Effect of Heat Stable Salts on Steam Stripping Rate

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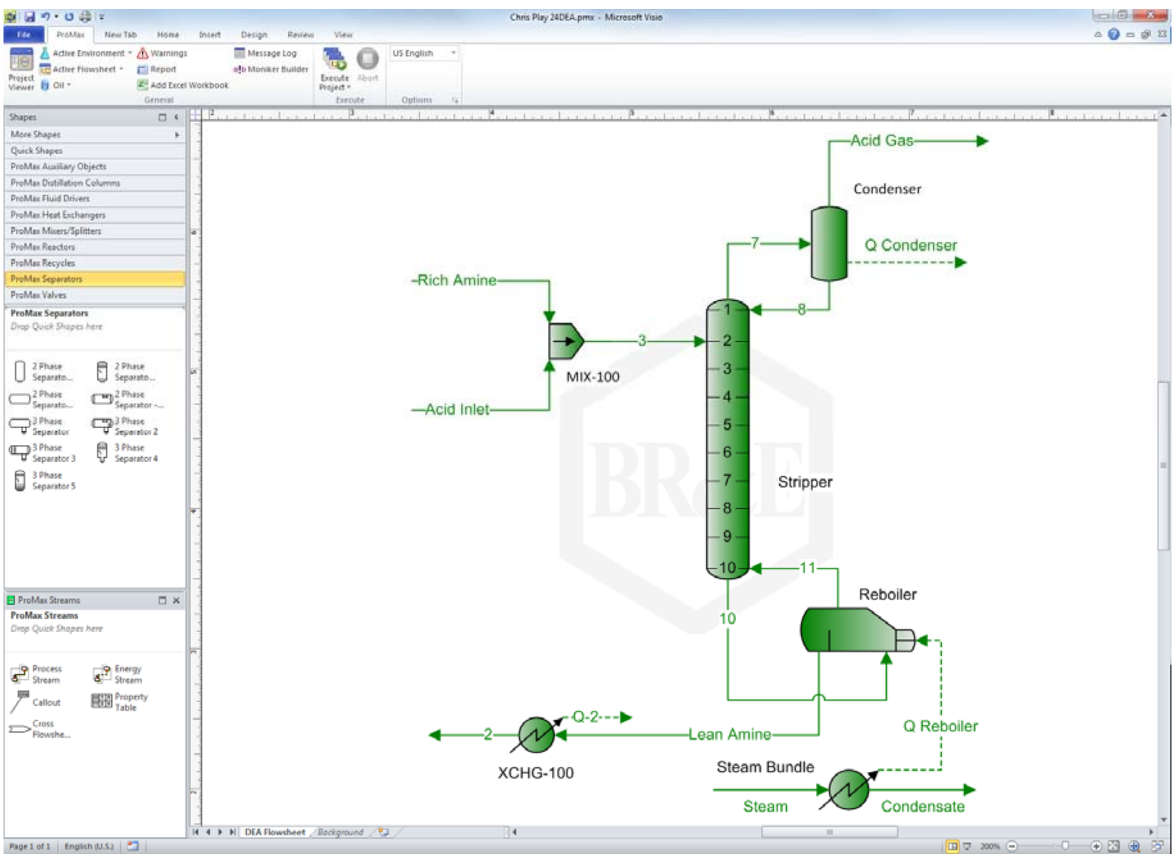
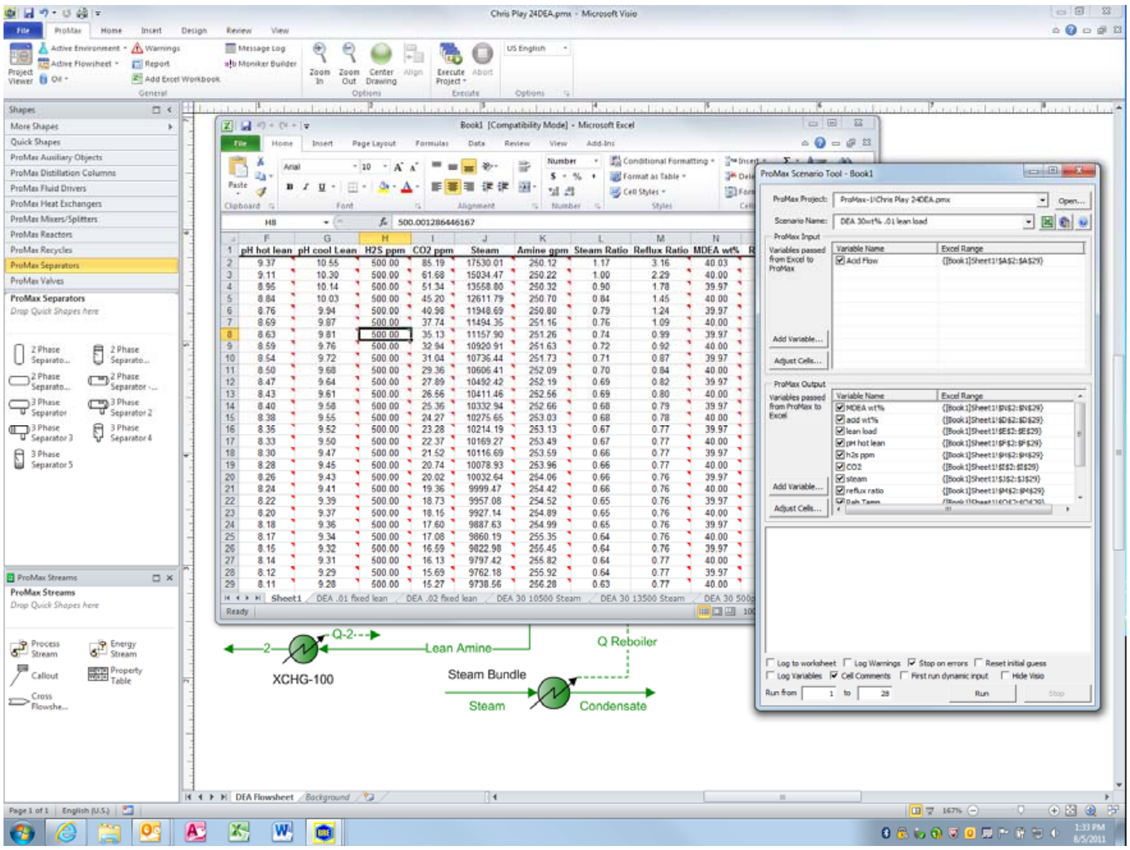
Heat Stable Salts are often implicated as the culprit for an assortment of amine issues such as corrosion, foaming, reduced performance and operational difficulties, and rightly so. However, the presence of heat stable salts does reduce the pH of the amine solution resulting in improved regenerator stripping. Thus the question arises: What is the optimal level of heat stable salts that will balance improved stripping and reduced energy cost with maintaining proper amine hygiene? Presented here are a series of simulations evaluating stripper performance and energy savings as a function of wt% HSAS.

