NEUTRALIZATION OF HEAT STABLE SALTS REVISITED

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ABSTRACT

Neutralization with caustic in amine systems has long been a debated topic and there is no shortage of experts weighing in on the pros and cons. This paper will revisit the historical practice of intentionally adding caustic to amine with the purpose of improving performance and reducing corrosion by "neutralizing" Heat Stable Amine Salts (HSAS) which have accumulated in the amine. The paper will briefly cover introductory concepts including electrolyte reactions, corrosion reactions, chelation, and the relationship between soluble iron and corrosion rate. Common terms, including HSAS and % neutralized, are defined in an appendix.

A series of simulations will be used to demonstrate the effects of heat stable salts on the ionic speciation of amine, how adding NaOH affects the speciation, and what happens when too much NaOH is added to an amine system. Plant data from several amine units will be presented to show the effect of neutralization on soluble iron concentration as well as the impact of over-neutralization on lean loading.

We will also use simulations to explore other relevant topics including the impact of neutralization on ionic strength / activity coefficients, and on potential volatility of HSS species such as acetate and formate in the regenerator reboiler.

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Introduction

Neutralization with caustic in amine systems has long been a debated topic in the gas sweetening industry. *Neutralization* is the practice of intentionally adding a strong base (NaOH, Na_2CO_3, KOH, etc) to amine for the purpose of improving performance and reducing corrosion by "neutralizing" Heat Stable Amine Salts (HSAS). While this paper is not likely to resolve all differing opinions on this topic, the authors hope that it will serve as a useful reference by summarizing the current state of understanding.

The paper will approach the topic in four parts which are supported by simulation case studies and plant data as applicable:

i) Chemistry review to explain theoretical considerations and list relevant chemical reactions which will be referenced throughout the rest of the paper.
ii) Heat Stable Salt (HSS) effects on amine chemistry and corrosion.
iii) NaOH effects on amine chemistry and corrosion.
iv) Effects of adding too much NaOH.

For brevity's sake, this paper focuses on a representative subset of the chemicals which are currently in use in industry. The only acid gas addressed extensively is H_2S, the only amine considered is MDEA, and the only strong base discussed is NaOH. While there are other acid gases, amines, and strong bases that are important in industry, it is hoped that all of the relevant points can be made more effectively by focusing on the underlying chemical principles rather than juggling a larger list of similar reactants.

The main conclusions of this paper are:

1. HSS are common contaminants in amine units. They increase corrosion rate, chemically bind or neutralize amine, and often they accumulate over time. Dealing with HSS is a typical challenge in operating an amine unit.
2. There are several established methods for handling HSS. Neutralization is one option. It has the goal of neutralizing HSAS (converting HSAS into Inorganic HSS) and extending the time before the more effective (and expensive) methods are used. Neutralizing does not get rid of HSS anions, but tries to mitigate some of their negative effects.
3. Published studies and reports from operating plants are not unanimous about whether or not neutralizing reduces corrosion rate. However, there are several effects which are generally accepted to happen:
    a. Neutralizing can convert bound amine to free amine, which restores incremental acid gas pickup capacity.

   b. Neutralizing can increase lean loading. In some cases, this can hurt the solvent's treating performance.
   c. Injecting too much or too fast creates a risk of precipitation, pluggage, and alkaline Stress Corrosion Cracking (SCC).
   d. Neutralizing is not a permanent solution for on-going HSS contamination. It is intended to be a coping mechanism for extending the time between reclaim / purge events. Neutralization is commonly used as one part of a comprehensive HSS management strategy.
4. A significant number of operating sites neutralize their amine, and contend that they get benefits which out-weigh the risks.

Part 1 - Chemistry Review

The conclusions of this paper rest on several concepts from chemistry, which are reviewed here for convenience.

Electrolyte chemistry concepts

There are several important electrolyte, or ionic, chemical reactions which happen in the aqueous amine solutions used in gas treating. These reactions are responsible for the primary function of the amine: absorb acid gas in the contactor then release the acid gas in the regenerator.

For example, Equation 1 and Equation 2 below demonstrate how H_2S is chemically trapped in an MDEA solution. In Equation 1, aqueous H_2S lives up to the name *acid gas* by giving an H^+ ion to the solution. This renders the remaining HS^- ion as completely non-volatile and chemically traps the H_2S in solution. In a complementary reaction, MDEA acts as a base by accepting H^+ ions to create a *protonated MDEA* molecule, $MDEAH^+$.

$$H_2S_{(aq)} \leftrightarrow HS^- + H^+ \qquad \text{Equation 1}$$

$$MDEA + H^+ \leftrightarrow MDEAH^+ \qquad \text{Equation 2}$$

These reactions underscore two important concepts:

1. Equation 1 is the underlying mechanism for chemically capturing acid gas in amine. Ionic charged species such as HS^- are not volatile; they are chemically trapped in solution. Conversely, non-charged molecules are volatile to the extent allowed by vapor pressure or Henry's constant. This is a key concept for how acid gases get captured in amine, but in the context of this paper, it also drives the influence of neutralization on the volatility of HSS species in the regenerator's reboiler. This effect is also responsible for one of the undesired consequences of over-neutralization, which is elevated lean loadings.

2. Reactions affect each other through the common ion effect. In water, Equation 1 does not proceed very far to the right. However, the presence of MDEA greatly increases the amount of H_2S which can be held in the aqueous phase by a factor on the order of 1000x. This is accomplished through Le Chatelier's principle: If an equilibrium is disturbed, the system will shift to counteract that change and establish a new equilibrium. In the case of Equation 1, as H^+ ions are produced by H_2S, those ions are captured by MDEA through Equation 2. This drives Equation 1 further to the right, making it harder and harder for the volatile $H_2S_{(aq)}$ molecules to exist in solution, since they're preferentially converted to non-volatile HS^- ions after giving up their H^+ ions to MDEA. Le Chatelier's principle will be important in several aspects of the discussions below.

Ionic vs covalent bonds

The following discussion draws heavily on Chapter 3 of Reference [1].

The term *chemical bond* encompasses two distinct modes through which atoms are held together: covalent bonding and ionic bonding.

