Thermal Reactor Refractory Enhancements for O_2 Enriched Service

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** Due to significant confusion in the marketplace concerning various "Thorpe" named entities in the USA, we are clarifying that Thorpe Specialty Services Corporation (TSSC), headquartered at 3702 Mykawa Rd., Houston, Texas, 77033 is the parent holding company of J. T. Thorpe Company, Thorpe Plant Services, Inc., Thorpe International Services, Inc. and Thorpe Engineered Products Company. These entities can be accessed at www.ThorpePME.com.

Abstract

Chevron's Richmond Refinery instituted Oxygen Enrichment in two older tangentially fired thermal reactors, modified one after the other in separate periods of downtime to minimize refinery throughput impact. In the first outage, a new thermal reactor was fabricated and lined by a local refractory contractor. The old refractory design with a flat wall on the burner end was used. Upon startup of the first unit, oxygen could not be introduced due to hotspots that developed at the burner nozzle connection. It was determined that to reach the design rate with oxygen enrichment, an enhanced refractory lining was needed on the burner end of the unit along with burner placement modification. This was performed on both units resulting in reliable operations with no hotspots at the design oxygen level. We will discuss the operation and history of these units, the changes made, and the performance of these units since the enhanced linings were installed.

Introduction

Today's engineers must deal with many issues that were of little concern decades ago. Thermal Reactors operating below 2000°F did not face the same chemical, thermal or mechanical concerns or challenges of present-day units running at higher temperatures. It is important to understand that mechanical designs, high intensity burners and the operating requirements of today can easily exceed the capabilities of the refractory lining systems. It is essential that the refractory designer be involved early on, preferably at the mechanical and process design stage, in order to circumvent seemingly benign decisions that can result in ongoing refractory maintenance issues for years to come. In addition, oftentimes simple modifications can have a dramatically positive impact on service life and reliability of the unit, saving unexpected downtime and maintenance costs. This point has been introduced in the new API 565 Standard for Thermal Reactors which has just been published this year.

> Per API 565 4.1.5: The owner / operator shall ensure that the process licensor, burner manufacturer, vessel manufacturer, **refractory designer** and suppliers of reaction chamber auxiliary components collaborate to develop a comprehensive thermal reactor design package sufficient to meet the specified process and mechanical design parameters of the process unit.

We recognize that in the subject units, much of today's technology was not available when the units were built. However, in order to emphasize the importance of the new Standard, even for older existing units, references to the new API Standard will be made. For this paper, we address the mechanical challenges imposed on the refractory lining by the flat end wall and burner connection design, all compounded by the effects of higher operating temperature.

Refinery Background

The Chevron Richmond Refinery was built on a peninsula of low hills rising from the San Francisco Bay in 1902. Chevron's earliest predecessor, the Pacific Coast Oil Company (PCO), found an ideal site along a dusty country road that terminated near a tiny railroad settlement called East Yards.[1] At a tract of land just north of the village stretched 600 acres of rolling abandoned farmland.

The original plant contained 19 stills that could process 10,000 barrels of crude oil a day. The refinery had an original staff of 80 employees including engineers, mechanics, technicians, inspectors and managers. Their presence transformed the small village which had just 200 occupants at that time and would later become the City of Richmond.

The new century brought a major celebration: the 100th anniversary of the Richmond Refinery in 2002. At the time of its centennial, the plant had more than 1,300 employees and was spread over 2,900 acres. One hundred and twenty years later, the crude oil processing capacity is now approximately 240,000 barrels per day and the Refinery has a workforce of 3,000.