The simulations were performed using Bryan Research and Engineering's process simulator ProMax depicted below.



Both the absorber and regeneration process are affected by the presence of heat stable salts. However, their effect on absorption is typically not limiting to the process, so for purposes of simplicity only regeneration was simulated. ProMax' Scenario Tool was used to run the hundreds of simulations needed to prepare the plots contained within. Using the Scenario Tool the percent phosphoric acid was varied from 0 to 2.5 wt% while maintaining other fixed parameters such as steam rate, lean loading, or ppm H_2S. ProMax saved the selected results from each simulation in an Excel spreadsheet which was later used for convenient plotting. The "rich amine" was ~2.5 wt% H_2S and ~1.0 wt% CO_2 for all regenerator simulations which corresponds to a 0.34 and 0.28 mol/mol loading for DEA and MDEA, respectively.



The common heat stable salts in a refinery process vary from organic anions such as acetate and formate to inorganic anions like thiocyanate and thiosulfate. There are at least a dozen different anions found in most refinery systems. Again, for simplification purposes, phosphoric acid was used to generate the heat stable salt in the simulations. To standardize the effect of the phosphate, the "Bound Amine" or Heat Stable Amine Salt (HSAS) was monitored versus the actual weight percent phosphate. The weight percent HSAS was calculated based on the amine that would be tied up by the phosphate anion. For example, in the case of a DEA system:

Phosphate = 95 lb/lb-mole
One mole of Phosphate would "bind" three moles of DEA
DEA = 105 lb/lb-mole