The term *covalent bond* refers to the bonding mechanism in which the outer orbitals of the bonded atoms overlap, resulting in increased electron density between the atoms. There are several sub-types of covalent bonds, including the metal-ligand bonds discussed later in this paper. All atoms are not created equally when it comes to covalent bonding: some atoms are much more available for covalent bonding due to their electronic configuration whereas others are less able to do so. For example, the Fe^{+2} cation can readily form coordinate covalent bonds with various ligands when it is in an aqueous solution, because it is a transition metal and therefore has d-orbitals in its outer shell. In contrast, the Na^+ cation's outer electronic configuration is much less available for covalent bonds.

The term *ionic bond* refers to bonds where atoms of opposite charge are attracted to each other by electrostatic forces. The concept of an ionic bond is an idealization which does not perfectly reflect real world solutions. In actuality, all ionic bonds also include some amount of covalent bonding, though the relative importance of those covalent bonds is much smaller.

Cation behavior in solution

Two cations are of special interest for the purposes of this paper: iron and sodium. These species behave quite differently in amine solutions. The Fe^{+2} cation enters the solution through corrosion, and Na^+ might be intentionally added during neutralization, or it may unintentionally enter the amine through contaminated makeup water, leaking isolation valves, amine reclamation etc.

When Fe^{+2} enters the solution, it enters as a complex surrounded by water molecules. Because of its electronic configuration, which includes the d-orbitals of a transition metal, each central

Fe^{+2} cation is surrounded by six water molecules. The water molecules serve as ligands, as shown below in Equation 6 and Equation 8. The six ligands organize into an octahedral complex around the cation. Each ligand shares a *coordinate covalent bond* with the cation. Both electrons of the bond are donated by the ligand. The metal-ligand bonds are true chemical bonds with measurable bond enthalpy. The solubility of a metal is strongly influenced by the stability of the metal-ligand bonds. As we will discuss soon, ligands can be substituted: the water molecules can be replaced by other molecules such as HSS anions.

In contrast, the electronic configuration of Na^+ cations is relatively inert with respect to covalent bonds. In fact, the outer shell of Na^+ cation has the same configuration as the noble gas neon. Given its electronic configuration, Na^+ is not very likely to have orbital overlap or participate in covalent bonds. However, it has a concentrated electrostatic charge in a relatively small volume, so it exerts considerable influence on polar and charged molecules in its vicinity. Approximately 16 – 17 water molecules are attracted to each Na^+ cation to such an extent that they can be considered as bound to the Na^+ with an ionic / electrostatic force.

That being said, coordinate covalent bonds with Na^+ cations still form at a detectable concentration, though they are less favored than bonds with transition metals such as Fe^{+2}. For example, reference [3] documents the critical stability constant for complexes of K^+ cations with oxalate and complexes of Na^+ cations with acetate. By analogy, complexes of Na^+ and oxalate should be expected to exist as well.

Corrosion reactions

Iron corrosion proceeds through the anodic – or oxidation – reaction listed in Equation 3. Typically, in amine systems, the corresponding cathodic – or reduction – reaction involves protonic acids, which provide H^+ ions that react as shown in Equation 4. Adding these two reactions together, we get Equation 5 which shows a simple corrosion reaction for iron. The H^+ ions in Equation 5 can come from the surrounding solution or from protonic acids like H_2S or HS^-.

$$Fe_{(s)} \rightarrow Fe^{+2} + 2\,e^- \qquad \text{Equation 3}$$

$$2\,H^+ + 2\,e^- \rightarrow H_{2,(g)} \qquad \text{Equation 4}$$

$$Fe_{(s)} + 2\,H^+ \rightarrow Fe^{+2} + H_{2,(g)} \qquad \text{Equation 5}$$

Iron cations from Equation 5 can go into solution surrounded water ligands as shown in Equation 6. In an amine system with H_2S present, it is also likely that the iron could be converted into a solid corrosion product as in Equation 7, with HS^- serving as the source of H^+ for corrosion. (Recall that chemically captured H_2S primarily exists as HS^- in amine solutions.) Iron sulfide created in Equation 7 also has some solubility, which can be expressed as Equation 8. [2]

$$Fe_{(s)} + 2\,H^{+} + 6\,H_2O \rightarrow\ [Fe(H_2O)_6]^{+2} +\ H_{2,(g)} \qquad \text{Equation 6}$$

$$2\,HS^{-}_{(aq)} +\ Fe_{(s)} +\ H_2O \rightarrow\ FeS_{(s)} +\ H_{2,(g)} +\ HS^{-}_{(aq)} +\ OH^{-}_{(aq)} \qquad \text{Equation 7}$$

$$FeS_{(s)} + 7\,H_2O \leftrightarrow\ [Fe(H_2O)_6]^{+2} +\ HS^{-}_{(aq)} +\ OH^{-}_{(aq)} \qquad \text{Equation 8}$$

Equation 6 shows the general principle that everything else being equal, more acidic solutions will be directionally more corrosive to iron. Equation 7 shows how amine solutions with higher acid gas loading become more corrosive, and also how captured H_2S leads to the formation of solid iron sulfide. Iron sulfide can be deposited as a layer coating the inner surface of pipes and equipment; it can also (through Equation 8) form as a particulate floating in the amine. The adhered layer of solid iron sulfide is known to significantly slow down the overall corrosion rate by slowing down mass transfer between the bulk amine solution and fresh, uncorroded iron underneath.

Equation 8 is a reversible reaction. This fact is one reason for the common observation that even when the lean amine is clear when it enters the absorber, the rich amine leaving the absorber will often have a significant amount of iron sulfide particles leading to dark or green appearance. In the absorber, as the amine picks up H_2S, the equilibrium of Equation 8 will naturally shift to the left due to increasing concentration of $HS^{-}_{(aq)}$ ions, causing more of the dissolved iron cations to precipitate as FeS solids.

