New Insights with Rate-Based Claus Waste Heat Boiler Modeling[1]

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ABSTRACT

The Claus Waste Heat Boiler (WHB) is a critical piece of equipment in the sulfur recovery unit (SRU). As refiners and gas producers have pushed towards higher sulfur feedstocks placing more load on the SRU, WHB failures have become more common. These higher failure rates have come at a time when uptime metrics and environmental constraints have become concurrently stricter.

In this work, a set of case studies were run using a newly developed rate-based heat transfer and chemical reaction model of the Waste Heat Boiler. The rate-based model provides quantitative insights into several aspects of the WHB that impact the sulfur plant performance:

- Recombination reactions that occur at the front of the WHB are as follows:

  $H_2 + \frac{1}{2} S_2 \rightleftharpoons H_2S$
  $CO + \frac{1}{2} S_2 \rightleftharpoons COS$

  These reactions not only influence sulfur recovery, air demand, and hydrogen production in the SRU, they also impact the heat flux and performance of the WHB. These reactions occur towards the front (inlet) side of the WHB and are exothermic. The "hidden" heat associated with these reactions tends to increase heat flux towards the critical tube-to-tubesheet joint.

- Radiation impacts on heat transfer also occur primarily towards the inlet of the WHB.

Radiative heat transfer, coupled together with the exothermic recombination reactions collectively increase the peak heat flux at the front of the boiler well above predictions from models that ignore or discount these factors. Tube wall temperatures, pressure drop, and heat flux predictions from the model are examined down the length of the tubes for an oxygen-enriched and air-only sulfur plant as a function of tube size and mass velocity. Surprising findings show elevated tube wall temperatures well downstream of the area of protection provided by ceramic ferrules for the higher mass velocity cases, validating documented failures in the industry. The implications of sulfidic corrosion and the resulting impact on boiler tube life and sulfur plant reliability economics are examined with this new information.

BACKGROUND

The WHB (Figure 1) is arguably the most fragile part of an SRU and can be subject to sudden and very costly failure. The most common failure point is the tube-to-tubesheet joint where

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[1] Brimstone Vail, Vail CO, 2017

temperatures can become unacceptably high, causing the welds there to fracture and the joints to fail. To provide operability, this region of the WHB is protected by ceramic ferrules (Figure 2) inserted a short distance into the tubes and which usually also completely cover the face of the tubesheet (Figure 3). On the utility side, high or medium pressure steam is usually generated (heat recovery) by cooling the hot gas on the process side. Sulfur is not usually condensed in the WHB except at turndown conditions.

Figure 1 Waste Heat Boiler (courtesy Schmidtsche Schack, Düsseldorf)

