

Simulation of Claus unit performance

Simulating a sulphur recovery unit using a fundamental approach enables the effects of process changes on a host of performance metrics to be reliably assessed

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Whether at the level of an individual piece of equipment or an entire plant, optimisation is usually done using simulation tools. The first step, however, is to verify that the tools chosen are able to reproduce the measured performance of the unit under its present operating conditions. This article benchmarks the SulphurPro SRU simulator against the measured performance of a sulphur recovery unit (SRU) processing an ammonia-rich acid gas in which a significant concentration of COS is formed and recycled back to the reaction furnace. Combustion air is oxygen enriched and, at just over 6 mol%, the ammonia content of the combined acid gas stream, amine acid gas (AAG) plus sour water acid gas (SWAG), is greater than the CO₂ content. This provides a fairly stringent test of a model that relies on fundamental chemical reaction kinetics and heat transfer rate calculations to predict performance, rather than one that uses curve fits to forecast performance by looking in retrospect at how similar plants have performed in the past.

The discussion begins with the case study of a refinery SRU producing about 125 t/d of sulphur from 3.4 MMscfd of AAG with 91% H₂S plus 6.8% CO₂, balance nitrogen on a dry basis comingled with a sour water acid gas flow of 0.6 MMscfd that is 45 mol% H₂S and 55 mol% ammonia. This forms the base case. Simulation includes SRU feed gas preparation, the main body of the SRU itself, and the treatment of the effluent gas from the last sulphur condenser through the final burner, the hydrogenation reactor, and the quench tower. In other

Comparison between simulation and measured data: base case			
Parameter measured	Measured	Simulated	% Deviation
Enriched air + O ₂ flow, mscfh	284.4	267.4	-6.0
Enriched air O ₂ content, dry mol%	28.5	28.4	-0.35
Reaction furnace outlet temperature, °F	2300	2385	3.7
WHB feed water temperature, °F	280	280.0	0
WHB steam production flow, lb/h	32 000	30 398	-5.0
WHB process side outlet temperature, °F	512	510.9	0.2
Condenser-1 steam production flow, lb/h	3042	2871	-5.6
Condenser-1 process side outlet temperature, °F	329	325.6	-1.03
Converter-1 outlet temperature, °F	602	604.1	0.35
Condenser-2 steam production flow, lb/h	3138	2911	-7.24
Condenser-2 process side outlet temperature, °F	332	332.06	0.02
Converter-2 outlet temperature, °F	471	472.3	0.27
Condenser-3 steam production flow, lb/h	1409	1467	4.09
Condenser-3 process side outlet temperature, °F	317	312.3	-1.5
Converter-3 outlet temperature, °F	412	409.2	-0.7
Condenser-4 process side outlet temperature, °F	261	260.6	-0.2
H ₂ S content in Condenser-4 vapour outlet, mol%*	0.49	0.54	9.96
SO ₂ content in Condenser-4 vapour outlet, mol%*	0.26	0.27	3.55
TGTU air flow for RGG burner, mscfh	31.7	30.2	-4.7
Natural gas flow for RGG burner, mscfh	3.3	3.1	-4.7
Tempering steam flow for RGG burner, lb/h	164	156	-4.6
Hydrogen make-up for hydrogenation reactor, mscfh	7.4	7.6	3.3
Hydrogenation reactor inlet temperature, °F	570	562.0	-1.4
Hydrogenation reactor outlet temperature, °F	603	614.7	1.9
Quench tower vapour overhead temperature, °F	85	86.4	1.7

*Measured ratio is 1.88, forced to 2.00 in the simulation

Table 1

words, the SRU from introduction of AAG, SWAG, air, and enriching oxygen through to the point of entry of the tail gas into the tail gas treating unit (TGTU). The TGTU was not part of the study so it was not simulated; however, it could have been completely integrated into the SRU model in a single flowsheet and simulated on a mass transfer rate basis with recycle of the recovered H₂S back to the start of the SRU.

Base case

Figure 1 shows the flowsheet for the base case. Pure oxygen is used to enrich the oxygen content of the intake air to 28.5%. The total combined (enriched air) flow is adjusted

using the solver block marked ADA (air demand analyser) to ensure the total air flow rate from the flow multiplier (marked MULT) in the figure results in a H₂S to SO₂ molar ratio of 1.9 in the gas leaving the final sulphur condenser.