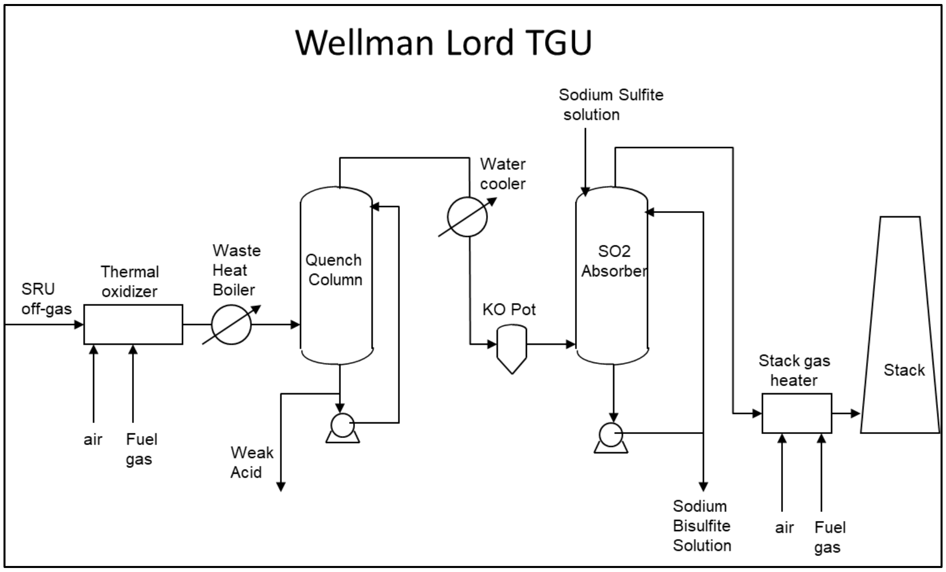
Sulfur Recovery Unit Configuration and Operations

The Chevron Richmond Refinery has 3 SRU parallel trains, SRU #1, SRU #2 and SRU #3. All three SRUs were built in the early 1970s with each utilizing the modified Claus process containing a single stage thermal reactor with a tangentially mounted burner and flat endwall. All three SRUs have two stage catalyst converters and acid gas reheaters. Each SRU contains a Wellman-Lord tail gas unit.

A process overview of the Wellman-Lord tail gas unit is displayed in Figure 1. The Wellman-Lord tail gas process is a regenerable process and runs in an oxidizing atmosphere. In this process, the sulfur compounds in the Modified Claus tail gas are first converted to SO_2. The resulting gas is cooled and then the SO_2 is removed in the absorber by contact with an aqueous solution of sodium sulfite forming sodium bisulfite.[2] The clean gas, containing less than 250 ppm of SO_2, is heated and allowed to discharge to the atmosphere by its operating permit. In a separate plant, the sodium bisulfite is heated and the absorption reaction is reversed to form SO_2 and sodium sulfite. The SO_2 is reintroduced back to the front of the Modified Claus unit to enhance the sulfur plant recovery to over 99.9%.

The acid gas feed to all three SRUs comes in a common header with typically H_2S content of over 90%. The other compounds in the acid gas are CO_2, water, and light hydrocarbons. The SRU thermal reactors operate at approximately 2,000^{o}F and are not designed to burn ammonia. The temperature of the thermal reactors is monitored by two Delta thermocouples and one E^2T pyrometer. The Claus tail gas is typically kept at the optimal sulfur conversion with H_2S to SO_2 ratio of 2 to 1.

Figure 1



Thermal Reactor Configuration and Flat Endwall Refractory Issues

The thermal reactors in each SRU are designed with a tangentially mounted burner and flat endwall located near the burner as displayed in Figure 2. The thermal reactor contains two layers of refractory bricks, an insulation layer and a hotface layer. Internal inspection of the thermal reactor refractory occurs approximately once every 3 years due to the boiler recertification requirement. Some maintenance work on the flat endwall refractory has been a consistent theme during just about every maintenance event. Maintaining good refractory on the flat endwall has been problematic.