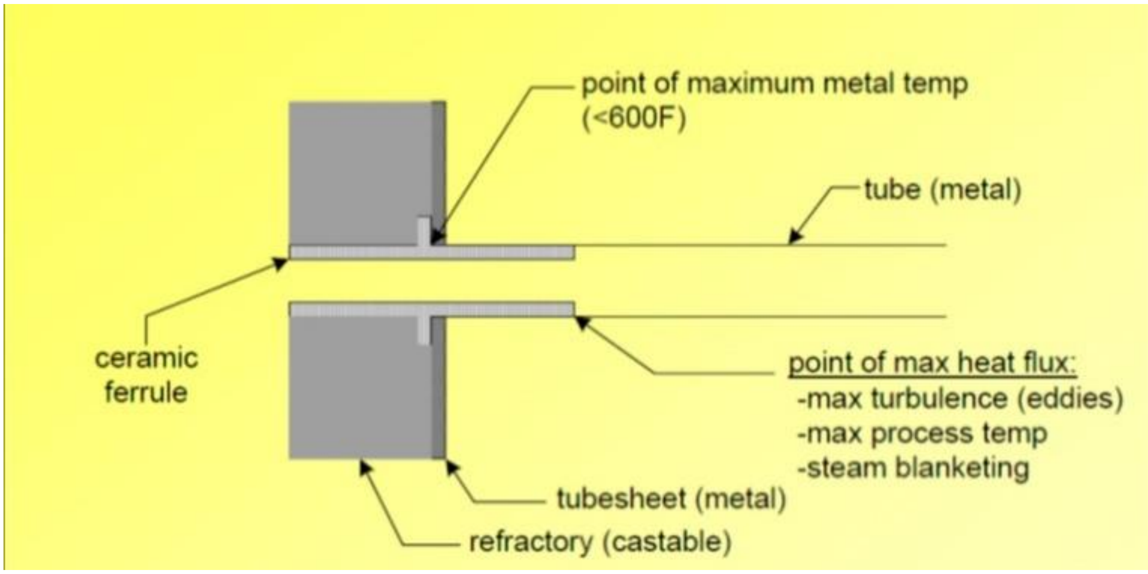
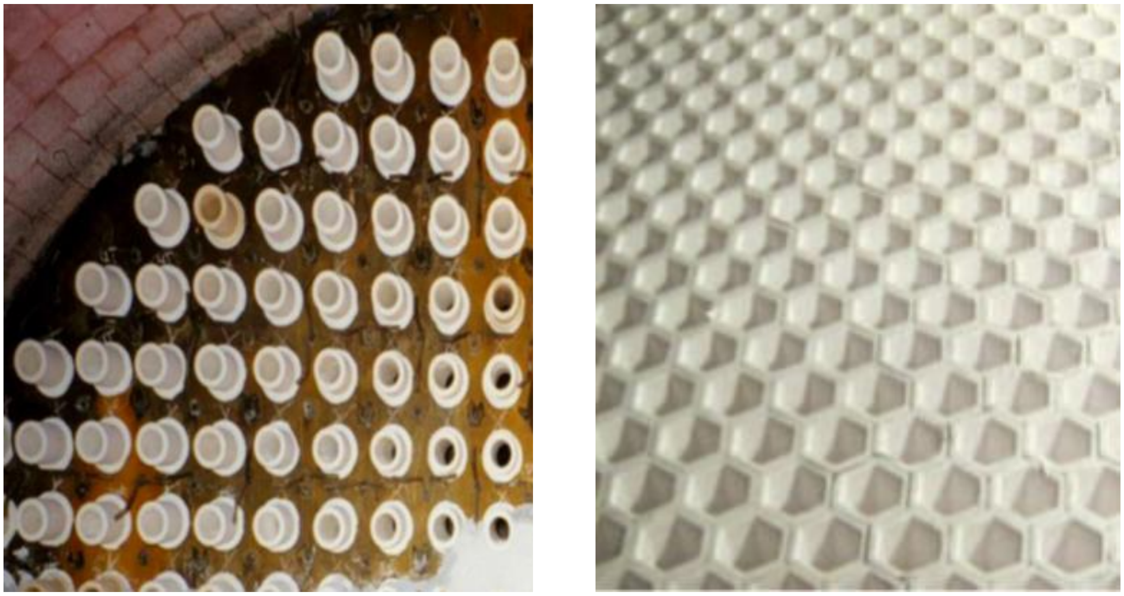


Figure 2 Thermal Protection by Ceramic Ferrules



Conventional Ferrules before Final Refractory Installation

Hex-Head Ferrules

Figure 3 Types of Ceramic Ferrules, Installed View

In the WHB a number of interesting reactions take place as heat is removed. It is well known that the S_2 vapor allotrope is exothermally converted into the S_6 and S_8 forms as the gas is cooled (Reactions i and ii below). Reactions of at least equal importance involve hydrogen recombination with S_2 vapor (reaction iii) and COS formation from carbon monoxide and S_2 vapor (reaction iv). These reactions are also exothermic and take place primarily at the WHB's front end. [1]-[5]

$$3S_2 \rightleftharpoons S_6 + heat\ (i)$$

$$4S_2 \rightleftharpoons S_8 + heat\ (ii)$$

$$2H_2 + S_2 \rightleftharpoons 2H_2S + heat\ (iii)$$

$$2CO + S_2 \rightleftharpoons 2COS + heat\ (iv)$$

Because of the high inlet temperature of the process gas, radiation is also significant to heat transfer in the Waste Heat Boiler, unlike the heat exchangers further downstream.