The purpose of this article is to use simulation to quantify the effect of oxygen enrichment on the sulphur processing capacity of the plant, and in the same processing show unit how sensitive such parameters as SRU throughput, ammonia destruction, and WHB performance parameters are to the level of oxygen enrichment. To this end, an additional computational (solver) loop was added to the flow-

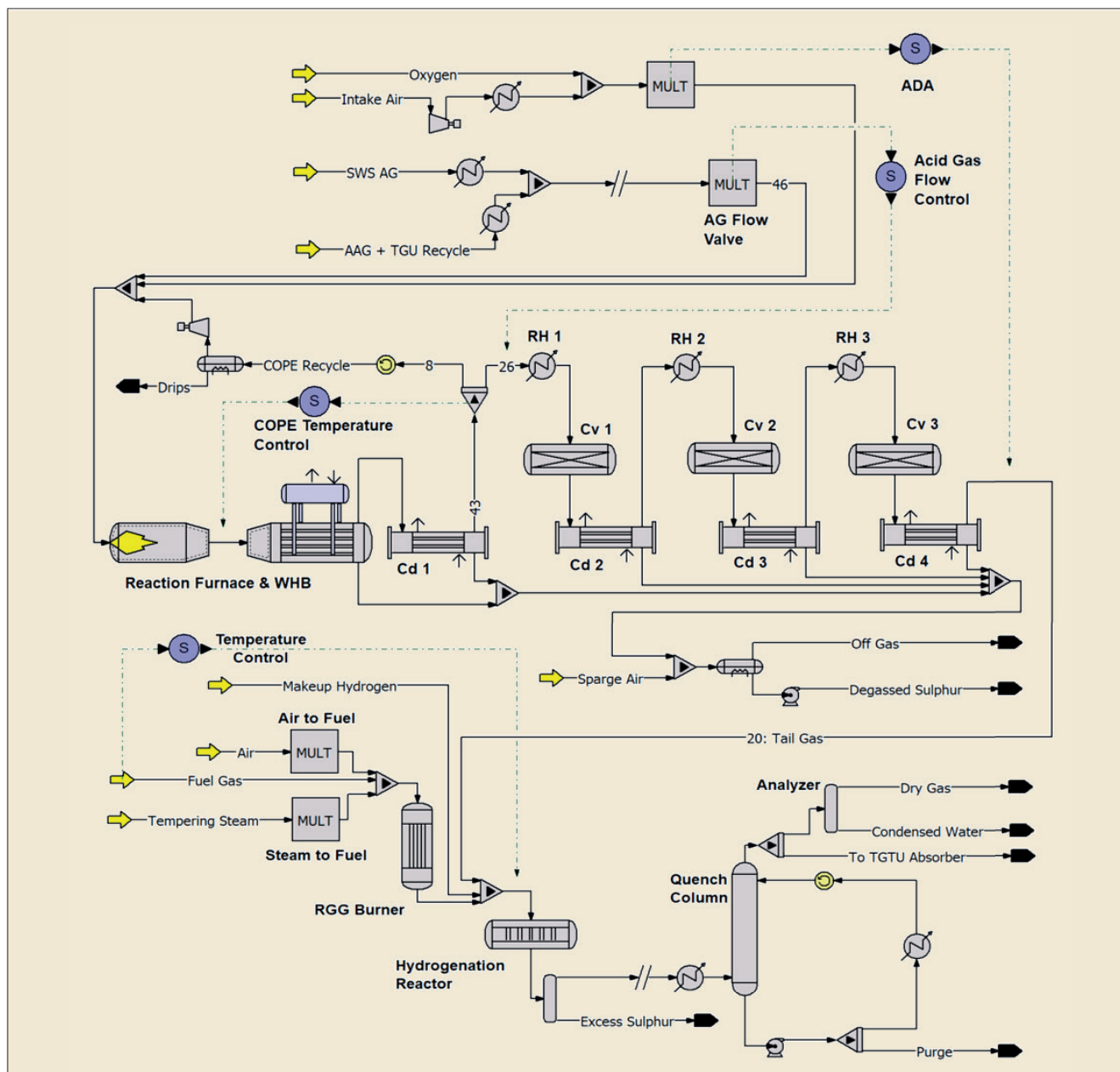


Figure 1 Refinery SRU with partial TGTU flowsheet

sheet in order to calculate the plant feed sulphur flow necessary to have the same total molar flow rate of gas from the first condenser into the converter (Stream 26 in Figure 1). The flow rate of this stream is taken to represent the SRU's gas handling capacity, as discussed more fully below. For the base case study, however, this solver block was left disabled, and the gas flow calculated from the first condenser (but with the COPE recycle removed) formed the capacity basis for other levels of oxygen enrichment.