Ligand Substitution and Chelation

As discussed above, in amine solutions, dissolved iron cations exist as the central metal cation surrounded by ligands, which are covalently bonded to it. For many cations, these ligands will be water as shown Equation 6 and Equation 8. However, other species can displace water to serve as a ligand. Equation 9 shows an example of a ligand substitution reaction where formate ($HCOO^{-}$) enters the complex to become a ligand. While Equation 9 shows one water molecule being displaced, it is also possible for more than one displacement to happen for the same central iron cation.

$$[Fe(H_2O)_6]^{+2} +\ HCOO^{-}\ \leftrightarrow [Fe(H_2O)_5(HCOO)]^{+} +\ H_2O \qquad \text{Equation 9}$$

Researchers have catalogued equilibrium constants for reactions such as Equation 9, which can be found in published tables of Critical Stability Constants, for example Reference [3]. Substitution reactions such as these are one way that HSS anions increase the net corrosion rate: they stabilize iron cations in solution, i.e., they shift Equation 6 and Equation 8 further to the right.

An additional effect, called *chelation*, happens when one ligand molecule is able to form more than one bond with a central metal cation. The oxalate anion, which is sometimes present as a contaminant in amine solutions, is an example of a chelating anion. Each oxalate anion ($C_2O_4^{-2}$)

has two carboxylic acid groups, each of which carries a -1 charge. Oxalate can displace two water molecule ligands as shown in Equation 10. Ligands in chelate structures make more stable complexes. This stability is at least partially due to statistical / entropic considerations: If a random encounter leads to a bond with one of oxalate's sites, then the oxalate's second bonding site will stay in close proximity and have a much better chance of creating a second bond. The reverse reaction, i.e., displacement of one oxalate ion by two water molecules, is similarly less likely because it requires the concurrent displacement of two bonds. The chelation effect explains why, relative to other HSS anions, oxalate has a significantly higher critical stability constant with iron [3] and has been observed to lead to significantly faster corrosion rate in amine solutions, as shown in Figure 1.

$$[Fe(H_2O)_6]^{+2} + \ C_2O_4^{-2} \ \leftrightarrow [Fe(H_2O)_4(C_2O_4)] + \ 2\ H_2O \qquad \text{Equation 10}$$

Soluble metal vs Corrosion Rate

Even though soluble metal concentrations are frequently reported for amine solvents, there is some nuance to understanding what this measurement tells us. There is not a rigorous direct relationship between the concentration of metal held in solution and the corrosion rate experienced in an amine unit. The corrosion rate in an amine unit depends on many parameters which are well documented in literature, for example in Reference [4]. In general, the corrosion rate will vary quite significantly from one place to another within the same amine unit. Local factors typically govern the severity and location of the worst corrosion in the unit. For example, the following factors are common culprits in corrosion failures: high rich loading, high velocity / turbulence from flashing 2-phase flow, high wall shear due to mechanical design that creates eddies and / or impinging flow [5]. These local factors must be identified through a unit review and cannot be identified through laboratory analysis of the amine.

The effect of the various local corrosion factors are additive in an operating unit. A unit which has a step change increase in rich loading will have an incremental increase in corrosion rate in the rich amine circuit. Similarly, a unit which has a step change increase in soluble iron concentration should be expected to have incrementally faster corrosion rate. The significance of any specific increase in corrosion rate will include considerations of the remaining corrosion allowance in the specific pieces of equipment, the quality of the inspection program in the plant, etc.

The cycle of taking Fe^{2+} cations from the internal surface of equipment / pipe, then precipitating that iron as FeS fouling is described as an "iron pump" in Reference [8]. Under this paradigm, we can think of a solvent that holds more iron as a higher capacity iron pump. Therefore, we should expect a directional relationship between iron solubility and corrosion rate: higher soluble iron concentration is directionally worse than lower soluble iron concentration. Nonetheless, it is not easy to determine when the difference is significant enough to justify taking action. Good unit monitoring practice is to watch trends of soluble metals over time and to interpret step changes or shifts as potentially serious signs of increased risk.

Important Chemical Reactions

The list of chemical reactions below shows the primary reactions in a typical amine solution. Acetic acid, H_3C_2OOH, is included as a typical HSS. These reactions are listed here as an introduction and for easy reference in the rest of the paper.

One important feature of this reaction set is that the acid H_2S and stronger acids such as acetic acid H_3C_2OOH, do not react directly with the amine MDEA. Instead, these acids donate H^+ cations to the solution, and the basic amine MDEA accepts H^+ cations from the solution. It is important to realize that the H^+ cations in solution are all equivalent to each other regardless of which molecule they came from. This relationship between different reactions is called the *common ion effect*; it is the mechanism through which the concentration of one ionic species affects the concentration of another across a network of reactions.

For example, consider the impact of increasing the amount of acetic acid H_3C_2OOH in a solution with H_2S and MDEA. Acetic acid is a stronger acid than H_2S. Increasing the concentration of acetic acid in solution will increase the concentration of H^+ ions, which in turn will both increase the extent of MDEA's protonation (Equation 14 moves further to the right) and it will also decrease the extent of H_2S's dissociation (Equation 12 moves further to the left). Both of these effects of HSS (i.e., more protonation of amine, less dissociation of acid gas) will be discussed further soon.

Another key aspect of this set of reactions is that NaOH can be assumed to completely dissociate into Na^+ and OH^- in the aqueous solution. These dissociated ions are not tightly bound to each other, so they will move independently through the solution. The reader is encouraged to look through the list of reactions and identify the ones which involve Na^+ and OH^-. In the case of OH^-, its only reaction is the reversible reaction with OH^- to make water. (OH^- also appears in Equation 7 and Equation 8, but these are less significant side reactions due to the low concentration of soluble iron, which is typically 10s of ppmw Fe or less.)

Reactions between Na^+ and HSS anions, such as Equation 16 are not extensively documented, but they do seem to happen. These complexes are important for considering corrosion phenomena related to neutralization. Any HSS anions which are complexed with Na^+ ions will be less available for complexing with iron in reactions such as Equation 9 and Equation 10. Therefore Equation 16 is a mechanism for neutralization to slow down corrosion.

