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Corrosion Control in Sulphur Recovery Units – Claus Process
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Abstract

Today there are more than 100 Sulphur Recovery Units in the Middle East and many of them have been in operation for 10 years or longer. Corrosion can be one of the most challenging issues in these units due to the presence of hydrogen sulfide, sulphur dioxide, elemental sulphur and water. If operated within the normal operating temperature range, corrosive conditions should not occur; however, if upset conditions result in temperatures which are too high or too low, several corrosion mechanisms are possible. This issue has resulted in many instances in which existing units have been forced into emergency shutdown for several days to perform maintenance. This results in production loss and the potential for significant environmental impact due to flaring acid gases.

API 571 documents most of the major corrosion mechanisms in the Claus process such as sulfidation, oxidation, flue gas dewpoint corrosion and wet sulphur corrosion. However, it does not address specific means of controlling corrosion, taking into account different technologies available for tail gas treatment. This paper demonstrates the fundamental corrosion issues encountered in SRUs and proposes protective actions. Guidance related to start-up, shutdown and normal operation is also provided for establishing appropriate operating limits to achieve safe and reliable operation for corrosion avoidance.

This paper takes a unique approach which considers both theoretical and practical, real-world experience in the mitigation and monitoring of corrosion control. Operators are provided with tangible recommendations that can be applied to their facilities. Protection against atmospheric corrosion is not in the scope of this paper.

This paper has been prepared based on a review of several industry publications, which address specific corrosion mechanisms in SRUs. The main objective of this paper is to provide a high-level overview of these works, while also offering guidance on the safe operating envelope of the facility, to avoid excessive corrosion. Most of the metallurgy in an SRU is typically specified as carbon steel, which is adequate when the unit is operated within safe operating limits. However, if operated outside the acceptable range (above or below), corrosion can be swift and severe, as will be described.
**Introduction**

Sulfur recovery refers to the conversion of hydrogen sulfide (H₂S) to elemental sulfur. Hydrogen sulfide is a by-product of processing natural gas and refining sulfur-containing crude oils. The feed gas to a sulfur recovery unit (SRU) is considered ‘acid gas,’ as the components will form acids in the presence of liquid water. Such streams emanate from amine regenerators and sour water strippers located in various refinery and gas processing unit operations upstream of the SRU. The SRU is based on the Modified Claus Process. Approximately one third of the H₂S in the acid gas feed is burned in the reaction furnace to form SO₂. The SO₂ and remaining H₂S then react, at an optimal 2:1 ratio, to form elemental sulfur (Sₘ) across the Claus reactors. After each catalytic stage, liquid sulfur is recovered in the Claus condensers. It should be noted that SRUs have very complicated sulfur chemical reactions resulting in many sulfur species existing at any one condition or process step.

![Figure 1 Typical Three Stage Claus Sulphur Recovery Unit](image)

As shown in Figure 1, acid gas enters the unit in the knock out vessel at low pressure (usually less than 1 barg). This drum is utilized to remove condensed and entrained liquids which are mostly water, with some hydrocarbons (and amine if from an amine stripper). The acid gas is carefully combusted with air in a reducing atmosphere in the reaction furnace. Temperatures in the reaction furnace range from 950 to 1400 °C (1742 to 2552 °F) depending on the composition of the specific acid gas feed. The combustion gases typically pass through a Waste Heat Boiler (WHB) where temperature will be reduced to about 320 °C (608 °F) via production of HP steam. Most of the elemental sulfur formed during combustion is condensed, separated and drained to storage in a downstream sulfur condenser which produces LP steam. The process stream is reheated and passed through the first catalyst bed where additional sulfur is formed. The process gas is again cooled and sulfur condensed, separated and forwarded to storage. Typically two or three catalyst beds, with condensation after the beds, are utilized in the Claus unit. To remove as much sulfur as possible from the process gas, the final condenser outlet temperature is typically less than 140 °C (less than 284 °F), which is accomplished by producing LLP steam or heating BFW.

