Top Five Fundamental Integrity Issues for SRU Waste Heat Exchangers (Boilers)

Panel Discussion

Presented at the 2011 Brimstone Sulfur Symposium, Vail Colorado

ABSTRACT

The SRU Waste Heat Exchanger (boiler) continues to be a significant operational integrity consideration. The panel members will present a brief summary of the past integrity issues, state of the art solutions, and current limitations. After the presentations, there will be a combined question and answer session where each of the panel members will poll the audience to share relevant experiences and respond to specific questions.

The top five fundamental integrity issues addressed for the SRU WHE (WHB) are as follows:

1. **Burner Flame Temperature During Warm Up and Hot Standby** – Alan Mosher, KPS Technology & Engineering LLC

   Alan will present calculated flame temperatures for different fuels used during SRU warm up and hot standby and review the limitations of current SRU refractory systems. He will discuss methods to control the flame temperatures through the use of tempering media.

2. **Ferrule Design and Installation for Insulation of SRU Tubesheets** – Domenica Misale-Lyttle, Industrial Ceramics Limited

   Domenica will share her considerable experience with successful ferrule systems and the pitfalls that result in unsuccessful ferrule service. She will address what she considers are the key aspects to overcoming these pitfalls.

3. **Boiler Water Level Safety Considerations & Tube Collapse** – Lon Stern, Consultant

   Lon will review the evolution of the WHB designs highlighting significant advancements. He will share his knowledge of current water level control designs and safeguarding to avoid tube damage and nuisance trips of the SRU.

4. **Tube & Tube Weld Corrosion and Tube Collapse** – Dennis Martens, Porter McGuffie, Inc.

   Dennis will discuss the important aspects of current successful industry practices for reliable service of the WHE from the standpoint of high temperature corrosion and tube collapse. He will review the three most common corrosion issues and share his proposed Claus SRU Service Sulfidation Corrosion Curve for Carbon Steel.

5. **SRU Overpressure in a Waste Heat Boiler Failure** – Justin Lamar, Black & Veatch

   Justin will discuss the aspects of WHE tube failure, API 521 evaluations, and SRU pressure buildup. He will review a case history of a reported tube failure and associated SRU pressure buildup. The review creates a perspective on a viable tube failure and boiler depressuring mode that could be used for evaluation of an SRU pressure buildup.

KPS TECHNOLOGY & ENGINEERING

BURNER FLAME TEMPERATURE DURING WARM UP AND HOT STANDBY

Alan D. Mosher
KPS Technology & Engineering LLC

Presented at the Brimstone Sulfur Symposium
Facilitated by Brimstone STS Limited
Vail Colorado

September 12 to 16, 2011

Summary

Typically, more damage occurs in an SRU during start-up and shutdown than any other time. Hot Standby is another Thermal Reactor and WHB killer. One of biggest concerns is operating the Thermal Reactor Burner at stoichiometric natural gas and air flame temperatures. The best available refractory cannot withstand the temperature of a stoichiometric flame. An understanding of the potential flame temperatures is critical since you cannot fully trust the temperature measurement devices. These flame temperature concerns can be successfully addressed by using a proper flow rate of tempering media (steam or nitrogen) whenever natural gas or other fuels are used during start-up, shutdown or hot standby.

Stoichiometric Flame Temperatures

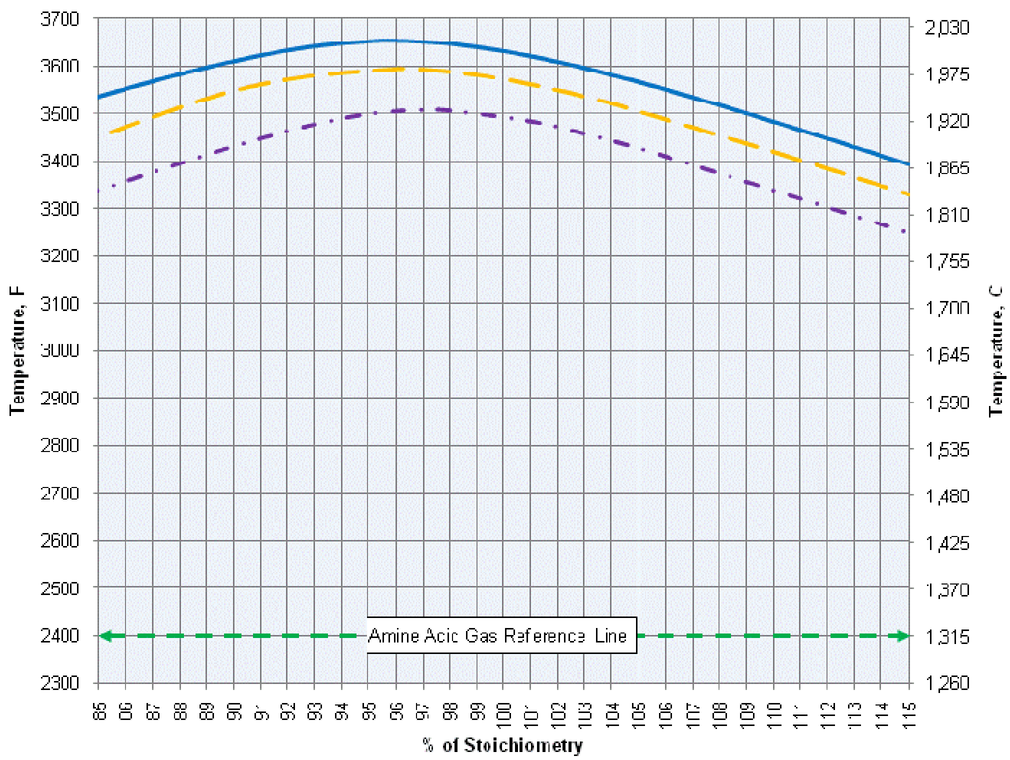
Start-up of an SRU Thermal Reactor involves operating the main burner with natural gas and air to heat the Thermal Reactor, WHB and downstream equipment. The ratio of air to natural gas is adjusted to stoichiometric conditions. If the unit was properly shutdown including operation to purge sulfur (heat soak) from the catalyst beds then the subsequent start-up of the Thermal Reactor burner can operate with some excess air until the catalyst beds approach 330F (165C). Typical start-up and shutdown steps were described by d'Haêne and Cicerone [1] at this conference in 2010. If the unit was shutdown without a sulfur purge then the main burner will need to be started and quickly adjusted to stoichiometric conditions. The headaches associated with a restart after a shutdown with no heat soak were discussed by Young [2]. Hot standby involves operating the Thermal Reactor Burner at stoichiometric conditions for a day or so while waiting to recharge acid gas feed.

As shown in Figure 1, the temperature of a stoichiometric natural gas and air flame is quite high at 3500F (1925C). The X axis is percentage (%) of stoichiometric air and the Y axis is flame temperatures.

The flame temperatures are simulated values from a Gibbs Minimization reactor in ProMax®. Typical refinery fuel gas produces a similar stoichiometric flame temperature. Some units are forced to use high hydrogen content fuels which have even higher stoichiometric flame temperatures 3655F (2010C). SRUs for Syngas units may have no choice other than to use LPG for start-up fuel that has a stoichiometric flame temperature of about 3600F (1980C). The reader may notice that the peak flame temperatures are occurring in the range of 96-97% of stoichiometry. The definition used for the stoichiometric air is that all carbon is combusted to carbon dioxide (CO_2). As excess air is reduced some of the carbon is combusted to carbon monoxide (CO). This effect shifts the peak temperature slightly to the left of 100% stoichiometric air.

In comparison to the stoichiometric fuel and air temperatures, operating with a typical refinery amine acid gas feed with air only combustion produces a temperature of about 2400F (1315C). Oxygen enriched combustion can produce very high temperatures and the oxygen concentration is typically limited so the flame temperatures due not exceed the capability of the refractory system.

Figure 1
Temperature Versus % of Stoichiometry



Hydrogen	
Composition	Mole %
H2	74.00
Methane	12.00
Ethane	6.91
Propane	4.55
nC4	2.54

LPG	
Composition	Mole %
Ethane	0.34
Propane	23.13
iC4	33.38
nC4	30.09
Butene-1	9.14
Water	3.38
Dimethyl Ether	0.54

Natural Gas	
Composition	Mole %
N2	0.89
CO2	1.13
Methane	94.30
Ethane	2.44
Propane	0.70
iC4	0.19
nC4	0.16
iC5	0.07
nC5	0.05
nC6	0.07

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Refractory Use Temperatures

Determining the hot face refractory maximum use temperature is not an exact science. Refractory datasheets may list a maximum use temperature but these values are based on an oxidizing environment and no applied load. In a Thermal Reactor the burner is operated in a reducing environment and the refractory is under varying compressive load. The refractory maximum use temperature needs to be lowered to account for these conditions. Arriving at a realistic maximum use temperature is a complex analysis requiring experience and an overall understanding of the entire refractory system and how the system will react (move and grow) as the system heats up, temperatures fluctuate during operation, and the system cools down. Also the composition of the refractory material will vary from the composition of the refractory sample used to generate the datasheet. Changes in the trace compounds in the refractory material can have a significant impact on the properties of the refractory. Bottom line is that not all 90% alumina bricks perform the same. Not even all 90% alumina bricks of the same type and brand name will perform the same due to slight differences in the trace compounds. If the design is going to push the limits of the refractory, testing of each lot is needed to confirm properties.

Table 1 shows some approximate maximum use temperatures for some common brick materials that have been used in Thermal Reactors.

	Table 1 Brick Maximum Use Temperatures	
Hot Face Material	**Korundal XD (90% alumina)**	**Greenal 90 (90% alumina)**
Stated Maximum Use Temperature (oxidizing environment)	3250F	3100F
Reducing Environment	-200F 3050F	-200F 2900F
Mechanical Allowances and Temperature Measuring Differences	-200F ***2850F****	-200F ***2700F****

Note: All temperatures are approximate and must be verified for each specific application and specific system design.
* Mean Temperature of Lining

Table 2 shows some approximate maximum use temperatures for some common castable materials that have been used in Thermal Reactors.

	Table 2 Castable Maximum Use Temperatures	
Hot Face Material	**GreenCast 94 (94% alumina)**	**Mizzou Castable (60% alumina)**
Stated Maximum Use Temperature (oxidizing environment)	3400F	3000F
Reducing Environment	-200F 3200F	-200F 2800F
Mechanical Allowances and Temperature Measuring Differences	-400F to -500F ***2700F to 2800F***	-500F ***2300F***
Note: All temperatures are approximate and must be verified for each specific application and specific system design.		

Castable materials require a larger deduct for mechanical allowances because of the following items.