Approaches to Recombination Modeling

The recombination reactions can generate significant heat near the front of the WHB, i.e. close to the fragile tube-to-tubesheet joint area, so getting the simulated temperature there as correct as possible is important. Until very recently, the models used by all commercially available SRU simulators handled recombination by one of several obfuscation techniques:

- Ignore local recombination and assume the reaction furnace (RF) is at equilibrium, or
- Lump these reactions into the RF effluent, or
- Freeze the reactions by assuming they reach equilibrium at a user-supplied quench temperature.

The only correct approach is to model the reactions as they truly are: fully reaction kinetics rate-based. With the advent of the Sulphur package in Version 6.4 of the ProTreat® simulator, this approach is now available.

The first-principles, rate-based model in ProTreat® incorporates the effects of reaction kinetics, rigorous heat transfer (including temperature, composition, and geometry-dependent radiation), and condensation calculations of liquid Sulphur (including thermodynamic and physical property effects resulting from the varying distribution of Sulphur allotropes.) The interdependency of physical properties, reaction rates (and their heats of reaction/redistribution), bulk heat transfer, and stream enthalpies (both latent and sensible) are solved together to provide a consistent and powerfully predictive modeling tool.

In brief, the set of equations governing the WHB, including recombination reactions, are numerically integrated along the boiler tube length. Adaptable segmentation is used to yield more accurate results by placing more segments in the locations where properties are changing fastest and consequently require higher numerical resolution.

Reaction kinetics modeled in ProTreat® are based on a collection of literature sources whose main purpose was exploration of the two main recombination reactions which occur in the WHB.[1]-[4]. In those works, sets of Arrhenius kinetic constant parameters were tuned to match sets of experimental, pilot, and full-scale SRUs. Implementation of kinetics in ProTreat® are consistent with ProTreat's® thermodynamics, and additional adjustments were made to match internal sets of plant data for both normal operations and off-spec conditions in real operating sulfur plants. All other transport coefficients and physical properties are calculated from proprietary or well-established literature correlations.

To illustrate the importance and relevance of these reactions, we turn next to a set of case studies.

CASE STUDIES

The flowsheet in Figure 4 was used as the basis for the case studies in this work. Since WHB failures have tended to be more common during the harsher conditions of oxygen enrichment, we took a plant initially designed for approximately 100 LTPD sulfur on air operations that would be revamped using low-level oxygen-enrichment (to 30% O_2 wet-basis) to process 25% more throughput. Typical compositions of refinery amine acid gas (90% H_2S, 0.5% C_1, balance CO_2, water saturated) and SWS gas (55% NH_3, 45% H_2S, water saturated) were used with a 5.6:1 ratio of amine acid gas to SWS gas. This resulted in nominally 6% NH_3 in the combined acid gas feeds.

Table 1 lists the WHB tube configuration chosen for rating. Failures above mass velocities of 5.0 lb/sec-ft^2 have been reported to be more common.[6] We chose a design that would target a mass velocity just under this value on air operations.

