The Seven Deadly Sins of Sulphur Recovery

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Introduction - The availability of information regarding the operation and optimization of Claus sulphur recovery units has increased significantly over the past years. For individuals involved in the day to day operation of the Claus unit, however, the sheer volume of information can often be overwhelming, and it is difficult to determine what is of direct importance to the plant performance.

This paper attempts to reduce the topic of sulphur plant optimization down to its basics. Viewed in this way, it can be seen that there are only seven key items that can reduce sulphur plant efficiency, the Seven Deadly Sins of Sulphur Recovery. Each of these seven sins is analyzed in detail, providing some indication of typical losses in each case based on test results obtained by Sulphur Experts. Additionally, "worst case" examples from Sulphur Experts' files showing the potential for efficiency losses in each of these cases are also presented. This paper can be used as a simple checklist by sulphur plant operators and engineers to determine the potential for efficiency losses in their own facilities, and conversely the potential for optimization of recovery efficiency.

The Starting Point - Ideal and Practicable Efficiencies

In order to show the effect of the Seven Deadly Sins on recovery efficiency, it is important to first establish the maximum capability of the Claus process. The ideal capability, which has been determined in the past using the Sulsim® simulation program and ideal operating conditions (Figure 1), represents the true maximum capability of the standard Claus process[1]. The ideal values presented in Figure 1 are not achievable on a regular basis, however, they do represent the true upper limit for the Claus process and should be considered as the goal of the sulphur plant operator.

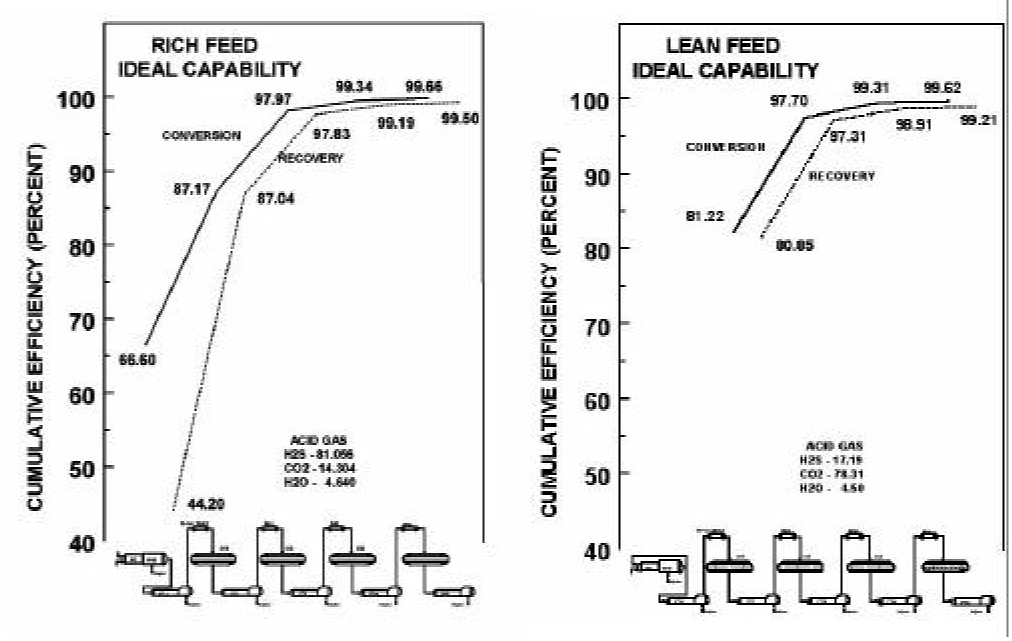
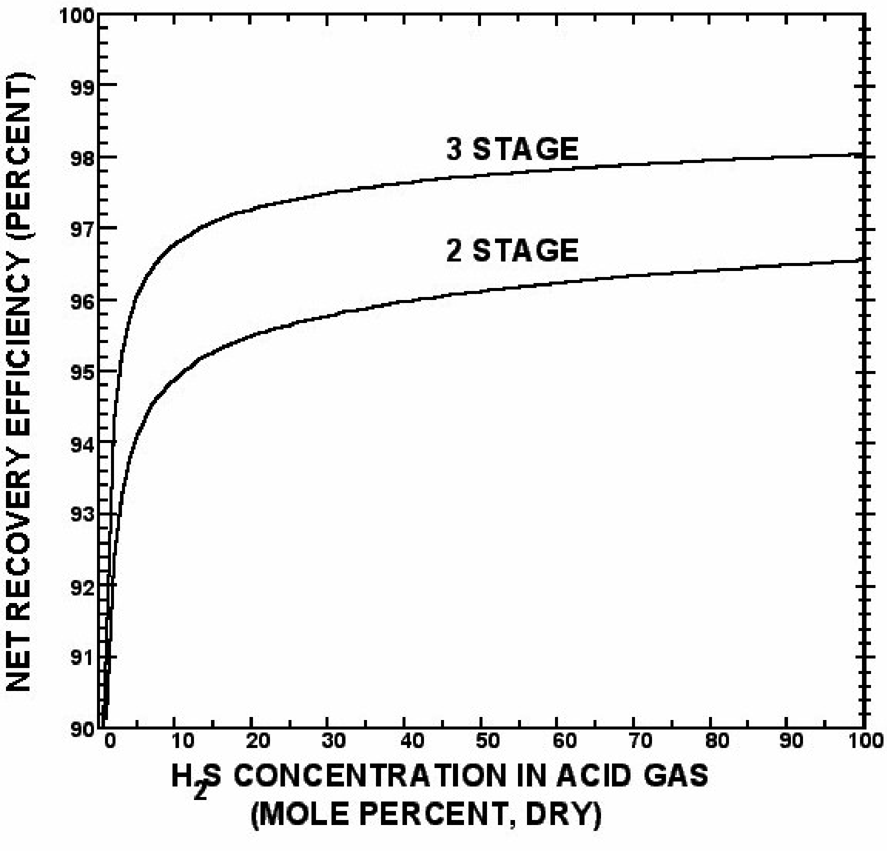