Evidence for reactions such as Equation 16 can be found in the literature, though it takes some research to find. Reference [3] gives the critical stability constant for a complex of potassium cation with oxalate anion; presumably complexes of sodium and oxalate also exist, though they are not listed. Reference [9], which focuses on bicine corrosion, documents that critical stability constants for complexes between alkali metals and amino acids are available from the public data resource NIST SRD 46 – which the authors of the present paper were not able to confirm due to time and IT constraints (the freely available NIST SRD 46 database is accessed through an executable compiled to run on Windows XP or earlier). The authors of Reference [9] note that the NIST database does not contain a critical stability constant for complexes of sodium and bicine, but it does contain constants for complexes of sodium with related or analogous amino acids. They reasonably conclude that, by analogy, some amount of coordinate covalent bonding would be expected between sodium and bicine as well.

$$H_2O \leftrightarrow H^+ + OH^- \qquad \text{Equation 11}$$

$$H_2S_{(aq)} \leftrightarrow H^+ + HS^- \qquad \text{Equation 12}$$

$$H_3C_2OOH \leftrightarrow H^+ + H_3C_2OO^- \qquad \text{Equation 13}$$

$$MDEA + H^+ \leftrightarrow MDEAH^+ \qquad \text{Equation 14}$$

$$NaOH \rightarrow Na^+ + OH^- \qquad \text{Equation 15}$$

$$Na^+ + H_3C_2OO^- \leftrightarrow Na(H_3C_2OO) \qquad \text{Equation 16}$$

Part 2 - HSS effects on amine chemistry and corrosion

More acidity, more iron complex stability

It is well-documented in industry that amine solutions become more corrosive as HSS anions accumulate. This general principle can be seen in Figure 1 which shows how corrosion rate increases as an amine solution is progressively acidified by HSS. This lab study did not reflect all aspects of typical industrial conditions - especially the presence of H_2S. Since there was no H_2S present to create a protective iron sulfide film in the experiments, an important factor that influences corrosion rate in real world amine units was missing. Nonetheless, there is a clear relationship for each acid showing that corrosion rate increases as pH falls. In the limiting case of a completely absent or destroyed FeS passivation layer, this corrosion behavior could be expected. This study also shows that oxalate and bicine are significantly more corrosive than other anions at the same pH, which is attributed to the ability of oxalate and bicine to chelate iron.

Other studies [2] and [6] present data showing an analogous relationship between increasing HSS concentration and increasing corrosion rate in the presence of H_2S and CO_2. Since the accumulation of HSS will reduce the solution's pH (more H^+ available, less OH^- available), corrosion rate from Equation 6 and Equation 8 should naturally increase. Additionally, HSS will increase corrosion rate by stabilizing iron in solution through reactions similar to Equation 9 and Equation 10. This effect will act to stabilize any iron cations in solution, regardless of how they got there, but it is thought to be especially damaging to process equipment in amine service because – through the common ion effect and Equation 8 – increased HSS concentrations damage the protective iron sulfide layer which has a strong influence on overall corrosion rate.

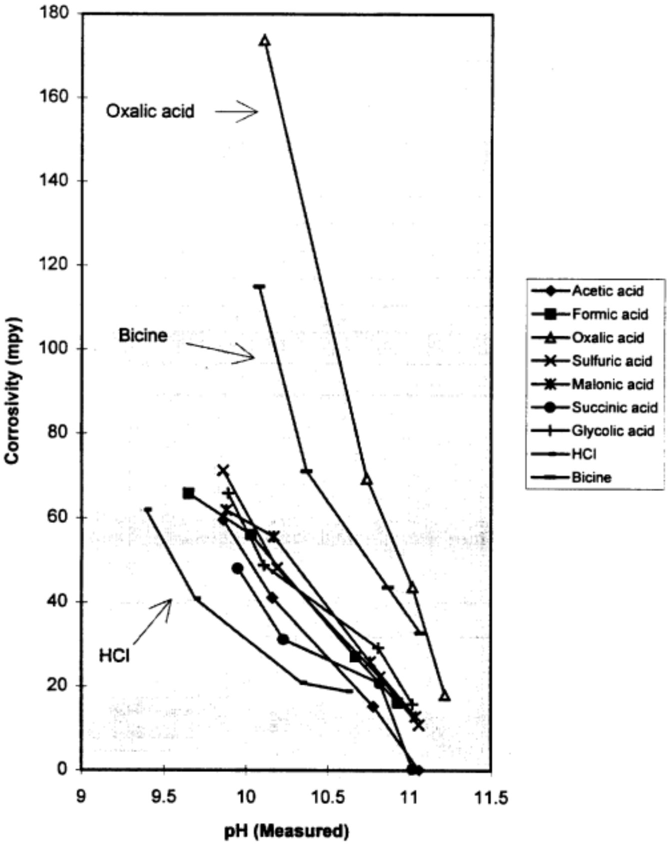


Figure 1 – From Ref [7] shows that corrosion rate increases as an amine solution is progressively acidified by strong acids. These particular data points come from carbon steel corrosion coupons in a closed stirred reactor containing 50 wt% MDEA in water with varying concentrations of acid at 250°F for 7 days.

Figure 2 shows the effect of HSS on the speciation of a rich MDEA solution with increasing acetate content. The acetate (and acetic acid) increase, causing a rise in $[H^+]$ and a decrease in $[OH^-]$. Increasing $[H^+]$ increases $[MDEAH^+]$ at the expense of MDEA. The $[HS^-]$ remains roughly constant, while H_2S rises and $[S^{--}]$ falls. These results demonstrate how increasing amounts of HSS lead to more bound amine (more $MDEAH^+$) and less solubility of H_2S (molecular uncharged – and therefore volatile - H_2S is a larger fraction of total H_2S).

