New insights into Claus waste heat boilers

The real plant performance of a waste heat boiler depends on many factors besides heat transfer

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The Claus waste heat boiler (WHB) is a critical piece of equipment in the sulphur recovery unit (SRU). As processors move towards higher sulphur feedstocks, more load is placed on the SRU, and WHB failures are becoming more common. Higher failure rates have come at the very time when uptime metrics and environmental constraints have also become stricter.

A set of case studies is reported using a newly developed rate based heat transfer and chemical reaction model of the WHB which provides quantitative insights into several aspects of the WHB that affect SRU performance:

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

$$H_2 + ½ S_2 \rightleftharpoons H_2S$$
$$CO + ½ S_2 \rightleftharpoons COS$$

These reactions not only influence sulphur recovery, air demand, and hydrogen production in the SRU, but they also affect 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 them tends to increase heat flux near the critical tube to tubesheet joint.

- Radiation affects heat transfer, primarily towards the inlet of the WHB.
- Radiative heat transfer, coupled 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, heat flux, and corrosion rate predictions from the model are examined down the length of the tubes for an oxygen enriched and air only sulphur 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 sulphidic corrosion and the resulting impact on boiler tube life and sulphur plant reliability are examined with this new information.

Figure 1 Waste heat boiler (*courtesy of Schmidtsche Schack, Düsseldorf*)

Background

The WHB (see **Figure 1**) is arguably the most fragile part of an SRU and is subject to sudden and very costly failure. The most common failure point is the tube to tubesheet joint where 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 (see **Figure 2**) inserted a short distance into the tubes and which usually also completely cover the face of the tubesheet (see **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. Sulphur is not usually condensed in the WHB except at turndown conditions.

As heat is removed in the WHB, a number of interesting reactions take place (see **Equations 1-4**). The S_2 vapour allotrope is exothermally converted into the S_6 and S_8 forms as the gas is cooled (see **Equations 1** and **2**). Reactions of at least equal importance involve hydrogen

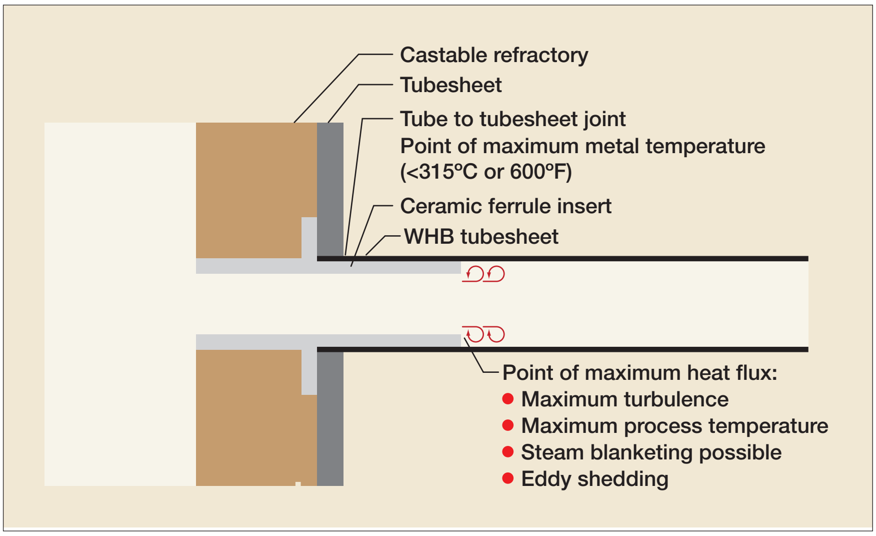

Figure 2 Thermal protection by ceramic ferrules

recombination with S_2 vapour (see **Equation 3**) and COS formation from carbon monoxide and S_2 vapour (see **Equation 4**). These reactions are also exothermic and take place primarily at the WHB's front end.[1-5]

$$3S_2 \rightleftharpoons S_6 + heat \quad (1)$$
$$4S_2 \rightleftharpoons S_8 + heat \quad (2)$$
$$2H_2 + S_2 \rightleftharpoons 2H_2S + heat \quad (3)$$
$$2CO + S_2 \rightleftharpoons 2COS + heat \quad (4)$$

Because of the high inlet temperature of the process gas, radiation also plays a significant role in heat transfer in the WHB. This is quite unlike the heat exchangers further downstream.

Approaches to recombination modelling

The recombination reactions can generate significant heat near the front of the WHB (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 is at equilibrium
- Lump these reactions into the reaction furnace effluent
- 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 SulphurPro simulator, this approach is now available.