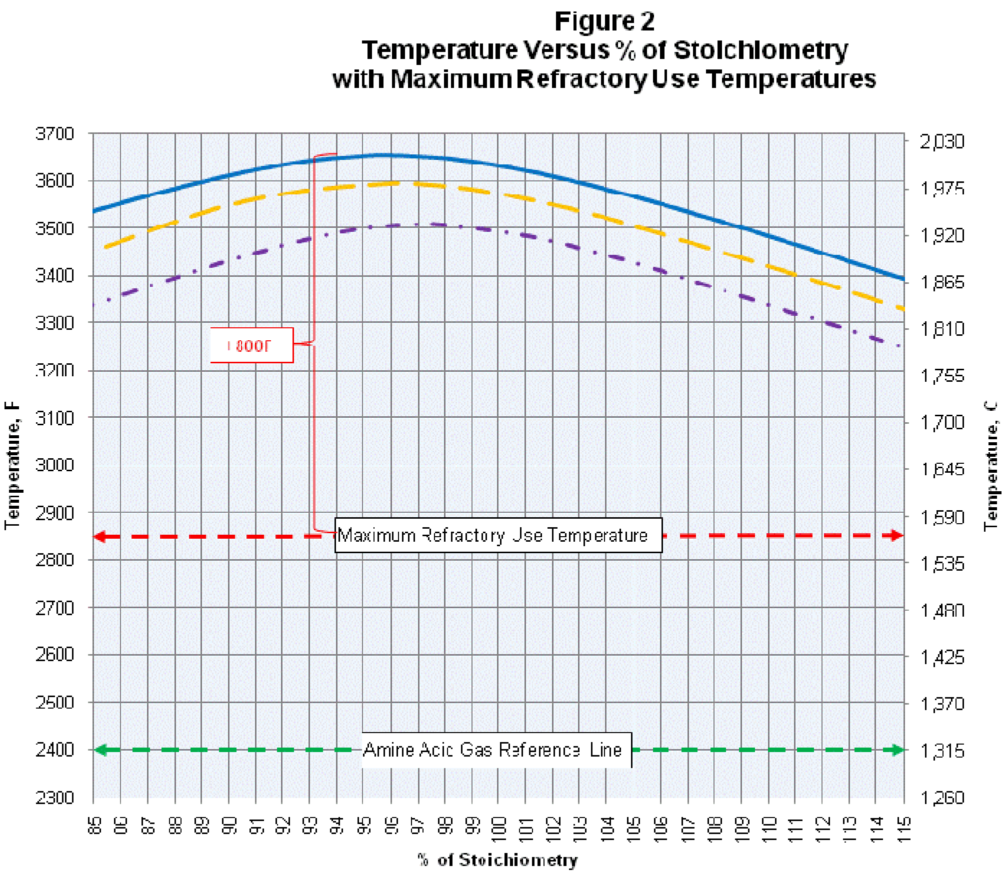
- The brick temperature numbers include some hot loading on the brick in operation while the castable numbers are from technical data sheets that do not have any hot loading.
- Castables will have calcium oxide (Ca0) within them that comes from the calcium aluminate binder which acts as a flux at high temperatures and will excessively deform the castable when loaded during high temperature Thermal Reactor operation. *Flux materials are very active at high temperatures and combine with the surface molecules of a crystal and cause the crystal to dissolve.*
- Metallic anchor support systems to stabilize the castable construction can be easily overheated causing unpredictable cracking and slumping.
- Quality control over the water content during mixing, forming, and dryout is moved to the field versus the more easily controlled brick manufacturing. *This can be a major factor.*

Table 3 shows some approximate maximum use temperatures for some common ferrule materials that have been used in Thermal Reactor WHBs.

	Table 3 Ferrules Maximum Use Temperatures	
Hot Face Material	**Industrial Ceramics (90% alumina)**	**Industrial Ceramics (94% alumina)**
Stated Maximum Use Temperature	No longer offered	3250F
Mechanical Allowances and Temperature Measuring Differences		-300F ***2950F***
Note: All temperatures are approximate and must be verified for each specific application and specific system design.		

The purpose of this paper is not to attempt to explain how to select the proper refractory for every application of a Thermal Reactor. There are others that are far more experienced than this author in selecting the correct materials and completing a good overall system design. Instead, the purpose of this paper is to point out that there is not a single refractory available that can withstand a stoichiometric fuel and air flame temperature.

As shown in Figure 2, the stoichiometric flame temperatures are much higher than the refractory maximum use temperatures.



Hydrogen Composition	Mole %
H2	74.00
Methane	12.00
Ethane	6.91
Propane	4.55
nC4	2.54

LPG Composition	Mole %
Ethane	0.34
Propane	23.13
iC4	33.38
nC4	30.09
Butene-1	9.14
Water	3.38
Dimethyl Ether	0.64

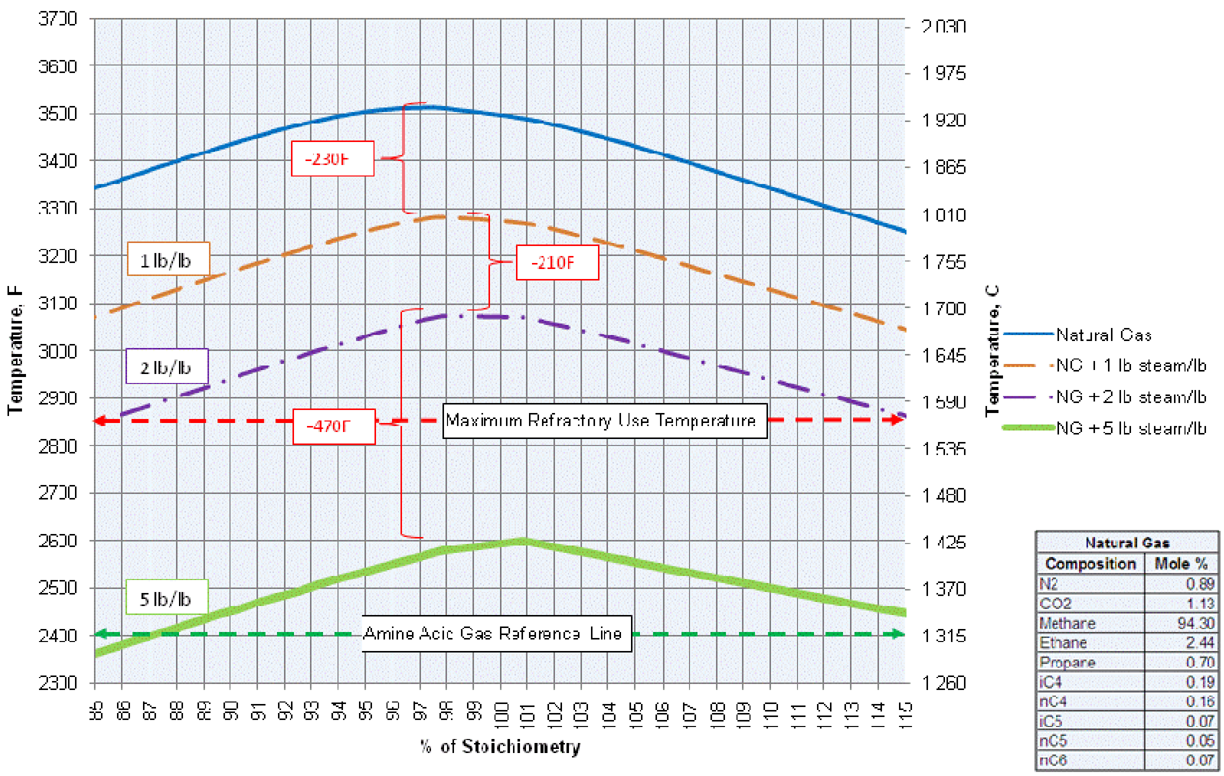
Natural Gas Composition	Mole %
N2	0.89
CO2	1.13
Methane	94.30
Ethane	2.44
Propane	0.70
iC4	0.19
nC4	0.16
iC5	0.07
nC5	0.06
nC6	0.07

Tempering

Some type of tempering of the flame is required to keep the temperature at a level that the refractory can handle. Nitrogen tempering is possible but in most applications it is expensive. Steam tempering is more commonly used because an SRU typically has an excess of steam available. Steam also has an added advantage in that the heat capacity is roughly double that of nitrogen and therefore takes half the mass flow to achieve the same tempering effect. Steam also will condense at the Quench Column and not add load to the downstream equipment (i.e., Incinerator).

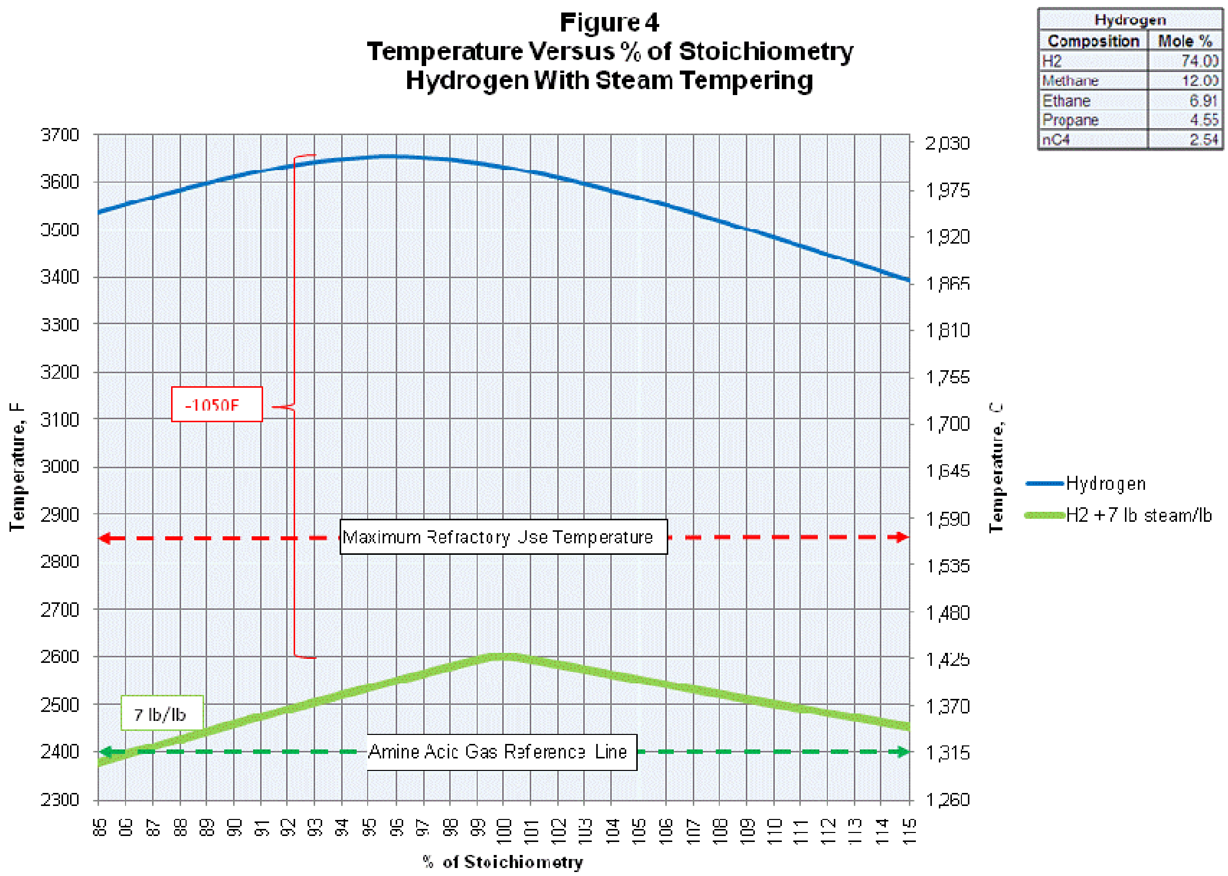
Figure 3 shows the stoichiometric flame temperatures for natural gas at air with difference amounts of tempering steam injection. The data shows that it would take at least 5 lbs of steam for every lb of natural gas burned at stoichiometric conditions to keep the flame temperature below 2600F (1425C) to provide a safety margin under the refractory maximum use temperature.