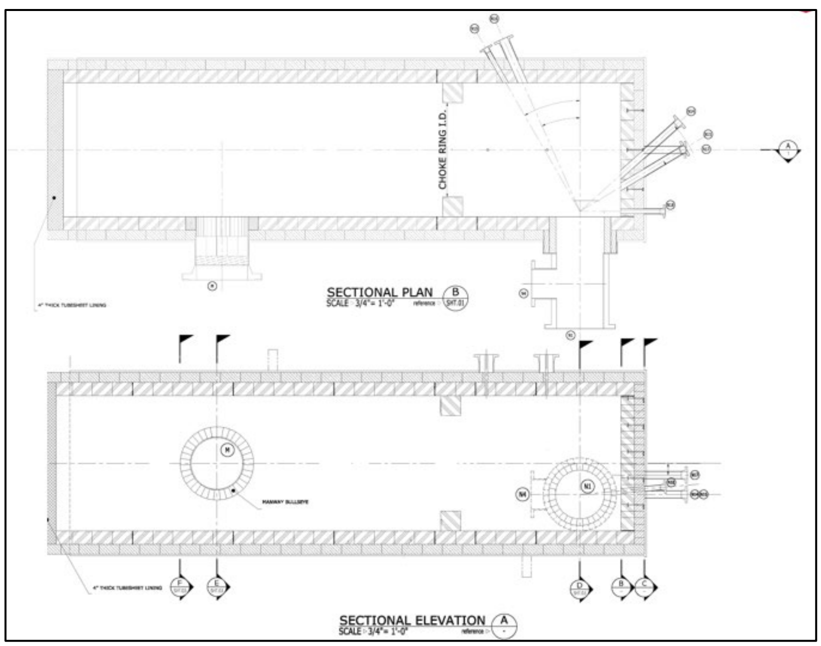


Figure 2

During past inspections, the flat endwall refractory has often been found to have major cracks as displayed in Figure 3, and sometimes bricks found fallen off as in Figures 4.

Figure 3

Figure 4

At times, even when an initial inspection of the flat endwall appeared good, it turned out to be not as good, as displayed in Figures 5 and 6. The flat endwall refractory in Figure 5 appeared to be in good condition at first glance, but was found to have major issues as shown in Figure 6. The inspection report findings were as follows.

> "Thermal imaging of the endwall prior to unit shutdown indicated a hot spot around the viewport nozzle. Upon entry, after unit shutdown, a hammer test of the brick indicated a void in the lining. Subsequent removal of the hotface brick revealed a 1" to 1-1/2" separation between the insulation bricks and the hotface bricks as the hot face bricks bowed inward. Metallic anchors tying the service lining to the shell were found to have failed, with some of these anchors having burned up. Even though the overall condition of both bricks was determined to be in serviceable condition, approximately 65% of the flat wall refractory had to be removed to repair the anchors."

Figure 5

Figure 6

Many past thermal scans of the flat endwall revealed similar findings, with higher temperatures around the viewport, as displayed in Figures 7 and 8.

Figures 7

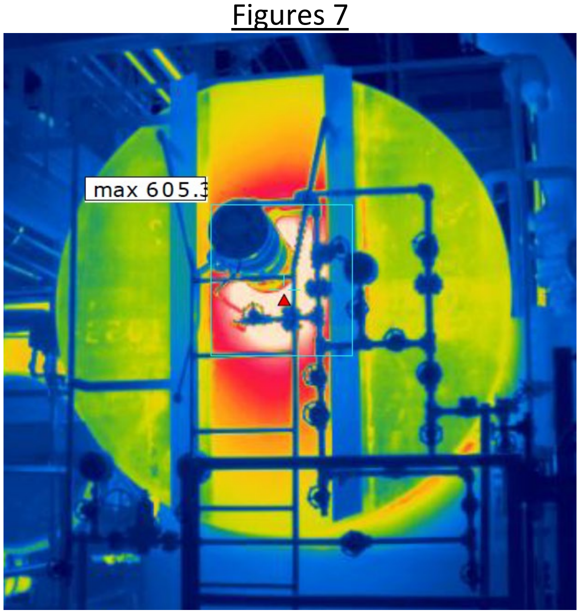
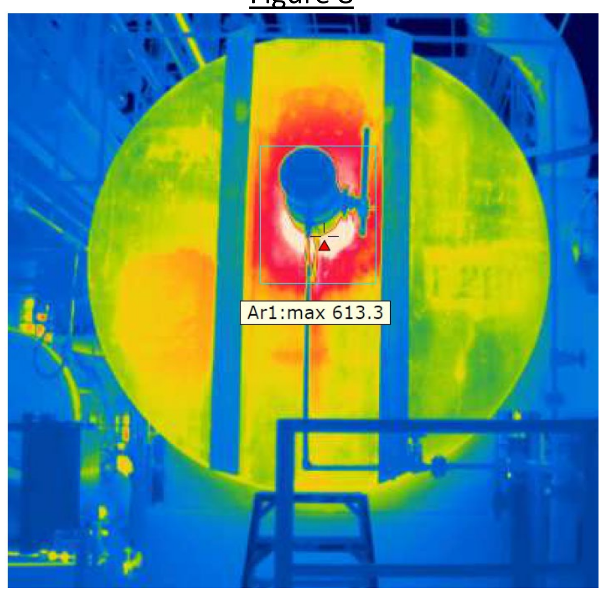


Figure 8



Project Goal and Objective

The project to modify the SRUs was a part of the Chevron Refinery Modernization Project (Modernization Project). Part of the Modernization Project goal was to install a collection of new sulfur removal equipment improvements that remove naturally occurring sulfur contained in the feedstocks.