The SulphurPro simulator uses a first principles, rate based model that incorporates the effects of

- Reaction kinetics
- Rigorous heat transfer (including temperature, composition, and geometry dependent radiation)
- 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 all considered together to provide a consistent and powerfully predictive modelling tool. The set of equations governing the WHB, including recombination reactions, is 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 greater numerical resolution.

Reaction kinetics modelled in SulphurPro are based on work whose original purpose was exploration of the two main recombination reactions that occur in the WHB, and in which Arrhenius kinetics parameters were tuned to match sets of experimental, pilot, and full-scale SRU data. Implementation of kinetics in SulphurPro are consistent with the ProTreat simulator's thermodynamics, with additional refinements made to match internal sets of plant data for both normal operations and off-spec conditions in real operating sulphur plants. All other transport coefficients and physical properties are calculated from proprietary or well-established literature correlations. Case studies will illustrate the importance and relevance of these reactions.

Case studies

The case studies are based on the flowsheet in **Figure 4**. Because WHB failures have tended to be more common during the harsher conditions of oxygen enrichment, the basis plant selected for study was

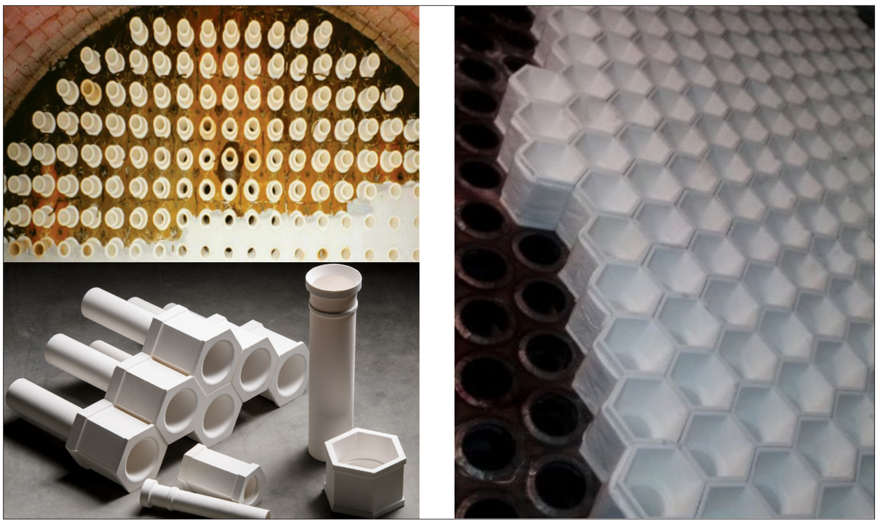

Figure 3 Types of ceramic ferrules, installed view: **(a)** Conventional ferrules before final refractory installation; **(b)** Hex-head ferrules (*courtesy of Blasch Precision Ceramics*)