There are several types of tail gas treating technologies which are designed to recover up to 99.99%+ of the sulfur entering the SRU. Technologies include selective oxidation (efficiency up to approximately 99.4%), sub-dewpoint (efficiency up to approximately 99.4%), amine-based H₂S removal (efficiency up to 99.99%+) and amine-based SO₂ removal (efficiency up to 99.99%).
The remaining process gas from the tail gas treating section flows to the incinerator. The incinerator typically heats the process gas to 650 to 815 °C (1200 to 1500 °F) by using a fuel fired burner in an oxidizing atmosphere. The small amount of remaining H₂S is converted to SO₂ and released to the environment through a stack. In some incinerator applications, a waste heat recovery boiler is utilized which cools process gas to around 350 °C (500 °F) to recover heat, while also ensuring high enough temperature to avoid acid condensation in the stack. This paper focuses specifically on the corrosion issues in the thermal and catalytical stages of the Claus process only; tail gas treating is not explicitly discussed.

**Corrosion Mechanisms in SRUs and Their Control Methods**

In general, corrosion in an SRU involves one of the following four components [4]:

- **Anode (+):** This is where metal loss occurs and is the portion of the metal that loses electrons (oxidation takes place).
- **Cathode (-):** This is where chemical reaction takes place and is the portion of the metal that gains an electron (reduction).
- **Electrical Conductor:** This is typically the metal between the anode and the cathode and is a pathway for electrons.
- **Electrolyte:** This is the solution containing conductive ions, which is often water.

In the case of hydrogen sulfide, the corrosion mechanism can be represented by the following equations (Figure 2):

Anodic: \[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \]

Cathodic: \[ S + 2e^- \rightarrow S^{2-} \]

Overall: \[ \text{Fe} + S \rightarrow \text{FeS} \]

At anodic sites, iron readily goes into solution as iron ions, \( \text{Fe}^{2+} \), which combine with \( \text{O}_2 \), \( \text{H}_2\text{S} \), or \( \text{CO}_2 \), depending on the components of the electrolytic fluid. These form corrosion products or scales as rust-iron oxide \( \text{Fe}_2\text{O}_3 \cdot \text{H}_x\text{O}_y \), iron sulfides \( \text{FeS}_x \), or iron carbonate \( \text{Fe}_2\text{CO}_3 \). While this is happening, the electrons migrate to the cathode. At the cathode surface, they reduce oxygenated water to produce hydroxyl ions \( \text{OH}^- \) or reduce hydrogen ions to produce hydrogen gas \( \text{H}_2 \) [6].

In SRUs, the sulphurous and sulphuric acids can be formed as follows:

\[ \text{H}_2\text{S} + 3\text{O} \rightarrow \text{SO}_2 + \text{H}_2\text{O} \]

\[ \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 \]

\[ 2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3 \]

\[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \]

The following corrosion/damage mechanisms can be found in an SRU (all of which are summarized from API 571, except the last item. Some notes have been added to address specific SRU considerations):
1. **Sulphidation**: Corrosion of carbon steel and other alloys resulting from their reaction with sulfur compounds in high temperature environments. Sulphidation of iron-based alloys usually begins at metal temperatures above 260 °C (500 °F). Sulphidation is primarily caused by H₂S and other reactive sulfur species as a result of the thermal decomposition of sulfur compounds at high temperatures. This is one of the major corrosion mechanisms affecting SRUs and can take place in the reaction furnace, auxiliary burners, or thermal oxidizer, if inadequate design features are employed and/or if excursions outside of the recommended operating envelope are experienced.

   **Corrosion Control**: API 571 states that resistance to sulphidation is generally achieved by upgrading to a higher chromium alloy, and that solid or clad 300 Series SS or 400 Series SS can provide significant resistance. However, SRUs are typically designed to maintain metal temperatures below sulphidation temperature via the use of ceramic refractory and thermal shrouds. For this reason, typically all of the metallurgy in the process is carbon steel. In few places where metal temperatures cannot be controlled below sulphidation temperature, higher grade allow materials may be required (e.g. burner tips). This is discussed further in the “Guidelines for Corrosion Control through Construction and Fabrication” section.

