The CONTACTOR™

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Heat Stable Salts IV — Case Study

In this the final installment in the four-part series on heat stable salts (HSSs), we will present a simulation study to demonstrate the effects of HSSs on process performance.

Gas Treating Effects of HSS

The most immediate effect of HSS accumulation is lost chemical capacity for holding acid gases in the solvent from the HSSs permanently protonating the amine. The chemical capacity of the solvent for acid gases affects the VLE driving force at the rich-end of the column. Therefore, amine treating services that are sensitive to circulation rate are either rich-end pinched or mass-transfer pinched with respect to treating. Figure 1 shows plots of the actual versus equilibrium H_2S partial pressure above a solvent in normal operation (top), and a solvent starved for amine (bottom) because of a high HSSs level.

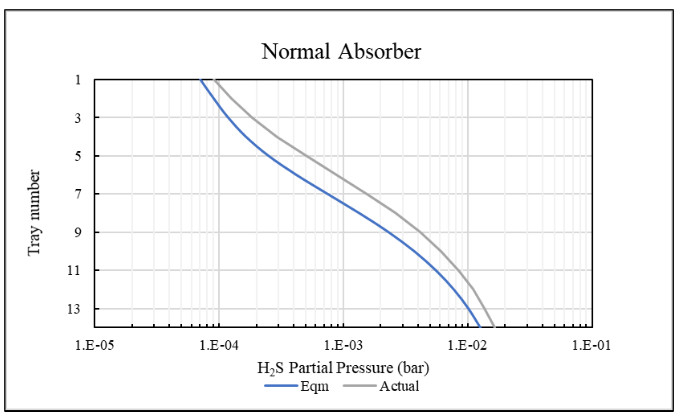

Figure 1a H₂S Profile in Absorber under Normal Operation

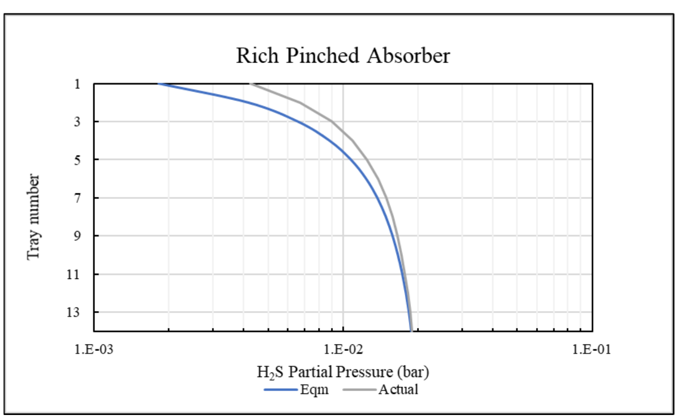

Figure 1b H₂S Profile in Absorber with Too Little Amine

If an amine contactor's treating performance is normally controlled by the lean loading and the lean loading drops over time due to heat stable salts, then some benefit can be seen in the treating as the HSSs accumulate.

By themselves, HSSs can carry a slight benefit in helping MDEA selectivity by slipping more CO_2 as we will demonstrate later. However, Jenkins and Critchfield provide evidence that MDEA exposed to SO_2 breakthroughs in Claus tail gas treating service degrades into MMEA and DEA, both of which are *less* selective than MDEA. The consequence of SO_2 breakthroughs hence is less selective MDEA, which was quantified in detail by Weiland et al. (see article here).

Case Study: Real World Application

A case study of a tail gas treating units is presented here. The purpose is to evaluate the robustness of a design in the presence of HSSs, from a few ppmw to nearly 2 wt%. The study was done using a typical Indian refinery TGTU feed gas composition as shown in Table 1. Figure 5 shows the PFD used. The callouts refer to performance with 10,000 ppmw thiosulfate HSS. Tower internals details are described elsewhere.

Table 1: Feed Gas Composition

H_2S	**1.54**	**mol%**
COS	25	ppmv
CS_2	2	ppmv
CH_3SH	15	ppmv
CO	750	ppmv
H_2	3.46	mol%
CO_2	3.82	mol%
N_2	82.76	mol%
Ar	0.94	mol%
H_2O	7.4	mol%
Total Gas Flow	70,0000	kg/h

CO_2 is minimally absorbed by MDEA because tertiary amines do not form carbamates making them nonreactive, whereas H_2S is quite strongly absorbed. This makes MDEA an excellent choice if selectivity towards H_2S is sought. A selective H_2S absorber is usually lean-end pinched. It is interesting to look at the H_2S profiles across the absorber and the effect that HSS has on them. Figure 3 shows two H_2S profiles.