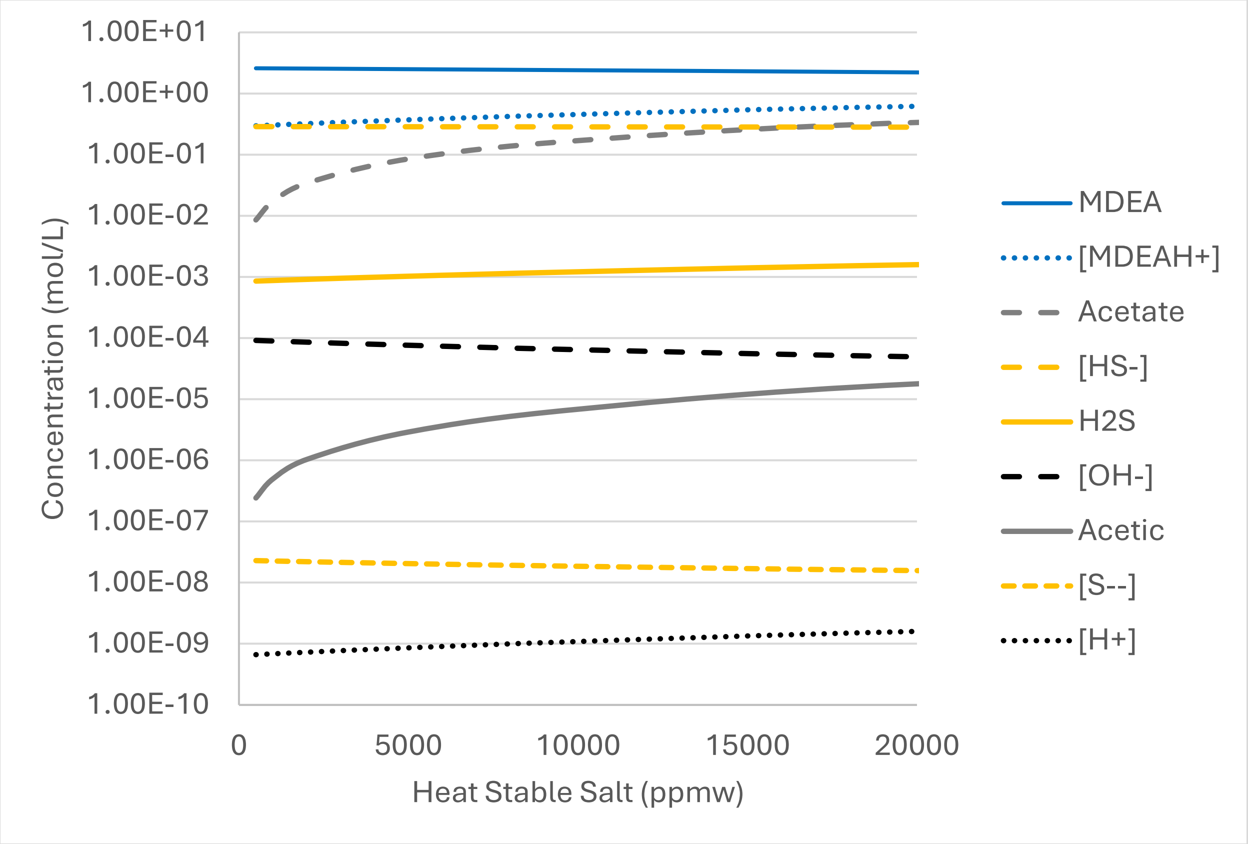


Figure 2 - – Speciation of 0.1 mol/mol loaded MDEA solution with increasing heat stable salts (Acetate)

Volatile acid in reboiler

There is another mechanism for HSS-driven corrosion, which specifically affects the bottom of the regenerator, the reboiler, and the reboiler vapor return line. This mechanism involves increased volatility of some acids as the overall concentration of HSS increases. Equation 12 and Equation 13 show how acids will find an equilibrium between the volatile molecular form and the non-volatile ionic form. The fraction of molecules that exists in volatile vs non-volatile forms is dictated by the temperature-dependent pKa value for each acid. Of course, the reason that we call these acidic contaminants *Heat Stable* Salts is that under normal operating conditions they are almost completely trapped in the non-volatile ionic form and cannot be steam stripped from the amine to a significant extent. However, some of the weaker acids (such as acetate with pKa = 4.76 and formate with pKa = 3.75) can sometimes achieve small but significant volatility in the regenerator's reboiler. Volatile acids pose a particular corrosion risk in the reboiler because the acid vapor can be absorbed into droplets of water which condense on the inner surface of the reboiler shell, reboiler vapor return line, etc. Since these water droplets contain much less amine than the bulk circulating solvent, the pH of the droplets is much lower than the bulk solvent, which can lead to increased corrosion rate. This effect is explored further in Part 3.

Beneficial side effect: Lower lean loading

Increasing concentration of HSS contaminants results in increased acidity (less basicity) of the amine solvent. As discussed above, increased acidity naturally shifts the ionic equilibrium of captured acid gas towards its volatile molecular form, with the net effect of making it easier to strip acid gas out of the solvent and achieve a lower lean loading. This effect is a natural consequence of Equation 12. In some units (especially TGUs), this effect can improve unit performance, but in other units the effect will not provide a significant benefit.