Figure 1: Ideal Capabilities

If the ideal capability represents the maximum efficiency for the sulphur plant, then the practicable capability (Figure 2) represents almost a minimum acceptable value since it allows both for typical efficiency losses (approximately 0.6 percent) plus additional losses due to poor operation or upset conditions (a further 0.6 percent). Unfortunately, these practicable efficiency curves have been misconstrued by designers, operators, and regulators, and are often misquoted to be maximum values. This has led to a certain degree of lethargy throughout the industry since plants achieving efficiencies at or near these practicable values are assumed to be optimized, and no further improvements are attempted.

Figure 2: Practical Recovery Efficiencies



Using these two curves as the baseline, the reasons why these ideal and practicable values are often not achieved are reviewed.

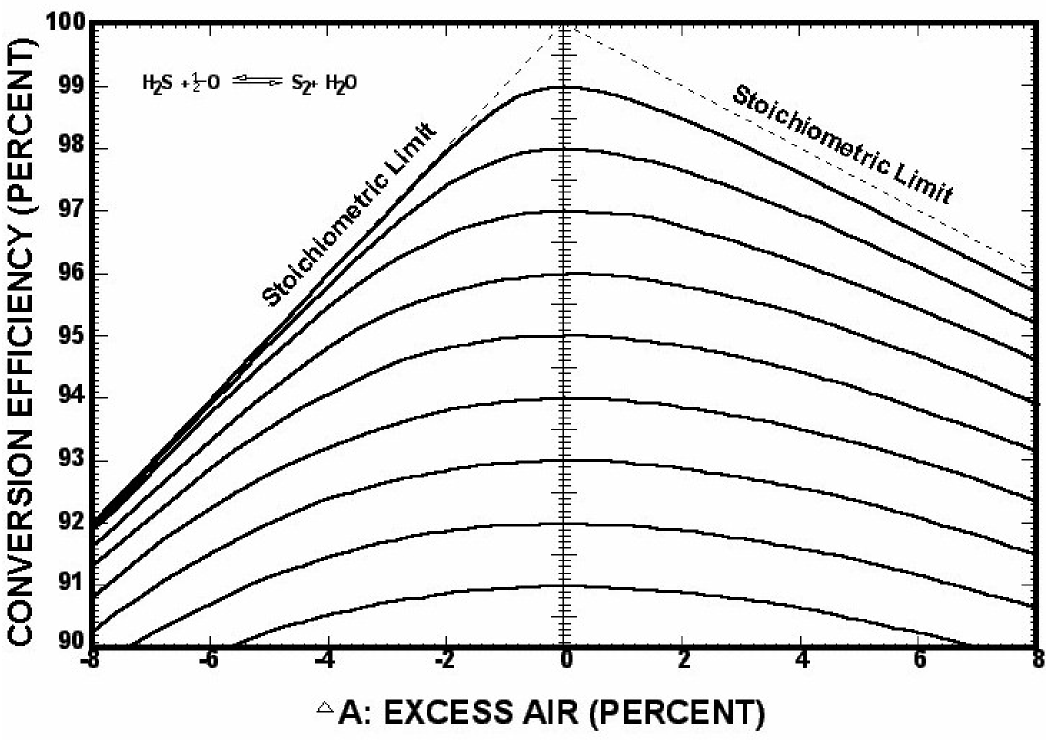
Sin # 1 - Poor Reaction Stoichiometry

The Claus process is a chemical process and exact control of the reaction stoichiometry is required in order to achieve maximum efficiencies.

$$3\ H_2S + 3/2\ O_2 \rightarrow SO_2 + 2\ H_2S + H_20 \rightleftarrows 3/x\ S_x + 2\ H_2O$$

The basic process chemistry appears simple but control of the process is complicated by a number of items including contaminants in the feed streams, varying feed composition and flow, side reactions in the furnace and catalyst beds, maintenance problems and inherent inaccuracies in the control instrumentation and logic. All of these items can be minimized or accounted for but never totally eliminated, and some deviation from perfect control is always encountered. Figure 3 quantifies the effect of these deviations, showing how recovery efficiency is affected as the actual air flow differs from the optimal value required to maintain the necessary Claus reaction stoichiometry.