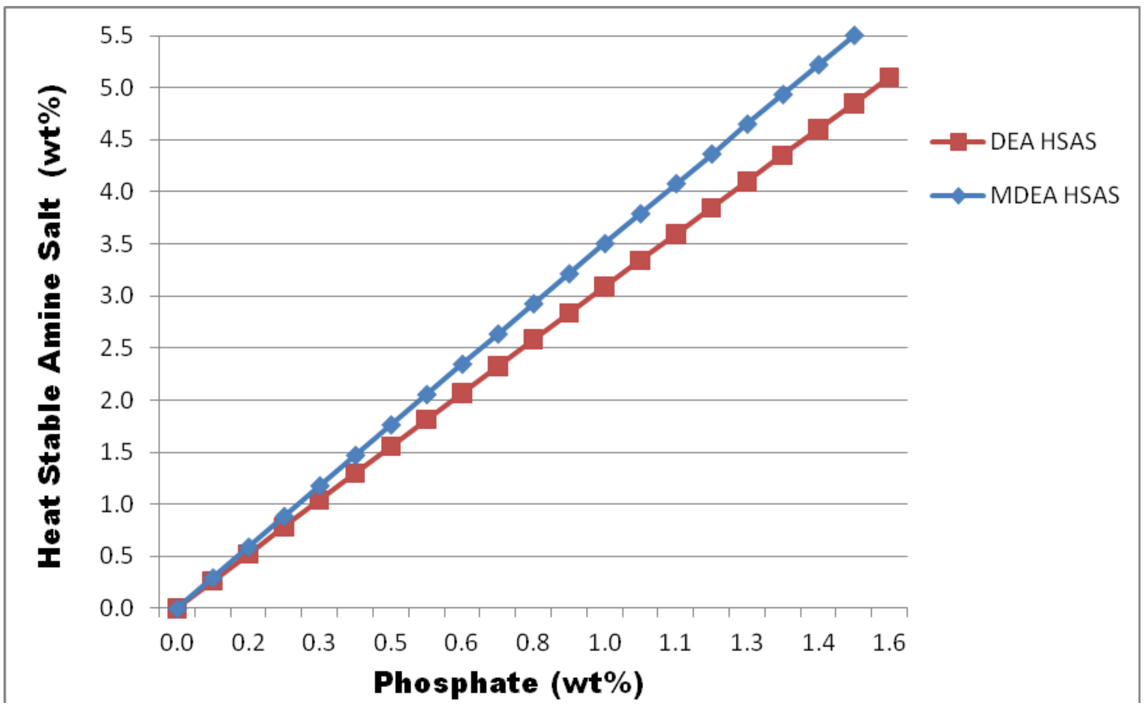
So the amount of “bound” DEA which corresponds to 1 wt% Phosphate is:

$$\left(\frac{1\text{ lb Phosphate}/100\text{ lb sol'n}}{95\text{ lb Phosphate}/\text{lbmole Phosphate}}\right) \times \left(\frac{3\text{ mole DEA}}{\text{mole Phosphate}}\right) \times \left(\frac{105\text{ lbDEA}}{\text{mole DEA}}\right) = \frac{3.32\text{ lb bound DEA}}{100\text{ lb sol'n}}$$

Thus, the presence of 1 wt% phosphoric acid would correspond to ~3.32 wt% HSAS in a DEA system whereas MDEA with a molecular weight of 119 lb/lb-mole would correspond to a slightly higher HSAS, i.e. 3.76 wt%.

