention.
5. Unplanned outages of the TGCU are much less likely.

If the modifications around the TGCU startup blower described in Option 3A are combined with the Option 3B steam heating modifications, still further improvement is possible. This combination of modifications has the following advantages:

1. During a TGCU shutdown, the "long" recycle can be used to re-circulate nitrogen for cooling the reactor through the TGCU back-end.
2. When new TGCU catalyst is installed and must be pre-sulfided, the gas leaving the reactor can be directed through the TGCU back-end, minimizing the SO<sub>2</sub> emissions while pre-sulfiding the catalyst.

### **2.2.3.5 Option C — Add a Tailgas Scrubbing Unit Downstream of the TTO**

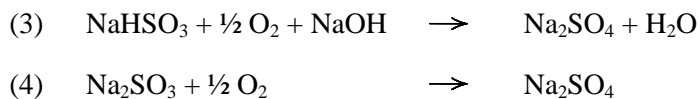
The third option studied for Level 3 was adding a scrubbing unit downstream of the TTO. In lieu of any of the changes discussed in the previous sections, the SO<sub>2</sub> emission exceedances could be eliminated completely by adding a tailgas scrubbing unit (TSU) to remove the SO<sub>2</sub> from the incinerated vent gases leaving the TTO.

A good example of this technology is the DynaWave<sup>®</sup> scrubbing process licensed by MECS. The TSU contacts the gas leaving the TTO with a circulating alkali solution (typically sodium hydroxide, NaOH). The SO<sub>2</sub> in the gas immediately dissolves into the solution and reacts with the NaOH to form sodium sulfite and sodium bisulfite. The resulting two-phase gas/solution stream enters a scrubber vessel where the gas is separated from the circulating solution and then vented to the atmosphere.

The chemical reactions between the caustic solution and SO<sub>2</sub> are as follows:



Most wastewater treating systems cannot accommodate water with a high chemical oxygen demand (COD). In such cases, oxidizing air can be sparged into the solution in the scrubber vessel to convert the sodium sulfite and sodium bisulfite to sodium sulfates according to the following chemical reactions:



### **2.2.3.6 New Capabilities Added by the Option 3C Modifications**

If the TSU is designed to process the TTO effluent when the TGCU is shut down, all of the following is possible:

- Near-zero SO<sub>2</sub> emissions while warming up the SRU, regardless of whether its burner is firing at or above stoichiometric
- Near-zero SO<sub>2</sub> emissions while switching the SRU from fuel gas to acid gas, regardless of whether the SRU is "coupled" to the TGCU
- Near-zero SO<sub>2</sub> emissions while pre-sulfiding catalyst in the TGCU reactor
- Near-zero SO<sub>2</sub> emissions during normal operations
- No SO<sub>2</sub> emissions excursion when upsets cause the TGCU to go off-spec or when the TGCU must be taken off-line

- Near-zero SO<sub>2</sub> emissions while flowing combustion products through catalyst beds to sweep out sulfur in the SRU (i.e., performing a "sulfur strip"), regardless of whether the SRU is "coupled" to the TGCU
- Near-zero SO<sub>2</sub> emissions while using nitrogen or air to cool the reactors in the SRU
- Near-zero SO<sub>2</sub> emissions while passivating the catalyst in the TGCU reactor

**2.2.4 Summary of Improvements for Level 3 Changes**

Table 2 summarizes the SO<sub>2</sub> emissions reductions achievable for each of the Level 3 options.

