

Dennis H. Martens

Consultant and Technical Advisor (martensdh@pm-engr.com)

Porter McGuffie Inc. (pm-engr.com)

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
 - o 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);
 - o 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].
 - o 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

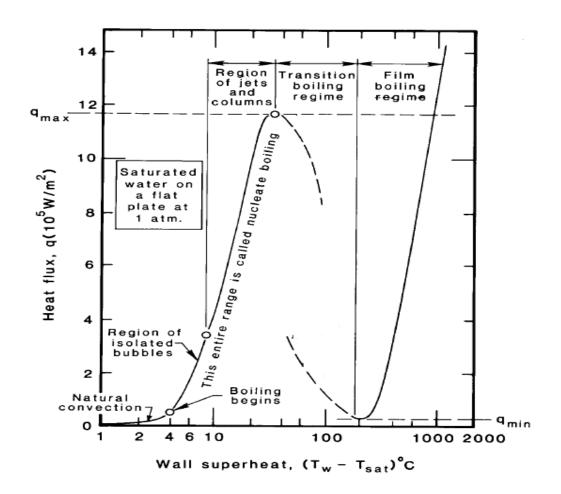
The analysis of partial collapse of tubes resulting from a Leidenfrost condition (steam blanketing of tubes) is reported in references 3 and 4. This analysis confirmed that a ~1200 F tube temperature creep collapse at one to two tube diameters after the end of the ferrule, could occur within minutes 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.

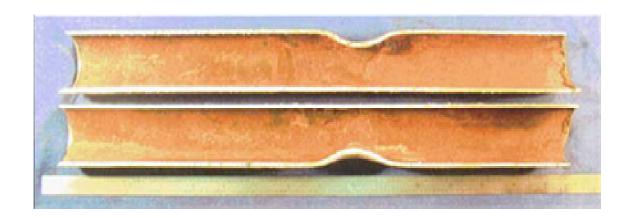
The WHE tube diameter is an important parameter for the effect of the turbulence at the end of the ferrule. The turbulence at the end of the ferrule will increase the local heat flux significantly. Computational Fluid Dynamic (CFD) analysis has confirmed heat flux increases in different tube to ferrule 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 and 4 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.



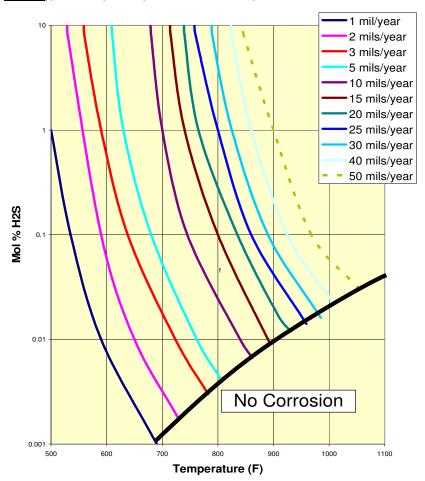






References []

- 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)
- 4. 2009 Brimstone "A Means of Avoiding Sulfur Recovery Furnace Fired Tube Boiler Failures" by Mike Porter (*Dynamic Analysis*), Dennis Martens and Sean McGuffie (*Porter McGuffie Inc.*) and John Wheeler (*Motiva Enterprises*)
- 5. 1996 ASME PVP paper :Analysis of Tubesheet Stresses in a Sulfur Recovery Unit, PVP-Vol. 336 ,(Structural Integrity, NDE, Risk and Material Performance for Petroleum, Process and Power), ASME, 1996, Dennis Martens, Charlie Hsieh and Christopher Brzon



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