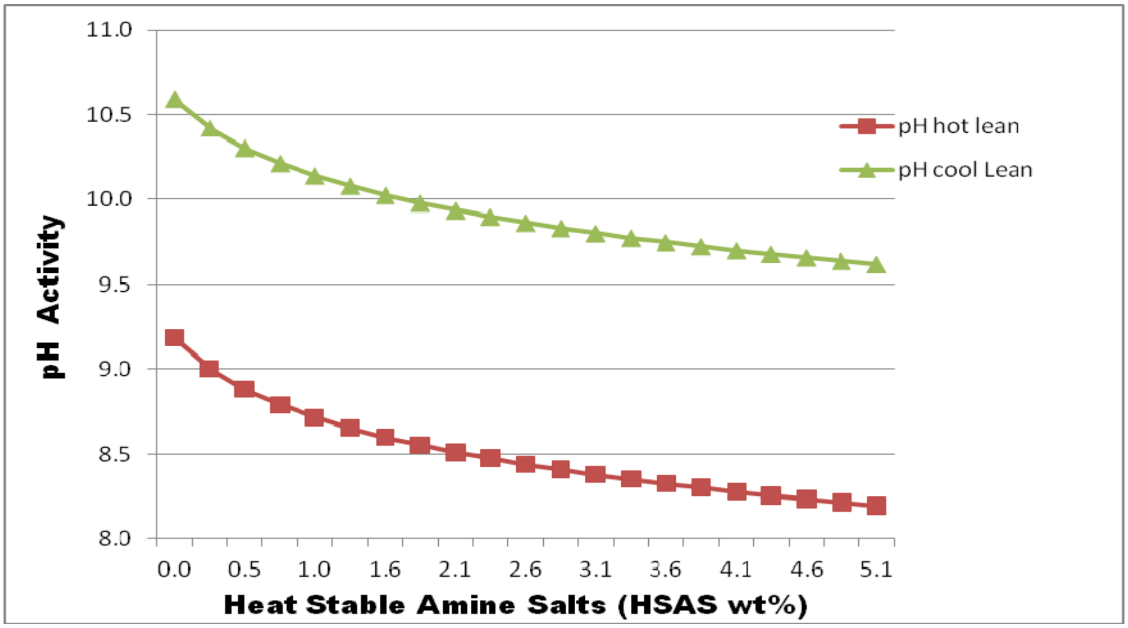
Figure 1 below shows the “bound” DEA and MDEA, i.e. HSAS as a function of the phosphoric acid present in solution (phosphate ions).

Figure 1: Heat Stable Amine Salts vs. Phosphate for DEA & MDEA



The presence of HSAS affects the pH of the amine solution as shown in Figure 2 below. In the case of absorption where temperatures are in the 120 deg F range, the pH is still sufficiently high to provide acid gas absorption. In the case of the regenerator where reboiler temperatures are typically in the 250-260 deg F range, the lower pH allows the amine to regenerate more easily and thus the energy required is significantly reduced.

Figure 2: pH Activity vs. HSAS for 30 wt% DEA System



To better see the effect of the HSAS at a fixed steam ratio, the H_2S and CO_2 were plotted for both a 30% DEA system (Figure 3) as well as a 40% MDEA system (Figure 4) at a typical fixed steam ratio. As you can see in Figure 3 below, at a fixed steam ratio of 0.9 lb steam/USG of amine, with no HSAS, the H_2S lean loading is above 1300 ppm whereas with approximately 2 wt% HSAS, the lean loading is 500 ppm H_2S.