The project goal for the Richmond's SRUs was to implement oxygen enrichment to increase the refinery's sulfur handling capacity. Only SRU #1 and SRU #2 were included in the Modernization Project. Since SRU #3 was not similarly modified during Modernization, it is not subject to the issues raised in this article. The SRU modifications were to be completed in two separate outages planned for fourth quarter of 2018 and third quarter of 2019.

The thermal reactors with oxygen enrichment required a new high intensity burner. With the expected higher operating temperature, it was recommended to increase the refractory lining thickness and to utilize a higher alumina content brick. The thermal reactor vessels were also replaced during the project.

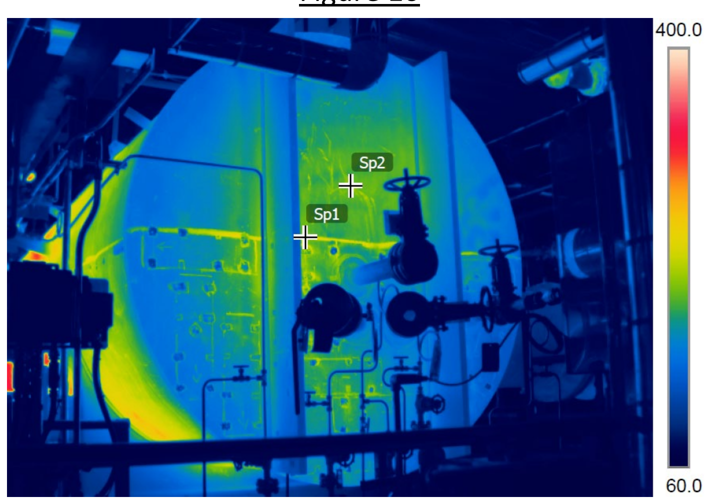
The SRU modification came with new updated environmental permit conditions that included lower stack H_2S and SO_2 limits, new CO and NOx limits and new PM limits including PM_{10} and $PM_{2.5}$.

SRU #2 – 2018 Outage and Results

During 3rd quarter of 2018, SRU #2 entered a scheduled outage as part of the Modernization Project modifications. The newly fabricated thermal reactor vessel with a shop installed flat refractory lining was installed as displayed in Figure 9. The outage was completed during mid-4th quarter 2018. The new refractory was dried out per manufacturer's recommendations. The unit was successfully commissioned and started up with air only. Upon start up, the flat endwall displayed a more uniform temperature profile without any hot spots, as displayed in the thermal image in Figure 10.

Figure 9

Figure 10



Shortly after startup and before oxygen was introduced into SRU #2, a hot spot was found at the burner nozzle as displayed in Figures 11. It was determined that oxygen, resulting in a higher thermal reactor internal temperature, could not be introduced due to the hot spot.