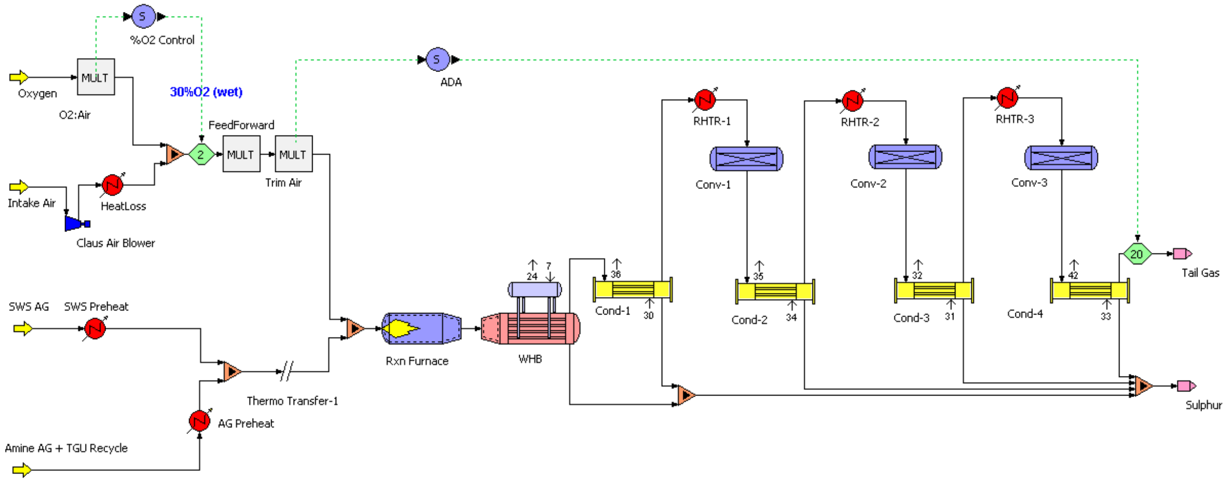


Figure 4 Flowsheet for Case Study

Table 1: WHB Configuration & Parameters

Number tubes	120
Tube OD/ID, inches	2 / 1.783
Tube length, feet	32
Steam generation pressure, psig	350
BFW temperature, °F	280
Mass velocity, lb/ft^2-sec	4.5
Inside tube wall emissivity	0.9
Fouling resistances, process /steam sides, hr-ft^2-°F/Btu	0.008 / 0.002
Steam side HTC, Btu/hr-ft^2-°F	150-1000

A range of utility-side heat transfer coefficients from the literature [7] were chosen as a sensitivity study to encompass expected ranges from the literature that would represent operating over a range from poor to good utility-side circulation.

Table 2 summarizes the results of the study specifically for the boiler rating. Quite profound differences between the air and oxygen-enriched operations can be seen. Inlet temperature from the Reaction Furnace climbs from 2360°F on air operations to nominally 2680°F on oxygen. Peak boiler tube wall temperatures and heat fluxes also elevate substantially on oxygen compared to air operations. Sulfidic corrosion rates at the ferrule outlet and the process piping outlet (assuming no refractory lining) were calculated by a curve-fit of the chart in reference 6 knowing the % H_2S and wall temperature. ***Expected corrosion rates under oxygen operations are on-the-order of two times higher than air-only operations***. It should be noted that the heat fluxes that were computed do not take into account the insulating effect of the ferrules, nor do they account for eddy effects that typically amplify heat flux at the ferrule outlet.