To ensure simulator credibility, the first task was to compare simulated versus measured performance indicators. Table 1 shows the rela-

tive percentage deviation of simulated results from measured data for some 25 of the parameters for which measurements were made. Every parameter is predicted within a few percent of measured levels.

The SulphurPro simulator can also provide a little more detailed picture of the operation of the catalytic converters by breaking the reactors into a number of discrete incremental depths of catalyst bed in order to assess temperature and conversion profiles across the beds. This can be done in both design and rating modes. SulphurPro allows the catalyst beds to have varying levels of activity relative to the fresh catalyst.

Figure 2 shows temperature profiles across the catalyst beds in the three converters. Points are the average of two thermocouple readings at opposite ends of a bed diameter. Converters-2 and -3 were simulated as having fresh catalyst beds. When Converter-1 was simulated this way, it was obvious that the catalyst was to some degree aged or deactivated. When simulated as just under 60% deactivated, the solid black line was obtained, so in an overall sense the bed does indeed appear to have a little over half of its original activity remaining.

It is interesting to note that, as measured, the temperature profile in the first converter actually

has two rather flat sections joined by a rapid transition from one to the other. This is a classic profile of what one would expect for a catalyst being poisoned by a contaminant in the feed. However, the contaminant, whatever it is, seems to be readily adsorbed onto the catalyst and deactivation will move through the converter's catalyst bed like a wave. Possible contaminants (poisons) might include BTEX components or even the soot formed from their decomposition.

SulphurPro gives a faithful rendition of what was actually observed in the operating unit; therefore, one can only conclude that at least in this instance it is a reliable model. It is important to emphasise that model calculations are pure predictions done completely without tuning of any kind. The basis for the predictions is fundamental laboratory measurements of chemical reaction kinetics combined with well-founded models for heat transfer. There is no direct reliance on tuning any parameters to plant performance

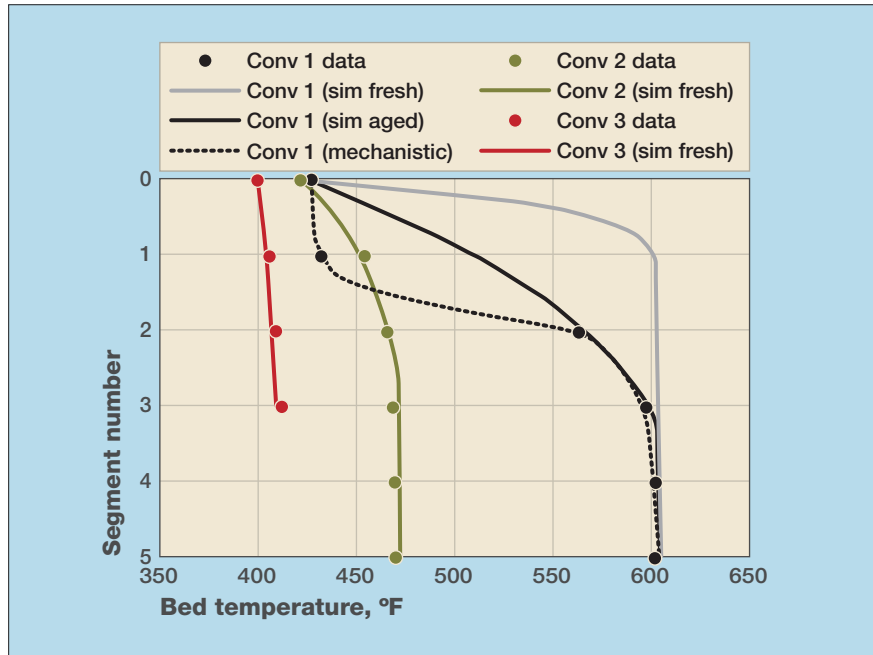


Figure 2 Calculated (solid lines) versus temperatures measured at stations every X feet through the catalyst beds in the three converters

data; thus, SulphurPro is solidly placed to predict the performance of individual units and the SRU as a whole, both robustly and with good accuracy.