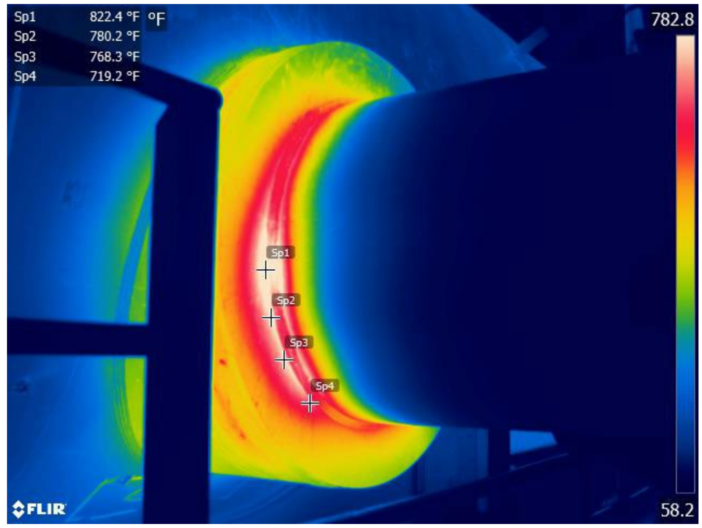


Figure 11

Upon further investigation, it was determined that the burner tip was too close to the nozzle metal causing the hot spot. It was determined that the burner could be moved further into the nozzle to eliminate the hot spot. A short outage was taken in early 2nd quarter 2019 to move the burner further into the nozzle and the hot spot was eliminated. Due to the hot spot and the prospect of higher operating temperature in the thermal reactor with oxygen enrichment, the project reconsidered the refractory design to avoid possible future hot spots and to ensure long term reliability. This led to discussions with Thorpe (Houston).

Thorpe Comments

Based on the problems with SRU #2 and the decision to now change the flat wall lining, Thorpe (Houston) was contacted in early June 2019, shortly before the planned SRU #1 replacement outage, to help Chevron install a more stable refractory lining on the flat endwall. Discussions were held to understand Chevron's situation and goals, as well as to discuss Thorpe concerns and suggestions.

Thorpe believes that the refractory lining is often a common limiting factor in the successful operation of an SRU. When we talk about "successful operation", we mean reliable service with shorter, less costly maintenance scheduled outages and avoidance of unscheduled shutdowns. With severe service units such as thermal reactors, it is importance to recognize that early (frontend) process and mechanical design decisions should be made with sufficient consideration for the long-term effects on the linings. Many of these decisions are difficult, or impossible, to correct after having been made. It is therefore critical to solicit input from the refractory designer during the process and mechanical design phases in order to optimize a unit for better reliability, thereby minimizing the risk of unscheduled shutdowns and fewer long-term maintenance issues.

Sample operating conditions that can affect the refractory include:

1. High and low operating temperatures
2. Type of burner
3. Burner turndown capability
4. Co-firing or fuel gas standby expectations
5. Use of steam (or not) during all fuel gas firing
6. Ramp rates (up and down)
7. Severity and frequency of thermal cycles

Some of the mechanical issues that can affect refractory linings include:

1. Roundness of vessel
2. Internal weld seams
3. Nozzle sizes, angles, projections (internally and externally), locations (grouping), etc.
4. Eccentric, tangential and off centered connections of any type
5. Manway nozzle sizes
6. Geometry of surfaces and transitions, and as in this case, the existence of flat walls

In the current case, the vessels were already fabricated and the refractory linings installed. Some of the points of discussion:

- Originally, a higher alumina brick was suggested to the plant for this project (and used for both initial new linings) due to the expected higher temperatures. There is a belief in the industry that a higher alumina brick will perform better at a higher temperature than a lower alumina content material in reaction furnace applications. However, while alumina content is one important attribute, there are many other considerations in arriving at the optimum SRU brick product, size and shape for a particular unit. In fact, there are many examples of higher alumina brick products significantly underperforming a lower alumina product. API 565 is attempting to introduce the concept of testing for the critical properties necessary for a design rather than assuming certain chemistries will provide the required properties. This is the concept Thorpe has used for decades, testing various bricks for critical projects under our proprietary high temperature testing regimen. This part of the API 565 Standard will need development and more testing for the group to better understand the behavior and performance of high purity, high alumina brick under SRU conditions. In this case, Thorpe utilized its standard of high purity SRU grade bricks utilized in many O_2 enriched units.
- A thicker refractory lining had also been recommended to the plant for this project for the expected higher temperature during O_2 enriched operation. Thorpe agreed with increasing the hotface lining thickness as recommended as this is a critical factor to stabilize the hotface lining.
- For any unit, especially a high temperature O_2 enriched service, one should also consider the value of having input to the full thermal envelope (the internal lining and the External Thermal Protection System, commonly, and incorrectly, referred to simply as a weather or rain shroud). The importance of considering the External Thermal Protection System (ETPS),

is discussed specifically in Section D.3 of the API 565 Standard, as well as other areas of the Standard.