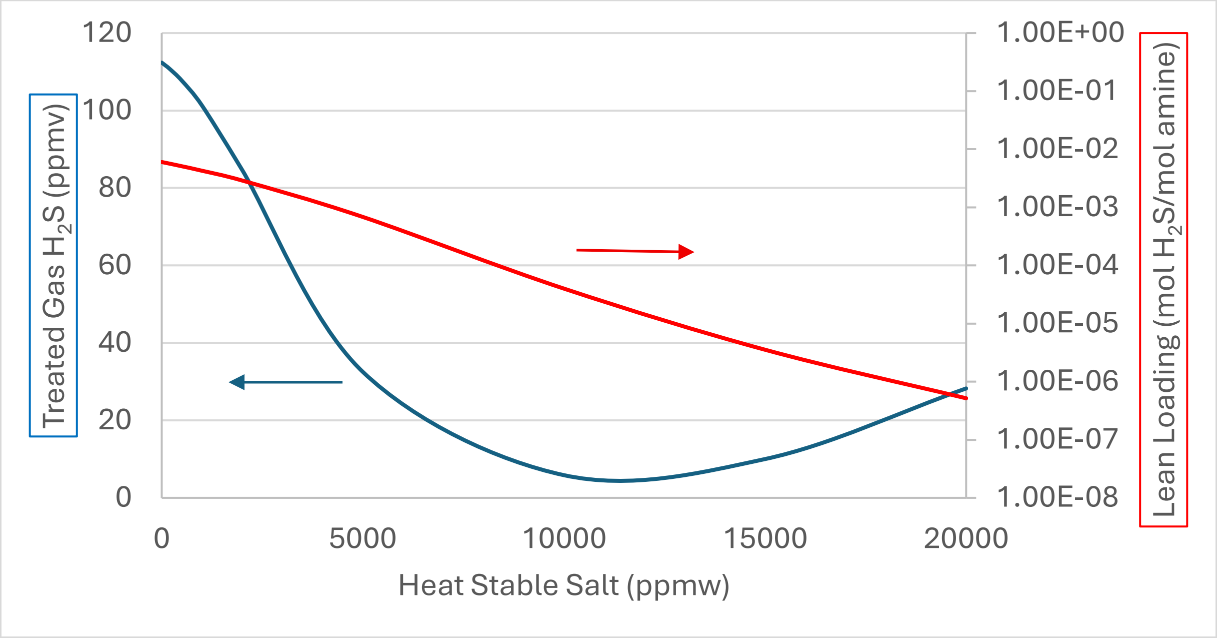


Figure 3 - Effect of HSS on TGTU performance, constant reboiler duty

Figure 3 shows the impact of increasing HSS on the overall behavior of a typical TGU. For a constant reboiler duty, as HSS increase, the lean loading goes down. This lower lean loading improves treating performance to a point. After sufficient MDEA is tied up in HSAS, the treating performance is degraded and the treated H_2S content increases.

Part 3 – NaOH Effects on Amine Chemistry and Corrosion

Simulation study

A Promax simulation study was used to investigate what happens to ionic speciation when NaOH is added to an amine solution with HSS. The example uses a 34wt% MDEA solution with acetate as a contaminant. To simplify the process, only H_2S is considered as an acid gas.

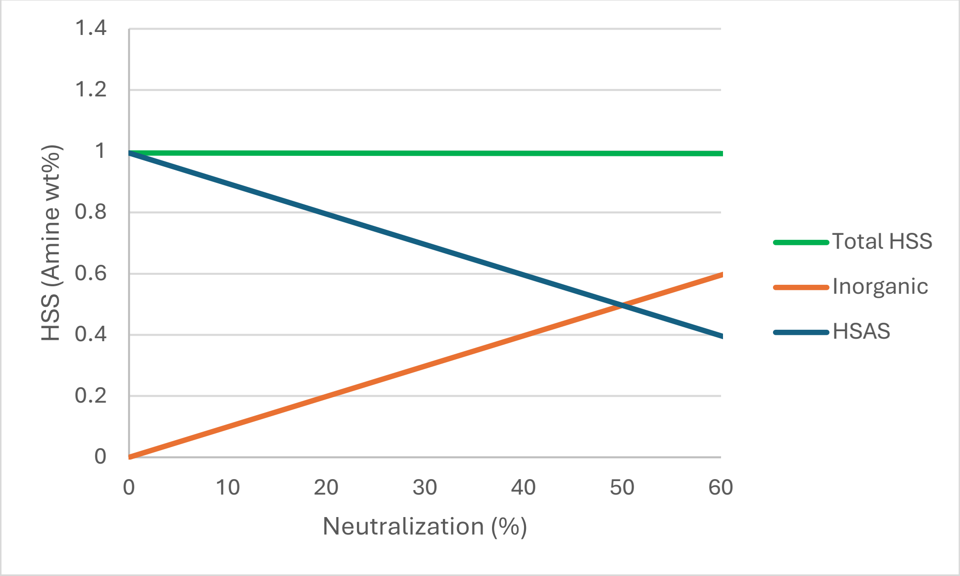


Figure 4-Effect of Neutralization on HSS (5000ppmw)

More free amine, no change to ionic strength

Figure 4 shows the primary intended effect of neutralization: Heat Stable Amine Salts are converted to Inorganic Heat Stable Salts – even though Total Heat Stable Salt content is not changed. The simulation study was used to explore what changes are happening at the ionic level. As shown in Figure 5, one clear and expected effect of adding NaOH is to raise the pH of the amine solution. The shift in pH is due to NaOH supplying OH^- anions to the solution, which consume H^+ through Equation 11. Due to the common ion effect, the increasing pH also frees protonated amine molecules by shifting Equation 14 to the left. This gives us one of the uncontroversial benefits of neutralization: It converts protonated amine (also called *bound amine*) into free amine, which restores some incremental capacity to hold acid gas.

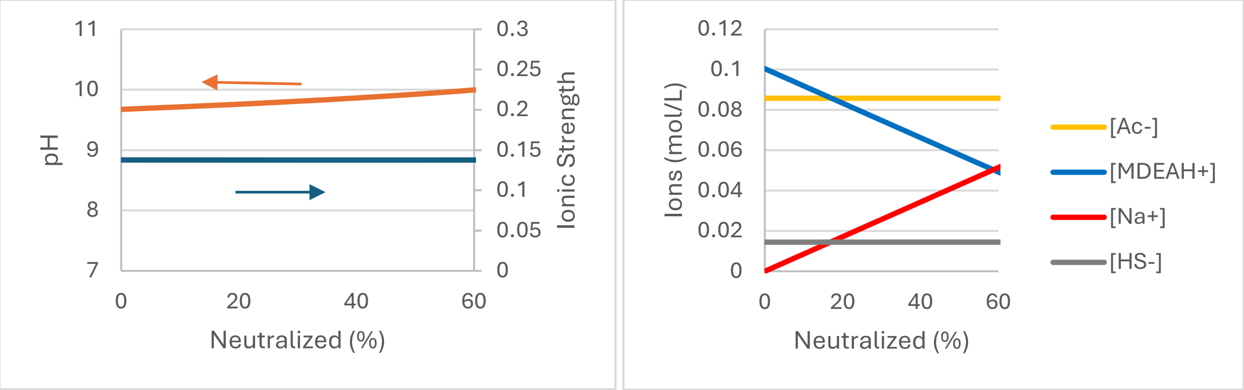


Figure 5 Effect of Neutralization at low loading (0.005 mol H_2S/mol amine)

An unexpected finding from the ProMax study is that ionic strength does not change appreciably due to neutralization, and therefore other properties that depend on ionic strength (electrical conductivity, activity of ions, etc.) should not be expected to change very much either. This makes sense upon reflection: As shown in Figure 5, the net effect of adding NaOH is to convert $MDEAH^+$ into Na^+, i.e., it changes one cation for another cation in a 1:1 swap without any net increase to the number of charged ions in solution. This simulation result is at odds with observations made in Reference [2] where adding NaOH to an HSS-laded amine solution resulted in higher conductivity in the lab. At this time, no explanation for this difference is offered – it could be an area for further investigation.