Effect of air enrichment on performance

The base case already discussed used 28.5% oxygen in the enriched air. The objective now is to deter-

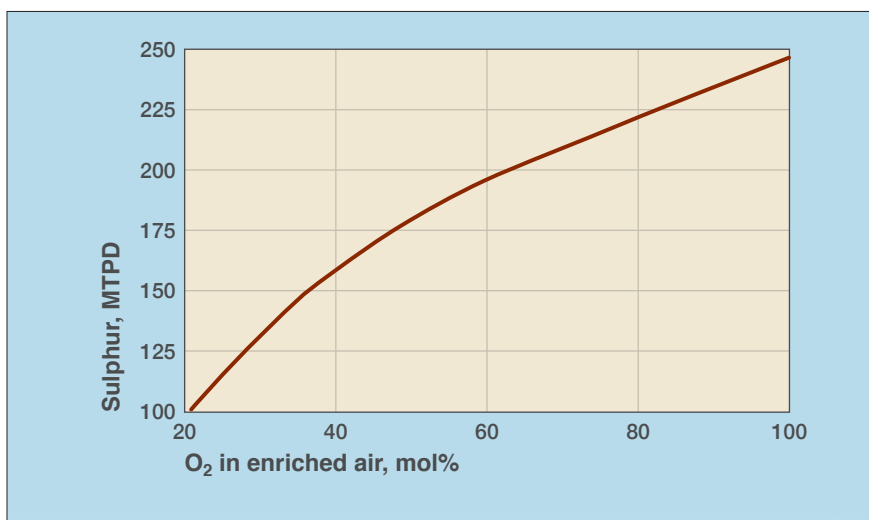


Figure 3 How oxygen enrichment of combustion air affects sulphur production

mine exactly how enrichment affects several key performance parameters in the as-built plant. Including the base case, six enrichment levels were considered: air containing 21%, 28.5%, 40%, 60%, 80%, and 100% O₂. It should be understood that this is not a design study; rather, the SRU under all the conditions being studied must operate within the constraints of the existing equipment and flowsheet configuration without modifications.

There are several solver blocks that could be used in the flowsheet solution process for this study. A solver block in SulphurPro is intended to determine the value of a parameter within an operating block needed to achieve a specified value of a specified parameter in a certain stream:

- The function of the solver labelled ADA is to calculate the

total enriched air flow to the reaction furnace needed to maintain the H₂S:SO₂ ratio of about two in the vapour from the final condenser (Stream 20).

- Another solver (acid gas flow control) could be used to calculate the total flow rate of sulphur-bearing gas into the SRU (Stream 46) corresponding to a given total flow rate of gas from the first condenser and into the converter/condenser bank (Stream 26). If no COPE recycle is needed (corresponding to zero to low enrichment), the gas flow from the first condenser (Stream 43) is often taken as a fair measure of the SRU's gas handling capacity. However, if higher levels of enrichment are contemplated, COPE recycle is necessary to keep the reaction furnace outlet temperature below the thermal limits of the furnace refractory.

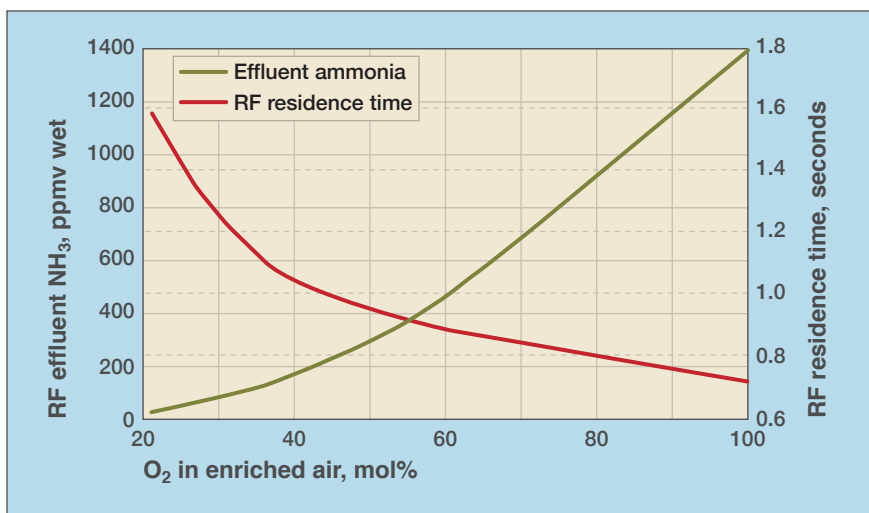


Figure 4 Effect of oxygen enrichment on residence time in the reaction furnace and the resulting ammonia concentration in reaction furnace effluent

If one is interested in high levels of oxygen enrichment, the gas flow in Stream 26 is the practical measure of capacity. Thus, acid gas flow control would ensure the SRU is fed with the right amount of gas to keep it at full capacity (Stream 26).