- Thorpe agreed with Chevron to change the flat wall to a shallow cone construction for multiple reasons. Table D.8 of the API 565 Standard discusses the importance of avoiding flat walls. Flat walls at elevated temperatures, and unrestrained, will pull towards heat due to the thermal gradient thru the lining. The "bending" or "bowing" of the lining toward the heat occurs as the hot surface of the lining (facing the process gas) expands more than the back surface. The "bowing" increases as temperature increases. A simple illustration of this effect is shown in Figure 12. In Chevron's case, history had already shown problems (repeated maintenance) with the flat wall at only 2000°F operation. While anchors can be installed to hold the brick back (and anchors were installed in these linings), Thorpe has not found any metallurgy to survive in thermal reactor environments when exposed to much over 2000°F. Inspection reports confirmed that anchors had been used and had failed. High operating temperatures in a thermal reactor will overheat/corrode any anchor used in the hotface lining. Unrestrained, the wall then pulls towards the heat. A concave geometry that forces the lining to expand outwardly during heatup is required to stabilize this wall in a self-supporting, non-anchored, fashion. The shallow cone is an option Thorpe has used many times in the past without any reported failures.

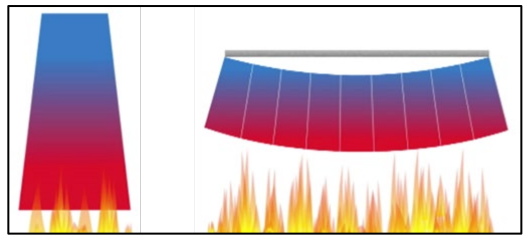


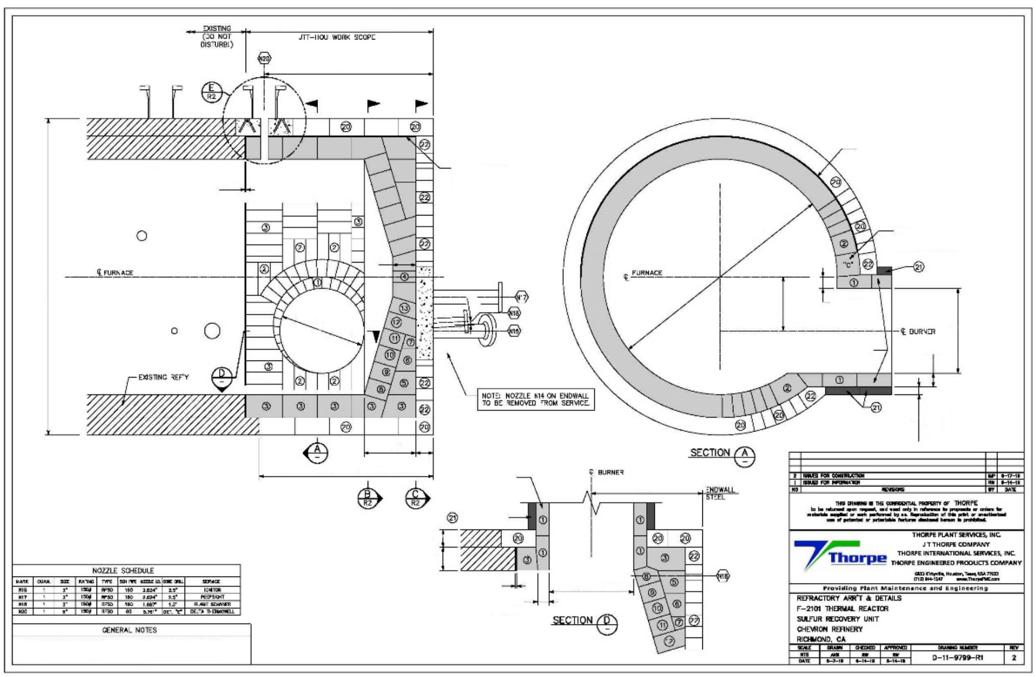
Figure 12

- Due to the close proximity of the burner nozzle to the flat wall and the space required to install a shallow cone on the endwall, it was also necessary to replace the existing refractory cylinder lining thru the burner nozzle, for overall integration and stabilization of the lining in this area.
- This decision led to discussions to explain the complexity of the connection at the tangential burner nozzle with the shallow cone brickwork. This is all possible to install but is considered very complicated brickwork to install properly. Properly means not just covering the steel shell (which can be done by installing brick in several different orientations) but being sure the geometry of the refractory lining construction results in the brickwork pushing back towards the steel shell during heatup and operation. This creates not only a self-supported lining, but a tight lining to better resist hot gas bypassing.