2. **Wet H₂S Corrosion**: There are four types of corrosion mechanisms that result in blistering and/or cracking of carbon steel and low alloy steels in wet H₂S environments: hydrogen blistering, hydrogen induced cracking, stress oriented hydrogen induced cracking and sulfide stress corrosion cracking. All of these damage mechanisms are related to the absorption and permeation of hydrogen in steels. Conditions which are known to promote these mechanisms are those containing free water (in liquid phase) combined with greater than 50 ppmw dissolved H₂S in the free water or more than 0.0003 MPa (0.05 psia) partial pressure of H₂S in the gas phase. Increasing levels of ammonia may push the pH higher into the range where cracking can occur. Equipment like the acid gas knock out drums and acid gas piping upstream of the reaction furnace are subject to this type of damage, if not properly protected. **Corrosion Control**: Effective barriers that protect the surface of the steel from the wet H₂S environment can prevent damage including alloy cladding and coatings.

3. **Oxidation**: Oxygen reacts with carbon steel and other alloys at high temperature, converting the metal to oxide scale. Oxidation of carbon steel begins to become significant above about 538 °C (1,000 °F). Rates of metal loss increase with increasing temperature. Oxidation may occur in fired equipment; however, the Claus process operates in a reducing environment, alleviating this concern. **Corrosion Control**: Resistance to oxidation is best achieved by upgrading to a more resistant alloy or insulating the steel from the processing atmosphere with a multi-layer refractory lining. As stated above, the entire SRU is designed to operate in a reducing environment with no free oxygen, with the exception of the incinerator, which is protected with a refractory lining to avoid achieving the metal temperatures indicated above.

4. **Refractory Degradation**: Thermal insulating refractories are susceptible to various forms of mechanical damage (cracking, spalling and erosion) as well as corrosion due to oxidation, sulphidation and other high temperature mechanisms. Refractory may show signs of excessive cracking, spalling or lift-off from the substrate, softening or general degradation from exposure to moisture. Coke deposits may develop behind refractory and promote cracking and deterioration. Refractory lined equipment should be designed for erosion, thermal shock and thermal expansion. **Corrosion Control**: Proper selection of refractory, anchors and fillers, combined with proper design and installation are the keys to minimizing refractory damage. Dry out schedules, cure times and application procedures should be in accordance with the manufacturer’s specifications to minimize refractory degradation concerns in SRUs.

5. **Steam Blanketing**: The operation of steam generating equipment is a balance between the heat flow from the combustion of the fuel and the generation of steam within the water wall or generating tube. The flow of heat energy through the wall of the tube results in the formation of discrete steam bubbles (nucleate boiling) on the ID surface. The moving fluid sweeps the bubbles away. When the heat flow balance is disturbed, individual bubbles join to form a steam blanket, a condition known as departure
from nucleate boiling (DNB). Once a steam blanket forms, tube rupture can occur rapidly, as a result of short term overheating, usually within a few minutes. This can happen in many types of steam-generating units, including fired boilers and waste heat exchangers in sulfur plants. Failures can occur in superheaters and reheaters during start-up, when condensate blocks steam flow.

**Corrosion Control:** Boiler tube configuration and layout are critical to ensure adequate flow through the water side of the boiler to avoid DBN. In addition, BFW treatment (and adequate blowdown) are crucial to provide water quality that will prevent scale build-up. Obviously, flame impingement on boiler tubes must also be avoided. All of these points must be considered in the design and operation of SRU boilers.

6. **Sulfuric Acid:** Sulfuric acid promotes general and localized corrosion of carbon steel and other alloys. Carbon steel heat affected zones may experience severe corrosion. While sulfuric acid formation is not normally expected in SRUs, off-design operating conditions may present some concerns.

**Corrosion Control:** Corrosion is minimized through materials selection and proper operation within design margins (as specified in coming sections). The Claus process is operated in reducing environment, and therefore sulfuric acid is not expected to be formed in normal operating conditions. However, refer to possible acidic corrosion in incinerator/stack in next point below.

7. **Flue Gas Dew Point Corrosion:** Sulfur species will form sulfur dioxide and possibly sulfur trioxide when combusted with excess air. At low enough temperatures, these gases and the water vapor in the flue gas will condense to form sulfuric acid which can lead to severe corrosion. The dewpoint of sulfuric acid depends on the concentration of sulfur trioxide in the flue gas, but is typically about 138°C (280°F). Metal surfaces allowed to cool near the condensation temperature during normal operation, shutdown, or startup operations will be subject to acid dew point corrosion.