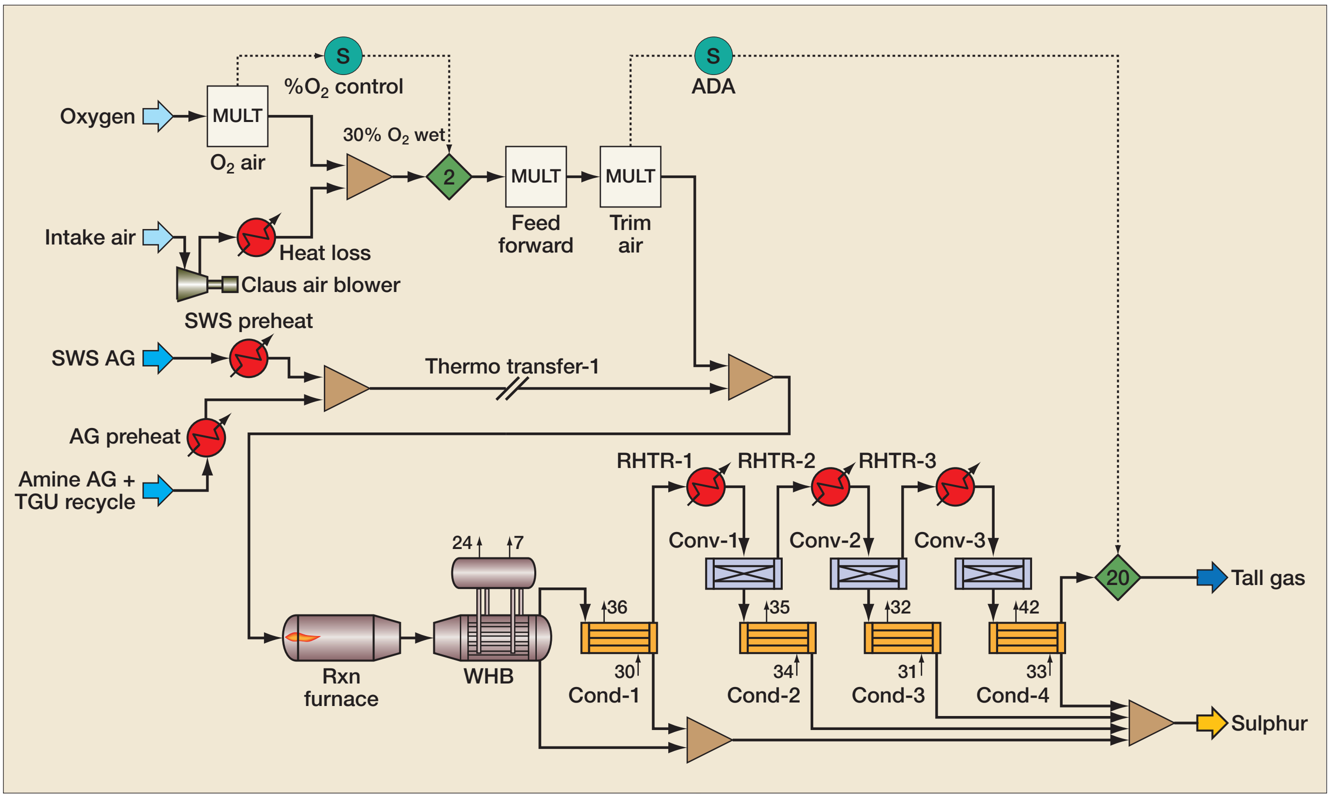

Figure 4 Flowsheet for case study

designed originally for approximately 100 lt/d (101.6 mt/d) sulphur on air operations, but that was to be revamped using low level oxygen enrichment (to 30% O_2 wet basis) in order to gain 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 shows the WHB tube configuration chosen for rating. Failures above mass velocities of 5.0 lb/ ft²·s (24 kg/m²·s) have been reported to be more common,[5] so a design was chosen that would operate at just under this mass velocity on air operations. A range of utility side heat transfer coefficients from the literature[6] was chosen for the sensitivity study to encompass expected ranges to represent operating over a range from poor to good utility side circulation.

Table 2 summarises the results of the study specifically for the boiler rating. Quite profound differences between the air and oxygen enriched operations can be seen. The inlet temperature from the reaction furnace climbs from 2360°F (1293°C) on air operations to nominally 2680°F (1471°C) on oxygen. Peak boiler tube wall temperatures and heat fluxes also elevate substantially on oxygen compared to air. Sulphidic 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 percentage H_2S and wall temperature. Expected corrosion rates under oxygen operations are about twice those for air only. 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 the effect of eddies that typically amplify heat flux at the ferrule outlet.

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 water circulation is poor near the tube inlet (150 Btu/h·ft²·°F case), then corrosion rates well above 10 mil/year can be expected

WHB configuration and parameters

Number of tubes	120
Tube OD/ID, inches	2/1.783
Tube length, ft	32
Steam generation pressure, psig	350
BFW temperature, °F	280
Mass velocity, lb/ft²·s	4.45/4.9
Inside tube wall emissivity	0.9
Fouling resistances, process/ steam sides, h·ft²·°F/Btu	0.008/0.002
Steam side HTC range, Btu/h·ft²°F	150 to 500

Table 1

WHB rating results

Parameter		Air only			30% O_2	
Steam side HTC, Btu/h·ft²·°F	150	350	500	150	350	500
% H_2S in/out		4.4/7.0			4.0/10.0	
Temperature in/out, °F	2361/598	2359/577	2358/572	2681/664	2678/631	2677/623
Mass velocity, lb·ft²·s (inlet)		4.45			4.9	
Max tube wall temp, °F	706	602	576	783	651	621
Max heat flux, Btu/h·ft²	37,400	39,900	40,500	48,200	51,900	52,700
Corrosion rate in/out, m/y	13/4.7	4.5/3.8	3.4/3.5	27/10	7.4/7.3	5.4/6.7