Figure 3
Temperature Versus % of Stoichiometry
Natural Gas with Steam Tempering



Natural Gas	
Composition	**Mole %**
N2	0.89
CO2	1.13
Methane	94.30
Ethane	2.44
Propane	0.70
iC4	0.19
nC4	0.16
iC5	0.07
nC5	0.05
nC6	0.07

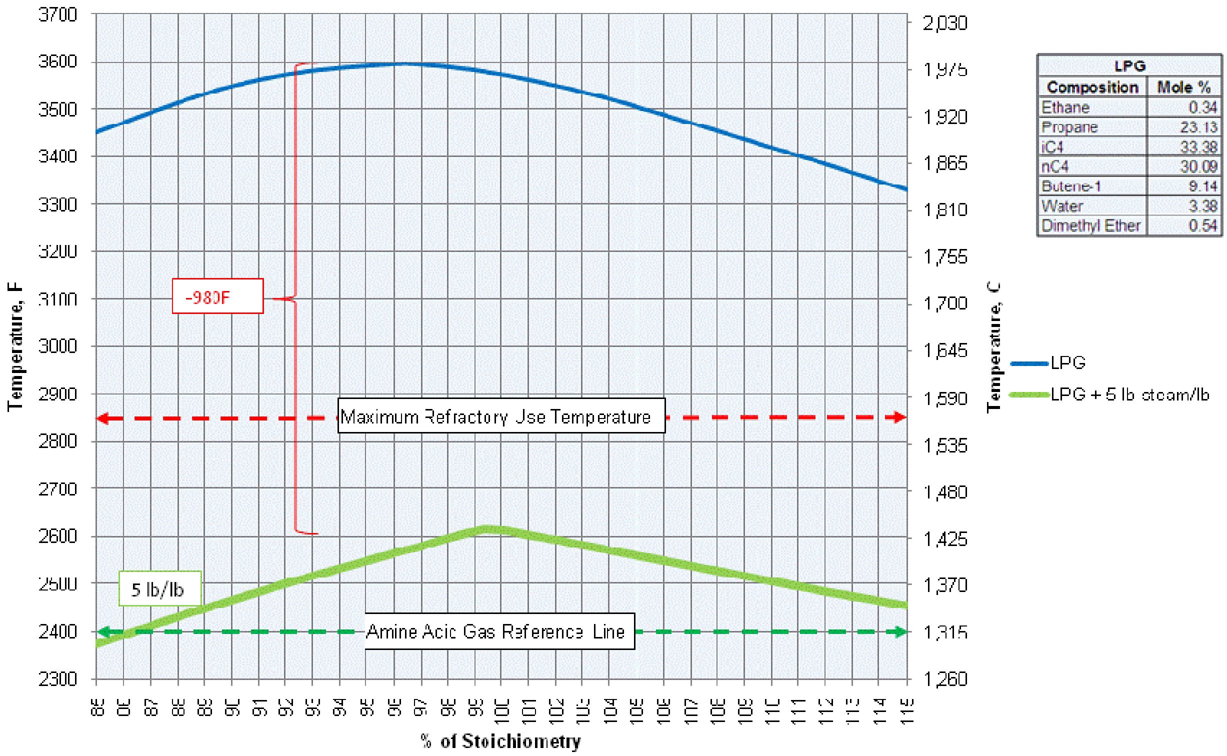
Figure 4 shows that 7 lbs of steam is required for every lb of hydrogen burned at stoichiometric conditions to keep the flame temperature below 2600F (1425C).



Hydrogen	
Composition	Mole %
H2	74.00
Methane	12.00
Ethane	6.91
Propane	4.55
nC4	2.54

Figure 5 shows that 5 lbs of steam is required for every lb of LPG burned at stoichiometric conditions to keep the flame temperature below 2600F (1425C).

Figure 5
Temperature Versus % of Stoichiometry
LPG With Steam Tempering



Addition of tempering steam also has the added benefit of improving mixing especially at turndown conditions that are experienced during start-up, shutdown or hot standby. The improved mixing helps to eliminate areas deficient in air and thereby reduces the chance of soot formation. Addition of steam and the high temperatures also promotes the methane shift reaction (reforming) where the carbon is shifted to carbon monoxide (CO). This reaction also reduces the chance of soot formation.

Adequate flow measurement of the fuel, air and tempering media (steam or nitrogen) is the best practice to avoid high flame temperatures.

Temperature Measurement

Accurate temperature measurement may be a problem at start-up and hot standby. On a cold start-up, the optical pyrometers cannot read until the temperature gets to about 600F (315C). Start-up thermocouples should be purchased from the optical pyrometer supplier and used during each cold start-up. The start-up thermocouples can use the same electrical connection as the optical pyrometers. Installation has to be correct, if you want any chance of accurate measurement. One of the keys to installation is making sure the optical pyrometer is aimed correctly or it could just report the temperature of the inside of the nozzle.

Also, operations need to be aware of the type of optical pyrometer that has been specified. Is it measuring maximum gas temperature, average integrated gas temperature or refractory surface temperature? Basic information on temperature measurement was presented by Hampsten [3] at the Brimstone Sulfur Symposium in 2009. The emissivity of the gas affects the temperature readings. The optical pyrometer is typically calibrated for the normal acid gas flames. How accurate is the reading while in start-up or hot standby with a natural gas flame, how accurate is it for operating with a high hydrogen content flame? More information on optical pyrometers was presented by Croom [4] at the Brimstone Sulfur Symposium in 2010.

Purged ceramic thermocouples are the other accepted measurement device for temperature measurement within the Thermal Reactor. Again, installation has to be correct if you want any chance of accurate measurement. Installation criteria were presented by Croom [4] in a past paper. One of the keys is location of the tip of the thermocouple. The outer ceramic wells should stick beyond the face of the refractory by about 1 ½" so the inner well and thermocouple tip will reside very near the hot face. One common mistake is that the overall length is not specified and the thermocouple tip is back from the hot face and therefore not an accurate indication of the temperature of the face.

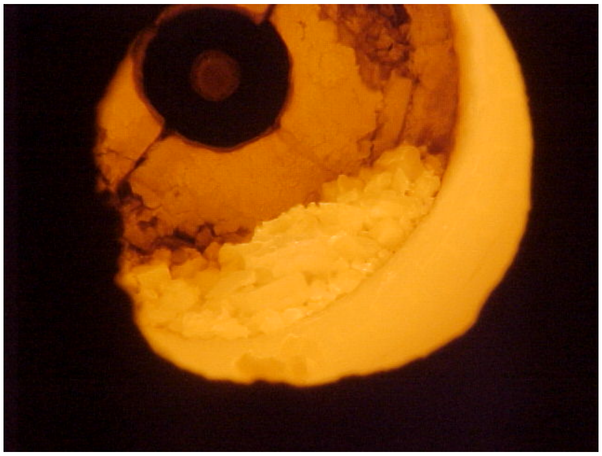
The best installation is to use both technologies.

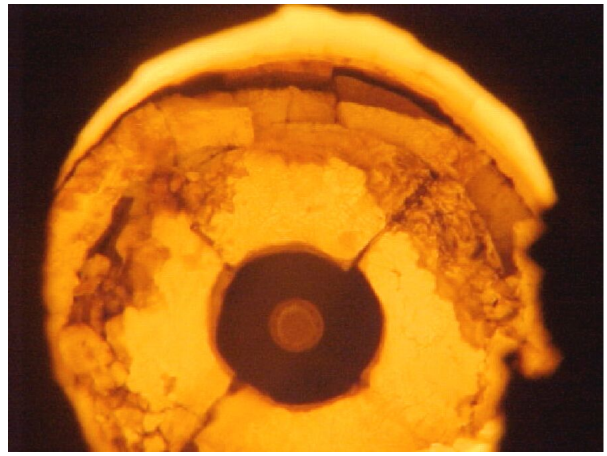
Several papers have been presented at this conference in the past showing CFD models of poor burner designs and good burner designs. The CFDs all show that there is a temperature profile throughout the Thermal Reactor Burner and Thermal Reactor. The temperature patterns are not necessarily what you might think they should be and they can change with changing load. The temperature measurement devices measure a temperature at a point. What are the odds that the temperature measurement is at the point of maximum temperature? Recognition of this issue is critical during start-up and hot stand-by.

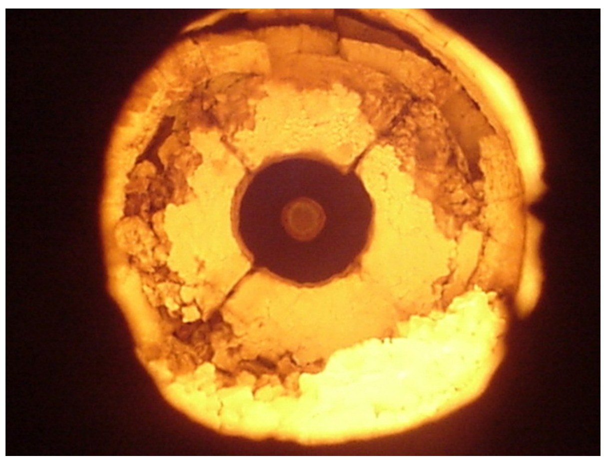
An understanding of the simulated flame temperatures, based on the actual fuel compositions, is an important factor in deciding whether the measured temperatures are realistic.