Figure 3: Lean Amine H_2S and CO_2 versus HSAS in DEA at a Fixed Steam Rate

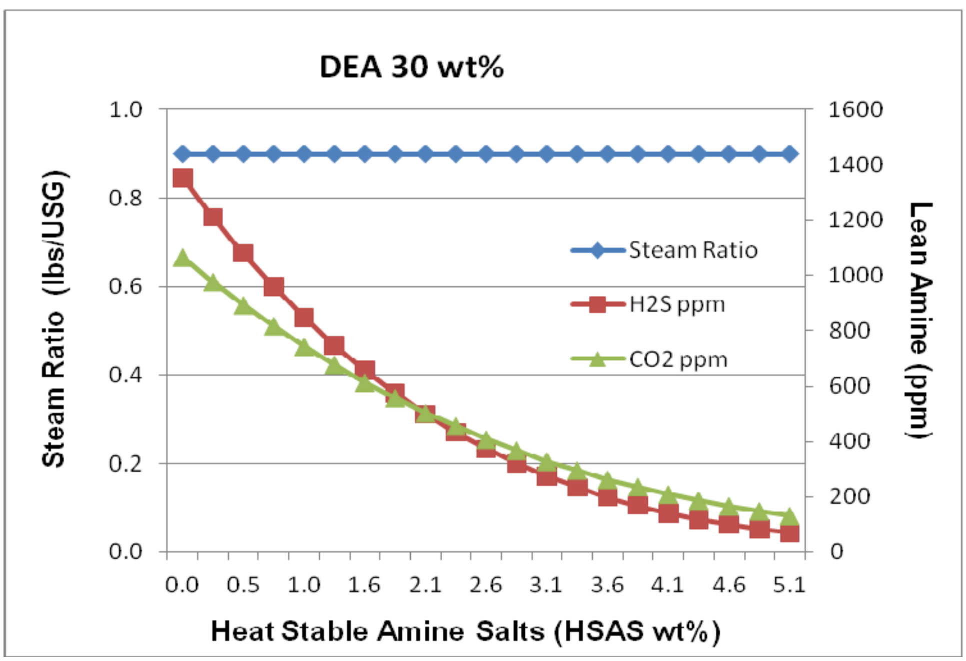
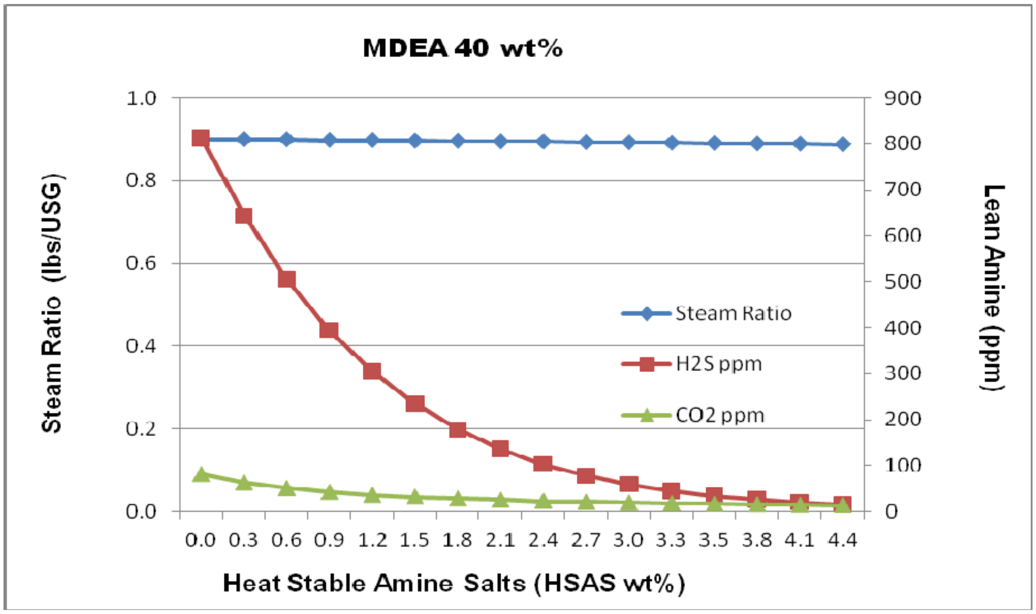


Figure 4 demonstrates a very similar effect though less HSAS needs to be present to produce 500 ppm H_2S in the lean amine. This is due to the fact that MDEA is much easier to regenerate than DEA so a 0.9 lb steam/USG MDEA is more than adequate.

Figure 4: Lean Amine H_2S and CO_2 versus HSAS in MDEA at a Fixed Steam Rate



Since it is more energy efficient to regenerate an amine solution with a high level of HSAS, why don't we let them build-up to 5-10%? One answer is immediately obvious: HSAS are corrosive and at high levels they can result in pitting, metal loss and ultimately leaks and failures. High levels of HSAS can also cause foaming issues and can limit absorber performance in cases where the absorber performance is nearing maximum load of the amine.

Another potential problem of high level HSAS is the inability to maintain an adequate sulfide protective layer. Many experts in the amine industry recommend a minimum of 300-500 ppm H_2S in the lean amine in order to provide a protective sulfide layer on piping and equipment. In the case of very high HSAS, it may become difficult to even maintain 300-500 ppm in the lean amine. Figure 5 shows a plot of Steam Ratio for a 30 wt% DEA system versus HSAS where the lean amine loading is maintained at 500 ppm H_2S. At ~5 wt% HSAS, the steam ratio is reduced below 0.7 lb steam/USG and the regenerator is most likely approaching minimum reflux. Thus in some systems, particularly overdesigned strippers, a 500 ppm H_2S lean loading cannot be achieved due to minimum reflux limitations. In a MDEA system which regenerates more easily, the problem can be even more pronounced. As shown in Figure 6, at HSAS levels above 4.1 wt%, the stripper was operating close to 0.6 lb steam/USG which in many regenerators may be at minimum reflux.