- Originally there were four (4) nozzles thru the back wall. Two of these were 3" nozzles at angles and in close proximity to each other, which were concerning. Again, comments are made to nozzles in the API 565 Standard, but we would specifically point again to API 565 Table D.8 Thermal Reactor Refractory Vulnerabilities. Higher operating temperatures and use of newer high intensity burners can cause operating conditions resulting in failure modes that are not common with the old pipe burners and lower operating temperatures. Higher temperatures combined with large nozzle openings brings radiant heat deeper into the linings. High intensity, high velocity burners can create pressure differentials that result in hot gas bypassing. Our other concern was the angle, close proximity and size of two of the

nozzles thru the endwall. Some designers have approached such an issue by utilizing pre-cast/pre-fired shapes installed in the hotface lining. Although this method is accepted by the API 565 Standard, Thorpe has never found such shapes to outperform a good quality hot face brick in sulfur recovery units. Thorpe therefore strongly emphasizes that precast/prefired shapes be avoided except as a last option. In this case it was agreed one of the interfering nozzles should be eliminated to further improve the overall lining integrity for the new endwall under these new operating conditions.

Due to the short window available for implementing the new design, a final challenge was to locate quality brick out of warehouse stocks that could be reliably utilized for the project. As we are often required to do for our maintenance customers, Thorpe was able to design around the high purity SRU grade brick that could be obtained immediately out of warehouse stocks. Figure 13 below shows the general outline of the work.

Figure 13



SRU #1 – 2019 Outage and Results

Within approximately one week of being contacted, Thorpe had technical discussions with Chevron Richmond, started the drawing design, found and shipped brick to site and mobilized to begin the modifications. Thorpe removed the existing lining (new flatwall) from the endwall, including the cylinder lining thru the burner connection in a local shop near the plant. The new Thorpe Houston shallow cone lining was installed in the vessel and handed back to the plant for the vessel to be installed in the unit. The newly installed shallow cone refractory is displayed in Figures 14 and 15.

Figure 14

Figure 15

A proper heat up and dryout of the refractory was performed on SRU #1. A successful startup followed soon after. The shallow cone refractory yielded a very uniform thermal profile when SRU #1 started up and operated with air as displayed in Figure 16. There were no hotspots to be found. Shortly after startup, oxygen was introduced into SRU #1. The acid gas feed rate reached close to the design with oxygen enrichment. The flat endwall still displayed a rather uniform thermal profile as displayed in Figure 17.

Figure 16

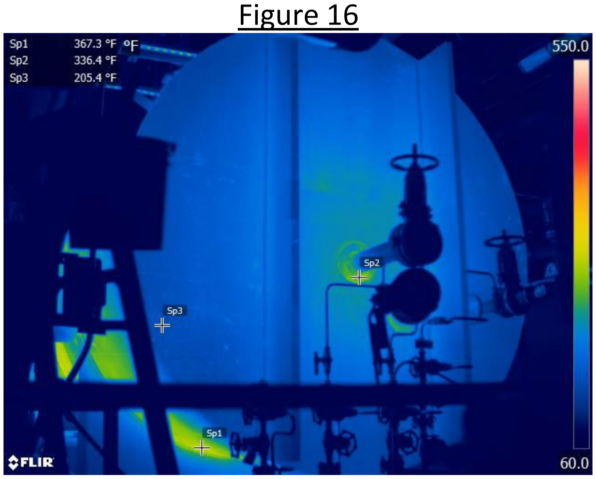
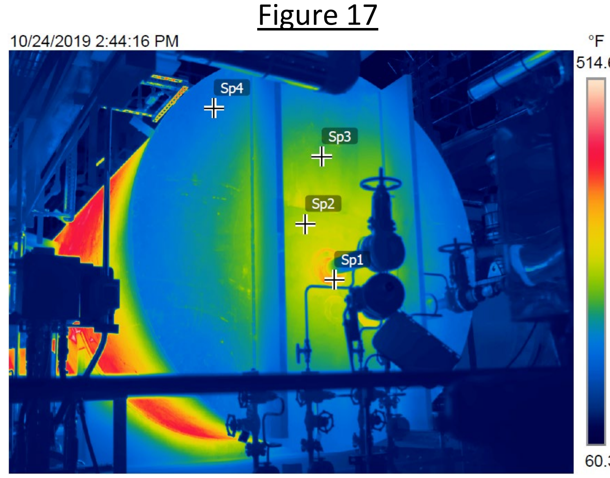