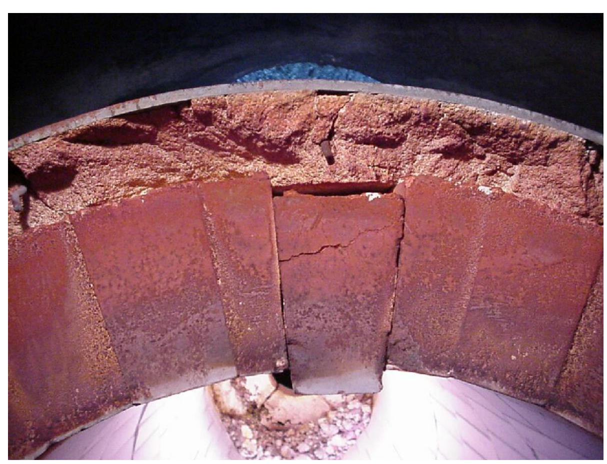
Failures

There have been some fairly spectacular failures when trying to operate with a natural gas and air stoichiometric flame without steam tempering. See photos below of one such case.









References [ ]

1. Sulphur Plant Startup and Shutdown by Paul E. d'Haêne (DANA Technical Services) and Doug Cicerone (Cicerone & Associates, LLC) presented at the 2010 Brimstone Sulfur Symposium
2. SRU Modified Cold Start-up From Emergency Shutdown by Mark Young (Suncor Energy) presented at the 2010 Brimstone Sulfur Symposium
3. Critical Instrumentation in Sulfur Recovery Units by Jim Hampsten (Principal Technology Engineering, Inc.) presented at the 2009 Brimstone Sulfur Symposium
4. Claus Reaction Furnace Temperature Measurement – An Overview by Steve Croom and Ted Keys (Delta Controls) presented at the 2010 Brimstone Sulfur Symposium.

Ferrule Design and Installation for Insulation for SRU tubesheets

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FERRULE DESIGN CONSIDERATIONS

Tubesheet refractory linings are traditionally difficult to construct and operate with complete success. However, industry experience has shown that tubesheet refractory linings can provide several years of reliable service if the installation is correct and the operation is controlled well.

In the late 80's, ferrule failure was identified as the primary source of WHB/SRU unreliability in gas plants, attributed to a combination of tubesheet refractory system designs and/or problems associated with installation. Although somewhat better, this statement is still valid today.

Several factors have contributed to this situation:

1. Tubesheet linings are large vertical walls ranging in diameter from less than 1 meter to >5 meters, with a several hundred degree temperature drop across a typical 100mm thickness.
2. SRU's operate as cost centers rather than profit centers and the trend has been to fix it the way it was rather than seek our real long term improvements.
3. Lack of continuity of information and staff from one turnaround to the next.
4. Ferrules are directly at the mercy of burner performance and any up-stream upsets.

Other factors compounding long term reliability is the industry trend toward oxygen enriched operation to increase unit capacities and achieve better ammonia and BTEX destruction. This has resulted in an increase in WHB temperatures from 1095°C-1200°C (2000°F-2200°F) to 1480°C-1590°C (2700°F-2900°F). Conversely, the maximum service temperatures of high alumina ceramic materials have remained constant at maximum of ~1750°C (3200°F). These values are further reduced when materials are used in SRU reducing environments, (see"Burner Flame Temperature during Warm up and Hot Stand-by", by Alan Mosher, KPS Technology, Brimstone 2011). As the gap closes between operating temperatures and maximum service potentials of ceramics remains the same, the probability of material upset increases. Another significant trend is to make SRU diameters larger; consideration must be given to underlying mechanical issues associated with tubesheet units with diameters larger than 4 meters.

The function of ferrules is to protect metal tubesheets and tubesheet welds from degradation due to high temperature sulphur corrosion. All ferrule styles, properly designed will minimize metal loss. Proper informed design also employs FEA analysis as a tool to evaluate thermal loading on ceramic ferrules in an effort to improve long term integrity. The use of thermal modeling has proven a valuable tool in examining the thermal gradient through a tubesheet insulation system and predicting peak metal temperatures. Examples illustrate that maintaining temperatures below metal sulphiding temperatures and reducing the thermal stresses through ceramic materials is critical in improving unit reliability.

Two factors contribute to the generation of thermal stresses: thermal conductivity, and thermal expansion. As a rule, metals generally exhibit higher thermal expansion and thermal conductivity values than ceramics, so any change in temperature from one part of a metal body to the other will be rapidly dispersed by its high thermal conductivity. In addition, any material expansion in metals will be accommodated by plastic deformation. In ceramics, however, the thermal conductivity is very low and as a result, any change in temperature from one part of the body to another will create a thermal gradient. Ceramic materials are unable to withstand significant plastic deformation, and are prone to brittle failure. Both the mechanical and thermal stresses in a ferrule are concentrated at the "shoulder"- the point where the ferrule enters the boiler tube; regardless of style. The differential thermal expansion (or contraction) created in a ceramic material resulting from a large temperature gradient may induce a crack at the ferrule refractory/tube joint. The portion of the ferrule imbedded in the refractory will separate from the portion in the tube; thereby exposing the tubesheet to hot gas impingent, resulting in hot sulphur corrosion and eventual tube leaks.

FERRULE INSTALATION CONSIDERATIONS

All ferrule styles, properly designed and installed will protect tubesheets from high temperature corrosion. Regardless of ferrule style, material and unit operating conditions, all ferrules should be used with a combination of ceramic fibre paper insulation to centre ferrules inside boiler tubes and ensure even heat distribution, as well as a ceramic fibre gaskets or board to isolate ferrule shoulder from coming into contact with tubesheet metallurgy.

Installation of Traditional Style Ferrules

Traditional style ferrules are installed using either a plastic or refractory castable to fill the spaces between the tubes. A quality installation of ferrules must focus on the details, some of which are listed below.

1. Qualified and experienced refractory contractors (sometimes you get what you paid for) (see API 936, Refractory Installation and Quality Control-Inspection and Testing monolithic refractory linings and materials)
2. Suitability of materials to environment and use.
3. Shelf life of materials used.
4. Quality and temperature of water used to mix castable refractory.
5. Ambient temperature conditions (difficult to install castable materials in very hot or cold weather)
6. Proper mixing of materials used to ensure adequate hydration
7. Proper placement of refractory material (use of pneumatic hammer and dummy ferrules to place plastic refractory)
8. Anchor quality, style and placement
9. Etc,,,,,,

10. And probably the most critical component to a quality lining controlled curing of the refractory lining and the initial dry-out to temperature.
11. Etc...

The disadvantage of traditional style ferrules embedded in castable is that any ferrule damage will necessitate the replacement of the entire lining.

Installation of Modular Style ferrules

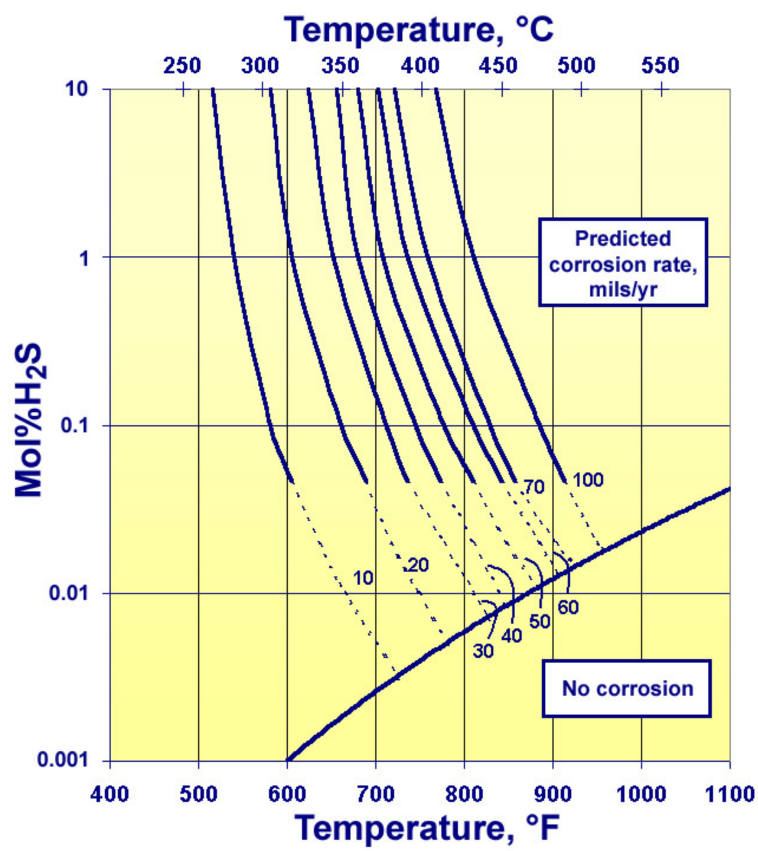
The industry trend has been to move towards modular style ferrules (2-pce hexagon) rather than traditional style ferrules embedded in castable. Hexagon and/or square style ferrules offer a maintenance and installation advantage include minimum installation labor, elimination of messy castable refractory systems. Inspection and repair of damaged ferrules can be completed without disassembling the entire lining. However, the area at the periphery of the unit is insulated using castable or plastic refractory; therefore a controlled curing and drying of castable must be performed to ensure no refractory damage.

Although tubesheet geometry is not important when using ferrules installed with refractory materials, it is important that modular style ferrules fit flush against tubesheet metallurgy; Voids at the tubesheet can accelerate metal loss.

The gap between hexagon (square faces) must also be addressed. Historically a number of methods have been employed with varying degrees of success. As always it is important the unit itself is examined.

1. The gap can be filled with a mortar; however, this negates the benefits of the modular style ferrules and its ability to accommodate tubesheet movement.
2. The dry—mount, gas tight approach relies on precise tolerances in the tubesheet and tubes in order to achieve a good dry-mount joint between the hexagon heads.
    a. Corrosion of the tubesheet metallurgy is dependent on 2 factors: 1) the concentration of the H_2S in the gas and 2) the temperature. The ferrule material is porous and the gas will diffuse through the ceramic and

therefore the H2S concentration will equilibrate at the tubesheet anyway. However, if the temperature at the tubesheet is below a threshold temperature (approx. 290 deg C) then the expected H_2S corrosion rate is 2 mils per year. See figure below which illustrates the effect of temperature and hydrogen sulfide content on high-temperature H_2S/H_2 corrosion of carbon steel) Thus managing the temperature at the tubesheet is the real issue.



b. Another factor to consider is that while tubesheet precision may be achievable with a brand-new tubesheet, subsequent unit operation results in warping, flexing and scale build-up of the tubes and tubesheet. This warping, flexing and scale leaves ferrules sitting in either of two ways: 1) such that the hexagon heads sit too far apart to properly seal the gap between the heads and leave the tubesheet exposed to process gas or 2) such that the hexagon heads sit too close together and then push against each other resulting in too much mechanical stress on the ceramic tube where it enters the tubesheet. This scenario can result in breaking of the ferrule and hot-as impingement on the tubesheet.