Figure 3: Efficiency vs Air Demand



Test work has shown that, with relatively stable feed compositions and flows and properly operating feedback control of the combustion air flow, control of the excess air to within +/- 0.5 percent is generally achievable. This results in typical losses of 0.1 percent for a two stage plant and 0.2 percent for a three stage plant.

Unstable feeds and poor or non-existent control can result in significant losses. Figure 4 shows test data from sulphur plant tests at 27 European refineries[2], and indicates losses of 10 to 20 percent due to poor stoichiometry control in the worst cases.

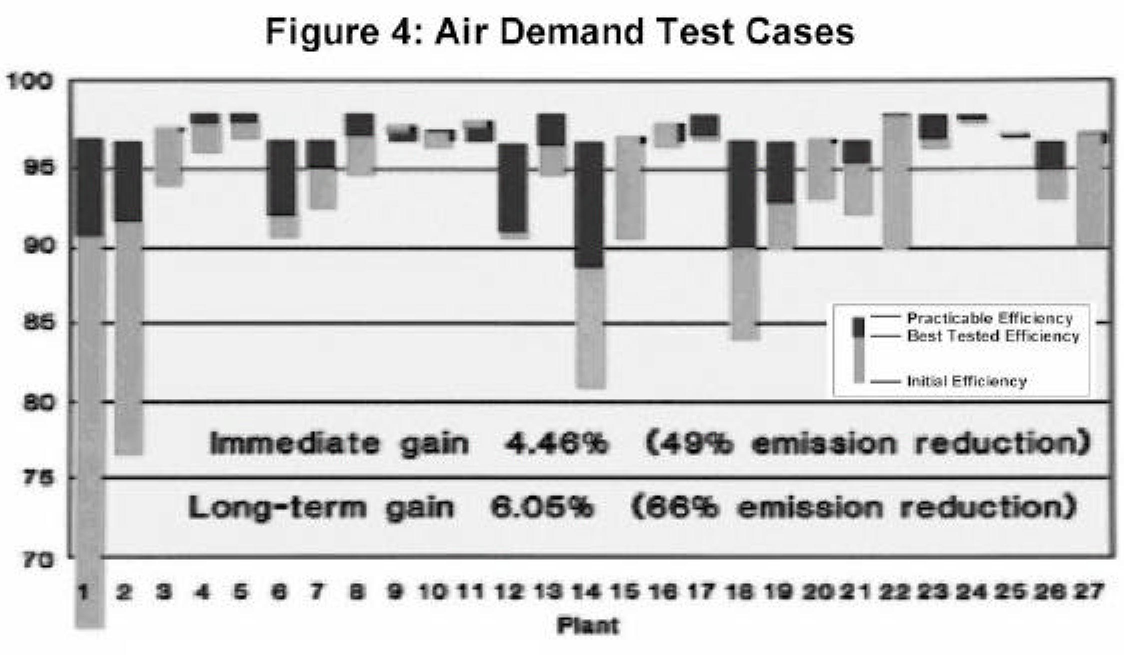


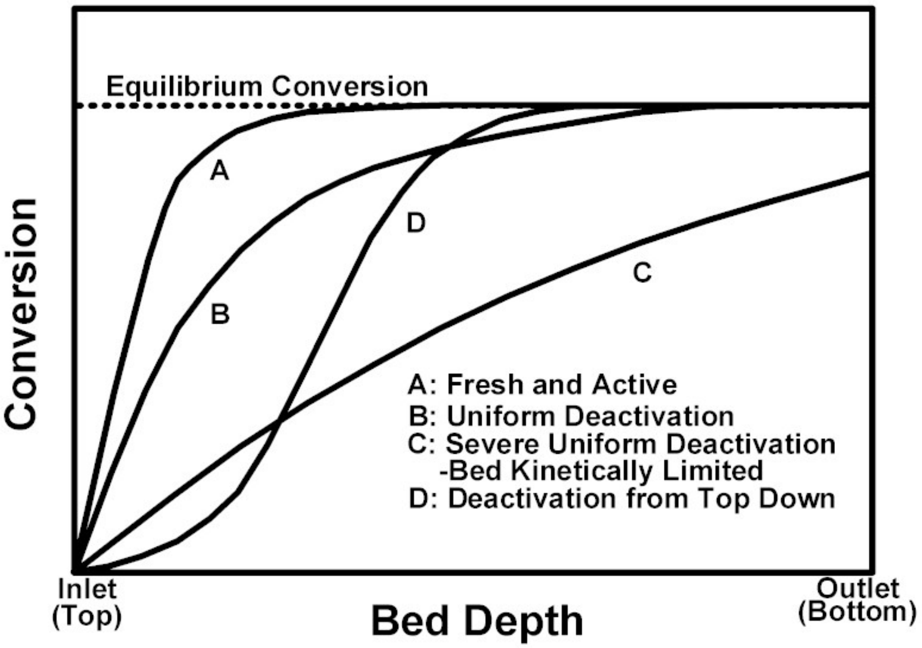
Figure 4: Air Demand Test Cases

The importance of controlling reaction stoichiometry in optimizing recovery efficiency is often affected by the choice of downstream tail gas clean-up unit (TGCU). For sub-dewpoint units (i.e Sulfreen, CBA, MCRC, Clauspol), where potential recovery efficiencies are pushed to nearly 99.5 percent through the use of cooler temperatures in the final conversion stage, even accurate control of the excess air to +/- 0.5 percent will still result in losses of approximately 0.3 percent. This significantly hinders the performance of these units, and even finer control is desired if these losses can not be tolerated. For amine based tail gas units (i.e. SCOT, BSR/MDEA, RAR, Sulften), the desire to protect the TGCU reactor from high SO_2 levels often necessitates operating the Claus plant in a slightly deficient air mode. For direct oxidation TGCU's (i.e. SuperClaus, Hi-Activity), the need to maintain an absolute Claus tail gas H_2S concentration completely replaces the need to maintain an excess air value.

Sin # 2 - Catalyst Deactivation

In the Claus converters, alumina or titania based catalysts are typically employed in order to allow the Claus reaction and COS / CS_2 reactions (discussed in the next section) to proceed to equilibrium in a reasonable length of time. Since deactivation of these catalysts can occur for a number of reasons (i.e. soot contamination, heavy hydrocarbon contamination, sulphation, liquid sulphur deposition, physical damage), converters are significantly oversized in order to allow for partial deactivation of the catalyst between turnarounds on the sulphur plant. As displayed in Figure 5, this means the reactions will still proceed to equilibrium across the catalyst beds even if a certain level of deactivation has occurred.

Figure 5: Catalyst Deactivation



Oversizing of catalyst beds results in typical losses due to catalyst deactivation being essentially zero. At some point, however, the level of deactivation is reached where the Claus and/or COS / CS_2 reactions no longer achieve equilibrium, consequently affecting the overall recovery efficiency.