**Table 2 – Summary of Improvements for Level 3 Options**

Operating Mode	SO <sub>2</sub> Emissions			
	<u>Option 3A</u> <sup>(1)</sup> startup blower piping "long" loop	<u>Option 3B</u> <sup>(1)</sup> steam heating	<u>3A+3B</u> <sup>(1)</sup> "long" loop + steam heating	<u>Option 3C</u> tailgas scrubbing
Warming up the SRU	Further Reduced	Further Reduced	Further Reduced	Near-zero
Switching the SRU to acid gas	No exceedance	No exceedance	No exceedance	Near-zero
Pre-sulfiding TGCU catalyst	No exceedance	No change	No exceedance	Near-zero
Normal operation	No change	No change	No change	Near-zero
Upsets during normal operation	No change	No change	No change	Near-zero
Cooling the SRU with nitrogen	No exceedance	No exceedance	No exceedance	Near-zero
Final SRU cooling with air	No change	No change	No change	Near-zero
Passivating TGCU catalyst	No change	No change	No change	Near-zero
NOTE 1. Assumes Levels 1 and 2 are also implemented.				

### 3 REFINERS' PERSPECTIVE

Refineries A and B both chose to proceed with Level 3 Option A, in addition to the recommended Level 1 and Level 2 changes, because these modifications could be accomplished at a lower cost, with less construction activity, and would not require any additional plot space. This section describes the Refiners' operating history with high SO<sub>2</sub> emissions, their economic evaluation, and the improvement in emissions following implementation of the Level 3 modifications.

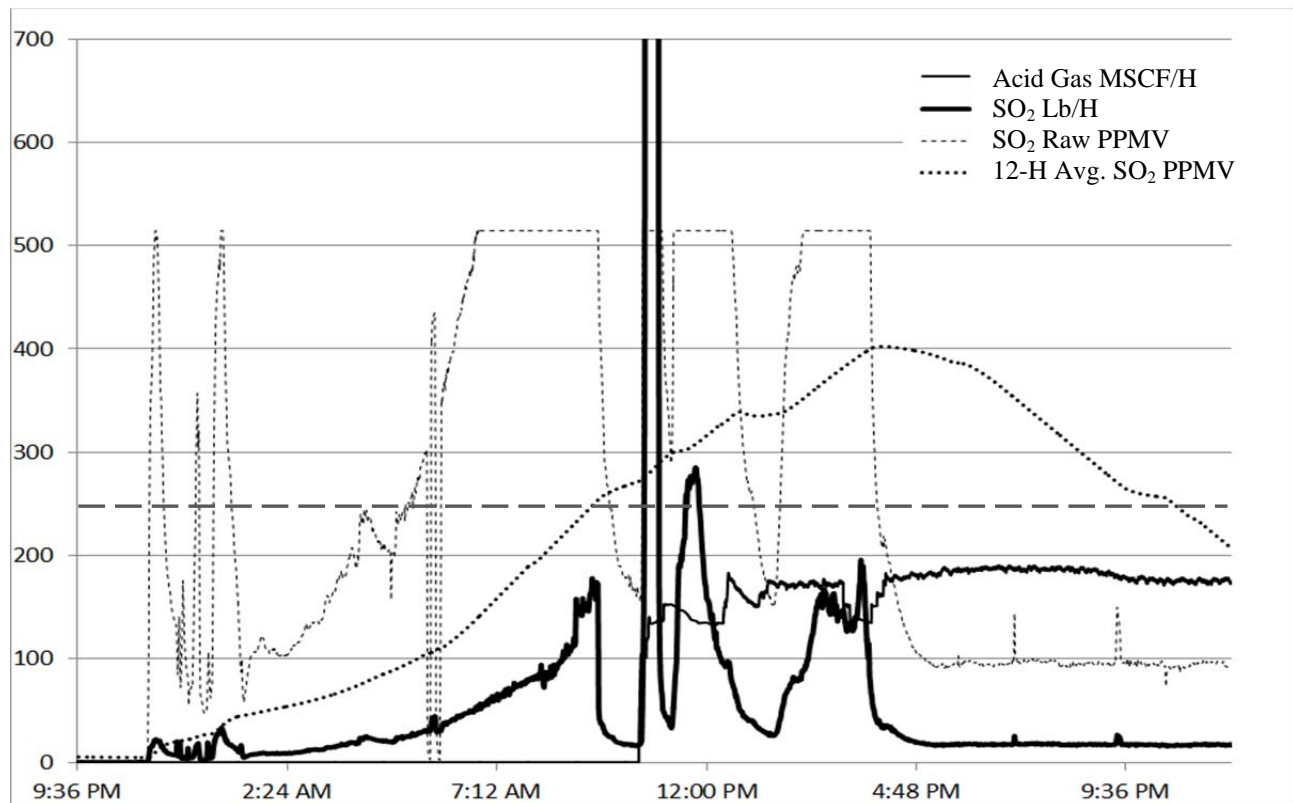
#### 3.1 Performance Before Low-Emission Changes / Modifications