- With oxygen enriched air, furnace temperatures can become high enough to exceed the thermal limits of the furnace's refractory and of the material in the waste heat boiler, especially with regard to corrosion. In the original case, 28.5% enriched air resulted in a simulated furnace effluent temperature of about 2400°F (1316°C). For each subsequent case in this study, the solver block COPE recycle could be set up to calculate the recycle gas flow by solving for the split of first-condenser gas between the COPE recycle (Stream 8) and the feed to the first reheater (Stream 26) necessary to keep the reaction furnace effluent at 2400°F.

Thus, the study was carried out by using the ADA solver to keep the H₂S to SO₂ ratio close to two, by keeping the plant's total gas throughput into the converter system constant, and by holding the furnace effluent temperature to 2400°F (which was roughly the simulated temperature of the reaction furnace in the base case) through adjusting the COPE recycle gas flow (Stream 8). This particular exercise was not to determine how to optimise each level of oxygen enrichment, but rather simply to compare each case on an apples-to-apples basis.

As expected, the SRU's acid gas processing capacity increases quite rapidly with enrichment level (see Figure 3). In principle at least, using pure oxygen instead of air can increase SRU capacity by nearly 250% in the case being considered here. However, there are other factors that must be taken into consideration that will limit the real potential of enrichment, and that will require adjustments to be made to at least partially overcome them. One of the most important ones is the effect of increased throughput (reduced residence time in the reaction furnace) on ammonia destruction.

In this case study, the gas being processed consists of a mixture of

AAG and SWAG. SWAG almost always contains a substantial ammonia concentration, 55% NH_3 in this example. The mixed feed is 6.65% ammonia on a dry basis. An often quoted guideline is that the reaction furnace effluent should be below 150 ppmv ammonia. As **Figure 4** shows, however, the NH_3 level can be 10 times higher than the recommended maximum when very high levels of oxygen enrichment are used and the reaction furnace outlet is kept at 2400°F. The problem with high ammonia levels is the propensity for ammonia to form ammonium salts in downstream equipment, most especially in sulphur condensers towards the end of the converter/condenser sequence. Ammonium salts cause increased pressure drop, which reduces plant throughput and eventually (maybe quite quickly) plugging of lines, and necessitating plant shutdown to clear.

For this particular case, since the SRU is an existing plant and equipment sizes are set, there are limited techniques to increase the ammonia

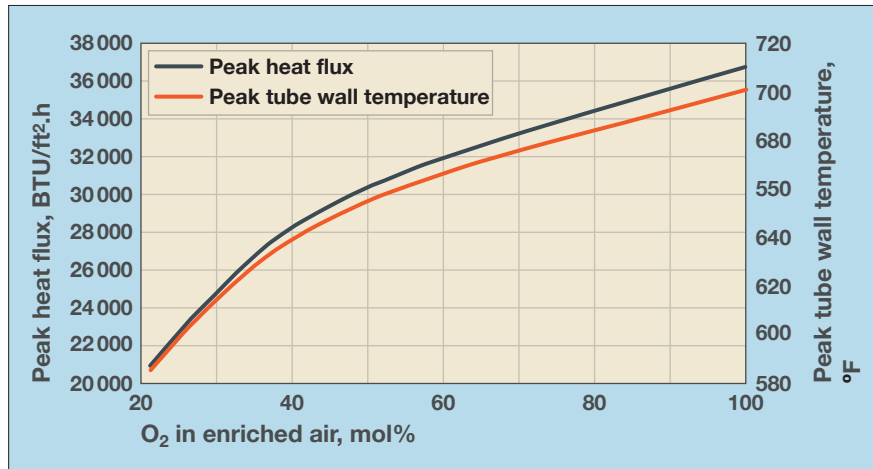


Figure 5 Effect of oxygen enrichment on peak heat flux and temperature in the waste heat boiler

destruction in the reaction furnace. Ammonia destruction is determined by reaction kinetics driven by three primary factors: the temperature within the reaction furnace, the residence time in the reaction furnace (also shown in **Figure 4**), and the mixing characteristics of the burner being used.