3. We strongly recommend installing hexagon head ferrules with a combination of ceramic fiber paper between the heads and then sealed by mortar. We generally specify a 3.2 mm joint between the heads, which is filled with ceramic fiber paper and then mortar. This proven installation method will accommodate variations in the tube pitch , scale/weld build-up, warped tubesheets and any expansion mismatch of the hexagon heads and metallurgy during service . It is the ceramic fibre insulation wrap that provides the thermal protection of the tubesheet and not the bulk ceramic itself. 94% alumina has a thermal conductivity of 10 W/mK whereas the thermal conductivity of ceramic fiber insulation is <1 W/mK. Therefore, ensuring the integrity of the ceramic fibre paper is of the highest importance in designing tubesheet refractory. Without the mortar protecting the ceramic fibre insulation, the binder will burn off the insulation and the insulation will dust out from between and behind the heads, leaving no thermal protection of the tubesheet. This fine grained mortar will then set and cure during heat up and ensure that the fiber material stays in place

CONCLUSIONS

SRU's and ceramic ferrules are being subjected to increasingly sever environments and conditions. Typically, many of the same problems are repeated from one unit to the next. Generally one can say that 60% of all ferrule damage occurs during the temperature extremes which can occur during an uncontrolled start-up or shut-down. Hot stand-by conditions or other in-process interruptions (resulting from either power outages, loss of burner flame etc) are the second largest cause of ferrule damage.

Although it is almost impossible to off-set ferrule damage resulting from upset conditions, tubesheet linings must be carefully engineered and installed to endure the temperature extremes present in most refineries and gas plants today.

List of publications and references:

1. **Brimstone Conference, Vail Colorado, September, 2010**
   Burner to Tubesheet an Evaluation of Reaction Furnaces
   Dave Sikorski / Nick Roussakis, HEC Technologies
   Andy Piper, Thorpe Engineering and Construction Group.
   Domenica Misale-Lyttle, Industrial Ceramics Limited.

2. **Hydrocarbon Processing, October 2002**
   Two Part Hexagon Style Ferrules, Design Considerations and Experience
   Domenica Misale-Lyttle, Industrial Ceramics Limited.

Brimstone Sulfur Symposium 2011

Boiler Water Level Safety Considerations & Tube Collapse

LH Stern

To paraphrase: *How do I Fail Thee….Let Me Count the Ways* ((in order to learn to AVOID FAILURES))

During the history of SRU operation, there have been a large number of incidents, including spectacular ones, of failure of Waste Heat Boilers (WHB's) connected to the Thermal Reactor that have failed, due to issues with boiler water level. Boiler damage resulting from loss of water level can be further exacerbated if BFW is re-started to the boiler after the tubes have been overheated and are beginning to lose mechanical strength. It is fortunate that typical SRU WHB designs place the high pressure water/steam on the outside of the tubes, resulting in overheated tubes tending to fail by collapsing with resultant small opening leakage, instead of large opening rupturing or total cleavage, opening up large pathways for the steam/water into the low-pressure process side.

Typical reasons for tube failures and leaks of steam/water into the low-pressure side are in my experience:

- Loss of water level
- Local overheating at end of ferrule
- Tube to tube sheet weld failure due to corrosion

This presentation is focused on the current industry practices for mitigation of the "loss of water level" event. From my perspective, the potential for a tube failure due to loss of boiler water level has been significantly reduced by the current industry practice of:

- use of HAZOP, LOPA, MOC and other safety analyses and processes, including extensive operator training
- use of multi level control devices,
  - more reliable instrumentation with voting and individual maintenance bypass abilities (i.e., not a single bypass for the entire level control/safeguarding system)
- unit shutdown on loss of level
- providing more reasonable operator reaction time between the first low level alarm and the shutdown of the unit.
- unit design pressure of 52 psi to 77 psi (3.6 to 5.3 bar)

First, a quick review of the fundamental WHB design challenges which are both numerous and evolutionary.

A few Early examples:

I. Early SRU boiler designs applied, with a bit of a priori logic, such notions as two passes in one shell and **thick tubesheets** which were required to provide strength for the harsh conditions of the typical boiler operation, namely:
   (a) a large deltaT of 2000+ ^{o}F (1100 ^{o}C) process-side temperature vs a water-side temperature of only 400-500 ^{o}F (200-250 ^{o}C)
   (b) a large deltaP of 10-20 psig process-side pressure vs a water-side pressure of 200-650 psig

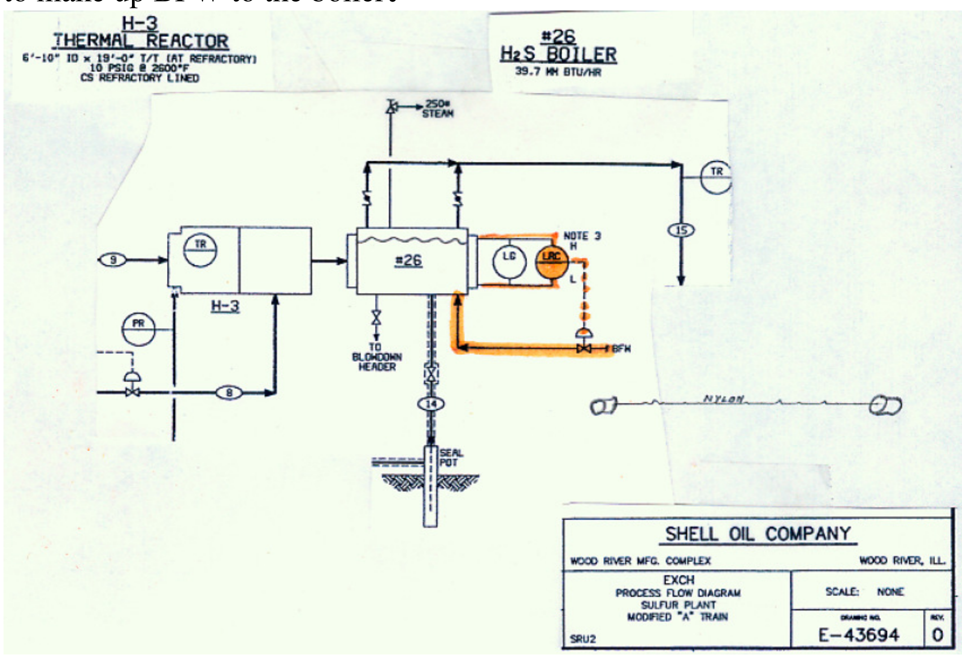
(c) lower furnace operating temperatures and no oxygen enrichment ability

II. Early SRU WHB's were contained in a single shell, utilizing a small area above the submerged tubes for separation of the steam from the boiling water, allowing a very limited water level above the top of the tubes

III. Early SRU boiler designs also incorporated "**small diameter" tubes**, say, 1 to1 ½", so that a tube failure would only have a small opening to deal with…and more heat transfer area could be built into a given boiler shell. The Leidenfrost effect on departing from nucleate boiling to film boiling was not as well applied to SRU boilers as to power plant boilers (this phenomenon demonstrated by Mike Porter at Brimstone in 2009)

IV. Until recently, there was no FEA or CFD modeling capability to simulate the design and operation of the boiler prior to building it

V. Early SRU boiler designs utilized a simple, straight-forward **level controller** to make up BFW to the boiler**:**



Over the past several decades, there have been a number Advances.

A few Improvements examples:

I. Modern SRU boiler designs now incorporate "thin" tubesheets, to provide more flexibility and greater heat transfer support

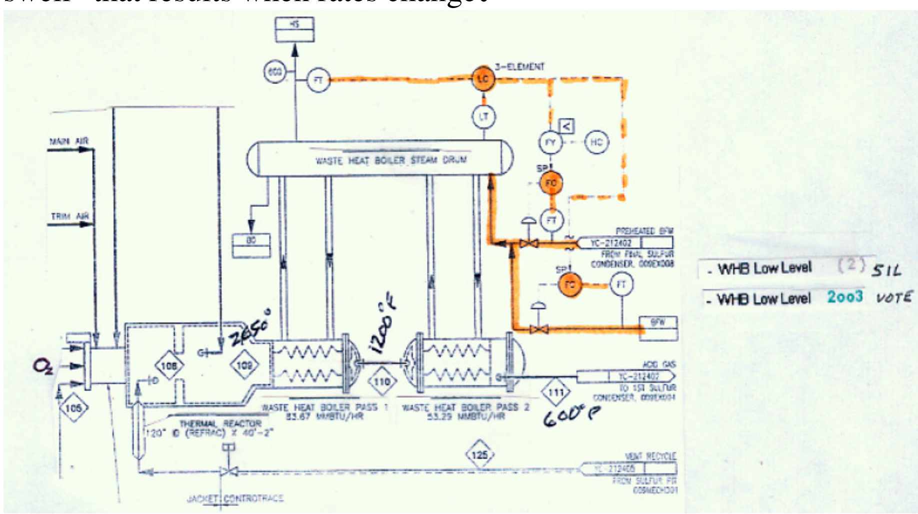
II. Modern SRU boilers incorporate larger diameter tubes (in some cases, they are actually pipe) to reduce heat flux and thus avoid the Leidenfrost effect of "steam-blanketing" the tubes caused by film boiling