In recent years, both refineries have experienced high SO<sub>2</sub> emissions during startups and shutdowns. Table 3 summarizes the emissions calculated by Refiner A during three previous startups. Likewise, Chart 1 shows the SO<sub>2</sub> emission trends from Refiner B during a previous startup in 1<sup>st</sup> quarter 2013. In each case, the SO<sub>2</sub> emissions significantly exceeded the refiner's allowable emissions.

**Table 3** – Refinery A SO<sub>2</sub> Emissions (Lbs of SO<sub>2</sub> above 250 PPMV)

Date	Lbs SO <sub>2</sub>
2 <sup>nd</sup> Quarter 2010	6,000
2 <sup>nd</sup> Quarter 2012	9,400
3 <sup>rd</sup> Quarter 2012	15,400

**Chart 1** – Refinery B SO<sub>2</sub> Emissions Trends 1<sup>st</sup> Quarter 2013



In an effort to reduce these high emissions during startup/shutdown, the following actions were taken by one or both Refiners, but none had a significant impact on environmental performance:

1. Provided senior process engineering support during startup and shutdown
2. Doubled the time spent on "sulfur stripping" (inert combustion products sweeping the SRU catalyst beds of residual sulfur)
3. Eliminated the final air cooling of the SRU catalyst beds and cooled only with supplied nitrogen
4. Verified no leakage from the SRU warmup bypass valves
5. Cleaned sulfur from sulfur condenser outlet channel during outages
6. Attempted to keep the TTO combustion air rate as low as possible during startup

Ironically, action 6 likely contributed to the high SO<sub>2</sub> emissions because reducing the air flow to the TTO reduces the amount of fuel gas consumed and the amount of combustion products produced by the TTO burner, which act as diluent and reduce the SO<sub>2</sub> concentration.

### 3.2 Implementation of Modifications

After obtaining Ortloff's initial study report outlining the various options and the expected levels of improvement in startup/shutdown emissions, Refiner A prepared cost estimates for each option. Table 4 below summarizes their results.

**Table 4 – Comparison of Options to Achieve Low-Emission Startups and Shutdowns for SRU A1 and SRU A2**

Level and Option	Capital Costs per Complex	Annual Impact on Emission Events
1 Modify Procedures	\$0	Nil – essentially 0% reduction
2 Quench Steam to SRU S <sup>o</sup> Condenser Heating	\$100,000 per SRU \$200,000 per Complex	Minimal – approx. 10% reduction = 0.9 Tons of SO <sub>2</sub>
3A Reconfigure S/U Blower Piping + 1 and 2	\$1,000,000	Substantial – approx. 60% reduction = 5.7 Tons of SO <sub>2</sub>
3B Convert RGG to Steam Heater	\$4,000,000	Substantial – approx. 40% reduction = 3.8 Tons of SO <sub>2</sub>
3A + B Options A and B Combined	\$5,000,000	Substantial – approx. 65% reduction = 6.2 Tons of SO <sub>2</sub>
3C Tailgas Scrubbing Unit (TSU)	\$8,600,000 <sup>(1)</sup>	Near zero emissions – 100% reduction = 9.5 Tons of SO <sub>2</sub>
NOTES		
1. Budget-quality TIC estimate for a DynaWave <sup>®</sup> TSU Flue Gas Scrubber provided by MECS		

The significantly lower cost for Option 3A (re-routing the TGPU startup blower piping), and the fact that it would require less detailed engineering, less construction activity, and no additional plot space, led both Refiners to choose option 3A for implementation. In addition, both Refiners elected to implement the

procedural changes described in Level 1 and the minor equipment/piping modifications outlined in Level 2 in order to obtain the full benefit of the changes associated with Option 3A.