Table 2

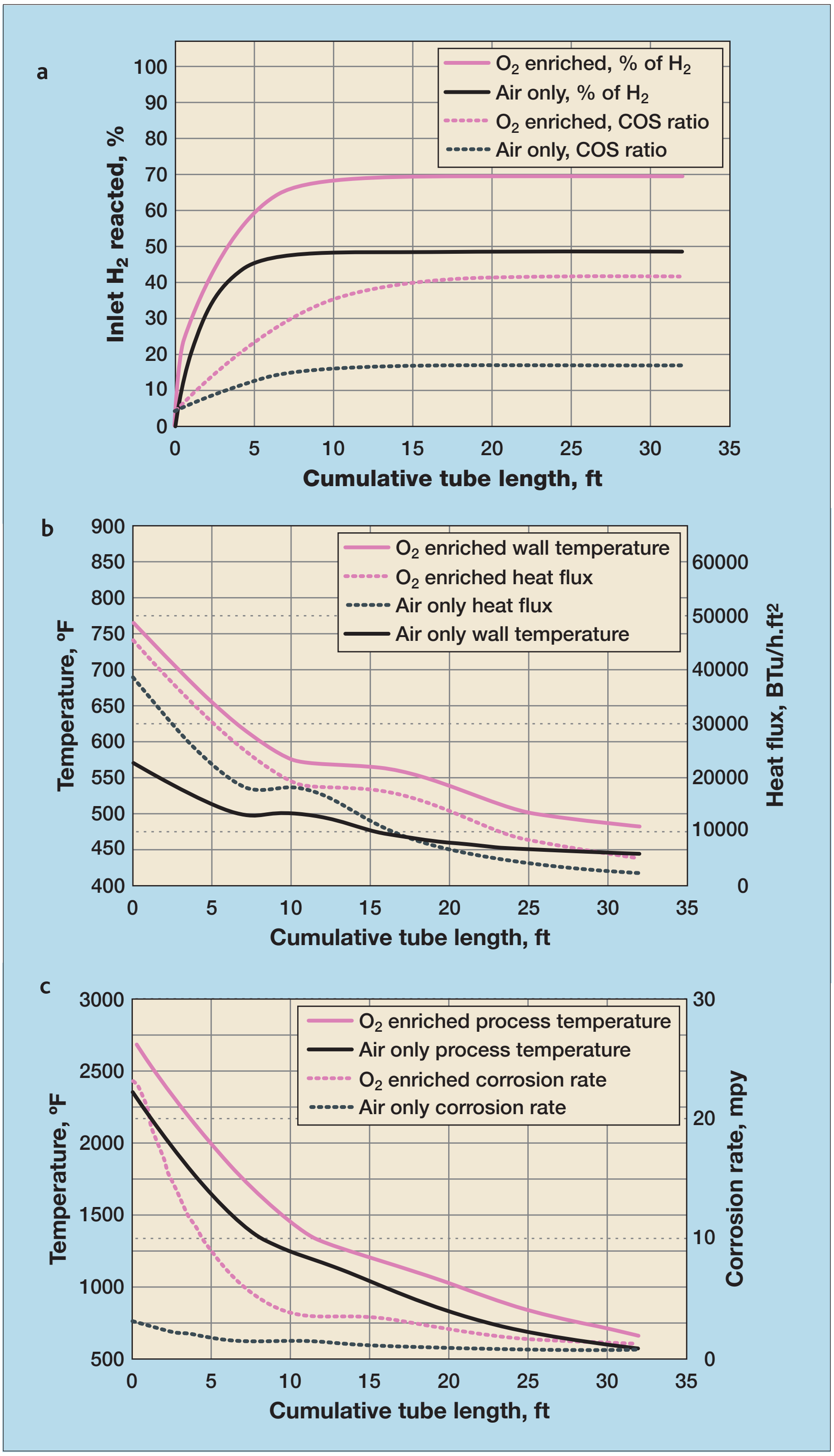

Figure 5 How process metrics change with distance along WHB tubes
(a) H_2 and COS vs cumulative length; **(b)** Tube wall temperature and heat flux vs length; **(c)** Process temperature and corrosion rate vs length

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/h·ft², which in the authors' experience can be a red flag for reliability. A CFD study of this boiler plus water side modelling would be wise.

Figure 5 shows sample plots of several parameters as a function of cumulative tube length. The lines for air only operations assume a steam side heat transfer coefficient of 500 Btu/h·ft²·°F while the lines for 30% O_2 operations assume a value of 150 Btu/h·ft²·°F for the steam side heat transfer coefficient. These 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).