III. Modern SRU boilers now employ full penetration strength welds for tube-to-tubesheet joints

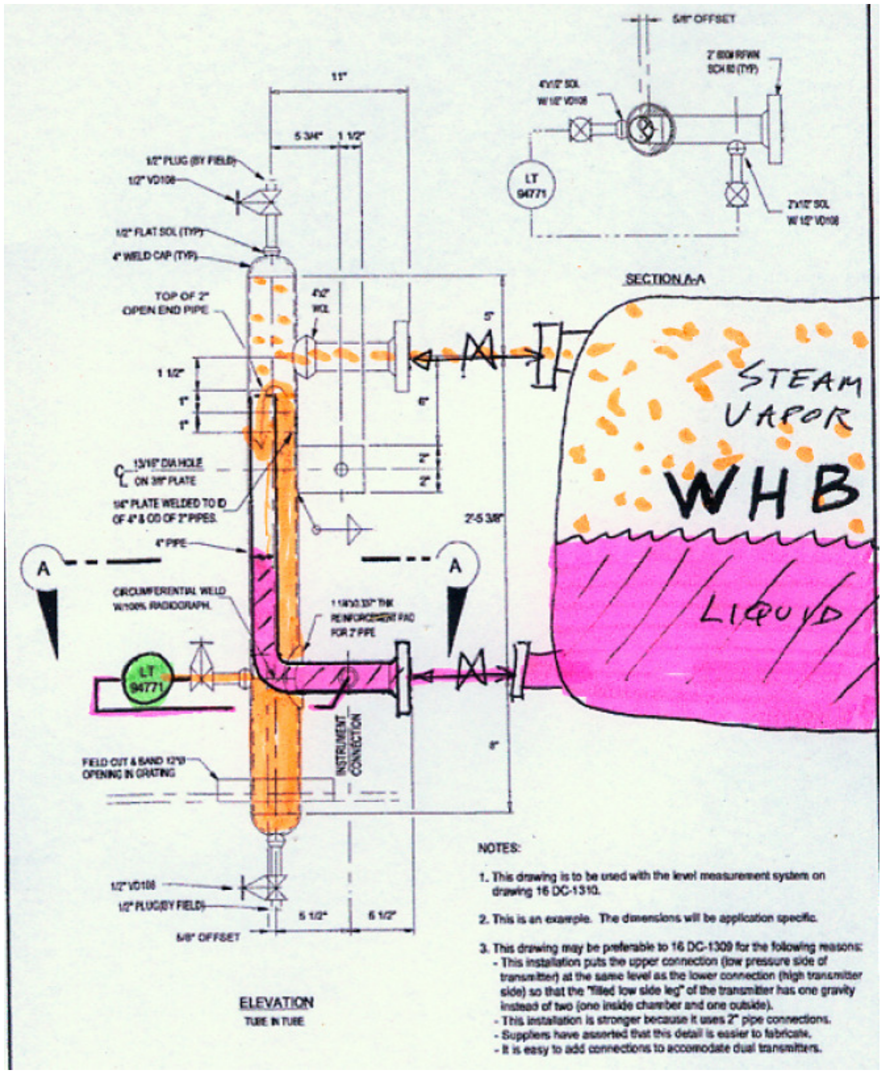
IV. Refractory and ferrule systems have evolved for the high temperature applications of oxygen enriched units and envoronmemntal operational aspects such as continued hot standby and hot restarts

V. Modern SRU boilers often incorporate two passes and an external steam drum, to provide better water circulation, better avoidance of steam blanketing behind the tubesheet, steam/water disengagement, more forgiveness for level swings, etc

VI. Modern SRU boilers incorporate a more sophisticated, 3-element, complex loop level control scheme, incorporating instrumentation to monitor steam production, boiler level and BFW flow, in order to reduce "boiler water swell" that results when rates change:



VII. Safeguarding schemes have evolved, as well as a significant reduction in meantime-between-failure of the instrumentation components.
Some examples:
(a) independent level bridles, often <u>at least three</u>
(b) voting logic, as well as deviation alarms, to improve reliability, while reducing false trips
(c) improved level bridles themselves, such as Shell's tube-in-tube design that is continuously self-purging:



Note: there are numerous papers providing much more detailed discussion of many of the topics noted above, A few examples from recent Brimstone Sulfur Symposiums include:

- 2005 Brimstone "SRU Overpressure in a Wasteheat Boiler Failure" by Justin Lamar *(Black & Veatch)*

- 2009 Brimstone "SRU Shutdown Systems - History & Basics" by Jim Hampsten *(Principal Technology Engineering)*

- 2009 Brimstone "A Means of Avoiding Sulfur Recovery Furnace Fired Tube Boiler Failures" by Mike Porter *(Dynamic Analysis)*, Dennis Martens & Sean McGuffie *(Porter McGuffie Inc.)* & John Wheeler *(Motiva Enterprises)*

And, this recent ASME paper: 2011 ASME PVP paper number 57625; Combining CFD Derived Information and Thermodynamic Analysis to Investigate Water Heat Boiler Characteristics by Sean McGuffie, Mike Porter & Dennis Martens (Porter McGuffie Inc (PMI) and Mike Demskie (Flint Hills Resources)

TUBE AND TUBE WELD CORROSION AND TUBE COLLAPSE

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Presented at the 2011 Brimstone Sulfur Symposium

Facilitated by Brimstone STS Limited

Vail Colorado

Significant unscheduled outages and extended shutdowns have resulted from SRU Claus Thermal Reactor Waste Heat Exchanger (WHE) tube and tube weld corrosion and from tube failure by collapse. Design operating temperatures in the Claus Thermal Reactor ranging from 2000° F (1090° C) to 2800° F (1540° C) are typical. In the last few decades the use of Oxygen enrichment and acid gas enrichment has resulted in more of the units being operated at the upper limit of this temperature range.

The current industry practices for the protection of the tube and tube weld from corrosion and tube collapse have proven to be sufficient to provide several years of reliable service between repairs or replacement. The important aspects of current successful industry practice necessary for reliable service of the WHE from a high temperature corrosion and tube collapse aspects are:

- WHE design utilizing conservative tube mass flow rates
- Design incorporating boiler water level controls and related shutdowns
- Operation within design parameters including startup, shutdown and hot standby
    - Reliable ferrule and ferrule/refractory designs including material selection for minimum of 200° F higher than design maximum operating temperature.
- Quality control of refractory and ferrule materials and installation
- Controlled initial dry out of castable refractory
- Boiler feed water quality, chemical addition control and drum water concentration management

Learning the hard way:

1. **The typical reason for tube ID corrosion occurring in the tube**, usually just downstream of the ferrule, is fouling of the tube OD (boiler water side) resulting in increasing the tube metal temperature into the sulfidation range.

Discussion:

The OD fouling of the WHE tubes results in an increased operating temperature of the tube. The fouling typically is not sufficient to significantly reduce the WHE duty so this condition may not be detected until a scheduled shutdown inspection. It is recommended that the tube ID and OD be inspected when ever assessable at shutdowns. Reference [1] reports the study and analysis of a corroded tube ID condition where up to approximately ½ of the wall had been corroded away. This paper concludes that OD fouling was the root cause for the corrosion. The reference document includes the authors' suggested SRU corrosion rate curves for carbon steel (reproduced at end of this paper). The picture below, reproduced from this paper, shows a significant FeS corrosion product and the tube wall thinning which was occurring about 1 to 2 tube diameters past the end of the inlet ferrule.

2 **The typical reasons for tube to tube sheet weld area corrosion**, resulting from excessive metal temperatures causing sulfidation, are listed below by the most common to least common reasons (in my opinion):

- improper ferrule or ferrule/refractory system installation and initial refractory dry out [2]
- loss of integrity of the ferrule or ferrule/refractory system
  - excessive operating conditions short and long term [3,4]
  - Hot restarts
  - Hot standby
- improper design or installation of the ferrule or ferrule/refractory system [1,2]

Discussion:
The subject of ferrules and ferrule/refractory systems is addressed in the presentation by Domenica Misale.

The following addresses the tube mass flux considerations:
The mass flux is important from a tube entrance pressure drop perspective as this pressure drop is a driving force for hot gas intrusion into the tube sheet protection system.

Reference [2] reports an analysis of the hot process gas flow potential around the peripheral gaps of removable ferrules that can result in corrosion of tube welds and the tube ends. Reference [2] determined that an inlet pressure drop (driving force) of 0.23 psi is sufficient to force up to 7% of the hot process gas flow through a 1/16” open peripheral gap. This rate of process gas flow resulted in a reported 835° F tube tip and weld temperature resulting in an approximate corrosion rate of 35 mil/yr. Similarly a refractory/ferrule system may also have a hot process gas flow potential but perhaps to a lesser extent.

Consideration for a design mass flow rates of 4.5 to 2.5 lb/square ft/sec, for higher operating temperatures, was reported in reference [5]. In one investigation the author found a mass flow rate of 5 to 7 lb/square ft/sec was suspected as the root cause of tube weld corrosion in a removable ferrule installation.

In a recent analysis it has been noted that the length of the tube extension beyond a minimum weld projection acts as a fin and can increase the tube tip and weld metal temperature significantly.

3 **The typical reasons for tube collapse are**;

- Maximum heat flux at the end of the ferrule exceeds the ability to maintain a stable nucleate boiling regime and development of a Leidenfrost condition (steam blanketing);
    - both mass flux and ferrule ID to tube ID step change at the end of the ferrule are significant factors in the increase in local high heat flux condition at the end of the ferrule [3,4].
    - excessive short term operating conditions resulting in Leidenfrost condition (steam blanketing of tubes) [3,4]
- loss of water level in boiler

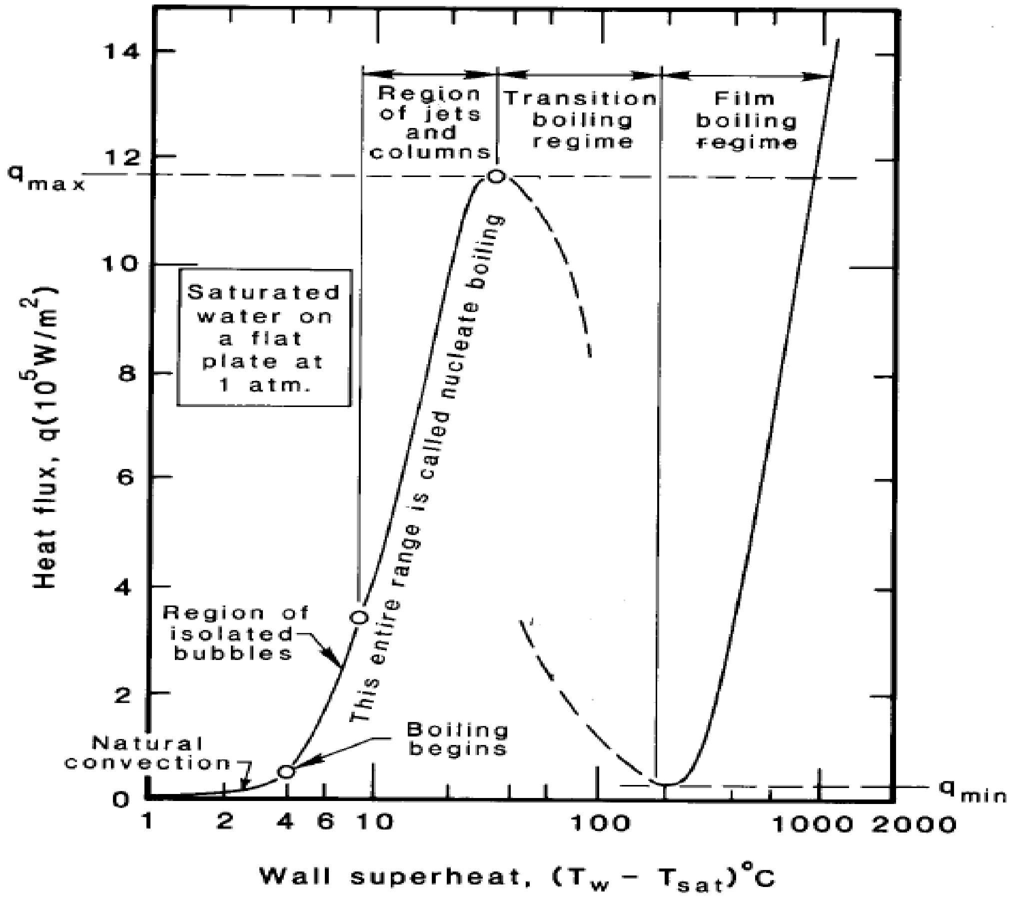
Discussion:
The loss of water level protection is addressed in the presentation by Lon Stern
The tube failure and plant pressure buildup is addressed in the presentation by Justin Lamar