Figure 6 shows the impact of neutralization of a solution with the same HSS content, but higher loading (0.1 mol H_2S/mol amine). The behavior of Figure 4 would be unchanged. However, at higher loading, the H_2S dominates the ionic character of the solution, and the pH is essentially unaffected by neutralization. Again, Na^+ ions replace the $MDEAH^+$ ions to provide an essentially unchanged ionic strength throughout the range of neutralization.

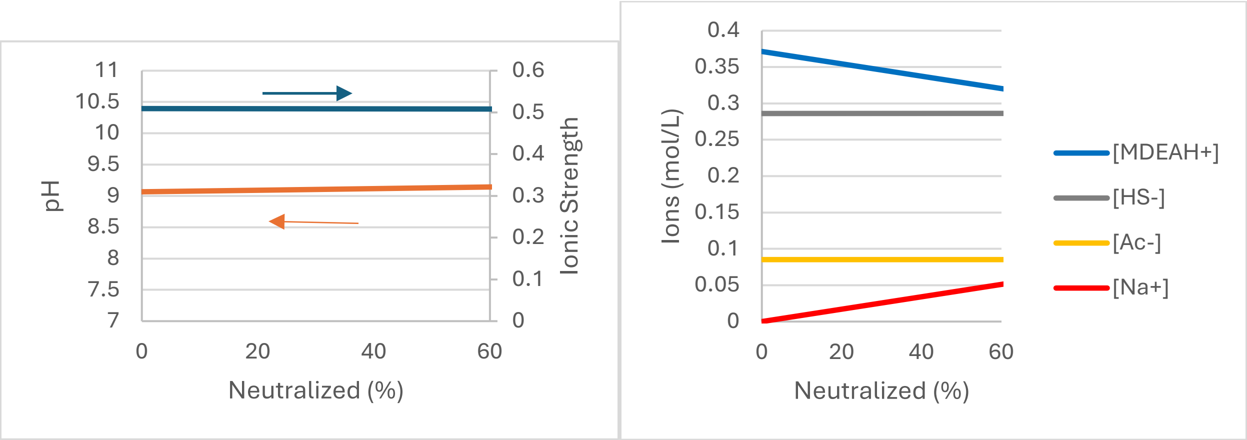


Figure 6- Effect of neutralization at higher loading (0.1 mol H_2S/mol amine)

Impact on corrosion rate

The effect of neutralization on corrosion rate is not completely clear, with some evidence existing on both sides.

On one hand, lab work presented in Reference [7] shows that corrosion rate correlates with pH as shown in Figure 1. This makes sense considering Equation 6, which shows that iron corrosion requires a source of H^+ ions, which are generally less available as pH increases. Notably, the experimental work in [7] was done in the absence of H_2S, so the protective influence of iron sulfide was not evaluated. Despite this fact, the data confirm that there is an acidic corrosion mechanism which would always be waiting to exert its influence any time fresh iron is exposed to the solution, e.g., when iron sulfide is removed by chemical solubility, flow-induced drag forces, or mechanical erosion.

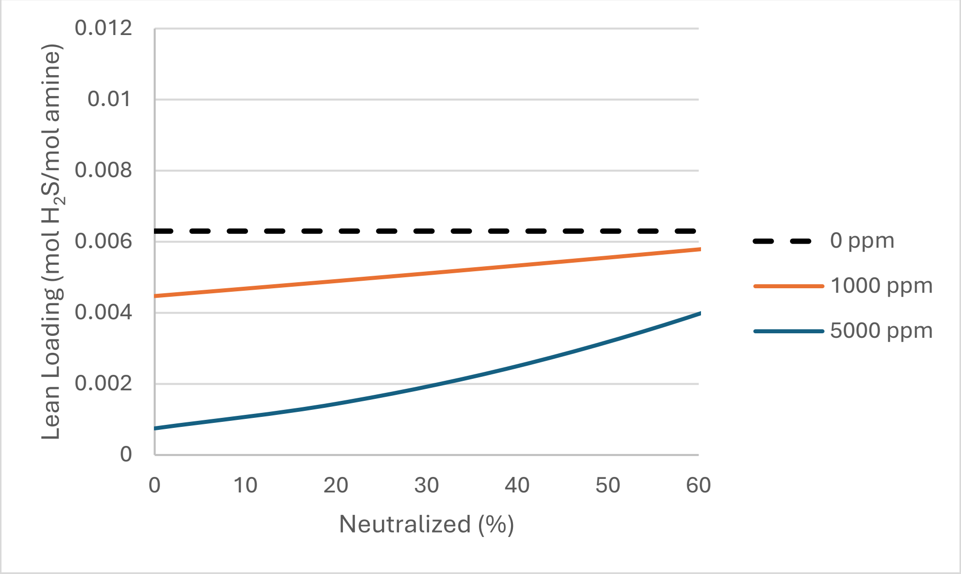
Also, reactions between sodium and HSS anions, such as Equation 16, are known to happen to some extent. For example, calculations done in Reference [9] suggest that caustic neutralization might chemically bind approximately half of bicine anions. HSS anions which are partially bound to sodium cations will be less available to participate in the iron complexes which accelerate corrosion, i.e., such HSS anions will be less available to participate in reactions like Equation 9 and Equation 10.

Finally, there are numerous anecdotal stories of operating plants who report lower corrosion rates and longer amine filter life when they maintain controlled levels of neutralization. Some of these plants have been following this practice for decades. Stories from the field are emphatically not the same as carefully collected data, but neither should they be rejected out of hand. There is a definite subset of our industry – professionals who operate real world process equipment year after year – which is convinced that neutralization helps reduce corrosion.

On the other hand, the lab study in Reference [2] concludes that neutralizing *increases* (not decreases) the overall corrosion rate in MDEA systems from 20 – 30 mpy before neutralizing to 40 – 50 mpy after neutralizing. Findings for DEA systems are less clear cut and may show reduced corrosion rate after neutralizing. The authors of Reference [2] also emphasize that the best way to reduce HSS-related corrosion is to get rid of the HSS – a conclusion that bears repeating. Even at its best, neutralization is a coping mechanism not a remedy. It can potentially extend the length of time between reclaiming or purging amine, but it does not remove HSS or other contaminants from the amine.