The potential for recovery efficiency losses due to catalyst deactivation varies significantly depending on the position of the catalyst bed and the level of deactivation. Deactivation of the first catalyst bed, which most commonly results from contaminants bypassing the flame in the reaction furnace either as a result of design or poor burner operation during both normal operations and shutdown and start-up procedures, will generally have the most significant impact on plant efficiencies. This is because this reactor is relied on to hydrolyze the COS and CS_2 in addition to catalyzing the Claus reaction, and recovery efficiency losses of over 5 percent due to significant deactivation of this bed have been measured.

Deactivation of the downstream converters, which is generally related to problems with direct fired interstage reheaters or dewpoint excursions, has only slightly less impact on efficiency. In the worst cases, complete deactivation of the third catalyst bed has resulted in a reduction in efficiency from 98 percent to 96 percent while the complete deactivation of both the second and third converters has resulted in a further reduction in efficiency to near 90 percent.

Most sulphur plant operators assume a lifespan of 1 or 2 turnaround periods before enough catalyst deactivation occurs to affect efficiency. The actual catalyst life, however, varies significantly with the exact operating conditions of the bed. In the worst case, significant deactivation can occur during the few days required to start-up a facility, especially if there is poor control of the fuel gas combustion resulting in carbon soot formation. Other extreme cases of significant deactivation during normal operation have resulted in regular catalyst change-outs every 45 days (in the case of a split flow plant with significant heavy hydrocarbon concentrations in the acid gas) or every six months (in the case of a plant using refinery fuel gas fired reheaters upstream of each converter). In the best cases, on the other hand, testing has proven a number of cases where second or third stage catalyst beds following indirect reheaters are still achieving equilibrium Claus conversions after 15 to 25 years.

Sin # 3 - Operating the First Converter Too Cold

H_2S and oxygen are the only two components involved in the Claus process but other species also comprise the feed to the Claus plant in acid gas, sour water stripper gas, and air streams. This results in a number of side reactions in the reaction furnace and waste-heat boiler. The products of many of these side reactions are COS and CS_2. In general, most plants have little or no control over these formation rates and some formation of these components can always be expected.

COS and CS_2 do not take part in the Claus reaction, but because they contain sulphur atoms they need to be converted back to H_2S or to elemental sulphur in order to be converted and/or recovered downstream. The expected conversion mechanisms for this are:

$$COS + H_2O \rightleftarrows CO_2 + H_2S$$

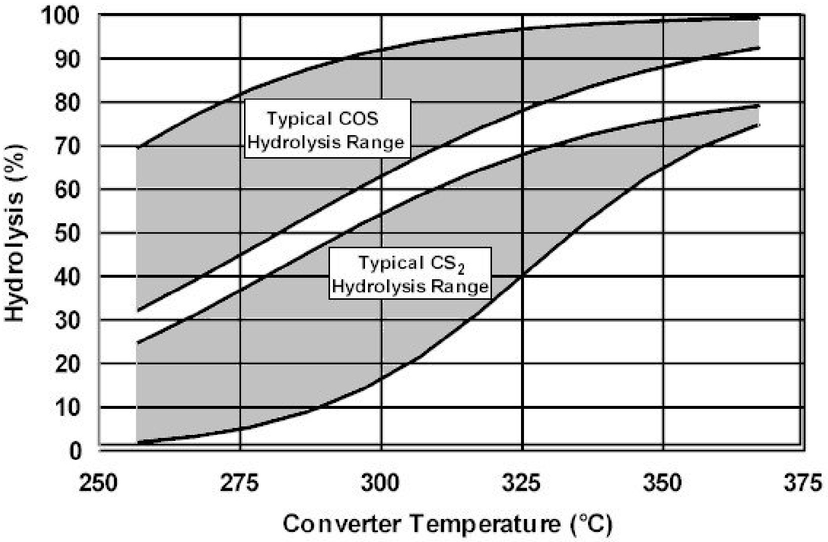
$$2\,COS + SO_2 \rightleftarrows 2\,CO_2 + 3/2\,S_2$$

$$CS_2 + H_2O \rightleftarrows COS + H_2S$$

$$CS_2 + SO_2 \rightleftarrows CO_2 + 3/2\,S_2$$

The equilibrium conversion rates for COS and CS_2 are roughly 99 percent and 100 percent respectively, but laboratory and test data have shown that these values are not regularly achieved due to kinetic limitation.

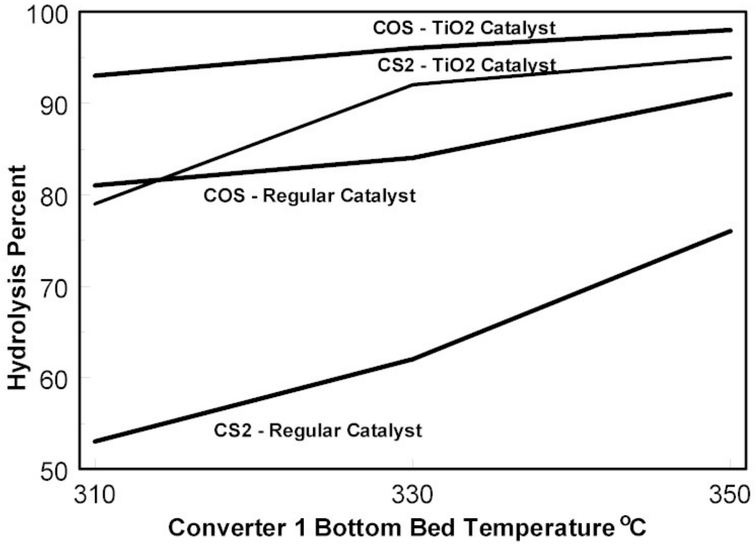
Figure 6: COS/CS₂ Hydrolysis vs Temperature



To overcome these limitations, the first catalyst bed is often run at an elevated temperature. Typical COS and CS_2 hydrolysis rate ranges over a variety of first bed temperatures (drawn from hundreds of Sulphur Experts' field test results) are presented in Figure 6. It should be noted that these curves are presented as ranges rather than as averages due to the significant deviation in actual measured results from plant to plant.

A second way of overcoming these limitations is through the use of special catalysts, either promoted alumina or titanium dioxide. An example of hydrolysis rates from a specific plant comparing standard activated alumina and titania is shown in Figure 7. It should be stressed that this is a single case study, and that these results can not be considered typical or average.

Figure 7: COS/CS_2 Hydrolysis vs Catalyst Type



Optimally, recovery efficiency losses due to COS and CS_2 could be kept under 0.1 percent assuming equilibrium conversion across the first converter. In reality this is seldom the case, with cooler than optimal temperatures or deactivated catalyst resulting in much higher typical losses. As an example, Table 1 presents COS and CS_2 losses from Sulphur Experts' last 10 gas plant and refinery tests. This tabular form is used instead of a single average value to illustrate the wide range of "typical" losses.

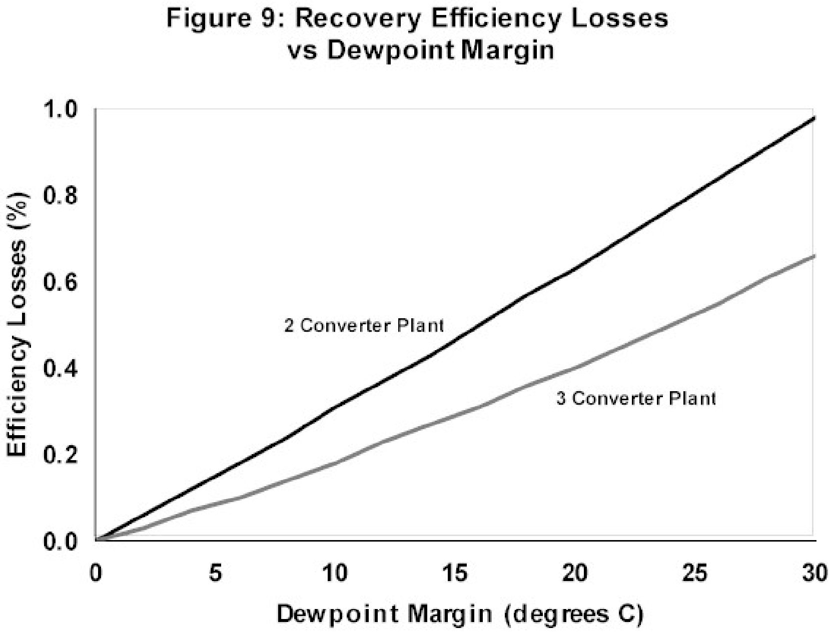
Table 1 - Recovery Efficiency Losses Due to COS and CS_2