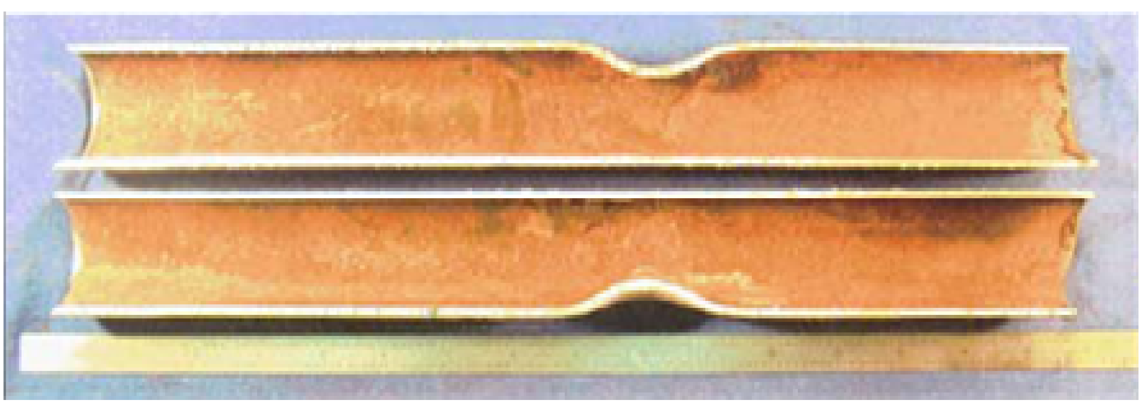
The analysis of partial collapse of tubes resulting from a Leidenfrost condition (steam blanketing of tubes) is reported in references 3 and 4. This analysis confirmed that a ~1200 F tube temperature creep collapse at one to two tube diameters after the end of the ferrule, could occur within minutes of initializing a steam blanketing on the tube. The heat flux versus wall superheat (temperature of the tube OD versus the saturation temperature of the boiling water) graph below is reproduced from these references, for a full discussion on this graph please refer to the references. The analysis reported in these references indicates that less than ~60 C (108 F) wall superheat may initiate a Leindenfrost condition in the 600 psi kettle type boiler investigated. The picture of a partially collapsed tube below is also reproduced from the references and is expected to have resulted in a very short term Leidenfrost condition. The partial collapse is thought to be unusual as recovery from a Leidenfrost condition is not considered to be a simple or stable activity therefore a significant step reduction in the operating parameters is expected to be required.

The WHE tube diameter is an important parameter for the effect of the turbulence at the end of the ferrule. The turbulence at the end of the ferrule will increase the local heat flux significantly. Computational Fluid Dynamic (CFD) analysis has confirmed heat flux increases in different tube to ferrule ID designs and mass flux rates by a factor of 1.7 to 3.5 (or greater) times than heat flux rates indicated by classical analysis such as HTRI. The use of small tubes in high operating temperatures typically have a significantly smaller ferrule ID with respect to the tube ID therefore creating greater turbulence and larger turbulence heat flux increase factors.

References 3 and4 reported a methodology that may be used to determine the maximum SRU operational parameters that would reasonably assure avoiding development of a steam blanketing condition.

The author considers lower mass flux and larger tubes to be key in reducing hot gas bypassing of the ferrules with corresponding corrosion damage to the tube to tube sheet weld and excessive heat flux developing at the end of the ferrule resulting in a Leidenfrost condition. This is contrary to what other papers may report regarding COS production in WHB tubes but nevertheless these are considered as key parameters in making a more robust mechanical system. The author would recommend that a minimum of 2 ½" diameter tubes be utilized for high operating temperatures.


Region of jets and columns
Transition boiling regime
Film boiling regime
q_{max}
Saturated water on a flat plate at 1 atm.
This entire range is called nucleate boiling
Region of isolated bubbles
Natural convection
Boiling begins
q_{min}
Heat flux, q(10^5W/m^2)
Wall superheat, (T_w − T_{sat})°C
0
2
4
6
8
10
12
14
1
2
4
6
10
100
1000
2000



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1. 2011 ASME PVP paper number 57625; Combining CFD Derived Information and Thermodynamic Analysis to Investigate Water Heat Boiler Characteristics by Sean McGuffie, Mike Porter and Dennis Martens (Porter McGuffie Inc (PMI) and Mike Demskie (Flint Hills Resources)
2. 2005 ASME PVP paper number 71143; Computational Fluid Dynamics Investigation of a High Temperature Waste Heat Exchanger Tube Sheet Assembly, Mike Porter, Dennis Martens, Sean McGuffie (PMI) and Thomas Duffy (Motiva Convent)
3. 2009 ASME PVP paper number 78073; A Means of Avoiding Sulfur Recovery Reaction Furnace Fired Tube Boiler Failures – Mike Porter , Dennis Martens, Sean McGuffie (PMI), and John Wheeler (Motiva Convent)
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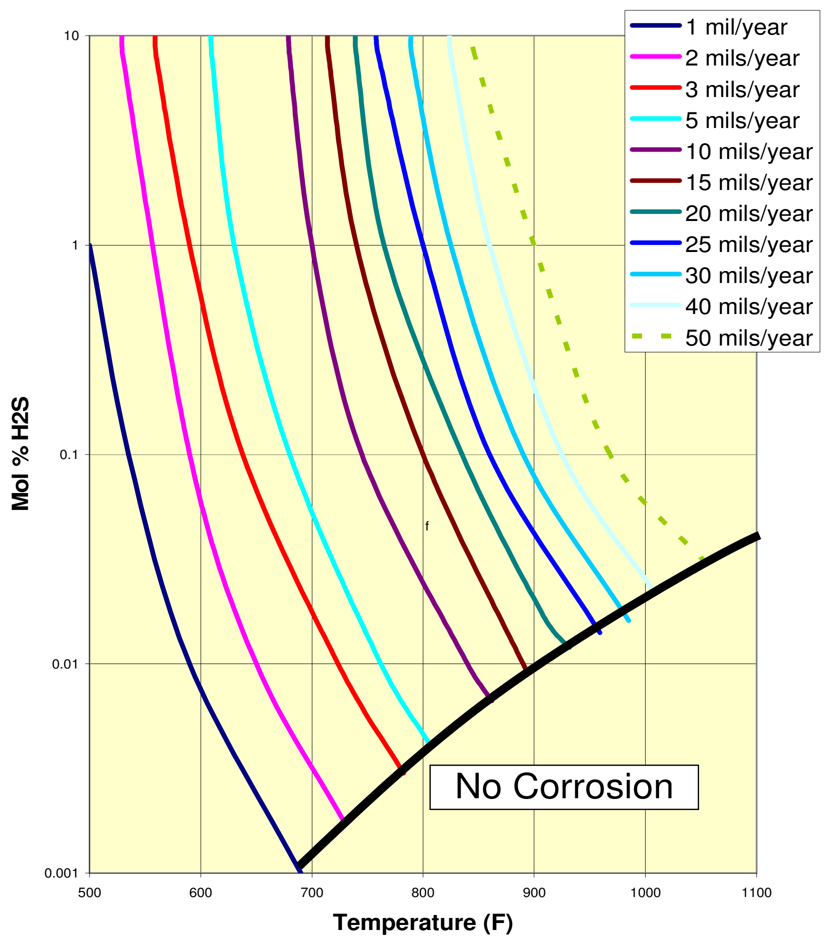

AUTHORS' PROPOSED CLAUS SRU SERVICE SULFIDATION CORROSION CURVE FOR CARBON STEEL

SRU OVERPRESSURE IN A WASTE HEAT BOILER FAILURE

Justin Lamar, Black & Veatch, Overland Park, Kansas USA

The SRU industry has reported many boiler tube leak and failure incidents. However, the industry has not reported vessel rupture or significant loss of containment because of these leaks and failures. The following discussion provides insight into some aspects which may be contributing to the industry's successful avoidance of major loss-of-containment incidents from these boiler tube leaks and failures.

Usually the largest sulfur plant pressure relief load to consider results from a tube leak in the high-pressure waste heat boiler installed downstream of the thermal reactor. The pressure relief path is usually the open process flow path to the atmosphere through the incinerator stack. Flashing boiler water is the chief source of steam flow supplying the tube leakage flow. The choked flow rate through a tube failure can be large for a big leak. However, the boiler's capacity for sustaining the high flow is limited. The principal effect occurring in a tube failure is a depressuring of the boiler. Falling boiler pressure reduces the differential pressure producing flow through the leak and consequently the leakage flow decreases. Also, there is a fixed amount of steam and water within the boiler supplying the leakage flow. The boiler discharge stop-check valve, if it operates, prevents steam header backflow to the boiler from maintaining boiler pressure. The boiler feedwater control valve may open in response to dropping water level; however, the maximum feedwater flow is typically much less than the tube leakage flow for a large failure. Low boiler water level or elevated SRU front end pressure typically will quickly shut down the thermal reactor feeds, and the absorbed duty from hot process gas flow through the tubes producing steam quickly diminishes. Although all these things limit the boiler's capacity to sustain leakage flow, the flashing water in the depressuring boiler is still a significant source of flow for a short period.