**Corrosion Control:** Maintain the metallic surfaces at the back end of the boilers and fired heaters above the temperature of sulfuric acid dewpoint corrosion. When designing a waste heat recovery system for an SRU incinerator, considerable care must be taken to ensure that flue gas temperature cannot drop below the acid dewpoint, in all operating conditions, including turndown.

8. **Boiled Water / Condensate Corrosion:** Corrosion and pitting in boiler feed water and condensate return systems is usually the result of dissolved gases, oxygen and carbon dioxide. Improperly treated boiler feed water and condensate may cause waterside corrosion and fouling on the water/steam side of the sulfur plant process, which may affect the steam drum, waste heat boiler, heat exchanger, and condensate drums.

**Corrosion Control:** Oxygen scavenging treatments typically include catalyzed sodium sulfite or hydrazine, depending on the system pressure level, along with proper mechanical deaerator operation. A residual of the oxygen scavenger is carried into the steam generation system to handle any oxygen ingress past the deaerator.

9. **Corrosion of Steel by Wet Solid Elemental Sulfur:** “This process requires certain conditions to exist before attack of the steel involving the sulfur will occur. These preconditions include the presence of moisture (steel and sulfur wetted by a free-standing condensed water phase) and direct contact between the surface of the steel and the sulfur. Under these conditions a corrosive interaction between the steel and sulfur will take place leading to the formation of the sulfur deficient iron sulfide, FeS(1-x), mackinawite, as the primary corrosion product.” [4].

Within an SRU, this type of corrosion can occur in sulphur tanks, condensers, rundown, bottom of sulphur seals and tail gas lines, and/or anywhere elemental sulphur is allowed to condense in the presence of liquid water.

**Corrosion Control:** In order for this corrosion mechanism to occur, there must be direct contact between steel and solid sulfur while liquid water is present. Maintaining temperatures above the water dewpoint throughout the entire process is critical to prevent this from occurring. In locations such as the sulphur pit, where the presence of liquid water may not be avoidable (due to humidity in sweep air), it is necessary to specify stainless steel materials of construction for any items which may come into contact with this water (e.g. vertical sections of steam coils).
In summary, corrosion in sulfur plants can be minimized if proper precautions are taken. However, if corrosion does occur, it usually results from either: (1) improper selection of materials of construction during plant design or (2) misoperation of the plant.

**Guidelines for Corrosion Control through Construction and Fabrication**

Cost effective corrosion control requires an integrated approach involving process and equipment design, material selection, and operating and maintenance practices (Figure 3). Changing or ignoring any part of this “triangle” without consideration for impact on the other elements can lead to premature failure of process equipment and poor unit reliability.

Material selection is an important step in the “triangle” and should generally follow a detailed process and equipment design step which is based upon a range of predetermined feed and operating conditions.

**A. Individual Equipment Items**

Although an SRU is constructed mostly of carbon steel, proper materials selection in several areas is important to reduce corrosion problems.

For example, burner tips, catalyst screens, sulfur pit piping, refractory anchors and mesh elements in sulfur condensers/coalescers should be specified as 316 stainless steel, or 309 stainless steel, which is better for very hot service. Carbon steel can be used in all other areas up to a temperature of 315 °C (600 °F). Carbon steel piping and vessels should be designed for minimum 3/8-inch wall thickness with 1/8- to 3/16-inch corrosion allowance. Refractory lined carbon steel should be used in services above 315 °C (600 °F). Recommended materials for process equipment with the justifications for these selections are given in Table 1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Materials of Construction</th>
<th>Justification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid gas piping &amp; knock out drum</td>
<td>CS with HIC resistant</td>
<td>H₂S service with potential for water condensation in feed gas system.</td>
</tr>
<tr>
<td>Burner tips, catalyst screens, sulfur pit piping, refractory anchors and mesh elements</td>
<td>Type 316 stainless steel, or 309 stainless steel</td>
<td>Very hot service</td>
</tr>
<tr>
<td>Reaction furnace</td>
<td>Refractory-lined CS with air shroud</td>
<td>Sulfidation corrosion due to high temperature exposure to H₂S and/or acid corrosion due to temperature below acid dewpoint</td>
</tr>
<tr>
<td>Reaction furnace waste heat exchanger system</td>
<td>Refractory-lined CS tubesheet and ceramic ferrules</td>
<td>Sulfidation corrosion due to high temperature exposure to H₂S and potential for DNB at high temperature differential interface close to tubesheet</td>
</tr>
</tbody>
</table>
### Component | Materials of Construction | Justification
--- | --- | ---
Reactors, Condensers | CS with partial refractory lining | Refractory lining for the concern of sulphur fire in the reactors and to avoid retained sulphur in low points in condensers during shutdown
Reheaters | CS for shell and tubes and sometimes SS for tubes | Hot service
Steam drums | CS and SS for internals | Liquid sulfur not containing any liquid water is only mildly corrosive to carbon steel
Rundowns and sulphur seals | CS | Sulphidation corrosion due to high temperature exposure to H₂S and/or acid corrosion due to temperature below acid dewpoint
Incinerator & stack | Refractory-lined CS with air shroud | Sulphidation corrosion due to high temperature exposure to H₂S and/or acid corrosion due to temperature below acid dewpoint