Gas Plants	0.48	0.34	0.09	0.35	0.16	3.53	0.20	0.21	0.24	2.45
Refineries	0.07	0.09	0.01	0.33	0.85	0.04	0.23	0.62	0.01	0.05

In the worst case, test results have shown plants where reaction furnace COS and CS_2 formation rates account for up to 13 percent of the total inlet sulphur, and where recovery efficiency losses due to COS and CS_2 have been greater than 6.5 percent.

Sin # 4 - Operating the Second and Third Converters Too Hot

At temperatures below 600°C (Figure 8) the equilibrium point for the Claus reaction improves with decreasing temperature. The operating temperature for the first catalyst bed is normally dictated by the need to maximize COS and CS_2 hydrolysis, however the operating philosophy for the second and third converters is to operate as cold as possible in order to maximize the equilibrium conversion efficiency. For all standard Claus plants (excluding sub-dewpoint processes), the lower temperature limit is dictated by the condensation point or dewpoint of sulphur, since the presence of liquid sulphur in the converters will result in deactivation of the catalyst. Figure 8 presents a dewpoint curve for one particular case, however the actual dewpoints for each converter in a particular plant will vary with a number of parameters (i.e. acid gas quality, upstream conversion and recovery, reheat type) and can only be determined accurately through the use of simulation programs or test work.



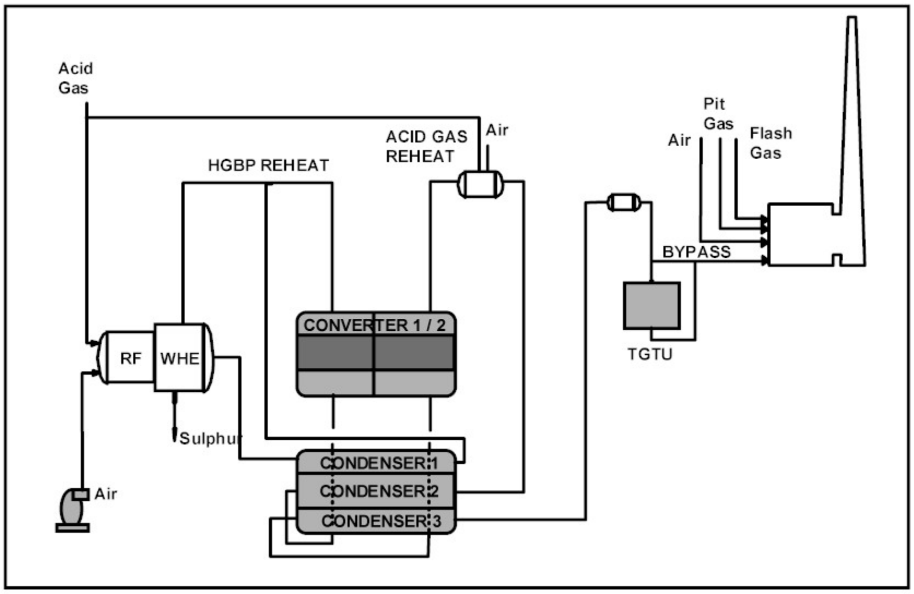
Ideally each converter should be operated at the dewpoint in order to maximize conversion across each bed. In reality, however, a temperature safety margin (referred to as the dewpoint margin) is required in order to allow for such things as heat losses, errors in dewpoint calculation, and capillary condensation of sulphur in the catalyst. Figure 9 shows the resulting losses in recovery efficiency over a range of dewpoint margins.

Knowledgeable plant operators will operate the second and third converters with dewpoint margins of 5 to 15 degrees C, resulting in typical efficiency losses ranging from 0.1 to 0.5 percent Much higher dewpoint margins ranging from 25 to 75 degrees C are quite common in the industry, resulting in worst case efficiency losses of over 3 percent.

Sin # 5 - Bypassing Gases Around Conversion Stages

Probably the least understood and least expected of the deadly sins is the intentional or unintentional bypassing of sulphur species around one or more conversion stages in a Claus plant. Figure 10 shows a number of ways in which this bypassing can occur. In general, any gas that does not go through all of the available conversion stages (thermal and catalytic) will have a negative impact on efficiency. In all of these cases, there are no typical values, however some worst case examples for each form of bypass are discussed below.