Figure 5: Steam Ratio versus HSAS in DEA at Fixed H_2S Lean Loading

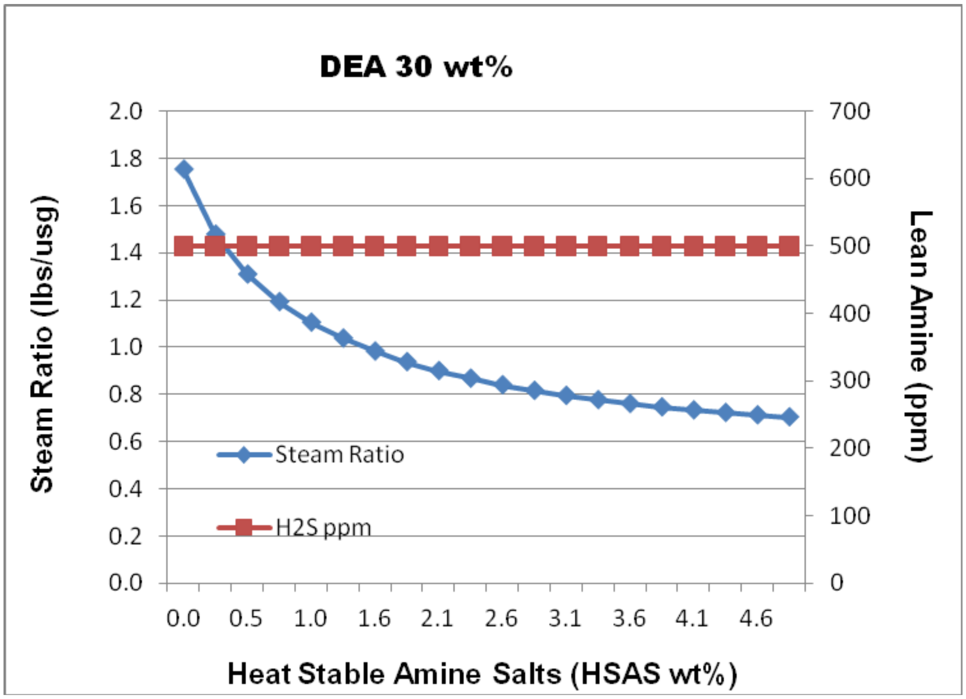
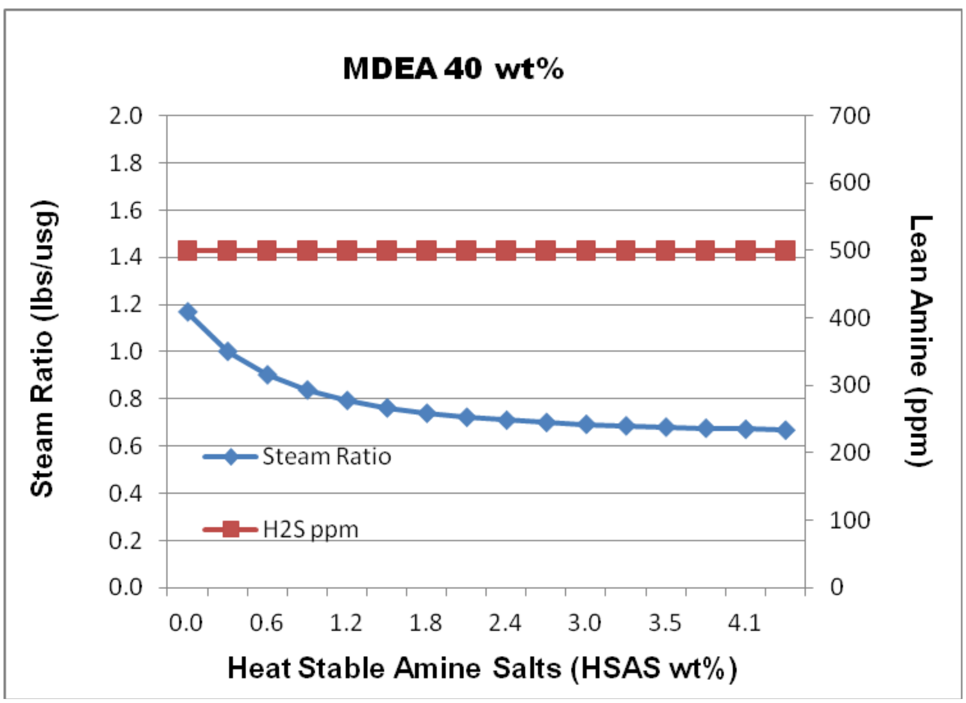


Figure 6: Steam Ratio versus HSAS in MDEA at Fixed H_2S Lean Loading



High levels of HSAS can wreak havoc on your amine system, resulting in corrosion, foaming, inability to obtain spec gas and over-stripping but steam energy savings may be a benefit from maintaining a low to moderate level of HSAS in your system. In Figures 7

& 8, the steam energy savings are plotted for DEA and MDEA, respectively. In the case of a DEA system, steam rates are reduced by 40% at 1.5 wt% HSAS as compared to a completely clean system. Thus maintaining your HSAS at 2.5 wt% vs. 1 wt% in a DEA would result in an approximate energy savings of 25%.