Refiner A began work on the SRU A1 complex in June 2015 and the modifications were completed in September 2015 during their 2015 turnaround. The work on the SRU A2 complex is expected to be completed during the 2017 turnaround. Refiner B began work on the SRU B3 complex in March 2016 and the modifications were completed in May 2016. The work on SRU B4 is also expected to be completed in 2017.

### **3.3 Performance After Low-Emission Changes / Modifications**

Both refineries experienced significant reductions in startup emissions following implementation of the selected changes.

Refiner A's estimated SO<sub>2</sub> emissions decreased to **290 lbs of SO<sub>2</sub> above 250 PPMV** during the September 2015 startup of SRU A1. However, startups are rarely perfect and SRU A1 experienced CEMS issues during warmup of the SRU. As soon as the TTO started up, the CEMS output was erratic, indicating an average of 167 PPMV SO<sub>2</sub> while swinging wildly. This continued for the first 18 hours until a plugged CEMS sample filter was replaced, then the CEMS settled down to around 25 PPMV SO<sub>2</sub>. If these erratic CEMS readings are included in the SO<sub>2</sub> emissions estimate, the total increases to 3,400 lbs of SO<sub>2</sub> above 250 PPMV, which is still a significant improvement from previous startups.

Refiner B also saw significant emissions improvement when starting up SRU B3 in May 2016. Chart 2 shows the SO<sub>2</sub> emissions trends for SRU B3 during the May 2016 startup. Unfortunately, Refiner B also experienced issues during startup that were unrelated to the modifications. Several days after introducing acid gas, the pressure drop across the packed bed in the TGPU absorber increased significantly. The unit was shut down and the column was opened up for inspection. At that time, they found significant plugging in the lower sections of the packed bed. Elemental analysis of the material indicated that it was predominantly carbon, iron, aluminum, sulfur, nitrogen and oxygen. The absorber packing and TGPU solvent were replaced and the unit was restarted in early June 2016. Chart 3 shows the SO<sub>2</sub> emissions during the subsequent startup in June.