Figure 10: Bypass Methods



Acid Gas or Hot Gas Bypass Reheaters - The use of acid gas fired or hot gas bypass reheaters results in the bypassing of sulphur species around the reaction furnace and/or catalyst beds. From the standpoint of recovery efficiency, both of these reheat methods have almost no detrimental effect when used only for the first converter. The use of these reheat methods for downstream beds, however, can result in significant losses. In the worst case, the use of acid gas fired reheaters for all converters in a three stage plant will directly cause recovery efficiency losses of 0.3 to 0.6 percent (depending on the burn stoichiometry used), with even higher losses noted in plants where additional COS and CS_2 formation has been noted from these units. For plants which use hot gas bypass reheaters to all three catalyst beds, even more significant efficiency losses of 1 to 3 percent have been noted. These losses are highly dependent on the reaction furnace COS and CS_2 formation since the use of hot gas bypass reheaters will bypass a portion of these components around the hot first converter.

Leakage of Gas Across Partition Plates - For economic reasons, two or more catalyst beds or condensers are often located within the same shell, with baffle plates used to physically separate the various process streams. A number of cases have been noted where these baffle plates leak or fail completely, with the resulting partial or compete bypass of gases around one or more catalytic conversion stages. In one recent worst case scenario, the baffle plate between the first condenser and the final condenser of a two stage plant had failed completely, reducing the efficiency from 96 percent to 72 percent.

Channelling of Gases through Converter Beds - It is generally assumed that the process gas is forced to pass through the entire catalyst bed in each converter. There are a number of cases, however, where this is not true. These cases primarily involve the channelling of gas through only a small portion of the catalyst bed, resulting from uneven catalyst depth or where low throughputs allow gas to proceed through a "channel" of low pressure drop. In the worst case, bypassing of gas around part of the catalyst bed can be complete, as experienced by one plant which had contained its entire catalyst load in a protective stainless steel mesh bag which subsequently contracted and pulled the catalyst load away from the walls.

Leakage of Gas Across Emergency Bypass Lines - The design of many facilities includes emergency bypass lines either around the entire Claus plant (enabling acid gas to be sent to the flare or to the incinerator) or around certain units (typically tail gas clean up units). These lines are closed during normal operation, but failure of the bypass valves to close completely can result in continued bypassing of process gas. This is especially true of bypass lines downstream in the Claus plant where the presence of elemental sulphur increases the risk of a poor valve seal. In the worst case, these leaks can allow for the complete bypass of entire stages.

Processing of Other Sulphur Containing Gases in the Incinerator - In addition to processing the tail gas from the Claus plant or tail gas clean up unit, the incinerator often processes additional sulphur bearing streams, most commonly flash gases and sulphur pit gases. Both of these cases, in effect, represent a bypass of gases around conversion stages. In the case of flash gases, H_2S is allowed to bypass the Claus plant entirely and contribute directly to emissions. These flash gases are sometimes scrubbed before being sent to the incinerator, however this scrubbing is often either incomplete or non-existent. These streams are generally small and low in H_2S resulting in maximum losses of 0.1 to 0.2 percent. In one case which involved only a three stage Claus plant, these losses were considered insignificant. In a second case involving a Claus plus SCOT facility, these losses resulted in a 10-fold increase in emissions from the facility.

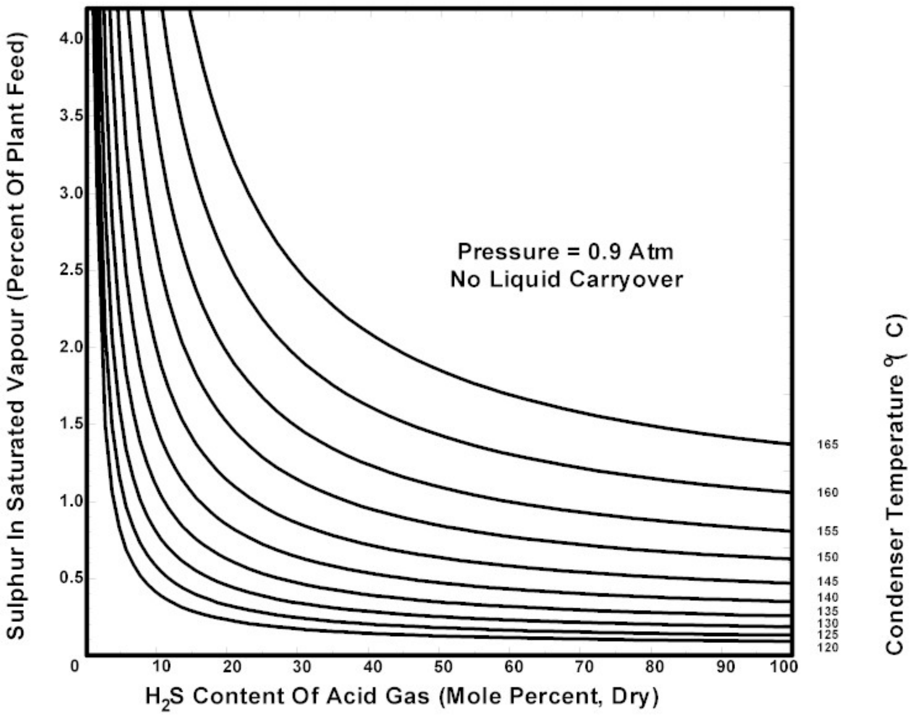
For sulphur pit gases, H_2S is naturally dissolved or chemically bound in the produced sulphur from every condenser and then is either naturally or intentionally released in the sulphur pit or storage tank. This too represents a fairly small maximum loss of less than 0.05 percent, relatively insignificant for a two or three stage Claus plant but a much greater relative source of emissions where tail gas clean up is used.