Metallurgy of individual equipment is provided in Figure 4. From this figure we can see clearly that SRU is constructed mainly of CS, with few exceptions, and refractory lining is used whenever temperature is expected to exceed 315 °C (600 °F).

### Figure 4 Metallurgy of Individual Equipments

B. General Design Guidelines
Industrial experience has shown that the following general guidelines should be followed in designing an SRU (Refer to Figure 4 for reference numbers):

1. In general, the plant should be designed so the operating conditions are always above the dew point of water. Apply heating in the unit, especially in areas where gases are near the dewpoint of water. Two key areas requiring significant heat maintenance attention are tail gas lines and vent gas lines from sulfur pits.
2. Generally carbon steel metallurgy with a 1/8” corrosion allowance provides acceptable service in sulfur handling equipment. However, it is important to maintain the vapor space hot and dry in an oxidizing atmosphere to prevent excessive corrosion and iron sulfide formation. [2]
3. Piping and equipment should be kept hot to avoid a wet environment or sulphur solidification. Heating can be done through steam jacketing, electric heat tracing, or steam tracing. Steam jacketing is the best, but may not be practical in some areas of the plant.

4. Gas piping should be designed to be free-draining to avoid accumulation of liquids that may condense and produce weak acid.

5. The burner and furnace are typically constructed of carbon steel. The high temperature, reducing atmosphere process operating conditions in the burner and furnace require protection of the carbon steel via insulation with a multi-layer refractory lining. The refractory lining/thermal shroud system should be designed to maintain the inside metal temperature between 150-315° C (300-600°F). Experience has shown this temperature range to be adequate to avoid both excessive acid and sulfide corrosion.

6. Where refractory is used, it is necessary to employ an external shroud to induce air flow around the outside of the equipment that will maintain the metal above the acid condensation temperature (Figure 5). The shroud also protects the carbon steel shell and internal refractory from thermal shock, which can occur from sudden rain storms or cold winter conditions. It should provide an insulating air gap that allows free air flow between the shell and shroud. The hot shell induces convective air flow. Louvers are installed in the bottom of the shroud and are used to regulate the air flow through the gap between the shell and shroud.

**Figure 5 Effect of Thermal Shroud**

7. WHB tubesheet ferrule design is very important to protect WHB tubes. If a crack develops, hot process gas may reach the tubesheet and/or tubes, resulting in high temperature sulfide corrosion and eventually tube failure. Figure 6 provides an example of cracked ferrules which can lead to formation of iron sulphide scale on the tubesheet, which is thermally insulating and must be removed to avoid failure. Upon failure, BFW leakage into the hot, refractory-lined reaction furnace causes additional damage.

8. The final condenser must be adequately heated and externally insulated to maintain a metal wall temperature above 120° C (250°F) to prevent formation of sulphurous/sulphuric acids which can severely corrode the metal wall.