Chart 2 – Refinery B SO<sub>2</sub> Emissions Trends May 2016

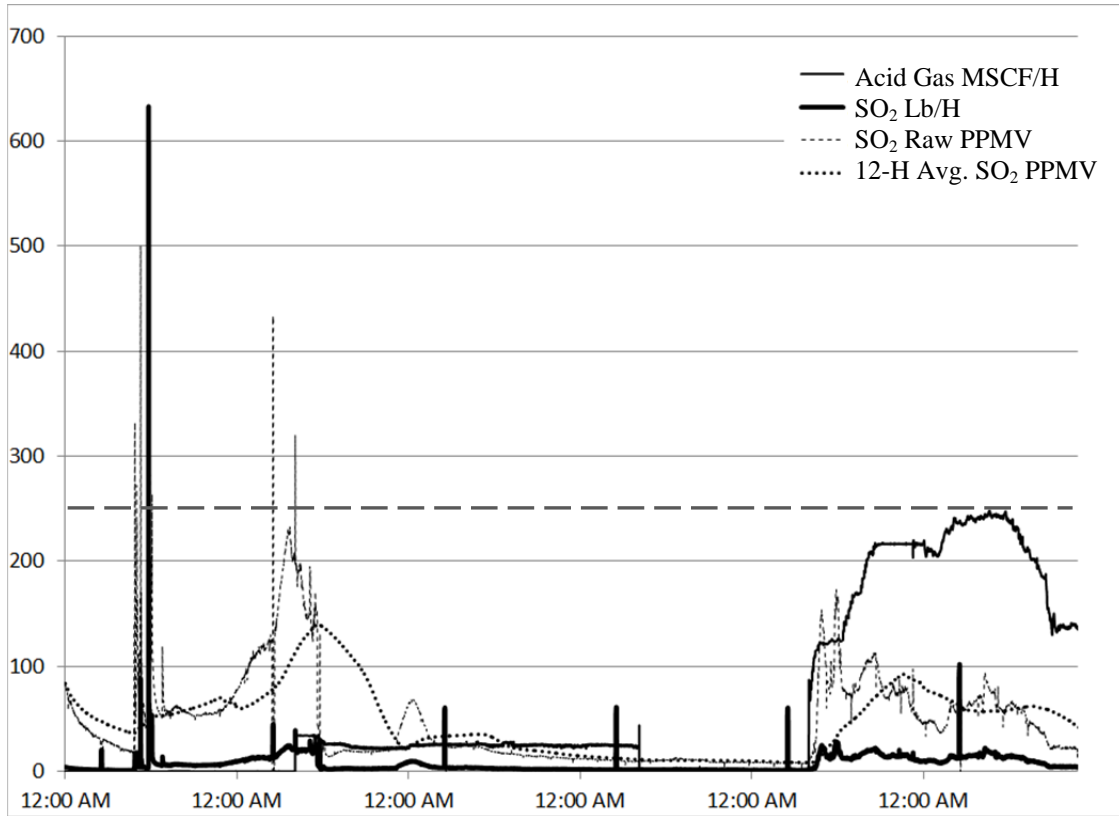
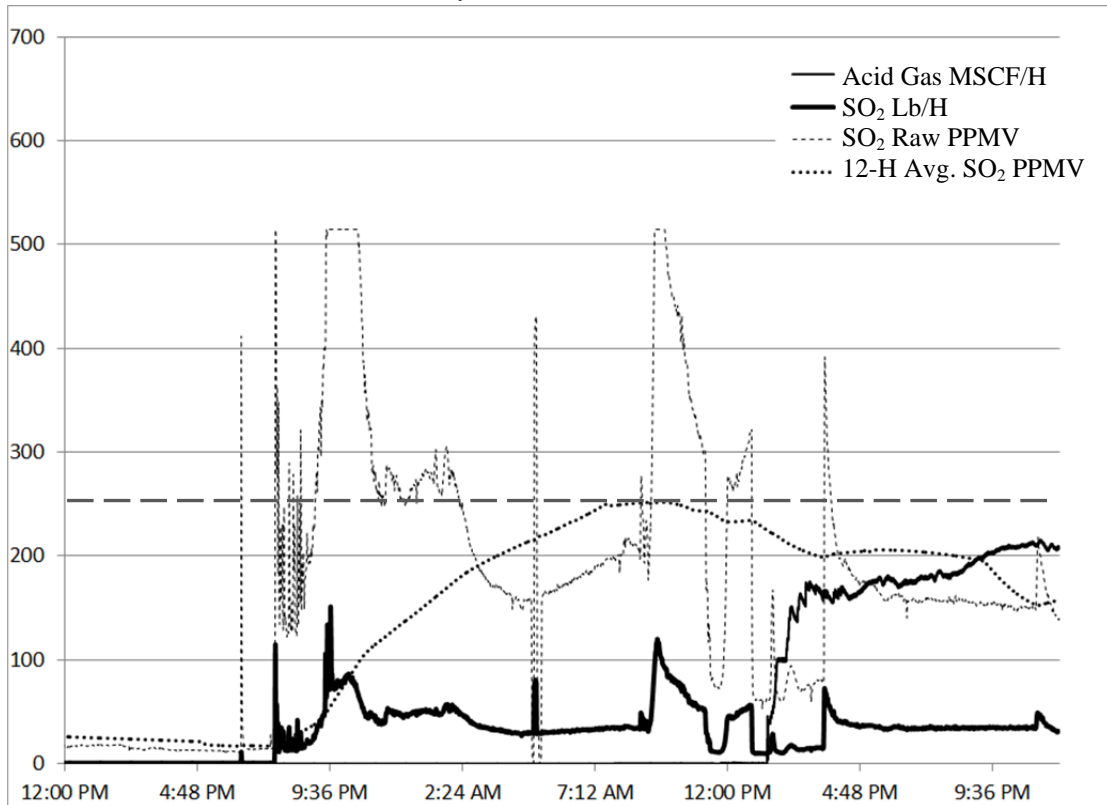