It is important to note that with high levels of oxygen enrichment,

special high efficiency burners from a reputable supplier are essential to ensure the reliability and operability of the SRU. Since the volume of the reaction furnace is set by the existing equipment, the residence time is determined by the flow rate through the furnace. One way to increase ammonia destruction would be to allow the reaction furnace to operate at a higher temperature. This

would mean reducing the amount of gas recycled from the first condenser and would subsequently require the throughput of acid gas to the SRU to be decreased in order to keep the hydraulic load at or below the plant's capacity. Because the residence time is determined by the flow rate of gas through the reaction furnace, reducing the throughput to allow for higher reaction furnace temperatures would also increase the residence time in the reaction furnace, so this optimisation move would have two beneficial outcomes. However, monitoring this effect on the rest of the plant downstream, particularly the heat exchangers (WHB and Cd-1 to Cd-4), would be crucial to ensure the operability of the SRU.

The SulphurPro SRU simulator is based on fundamental reaction kinetics and on heat transfer as a rate process. To assess reliably the effect of a planned change in process conditions, a fundamentals based simulator that addresses all the nuances of process chemistry is superior to one that uses heuristics and curve fits, even if the fits are to a plethora of plant performance measurements.

Heat flux and tube wall temperatures in the waste heat boiler are always of great interest because the waste heat boiler is subject to catastrophic failure, especially from high temperatures in the vicinity of the tube to tube sheet joint with associated sulphidic corrosion. **Figure 5** shows that with a high level of enrichment, even with COPE recycle, the peak tube wall average temperature (at the tube sheet) in the waste heat boiler can escalate into a dangerous region, and the peak heat flux can rise to 175% of the unenriched condition. This is highly concerning because the actual peak tube wall temperature is directly linked to the sulphidic corrosion rate. Furthermore, as the level of oxygen enrichment increases and more of the diluent gas that makes up almost 80% of natural air is removed, the H₂S in the reaction furnace effluent concentrates. This concentrating of H₂S combined with increasing temperatures at the front end of the waste heat boiler tubes will drive the corrosion rate up by a factor of

10x at 100% oxygen over the base case. Although the peak heat flux is under the recommended limit where a departure from nucleate boiling to Leidenfrost type boiling occurs, an increase of this magnitude would require a closer look at the utilities system of the waste heat boiler and further computational fluid dynamic analysis to ensure this change would not push the equipment to the point of failure.

Summary

Increasing oxygen content in the combustion air to an SRU is a great way to dramatically increase the capacity of the plant to allow a higher volume of acid gas to be processed. This is accomplished by increasing the concentration of the reactant (oxygen) and reducing the amount of diluent gas (nitrogen) entering the plant. There are precautions that need to be taken when increasing the oxygen content, however. One of great impor-

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tance is the temperatures within the reaction furnace. Without a process like COPE, the concentration of oxygen is limited to only a small increase without requiring further temperature mitigation measures to be taken. This cut-off concentration of oxygen is not the same for every plant and is determined by a number of factors, one of which includes the acid gas quality (how much H₂S is in the feed gas entering the plant). Low quality acid gas (less than 30% H₂S) can have a much higher level of oxygen enrichment without the need for further mitigation measures than higher quality acid gas and is in fact one way to boost the temperatures within the reaction furnace when processing low qual-

ity gas. However, this is a topic for another discussion.

SRU simulation using a completely fundamental approach is a modern reality that allows the effect of process changes on a whole host of performance metrics to be reliably assessed. Heretofore, one had to rely exclusively on extrapolations (and interpolations) of measured performance data. SRU performance is hard to assess accurately and this in itself leads to simulation models that are heuristic and truly reliable only for the conditions on which the simulation tool is based. When the opposite approach is taken and real reaction kinetics are used in modeling, greatly improved reliability and simulation accuracy are the result. Predictions become based on what the science says, devoid of the errors inherent in making plant measurements. Interactions between variables are not ignored; instead, they are automatically accounted for, and detailed SRU performance is reliably predicted.

Reliable simulation is an excellent way to assess the possible consequences of a proposed process change before the change is actually made. Simulation reliability is critical because, when changes to process conditions are being contemplated, decisions with significant downside potential must be made. Our contention is that simulation based on measured reaction kinetics for all the reactions taking place in the SRU while also accounting for heat transfer rates in condensers and waste heat boilers is the best approach available.

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