9. All liquid sulfur lines must be sloped to promote draining.
10. SRU tail gas piping from the final condenser to the incinerator or tail gas cleanup unit is often the source of plugging and corrosion, if not adequately heated. The outlet of the final condenser is the coolest point in the SRU. Furthermore, the tail gas is saturated with sulfur vapor and has a very high water content. Therefore, tail gas piping should be kept as short as possible and must be kept hot with steam jacketing or tracing.

**Figure 6 Tubesheet Failure**

**Guidelines for Corrosion Control through Process Operation**

This section contains suggested methods for startup, normal operation and shutdown, and includes special guidelines for avoiding corrosion. These instructions should be considered as a guide only, and are not intended to include all required preparatory details and operations.

**A. Normal Operation**

Under normal operation, minimal SRU corrosion is expected. In order to have active corrosion, liquid water typically needs to be present. As explained previously, all temperatures throughout an SRU should normally be above the water dewpoint; therefore, once the plant is operating, it should be kept running continuously as long as possible to avoid cooling the unit and condensing water. The following guidelines should be followed to minimize corrosion risks:

1. Do not purposely shut down an SRU unless it is for a scheduled turnaround. Most of the corrosion issues in an SRU occur during startups and shutdowns. It is far better to run an SRU at minimum design turndown than it is to shut the unit down (see the second point of shutdown guidelines for sweeping procedure).
2. When sufficient acid gas is available, operate the units as close to design capacity as possible. Operating at capacity does not expose the unit to increased corrosion; in fact, certain components (such as the acid gas burner) operate better at design rates.
3. Do not permit any equipment surfaces to be colder than 120°C (250°F) during normal operation to avoid sulfur solidification and wet sulfur corrosion.
4. It is necessary to operate the burner in a sub-stoichiometric combustion condition, for process performance and to avoid sulphur fires in catalytic reactors, which may lead to major damage in the catalyst support and/or the production of sulfurous acid. If hydrocarbon is present in acid gas feed and then suddenly removed, excess O₂ may then be present which can lead to these conditions. For this reason, some SRUs require hydrocarbon analyzers on acid gas feed streams.
5. Poor burner performance and unstable firing conditions can result in refractory damage, resulting in furnace hot spots (Figure 7) and there will be potential damage to carbon steel equipment and/or piping.

6. Reaction furnace and incinerator wall temperatures have to be maintained above 150°C (300°F) to avoid acid corrosion and below 315 °C (600 °F) to avoid high temperature sulfidic corrosion. Shroud louvers or lagging windows are provided normally to maintain wall temperature within these limits. Skin temperature is controlled by operation dampers that regulate flow of air through the annulus or jacket on the reaction furnace.

7. Operators should institute a program to use the intermittent blowdown connections on a routine basis to control solids accumulation in all boilers and condensers. This will reduce corrosion in the exchangers over time. At a minimum, intermittent blowdown once a week from all exchangers is preferable.

8. Operators should ensure continuous monitoring of the BFW in condensers and appropriate chemical injection.

9. Steam flow and pressure on steam jacket and steam tracing systems must be monitored and maintained to avoid cooling below the acid condensation temperature. The dewpoint of sulfuric acid depends on the concentration of sulfur trioxide in the flue gas. Figure 8 shows this type of corrosion when happening in SRU. It’s important also to maintain sufficient stack wall temperature above 175°C (350°F) to assure no SO₃ corrosion.

Figure 7 Refractory damage and furnace hot spot

Figure 8 Flue gas dew point corrosion in SRU reactor[8]
B. Startup
There is no doubt that more damage is done to sulphur recovery unit equipment during startup and shutdown than any other time. The following guidelines should be followed during startup to minimize corrosion risks:

1. Do not use or permit the use of excess oxygen on startup if there is any sulphur on the catalyst or in the unit. Excess air can only be allowed in the furnace during the initial startup and refractory dry out when fresh catalyst is installed in the unit. The unreacted oxygen may react with sulphur adsorbed in the refractory of the reaction furnace, or with sulphur adsorbed on the catalyst in catalytic reactors, which may result in formation of sulfurous/sulfuric acids.

2. Particular care has to be paid immediately after the main burner is lit to avoid a sudden spike in reaction furnace temperature. Burner vendor heat-up instructions should be followed and tempering steam should be utilized. Rapid warm up will not allow adequate time for refractory curing or thermal expansion, resulting in the potential for refractory damage (Figure 9).