Figure 7: Steam Savings versus HSAS in DEA at Fixed H_2S Lean Loading

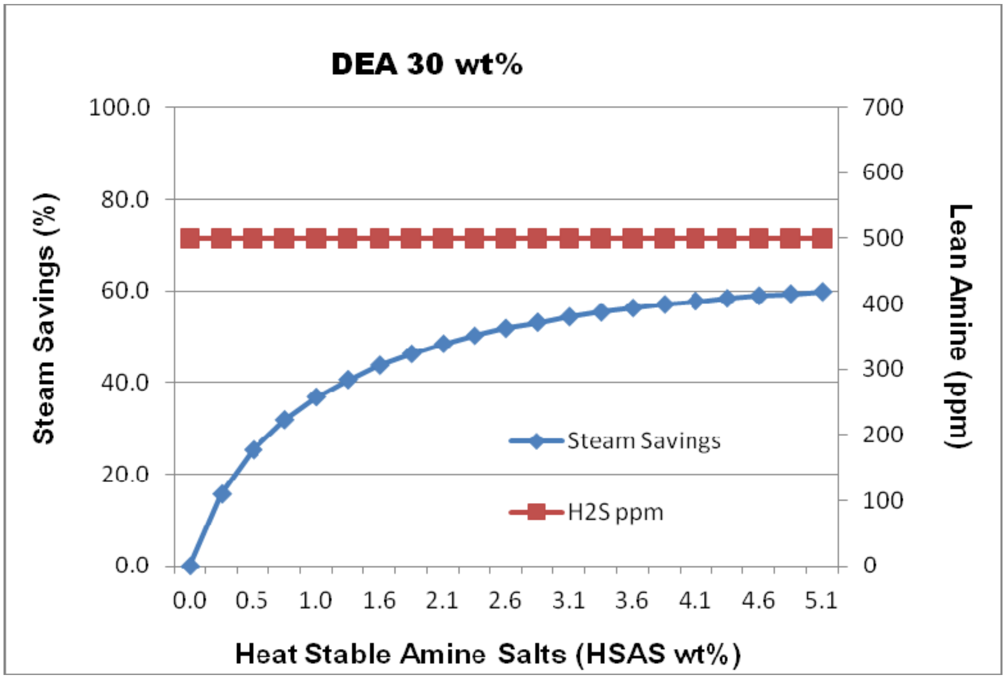
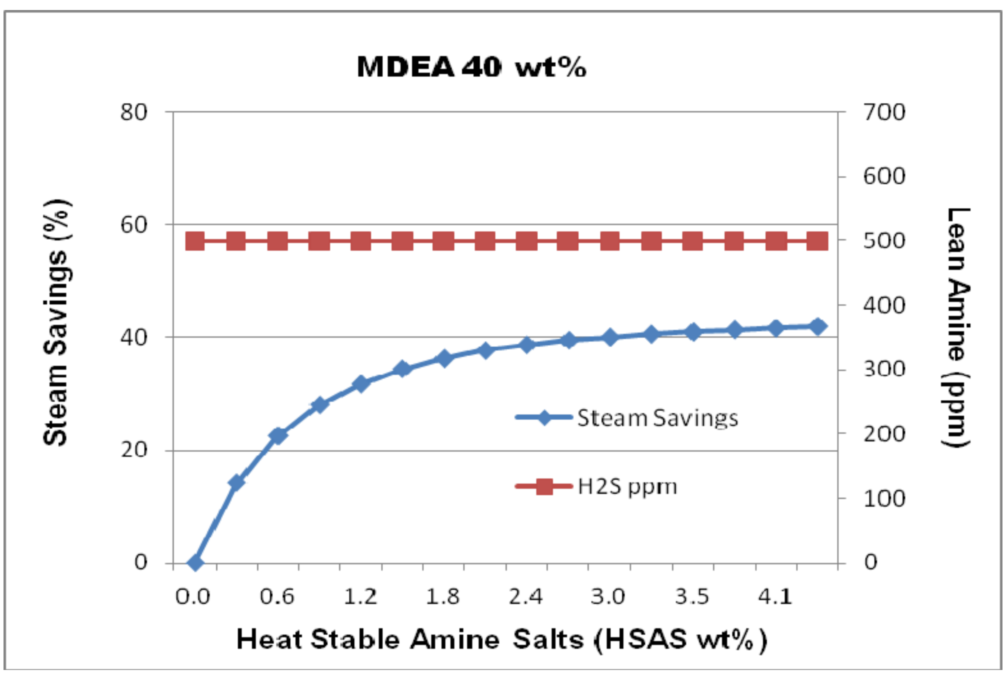
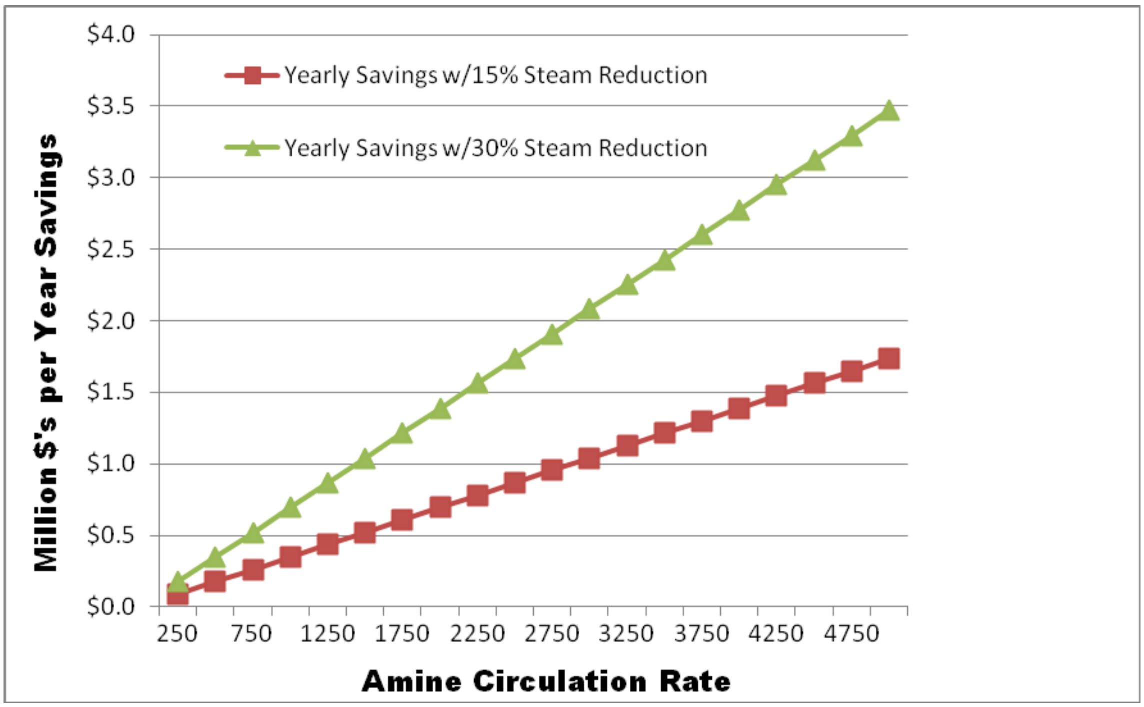


Figure 8: Steam Savings versus HSAS in MDEA at Fixed H_2S Lean Loading



MDEA requires less energy to regenerate as compared to DEA, thus the steam savings for a MDEA system (Figure 8) are not as pronounced as with DEA. However, steam savings of 35% can still be achieved with only 1.5 wt% HSAS present compared to a completely clean system. Since a system is rarely completely clean, a more practical comparison would be maintaining your HSAS at 2.0 wt% vs. 0.5 wt% in a typical MDEA system would yield an energy savings of 25%. Figure 9 shows the potential annual savings as a function of amine circulation rate for both a 15% and 30% steam reduction. The cost savings assume a steam cost of $4.00/MMBTU, regenerator steam rate of 1.0 lb steam/USG amine and 90% efficiency.

Figure 9: Annual Savings with 15% and 30% Steam Reduction



In summary, high levels of HSAS are not desireable in amine systems and can be the source of various operational and mechanical problems. However, maintaining low to moderate levels of HSAS in your amine system can provide significant energy savings. Therefore, proper management of HSAS in an amine system is essential and can yield tremendous benefits by avoiding problems while capitalizing on the available energy savings.