A number of interesting observations follow from **Figure 5**. First, the hydrogen and COS reactions are finished in the first 5-10ft 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 (~6in). 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 10ft along the tube length. Looking further at the bottom plots, the process temperatures are in the range where sulphur species begin shifting from S_2 vapour to S_6 and S_8 vapour (1200-1400°F, 649-760°C).

Process performance considerations

Table 3 outlines key process performance predictions from the rating study for the entire sulphur plant. Hydrogen in the Claus tail gas is a weakly increasing function of the assumed steam side heat transfer coefficient. Both hydrogen make in the Claus unit and COS production are higher under oxygen operations. In general, sulphur 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.

The SulphurPro ammonia destruction model predicts that ammonia concentration is higher leaving the thermal stage under oxygen enrichment than under air operations. This counter-intuitive finding results from two 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.

Sulphur recovery efficiency is a competition between the Claus reaction and tendency to COS formation in the thermal stage and efficiency of destruction in the catalytic stages. The minimum recovery efficiency on air only operations and maximum recovery efficiency on oxygen enriched operations at 350 Btu/h·ft²·°F steam side coefficient are a reflection of this competition.

Key process performance predictions

Parameter		Air only			30% O_2	
Steam side HTC (Btu/h·ft²·°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
Sulphur 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**			**63**	

Table 3

Weaknesses of less rigorous models

The study to this point has focused on the reaction kinetics rate based heat transfer model in SulphurPro. So the natural question most engineers will ask is: "What do less rigorous models predict in these two circumstances of air vs O_2 operations?" A sensitivity analysis was run using SulphurPro on the most severe oxygen enriched operating case with 150 Btu/h·ft²·°F steam side heat transfer coefficient. **Table 4** summarises the results.

Using a thermodynamic equilibrium based furnace without taking into account recombination underpredicts the air demand to the unit by a stunning 15%. The model also overpredicts unrecovered sulphur by 20%, and results in gross overprediction 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 SulphurPro's rate model both occur, but in the reaction furnace itself vs the WHB, results in the furnace temperature being overpredicted by 220°F (2902°F vs 2681°F). In the authors' experience, this is a common problem with most commercial sulphur simulation packages. Because the temperature prediction in the 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 select, a choice that is often unclear when process conditions overlap regression boundaries.

The freeze quench method works to capture the hydrogen make, combustion air demand, and sulphur recovery, but only for the one set of equilibration temperatures that is assumed for tuning the model. Because the reaction furnace temperature is contrived by the assumption of equilibrium, there is no true temperature to represent the real process stream entering the WHB, so the WHB simply cannot be rated rigorously. There is nothing predictive about this sort of approach. Again, the engineer is forced to use judgment as to how far away from the tuning point or rule of thumb the results can be safely 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 WHB depends on many factors besides 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 Claus unit downtime to re-tube the

Differences using less rigorous models (30% O_2 at 150 Btu/h.ft².°F steam side HTC)

Parameter	Kinetics rate model	Equilibrium furnace	Lumped reaction method	Freeze quench method
Enriched air flow, lbmol/h	698.3	603.5	698.3	698
Furnace temperature, °F	2681	2510	2902	2680
WHB outlet, °F	664	648	658.5	664 (spec'd)
WHB duty, MMBtu/h	30.2	25.8	30.3	30.2
Peak wall temperature, °F	783	736	796	N/A
Peak heat flux, Btu/h·ft²·°F	48,200	41,800	50,000	N/A
H_2 in tail gas, mole% (wet)	2.70	8.7	2.70	2.70
Sulphur recovery, %	97.57	98.05	97.58	97.62

Table 4

boiler with concomitant loss of production. SulphurPro's rate based model used here demonstrates the importance of water side hygiene – to maintain reasonable boiler tube life, keeping fouling in check is important under normal air operations, and even more so under oxygen enriched conditions.

A further 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 furnace effluent stream. Furnace temperature measuring devices have acquired a bad reputation over the years because they almost invariably read lower than most models predict. Some of this thumping may be undeserved. The SulphurPro approach to modelling completely eliminates the need to use lumped parameter empirical models to fit different operating modes such as oxygen enrichment.

Finally, equilibrium based furnace model predictions have been demonstrated not to reflect many important aspects of Claus unit performance. Air demand to the unit was underpredicted by nearly 15%. Unrecovered sulphur was missed by 20%, and hydrogen production was overpredicted by a factor of 3.7.

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