Figure 9 Some failures when trying to operate with natural gas and stoichiometric flame without steam tempering

3. Refractory heat-up rates shall respect curves provided by refractory vendors, to avoid refractory damage (Figure 10). Speeding up the process can and has resulted in refractory failures (from partial spalling to total collapse) leading to hot spots on the metal shell. Refractory linings must be dried very slowly prior to introduction of acid gas, to ensure that moisture is completely removed. If not properly dried out, moisture retained in the refractory may cause steam formation and can rupture the refractory.

Figure 10 Example of equipments drying out and heating up curves
4. To prevent overheating of the WHB during start up, it should be filled with BFW before establishing flame in the reaction furnace. Catalytic reactors and condensers should be bypassed during initial stages of heating (260°C (500°F) and below) to prevent excessive condensation and corrosion in the back end of the plant. During the initial stages of dry out, combustion gases are exhausted through the startup vent ahead of the Claus reactor.

5. Before acid gas can be burned in the reaction furnace, all metal temperatures in the plant must be above 120º C (250ºF) to avoid condensing corrosive sulfurous/sulfuric acids.

6. During start-up, the reaction furnace pressure should be monitored. An increasing pressure (above the design value) may indicate is the presence of a tube leak and/or solid sulphur accumulation in the downstream condenser (Figure 11).

7. Before any heat is applied, make sure all steam generators are filled to normal liquid level with BFW. In case of BFW cooling during startup (mainly in last condenser) due to ambient temperature, BFW should be warmed before admitting acid gas. Maintaining some continuous flow will help in avoiding this from happening.

8. Finding free standing water in the sulfur rundown during startup or shutdown is a sure sign of a leak in either the corresponding condenser or steam reheater and should be investigated/reppaired prior to re-starting the unit.

Figure 11 Condenser Failure[^4]

C. Shutdown
1. Following acid gas cut-off, closely control air flow from the combustion air blowers to the burners so that natural gas is burning with approximately 95% of stoichiometric air. Operation in a slightly reducing condition is required to prevent the possibility for sulphur fires in the unit. Nitrogen or steam must be used to temper the flame temperature below the refractory design temperature (approximately 1,375 ºC (2,500 ºF)) since excess air can’t be used. Oxygen content of the combustion gas downstream of the WHB may be monitored using a portable oxygen analyzer, and catalyst reactor temperatures should be closely observed to ensure that they are not increasing. Temperature excursions are indication of sulphur fires within the catalyst beds that can be extremely damaging to catalyst and equipment.

2. It should be noted that introduction of excess oxygen into a hot unit before sweeping will result in sulphur fire, as liquid sulphur is retained in the catalyst bed and in the pores of the catalyst. In shutdown procedure it’s required to heat soak the catalyst beds, i.e. operate at 30 – 45 ºC (50 – 80 ºF) above normal inlet temperatures for up to two days (the beds may also be run at H₂S rich inlet conditions, called “rejuvenation”, to remove some sulfate for a while also, if desired, typically using H₂S:SO₂ ratios of between 5:1 and 6:1). Then acid gas flow will be reduced, and finally
switch from acid gas to natural gas, this procedure is called seeping. Sweeping should be maintained at sub-stoichiometric conditions and at the maximum possible natural gas rate to ensure proper sweeping of all parts of the equipment and of the catalyst beds. Using low flows will allow channeling of the flow through the unit which will prevent all of the sulfur from being removed or will definitely extend the time required to remove it all. Sweeping is required until all the sulphur rundown stops flowing. An obvious result of a sulfur fire is damage to equipment. Sometimes the fire is limited, either by available sulfur or oxygen, and will give a noticeably higher temperature but no damage. Note however, that in the event of a sulfur fire, not only SO\textsubscript{2} but also SO\textsubscript{3}/sulfuric acid will be produced. Sulfuric acid can eventually lead to extensive corrosion damage in lines and equipment.

3. Once the unit has cooled down, it is not advisable to operate for an extended period below 120º C (250ºF) with steam as tempering. If sulfur has not been completely swept from the unit, water may condense in downstream, cooler equipment, leading to wet sulfur corrosion concerns.