Chart 3 – Refinery B SO<sub>2</sub> Emissions Trends June 2016



Refiner B considered both startups successful since they were able to stay below their limit of 250 PPMV of SO<sub>2</sub> for a 12-hour rolling average. However, during the June startup they came close to exceeding this limit for two reasons. First, there was a delay in sending the tailgas from the SRU to the TGPU during warmup and when switching to acid gas. Better sequencing of the startup procedure will likely mitigate this in the future. Second, the TGPU solvent was replaced prior to the June startup. The newer solvent did not contain any heat stable salts, and no stripping aid was added prior to startup. (SRU B3 and B4 are designed for low-level acid-aided regeneration of the TGPU solvent.) Consequently, the lean loadings were higher than normal during this startup, and the residual quantity of H<sub>2</sub>S in the absorber overhead was higher than it had been during the previous startup.

Neither refinery has shut down these units since completing the modifications, but both expect to stay in compliance while shutting down for the next turnaround. Overall, both Refinery A and Refinery B are very pleased with the results of implementing the Level 1, Level 2, and Level 3A modifications.



## 4 CONCLUSIONS

The Level 1, Level 2, and Level 3A changes had a positive impact on startup SO<sub>2</sub> emissions for both Refinery A and Refinery B. However, their experiences starting up the SRU complexes after making these modifications highlight several potential pitfalls of starting up in this manner. Their experiences also brought to light some questions for the industry at-large regarding low-emission startups and shutdowns.

### 4.1 Potential Pitfalls of Low-Emission Startups/Shutdowns

1. Proper procedures and training: Adherence to procedures and adequate training for operating staff are crucial in any sulfur plant startup or shutdown. However, the modifications described in this paper make these items even more critical to prevent significant equipment and/or solvent damage in the SRU and TGPU. These changes are designed to provide more flexibility to control or mitigate high SO<sub>2</sub> emissions during periods of off-design operation. However, they also require a greater level of operator attention and rely more heavily on procedural safeguards rather than automatic safeguards to ensure that the equipment is not operated outside of its design limits.

Proper sequencing of the startup and shutdown procedures is also crucial to achieving the desired emissions reductions. Failure to implement the procedures in the correct order or delays in moving from one step to the next can result in high SO<sub>2</sub> emissions despite the changes to the equipment, piping, and controls.

2. Inadequate quench steam: Both refiners reported warming up their SRUs with significantly less than the recommended ratio of quench steam to fuel gas when operating the burner at stoichiometric. While they were able to follow the recommended refractory warmup schedule with the lower steam rate and limit the heating rate of their refractory, questions remain about the consequences this may have for the burners themselves and the refractory adjacent to the burner where the temperatures were likely much higher than those measured further down the furnace.
3. Free Oxygen: None of these modifications mitigate the effect of oxygen on the catalysts or solvent in the SRU and TGPU. Likewise, they do not prevent an operator from inadvertently sending gas streams containing free oxygen into either the reactor beds or solvent system. In fact, they make it more likely that they will do so. Instead of flowpath limitations (which they had previously) or other automatic safeguards, these Refiners must now rely on training and procedural safeguards to prevent streams containing free oxygen from entering the catalyst beds and solvent system.
4. Less is not more: Both refiners previously reported limiting the air flow rate to their TTO during startup. It was also accepted practice to limit the hydrogen concentration in the absorber overhead during startup. These practices, and others like limiting the quench water circulation, solvent circulation, or the steam to the TGPU reboiler, may not be problematic during a traditional startup, but when starting up with the SRU "coupled" to the TGPU, they can have a detrimental effect on SO<sub>2</sub> emissions since they limit the "margin" available to handle upsets without going out of compliance. Using ample TTO air flow, TGPU hydrogen, quench water and solvent flow, and reboiler steam is always prudent during startup.