Figure 17

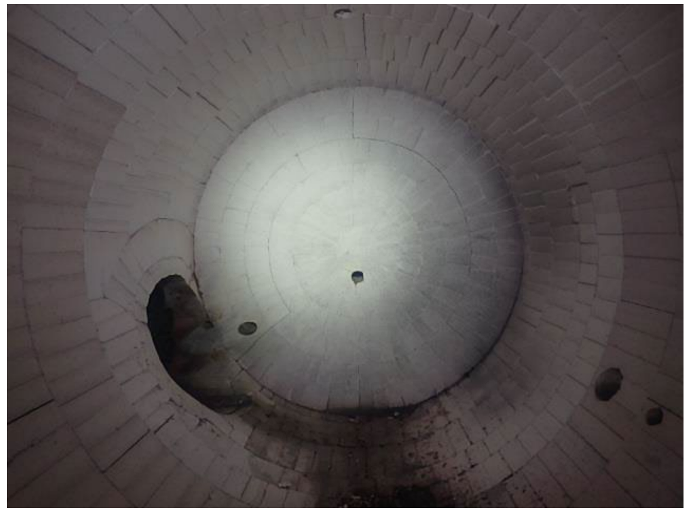


SRU #2 – 2019 Outage to Replace Flat Endwall

In late October 2019, SRU #2 was brought down for a planned short maintenance event and Thorpe Houston replaced the flat endwall with a shallow cone refractory lining just as in SRU #1. The work was completed well within the scheduled maintenance window.

Installation Updates and Results

Figure 18



In 4th quarter 2021, SRU #2 was taken down for the 3-year boiler recertification inspection. After 2 years of operation with intermittent oxygen enrichment, the shallow cone refractory on the flat endwall held up well, as displayed in Figure 18. The internal inspection noted the shallow cone refractory to be in serviceable condition with minor cracks (mortar joint separations) of up to a 1/16" in width. Such small cracks are not unusual and will close up in operation.

SRU #1 is due for its 3-year boiler recertification inspection in September 2022. The results are not expected to be available in time for inclusion in this paper.

Conclusions and Future Considerations

There have been no operational issues or hotspots with the new shallow cone refractory configuration. After 2 years of operations with the shallow cone refractory in SRU #2, internal inspection has determined the wall to be holding up well. No repairs were required. Only time will tell on the long-term reliability of the shallow cone wall.

As for the use of the shallow cone wall, the involvement of the refractory designer early in the project should be employed to prevent mechanical and process designs from limiting the performance of the refractory system. A properly designed refractory is critical, especially for oxygen enriched operations, to optimize the lining chemically, thermally, and mechanically in order to maximize reliability and minimize long term maintenance concerns and expenses.

As a point of reference, the shallow cone refractory requires more materials (due to increased refractory volume), and detailed engineering & BOMs to change from flat to a complicated three-dimensional shape. Due to the additional cutting and fitting involved to install the cone & burner nozzle, labor cost and installation time are also affected. The estimated cost differences to install the shallow cone refractory on the flat wall is approximately 15% higher for additional materials and approximately 50% higher for labor, due to the more complicated and therefore longer installation time. Thorpe's experience with these types of installations shows this is a minor upfront cost to improve reliability and reduce maintenance requirements for many years.

References

1. Chevron Richmond Refinery. History. The Early Years. http://richmond.chevron.com/about/history
2. Paskall, Harold G.; Sames, John A. (1990). "Sulphur Recovery". Western Research. Section 8, pp 14-16
3. API 565, Thermal Reactors for Sulfur Recovery Units in General Refinery Services, June 2022