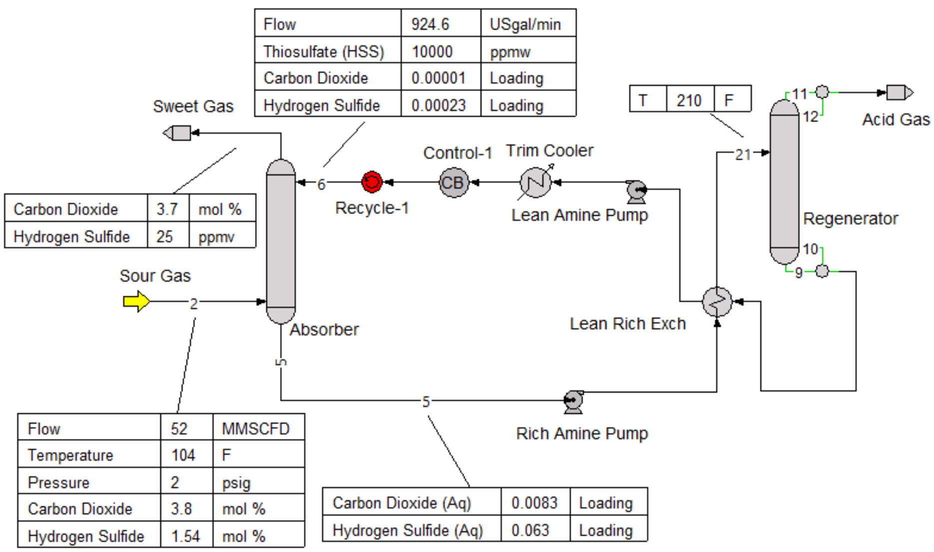

Figure 2 PFD For Case Study

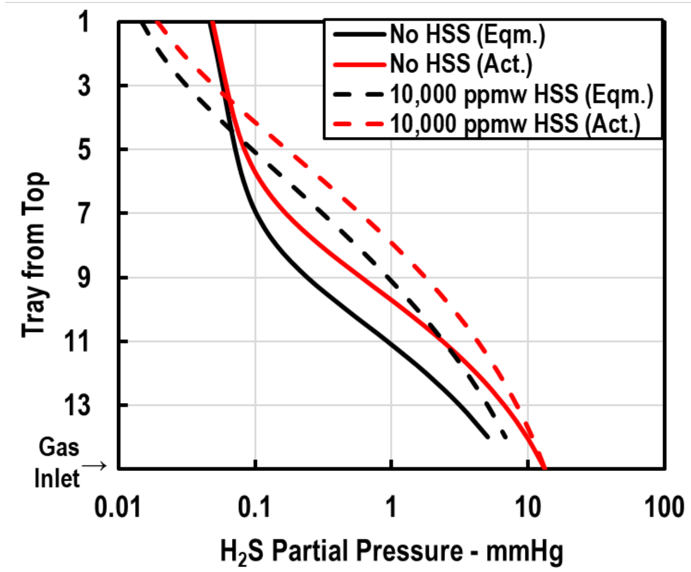

Figure 3 H_2S Profiles in the Gas Phase of the Absorber with 10,000 ppmw Thiosulfate (Dashed Lines) and without HSS (Solid Lines)

When no HSS is present the H_2S profile becomes almost constant near the top (lean end) of the column and the equilibrium and actual concentrations of H_2S become very nearly equal. The driving force for absorption virtually disappears and the treated gas emerges with a concentration of about 64 ppmv. When the solvent contains 10,000 ppmw of thiosulfate the lean-end pinch is relieved and the H_2S concentration in the gas continues to fall, reaching 25 ppmv in the column's outlet.

Figure 4 shows how the H_2S and CO_2 in the treated gas respond to varying thiosulfate concentrations. The HSS hardly affects CO_2 removal at all but there is a sweet spot for H_2S removal at around 10,000 ppmw thiosulfate. HSSs can be surprisingly beneficial to H_2S removal *if the absorber is lean-end pinched*. If is not lean-end pinched, HSSs are likely to be harmful to treating and when their concentration is too high, they exacerbate corrosion.

When HSSs improve H_2S treating they do so by forcing the solvent to be stripped better. The "How" lies in the chemistry. Acid gas absorption is accompanied by the production of protonated amine—so is solubilization of HSSs. The presence of HSSs results in an elevated level of protonated amine which drives the reaction equilibrium towards formation of molecular H_2S and CO_2. This is especially effective when loadings, and therefore protonated amine concentrations, are low

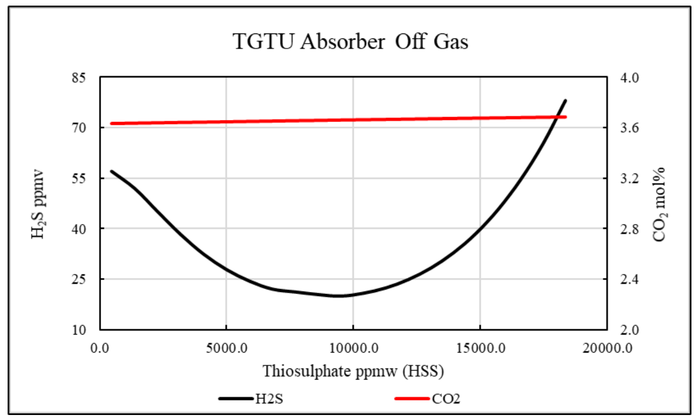

Figure 4 Response of H_2S and CO_2 Treating to HSS Concentration

Using a solid process simulator like ProTreat® allows us to learn much about gas treating and reveals numerous aspects that would otherwise remain hidden:

- Solvent contaminated with HSS *may* treat to a lower H_2S level than a clean solvent if the column is lean-end pinched.
- The presence of substantial quantity of HSS alters the solution chemistry allowing the regenerator to produce a solvent with much lower residual lean H_2S loading.
- It is prudent to assess the impacts of HSS on the treating units to ensure robustness of the design using rigorous heat and mass transfer rate-based simulations that also account for HSS chemistry.

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To learn more about this and other aspects of gas treating, plan to attend one of our training seminars. For details visit ogtrt.com/training.

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