Sin # 6 - High Final Condenser Temperature

Following each of the catalytic converters, condensers are used to cool the stream in order to condense and remove some of the sulphur product. For the interstage condensers, this removal of product is necessary to allow more sulphur to be formed in the next converter, and to lower the dewpoint temperature of each subsequent conversion stage allowing for colder operating temperatures. The decision on the operating temperature for these interstage condensers is often made by trading the need for product removal with the economics of reheating the stream for the next converter and the availability of suitable cooling medium.

For the final condenser, however, there is no trade-off unless a downstream tail gas clean-up unit is used. In this case, the aim is to remove as much product as possible since any residual sulphur vapour will contribute directly to emissions. As displayed in Figure 11, the recovery efficiency losses due to equilibrium sulphur vapour from the final condenser are directly related to the acid gas concentration and the final condenser temperature, with lower temperatures resulting in the highest recovery efficiencies.

Figure 11: Sulphur Vapour Losses vs Final Condenser Temperature



Typical sulphur vapour losses from a final condenser are set by the need to maintain a temperature safety margin above the freezing point of sulphur (approximately 119°C). Many plants will try to operate this condenser at 125 to 130° C, resulting in sulphur vapour losses of approximately 0.2 percent for relatively rich feed gases. Efforts have been made to develop a sub-freezing point condenser to reduce these losses effectively to zero.

Many plants operate their final condensers well above 125°C. Higher temperatures are often due to the final condenser being either in the same shell as or using the same cooling medium as the upstream condensers. Higher temperatures may also be used to minimize the possibility of ammonia salt deposition, which can occur at around 150°C when ammonia breakthrough from the reaction furnace is occurring. In these plants, final condenser temperatures of 155° C are common, resulting in recovery efficiency losses of at least 1.2 percent.

Sin # 7 - Liquid Sulphur Entrainment

As described earlier, the purpose of the sulphur plant condensers is twofold; both to condense the sulphur which has been produced in the upstream converters and to separate it and remove it from the process gas. The degree of condensation is strictly a function of temperature, while removal is more a function of design and kinetics. Any condensed sulphur which is not removed from the process will contribute directly to plant emissions.

Optimally, recovery efficiency losses due to entrainment of liquid sulphur from the final condenser can be kept to essentially zero through the use of proper condenser design mass velocities, appropriate separation residence times (possibly including the addition of a separate coalescing vessel), and through the use of mesh pads or mist eliminators. More typically, some minor entrainment should be expected and allowed for. This entrainment ranges from 2 to 4 kilograms of sulphur per 100 kmol of gas, resulting in efficiency losses of roughly 0.2 to 0.4 percent for a rich feed plant.

In the worst cases, sulphur entrainment levels from the final condenser of 50 percent (due to fogging problems at extremely low mass velocities) to 100 percent (due to mechanical blockage of the final rundown) have been measured, resulting in efficiency losses of 1 to 3 percent.

Conclusions

The “ideal” recovery efficiency capabilities for the Claus process are approximately 99 percent for three stage plants and 97.5 percent for two stage plants. Unavoidable losses due to the Seven Deadly Sins will slightly reduce actual recovery efficiencies but true recovery efficiency capabilities are still significantly higher than those traditionally expected throughout the industry.

Left unchecked, any one of the Seven Deadly Sins is capable of causing a significant reduction in plant efficiency. This summary of the potential causes of recovery efficiency losses into seven categories giving examples of typical and potential losses can be used as a check list by sulphur plant operators in order to determine the potential for optimization of their facilities.

Finally, as shown from the case studies, the deviations between typical and potential recovery efficiency losses are so great as to introduce tremendous risk for operators relying on “rules of thumb”, “design” or “average” values to estimate efficiency losses. Detailed sulphur plant testing is required to determine the exact effect on efficiency of each of the Seven Deadly Sins, and in turn to determine the potential for optimization.

References

1 “Capability of the Modifies-Claus Process” – H.G. Paskall – textbook published by Sulphur Experts Inc. (Western Research), Calgary, Canada 1980

2 “Optimizing European Sulphur Recovery Plants – a perspective” J.A. Sames and H.G. Paskall, - Sulphur ’91, New Orleans, November 1991

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