4. Lowering of the steam pressure during a unit shutdown in the WHB is identified as overstressing and cracking the tube-to-tube sheet welds that were already thinned due to corrosion. Lowering the pressure may cause sulphur condensation / solidification which will eventually cause corrosion in normal tubes (not thinned).

5. Maintaining and checking the steam jacketing regularly is highly important. After any shutdown or trip, it is critical to ensure that the jacketing is functioning properly to avoid off-design conditions that may lead to corrosion.

6. Liquid sulphur should be transferred from the sulphur storage drum/pit to minimum level during shutdown and steam heating coils should be put in service for the complete shutdown to maintain sulphur in liquid phase and prevent solidification and subsequent corrosion.

7. Long term shutdown would require eventual pressurization of the whole unit with dry nitrogen to prevent internal plant corrosion. However, this procedure is not recommended, as it is very difficult to ensure that no humidity will enter the piping/equipment if maintained in shutdown mode for an extended period of time. As mentioned previously, it is recommended to maintain SRUs in operation to minimize corrosion risks.

In summary, a key success factor for minimizing corrosion in an SRU is to keep equipment and lines in the unit hot. When a sulfur plant is operated above the melting point of sulfur and the dewpoint of water, the corrosion rates in equipment and piping are maintained within acceptable limits. Special precautions must be taken into account during off-design operating conditions and start-up and shutdown. Extended shutdowns of SRUs are never recommended; however, may be appropriately managed with adherence to strict nitrogen blanketing and monitoring procedures.

**Conclusions**

Despite the fact that SRUs are designed to operate without experiencing significant corrosion, damage from various corrosion mechanisms is prevalent in the industry. Few of these problems are related to design defects; the majority are related to operating conditions and non-adherence to startup and shutdown procedures.

Proper process control and understanding of operation modes (i.e. startup, shutdown, normal operation) of the SRU are essential for robust operation and prolonged service life. In addition, a comprehensive understanding of the most common damage mechanisms, and their possible locations, will help operators run their SRUs smoothly and will minimize operation outside of safe corrosion limits. To achieve these objectives, operator training and experience are critical.
Nomenclature

<table>
<thead>
<tr>
<th>symbol</th>
<th>description</th>
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<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>degrees Celsius</td>
<td>HID</td>
<td>Hydrogen Induced Cracking</td>
</tr>
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<td>°F</td>
<td>degrees Fahrenheit</td>
<td>ID</td>
<td>Internal Diameter</td>
</tr>
<tr>
<td>API</td>
<td>American Petroleum Institute</td>
<td>Mpa</td>
<td>Mega Pascal</td>
</tr>
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<td>barg</td>
<td>bar gauge</td>
<td>O₂</td>
<td>oxygen</td>
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<tr>
<td>BFW</td>
<td>boiler feed water</td>
<td>pH</td>
<td>potential Hydrogen (acid/alkaline balance)</td>
</tr>
<tr>
<td>CO₂</td>
<td>carbon dioxide</td>
<td>Psia</td>
<td>Pounds per Square Inch Absolute</td>
</tr>
<tr>
<td>CS</td>
<td>Carbon Steel</td>
<td>RF</td>
<td>Reaction Furnace</td>
</tr>
<tr>
<td>DNB</td>
<td>Departure from Nucleate Boiling</td>
<td>SO₂</td>
<td>Sulphur Dioxide</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
<td>SO₃</td>
<td>Sulfur trioxide</td>
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<tr>
<td>FeS</td>
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<td>SRU</td>
<td>Sulphur Recovery Unit</td>
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<td>SS</td>
<td>Stainless Steel</td>
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<td>elemental sulphur</td>
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<td>Sulfurous Acid</td>
<td>TGU</td>
<td>Tail Gas Unit</td>
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<tr>
<td>H₂SO₄</td>
<td>Sulfuric Acid</td>
<td>WHB</td>
<td>Waste Heat Boiler</td>
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References

2. Dennis H. Martens, Joe Livesay and Mark Tonjes, Sulphur Recovery Unit, 1998
3. Ellen Ticheler-Tienstra, Anne van Warners, Rien van Grinsven and Sander Kobussen; Risks of Accumulated Sulfur in Sulfur Recovery Units.