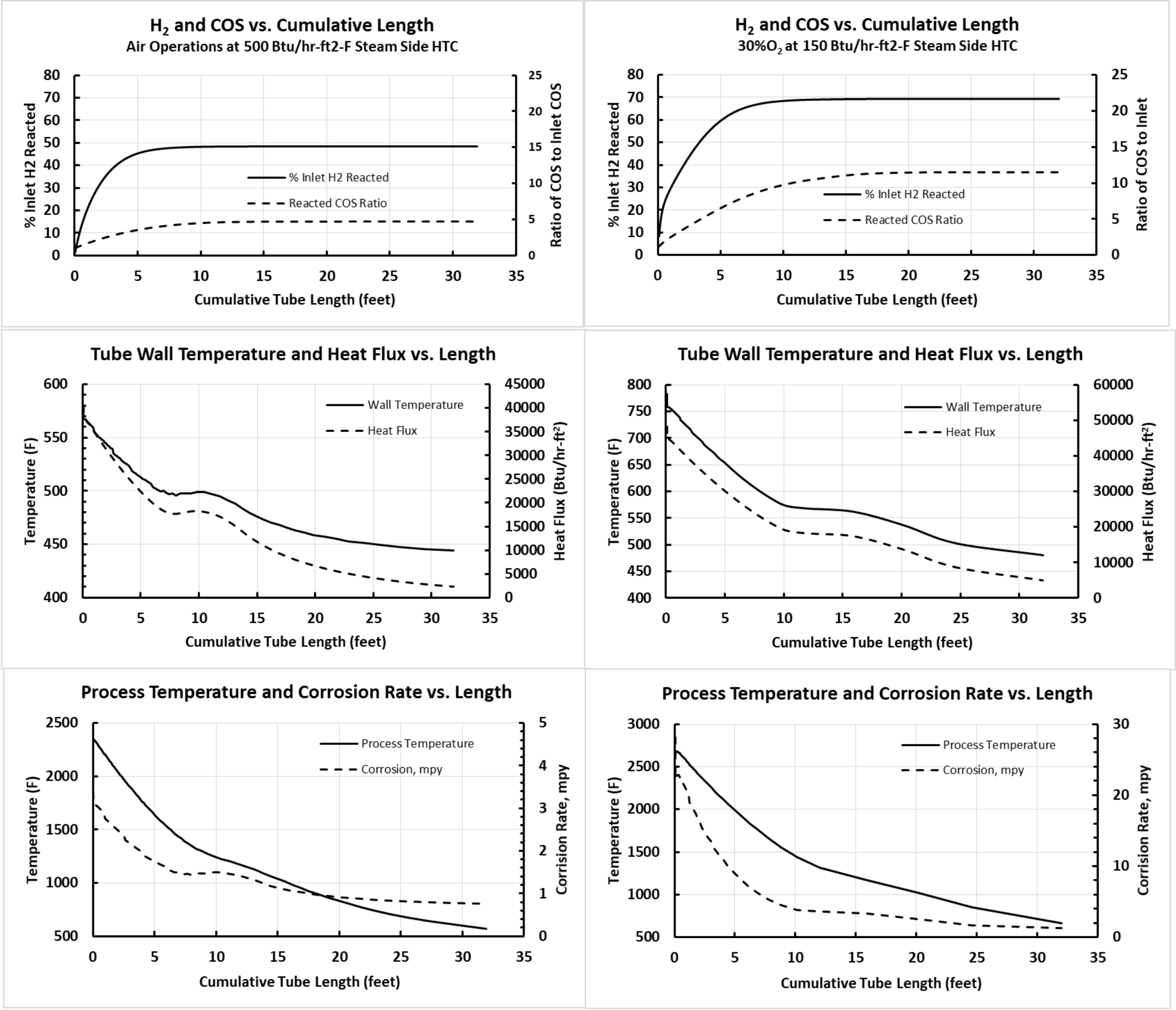
Table 2: WHB Rating Results

Parameter	Air-Only			30% O_2		
Steam side HTC, Btu/hr-ft2-°F	150	350	500	150	350	500
% H_2S in/out	4.4 / 7.0	4.4 / 7.0	4.4 / 7.0	4.0 / 10.1	4.0 / 10.0	4.0 / 10.0
Temperature in/out, °F	2361 / 598	2359 / 577	2358 / 572	2681 / 664	2678 / 631	2677 / 623
Mass Velocity, lb-ft^2-sec (inlet)	4.45	4.45	4.45	4.9	4.9	4.9
Max Tube Wall Temp, °F	706	602	576	783	651	621
Max Heat Flux, Btu/hr-ft^2	37,400	39,900	40,500	48,200	51,900	52,700
Corrosion rate in/out, mpy	13 / 4.7	4.5 / 3.8	3.4 / 3.5	27 / 10	7.4 / 7.3	5.4 / 6.7

Referring to Table 2, an unexpected finding is just how sensitive the results appear to be to the assumed steam-side heat transfer coefficient. If the water circulation is poor near the tube inlet (150 Btu/hr-ft^2-°F case), then corrosion rates above 10 mil/year can be expected for both air and oxygen enriched operations. Eddy heat flux amplification on the process side would undoubtedly make matters even worse. **These findings point to the importance of maintaining good water side circulation and water quality to prevent scale formation**. More steam-side resistance increases tube wall temperature while higher process-side fouling will tend to insulate the tube and lower the tube wall temperature. Better circulation (higher steam-side HTC) lowers the maximum tube wall temperature, but increases heat flux. The oxygen-enriched operations show heat flux in excess of 50,000 Btu/hr-ft2, which in the authors' experience can be a red flag for reliability. Further study of this boiler under CFD and water side modeling would be recommended as a wise thing to do.