Leakage flow rate is directly proportional to the total tube failure perforation size. Therefore the perforation size assumption is most important. In a failure one tube could have a tiny hole, several tubes could have tiny holes, one tube could have a larger hole, etc. API 521 addresses this uncertainty, saying, "In practice, an internal failure can vary from a pinhole leak to a complete tube rupture." API 521 [1] suggests a sharp tube break with flow through both ends for the design rupture flow basis for heat exchangers. A sharp tube break with flow through both ends is unrealistic for an SRU waste heat boiler failure, for several reasons:

- Sulfur plant boiler tubes are typically made from heavy-walled seamless pipe, which is sturdier than drawn heat exchanger tubes. API 521 [1] makes a distinction between gauge tubes and schedule pipe in heat exchangers; for instance, API 521 [1] Section 3.18.6 says, regarding double-pipe heat exchangers with inner tubes constructed of pipe material, "units that use schedule pipe for the inner conduit or tube are no more likely to rupture the inner pipe than any other pipe in the system."
- Sulfur plant boiler tubes have higher pressure on the outside and are in compression, and will tend to collapse before loss of containment occurs, obstructing the leakage flow path in a failure.
- Finally, an API 521-type break [1] depressures the boiler very quickly, as shown below, and has likely never occurred in a sulfur plant waste heat boiler. Assumed failure size for sulfur plant waste heat boilers should be based on failure analysis and examination

of actual failure events. An example study of a boiler failure is shown below and was reported in my technical paper [2] presented at the 2005 Brimstone Symposium.

The steam/water phase mixture supplying the leakage flow depends on what is in the boiler shell and where the failure occurs. A slowly dropping water level caused by instrument failure could expose, overheat, and fail top row tubes, leaking primarily steam. Or, corrosion from boiler solids accumulation could fail bottom row tubes, leaking primarily flashing water. Since we cannot anticipate what the leaking phase mixture will be, we must consider all possible mixtures and design for the worst effects. When considering all possible vapor/flashing liquid mixtures which could flow through the tube leak, we find that the worst case in terms of producing backpressure in the sulfur plant is likely the 100% vapor leakage case, since it produces the highest vapor flow rate downstream of the tube leak. Generally this is true for all rupture flows; the vapor flow rate is most significant. The water, if present, will settle out in the bottom of the SRU equipment, and to some degree will become entrained in the escaping steam flow through the unit.

We can combine methods for leakage flow calculation together with an unsteady-state material and energy balance calculation to obtain the pressure and leakage flow decay profiles for the ruptured boiler. First assume a set of conditions existing at the instant of boiler failure: mass of water in boiler, boiler pressure, boiler feedwater flow rate, boiler blowdown flow rate, absorbed process heat duty, and perforation size. Next calculate the rupture leakage flow rate. Then, over a small time increment, calculate the mass of steam released through the rupture, the mass of blowdown removed, the mass of boiler feedwater added, and the absorbed process energy. Perform an energy balance as follows to calculate the enthalpy of the boiler water after the small time increment:

$$New\ h_{bw} = \frac{M_{bw}\ h_{bw} - M_{stm}\ h_{stm} - M_{blowdown}\ h_{blowdown} + M_{bfw}\ h_{bfw} + Q}{M_{bw} - M_{stm} - M_{blowdown} + M_{bfw}}$$

where M_{bw}, h_{bw} = mass and enthalpy of water in boiler, lbs. and Btu/lb,
M_{stm}, h_{stm} = mass and enthalpy of steam released through the rupture, lbs. and Btu/lb.
$M_{blowdown}$, $h_{blowdown}$ = mass and enthalpy of blowdown, lbs. and Btu/lb,
M_{bfw}, h_{bfw} = mass and enthalpy of boiler feedwater, lbs. and Btu/lb,
Q = absorbed process energy, Btu.

The new boiler water enthalpy value is slightly lower than the starting value because some water flashes to produce the steam supplying the rupture flow. With the new boiler water enthalpy value after the small time increment, find the new saturation pressure of the boiler water. This is the new boiler pressure after the small time increment. Now repeat the calculation for succeeding time increments to find how the boiler pressure, rupture flow, and other variables change as time proceeds.

To illustrate the calculation, and the effects of various perforation sizes, consider the following example, taken from a paper presented by Joy Hansen and Ed Zamejc [3] at the Brimstone Conference in 2001. In that paper the authors present a case study of a failure incident in 1999, and provide a graph of measured boiler pressure data during the event, convenient to use for our example. Using the method outlined above, I applied a material and energy balance to that boiler, and calculated some pressure decay and rupture flow profiles with different perforation sizes. Figure 1 below shows some data points from the boiler pressure graph in the Hansen and Zamejc [3] paper, with my calculated profiles for different perforation sizes. The 5.91 in^2 size represents a double-ended sharp tube break per API 521 in a 2" schedule 80 tube. I calculated that a 0.85 in^2 perforation size best matched the observed boiler pressure decay profile. My calculated peak rupture flow rate resulting from a 0.85 in^2 perforation size is about 21,000 lb/hr, comparable with the normal process flow through the SRU, which may explain why the SRU pressure during the 1999 event did not blow the sulfur seal legs.

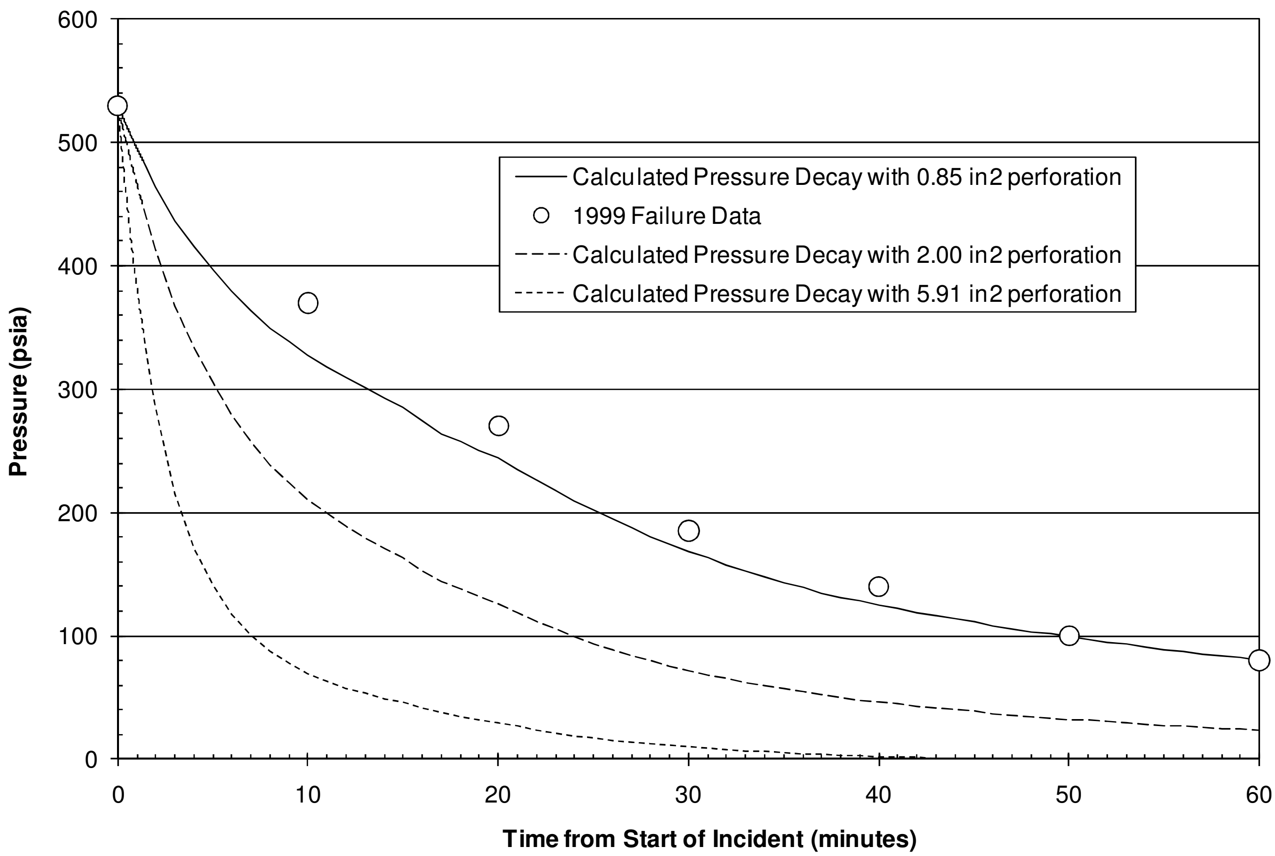

Figure 1: Calculated Pressure Decay Profile in Comparison with 1999 Failure Data.

With rupture flow estimates, we can calculate the backpressure developed in the SRU by the steam flow escaping to the incinerator stack. The easiest and most conservative backpressure calculation is to assume steady-state flow conditions develop through the sulfur plant and out the stack. Steady-state backpressure calculation is conservative for two reasons. First, the boiler drops in pressure from the instant of failure, causing the rupture flow to decrease, lowering the developed backpressure. Second, the accumulation of pressure within the SRU absorbs some of the rupture flow, and it takes a period of time for backpressure to build up in the SRU. These two effects combine to produce the actual peak SRU overpressure.

Dynamic backpressure calculations are more realistic than steady-state calculations because a waste heat boiler tube failure is not a steady-state occurrence. Dynamic calculation provides a lower backpressure result than conservative steady-state calculation because the dynamic approach takes into account the decreasing leakage flow and the build-up of pressure in the

SRU, which act together to reduce backpressure [2]. For SRU overpressure safety design, when steady-state calculations with reasonable assumptions provide unacceptable results, dynamic calculations provide a valid method to obtain a lower, more realistic, backpressure result which may be acceptable.

Some topics and questions regarding boiler tube leaks and SRU overpressure not addressed here are worthy of future consideration. Some examples include:

- Heating of the leaked, escaping steam flowing through the SRU to the incinerator stack by the hot catalyst beds and equipment inside the unit. Higher steam temperature and lower density would contribute additional overpressure.
- Boiling of leaked boiler water by the hot equipment and refractory surfaces, contributing additional steam flow and overpressure.

As a point of interest the API 520-521 committee initiated a working subcommittee in 2010 with two key objectives:

- Determine a viable tube failure mode for overpressure protection design, i.e. complete tube break or other failure
- Determine a viable path for mitigating the failure

Currently this subcommittee is gathering SRU boiler tube failure experience, and input from industry on the viable path for mitigating the failure. The next subcommittee meeting is scheduled for November 14-18, 2011, in Los Angeles, California.

For additional information, including how to provide your experience and suggested mitigation approach, please contact Michael K. Porter, Subcommittee Chair, at

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