## 4.2 Ongoing Questions and Concerns

The experiences of these two Refiners, and the practice of low-emission startups in general, reveals several issues and/or questions that have not been fully addressed by the industry and deserve further investigation.

1. How much quench steam is really enough?

Historically, quench steam has been added to control the refractory temperature and refractory warmup rate at some point downstream of the SRU burner, i.e. the measuring point of the thermocouple or pyrometer. However, this quantity of steam is often significantly less than what would be required to quench the flame temperature to the desired temperature. The presence of a temperature gradient between the flame and the refractory at the measured point is obvious, but the severity of that temperature gradient and how it changes during the warmup procedure is not as well understood. The concern with using too little steam is the integrity of the refractory very near the burner, its warmup rate, and the potential damage to the burner if the flame temperature exceeds the limits of the metallurgy and/or refractory for significant periods of time. It is possible that adding enough steam to quench the flame temperature to the desired value is not necessary. However, the amount required to protect the refractory along the entire length of the furnace and to protect the burner may be higher than what has traditionally been used.

2. Is stoichiometric firing sufficient to limit SO<sub>2</sub> emissions during SRU warmup, or is processing in the TGCU also required?

Earlier, two potential causes for high SO<sub>2</sub> emissions during warmup of these SRUs were discussed: oxidation of FeS and/or residual sulfur by excess oxygen in the combustion products, and vaporization/carry-over of residual sulfur by the hot combustion products. The former should only be a significant issue when firing the SRU burner with excess oxygen, but the latter would be an issue even when firing with stoichiometric air:fuel gas and quenching with steam.

Anecdotal evidence from other startups suggests that stoichiometric operation of the SRU burner (with quench steam) may be sufficient to reduce the SO<sub>2</sub> emissions during warmup even when the SRU tailgas is routed directly to the TTO. If oxidation is truly the greater contributor to high emissions during startup, then stoichiometric operation alone should be sufficient to control emission during warmup, which means that the SRU and TGCU could be warmed up in parallel, thereby shortening the overall time for startup. Although this hypothesis was discussed with the Refiners prior to startup, neither elected to bypass the TGCU while warming up the SRU during their recent startups.

3. What are the long-term consequences for the equipment, solvent, and catalysts in TGCUs that must operate at these off-design conditions?

Starting up with the SRU coupled to the TGCU puts the TGCU catalyst and solvent at greater risk for damage due to oxygen and/or SO<sub>2</sub> breakthrough. The long-term consequences of starting up in this manner and the impact on equipment life has yet to be determined, because for most refiners this is a relatively new requirement.

4. What is the best solution for smaller or remote facilities to accomplish low-emission startups/shutdowns if they do not have access to large quantities of nitrogen, activated (or partially activated) catalysts, or additional solvent or caustic?

Many small and/or remote facilities do not have to access to the personnel, facilities, utilities, or commodities that larger, more centrally located refineries have. This means that different (and potentially more expensive) modifications may be required to enable a smaller or more remote facility to achieve low-emission startups and shutdowns. However, that analysis has not been published to date.

### **4.3 Final Thoughts**

Although both Refiners were satisfied with the modifications that were made and the impact they had on their SO<sub>2</sub> emissions during recent startups, this paper is not intended to be the final word on the subject of low-emission sulfur plant startups. This is an area where the industry is continuing to evolve as regulations change and as we gain more experience and gather more operating data.

The changes implemented by Refiners A and B were effective at reducing their startup/shutdown emissions, but these new methods are less forgiving and rely more heavily on procedures and training to protect equipment and ensure that the units do not go out of compliance during startup/shutdown activities.

Finally, it is clear that as regulations for SO<sub>2</sub> emissions become more stringent, increasingly expensive modifications will be required for existing facilities to stay in compliance.

## **REFERENCES**

- (1) <https://www.epa.gov/enforcement/petroleum-refinery-national-case-results>