Figure 5 provides sample plots of several parameters as a function of cumulative tube length. The left plots are for air-only operations with an assumed steam-side heat transfer coefficient of 500 Btu/hr-ft^2-°F while the plots on the right show 30% O_2 operations at 150 Btu/hr-ft2-°F assumed steam side heat transfer coefficient. The conditions were chosen to bracket the extremes of the study that was conducted to contrast differences. Plotted parameters are:

- Reacting species, H_2 and COS (top most plots)
- Tube wall temperature and heat flux (middle plots)
- Process temperature and predicted corrosion rate (bottom plots)



H_2 and COS vs. Cumulative Length
Air Operations at 500 Btu/hr-ft2-F Steam Side HTC

H_2 and COS vs. Cumulative Length
30%O_2 at 150 Btu/hr-ft2-F Steam Side HTC

Tube Wall Temperature and Heat Flux vs. Length

Tube Wall Temperature and Heat Flux vs. Length

Process Temperature and Corrosion Rate vs. Length

Process Temperature and Corrosion Rate vs. Length

Figure 5 WHB Profiles vs. Tube Length for Air-Only (Left) and 30% O_2 (right)

A number of interesting observations follow from Figure 5. Firstly, the hydrogen and COS reactions are finished in the first 5–10 feet of the tube bundle. Hydrogen losses are much higher on oxygen than for air while the COS formation tendency is also much higher with oxygen.

Tube wall temperatures on oxygen operations remain quite high well past the insertion length typical for ceramic ferrules (~6"). Given the right conditions, such as poor water side heat transfer, corrosion rates and heat flux will also be high past the ferrule-protected length.

Tube wall temperature and heat flux (middle charts) exhibit an inflection at approximately 10 feet along the tube length. Looking further at the bottom plots, the process temperatures are in the range where sulfur species begin shifting from S_2 vapor into S_6 and S_8 vapor (1200-1400°F).

Process Performance Considerations

Table 3 outlines key process performance predictions from the rating study for the entire sulfur plant. Hydrogen in the Claus tail gas is a weak function of the assumed steam side heat transfer coefficient, increasing along with the heat transfer coefficient. Both hydrogen make in the Claus unit and COS production are higher under oxygen operations. In general, sulfur recovery efficiency under oxygen enrichment is higher than on air operation for the Claus unit. Note that SO_2 emissions from the TGU stack may not follow the same relationship since oxygen enrichment leads to more COS in the tail gas.

Table 3: Key Process Performance Predictions

Parameter	**Air-Only**			**30% O_2**		
Steam side HTC (Btu/hr-ft^2-F)	150	350	500	150	350	500
H_2 in tail gas, %wet	2.35	2.42	2.44	2.70	2.77	2.79
Sulfur Recovery, %	97.44	97.42	97.46	97.57	97.60	97.58
COS in tail gas, ppmv (wet)	401	387	384	587	570	566
Condenser-1 effluent NH_3, ppmv	36	36	36	63	63	63

The ProTreat ammonia destruction model predicts that ammonia concentration is higher leaving the thermal stage under oxygen enrichment than under air operations. This finding results from several factors:

(1) Although the Reaction Furnace runs hotter on oxygen, residence time for an overall hydraulic load equivalent to air operations is actually lower because of the higher temperature (lower actual gas density).
(2) While NH_3 destruction efficiency is comparable on oxygen, the lower concentration of inert gases from combustion air increases the concentrations of all the other species across the board.

Sulfur recovery efficiency is a competition between the Claus reaction and the COS formation tendency in the thermal stage and destruction efficiency in the catalytic stages. The minimum recovery efficiency on air-only operations and maximum recovery efficiency on oxygen-enriched operations at 350 Btu/hr-ft^2-°F steam-side coefficient are a reflection of this competition.

Weaknesses of Less Rigorous Models

The study to this point has focused upon the reaction kinetics rate-based heat transfer model in ProTreat. So the natural question most engineers will ask is "What do less rigorous models predict in these two circumstances (air vs. O_2 operations)?" A sensitivity analysis was run using ProTreat on the most severe oxygen-enriched operating case with 150 Btu/hr-ft^2-F steam side heat transfer coefficient. Table 4 summarizes the results.

Table 4: Key Process Prediction Differences using Less Rigorous Modeling Methods (30% O2 at 150 Btu/hr-ft^2-F steam side HTC)

Parameter	Kinetics Rate-Model	Equilibrium Furnace	Lumped Reaction Method	Freeze-Quench Method
Enriched air flow, lbmol/hr	698.3	603.5	698.3	698
Furnace Temperature, °F	2681	2510	2902	2680
WHB Outlet, °F	664	648	658.5	N/A
WHB Duty, MMBtu/hr	30.2	25.8	30.3	30.2
Peak wall temperature, °F	783	736	796	N/A
Peak heat flux, Btu/hr-ft^2-°F	48,200	41,800	50,000	N/A
H_2 in tail gas, mole% (wet)	2.70	8.7	2.70	2.70
Sulfur recovery, %	97.57	98.05	97.58	97.62

Using a thermodynamic **equilibrium-based** furnace without taking into account recombination under-predicts the air demand to the unit by a stunning 15%. The model also over-predicts unrecovered sulfur by 20%, and results in gross over-prediction of hydrogen production by a ***factor*** of 3.7. None of the equilibrium results reflect anything like what can be expected in a real operating plant.

Assuming that the same hydrogen and COS production predicted by ProTreat's rate model both occur, **but in the Reaction Furnace itself versus the WHB**, results in the Reaction Furnace temperature being grossly over-predicted by 220°F (2902°F vs. 2681°F). This is a common problem with most commercial sulphur simulation packages in the authors' experience. Because the temperature prediction in the Reaction Furnace is wrong to begin with, software using this reaction lumping approach will often require multiple regression models to predict the thermal section performance. The engineer then has to decide which regression model to choose from, and the answer is not always clear when process conditions overlap regression boundaries.

The freeze-quench method works to capture the hydrogen make, combustion air demand, and sulfur recovery, but only for the one set of equilibration temperatures that that is assumed for tuning the model. Because the Reaction Furnace temperature is feigned by the assumption of equilibrium, there is no **true** temperature to represent the real process stream entering the WHB, so the Waste Heat Boiler simply cannot be rated rigorously. There is nothing predictive about this sort of approach. Again, the engineer is forced to use their judgment as to how far away from the tuning point or rule-of-thumb the results can be applied.

A final test (not shown in Table 4) was conducted to ignore radiation in the WHB. The predicted outlet temperature would be about 20°F higher for the exchanger rating conducted in this manner.

CONCLUSIONS

The real plant performance of a Waste Heat Boiler depends upon many factors besides just heat transfer. When the chemistry of the recombination reactions is properly handled by the model as reaction kinetics-based, new insights into the performance of the WHB and the Claus unit can be gleaned. We have demonstrated, quantitatively, that corrosion beyond the ferrule outlet can become quite high, and it is highly sensitive to the steam-side heat transfer characteristics. Corrosion is excruciatingly costly when it results in tube failure and WHB downtime to retube the boiler with concomitant loss of production. The rate-based model used in this work demonstrates the importance of water-side hygiene — keeping fouling down is important under normal air operations, especially under oxygen-enriched operations to maintain reasonable boiler tube life.

Another important conclusion is that the true Reaction Furnace temperature on oxygen enrichment is considerably lower (220°F) than is predicted by many models that lump the recombination reactions into the Reaction Furnace effluent stream. Furnace temperature measuring devices have received a bad rap over the years because they almost invariably read lower than most models predict. Some of this thumping may be undeserved. The ProTreat approach to modeling eliminates the need to use lumped parameter empirical models to fit different operating modes such as oxygen-enrichment.

Finally, equilibrium-based furnace model predictions were demonstrated to not reflect many important aspects of the Claus unit performance. Air demand to the unit was under-predicted by nearly 15%. Unrecovered sulfur was missed by 20%, and hydrogen production was over-predicted by a factor of 3.7.

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