Higher lean loading

Another uncontroversial effect of adding NaOH is that it leads to higher lean loading. When HSS contaminants accumulate, they contribute additional H^+ ions to the solution, which drives Equation 12 to the left, converting more of the dissolved H_2S into its uncharged volatile molecular form, which has the net effect of making it easier to strip H_2S to very low levels. This effect was previously introduced in Part 2. Figure 7 shows the impact on a typical TGU of neutralization at three different levels of HSS contamination. As the neutralization increases, the beneficial effect of the HSS on lean loading and treated gas H_2S is diminished. This represents a fixed reboiler duty. For the case of trying to hold lean loading constant, the reboiler duty would be increasing with increasing neutralization.



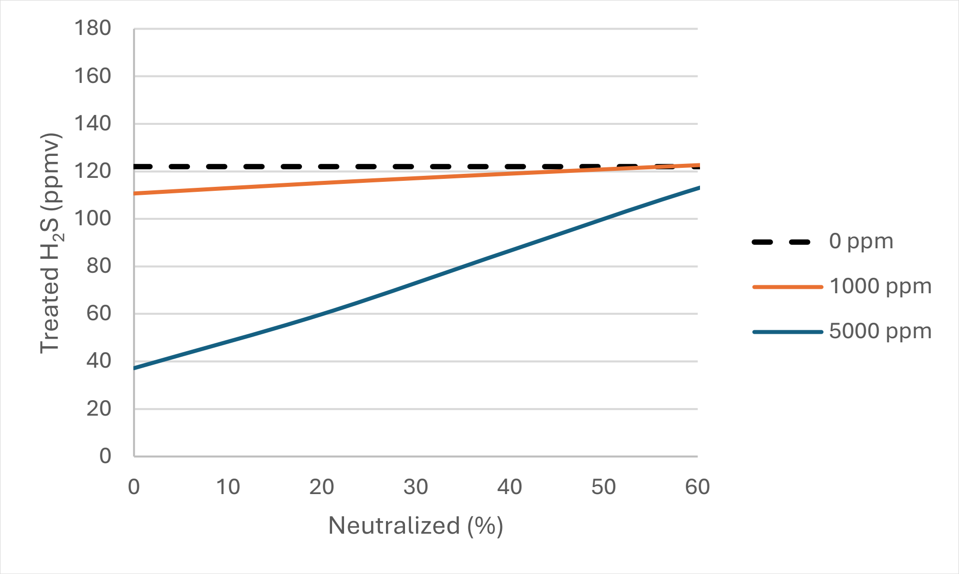


Figure 7 - Effect of neutralization on treating performance in a TGU

Adding NaOH reverses this effect by supplying OH^- ions that tend to consume H^+ to make water by Equation 11. Numerous real world plant experiences with both intentional and accidental addition of NaOH to the amine have observed this increase in lean loading.
As long as the solution is not neutralized to 100% or higher, i.e. when the molar quantity of NaOH added is smaller than the quantity of acid equivalents from HSS anions, this effect will be limited to cancelling out the beneficial side-effect of HSS. We will soon see that the effect can become more severe if the solution is over-neutralized to approach or exceed 100%.

Lower soluble iron

In plant data, it is often observed that neutralizing an amine solution leads to lower concentrations of soluble iron. The plant data sets below are examples.

Earlier we established two mechanisms whereby HSS anions increase the solubility of iron: i) by reducing the pH, which would affect the equilibrium of Equation 3 through Equation 8, and ii) by attaching to iron cations as ligands, which increase the solubility of iron through Equation 9 and Equation 10. Both of these HSS effects would be reversed by neutralizing, thereby leading to a reduction in iron solubility.

For systems with CO_2, another proposed mechanism for this effect was given in Reference [2] which noted that neutralization raises the solution pH. Higher pH shifts the equilibrium of dissolved CO_2, which primarily exists as bicarbonate HCO_3^-, to have a larger proportion in the form of carbonate CO_3^{-2}. The presence of carbonate and dissolved iron encourages the precipitation of iron carbonate.

Reduced volatility of acids in reboiler

Spooner and Costelow [10] described a regenerator at risk of failure by corrosion due to very high levels of formate at 15,000 – 20,000 ppmw, vs typical max limit of 2,000 – 5,000 ppmw. To extend the service life of the regenerator vessel, they employed a suite of changes to mitigate further damage, one of which was caustic neutralization. Caustic neutralization was used in this case to trap volatile formic acid in the bulk amine liquid where it is less corrosive due to the presence of amine. To investigate this claim, a ProMax simulation was created to roughly match the vapor phase formic acid profiles shown in the paper. The study was not meant to exactly mimic Reference [10], nor to critique the conclusions or methods there, but rather to investigate the claim through detailed analysis of simulation results. The simulated dewpoint liquid for the reboiler vapor was found to have a pH of 7.76 for the base case and 8.15 for the neutralized case. The difference was that neutralization reduced the volatility of formic acid, as expected. This result shows a directional benefit for neutralization in cases with severe formate contamination. For more typical levels of HSS contamination, there will be much less volatility of HSS acids, and therefore this effect will not be significant in most amine units – though it is a great trick to keep in mind for extraordinary circumstances.

Plant Data: Plant #1 – Neutralization leads to lower soluble iron

Data shown in Figure 8 demonstrates a correlation between % neutralization and soluble iron. Even when Total HSS are high, there is low soluble iron when neutralized. In this unit, HSS are predominantly formate and thiocyanate, which is typical for refinery service.

During the first time period, Total HSS are high at 3 – 6 wt%, the amine is 60-80% neutralized, and soluble iron is low at ≤ 2 ppmw. At the end of this time period, the amine was reclaimed, which resulted in lower HSS and soluble iron.

In the second time period, HSS began to accumulate in the solvent, but the plant did not neutralize the salts. During this time, HSS climb to 3-4 wt% and soluble iron climbs to 5 ppmw.

In the third and final time period, the plant resumes neutralizing. As the plant comes up to 40-60% neutralized, the soluble iron again falls to ≤ 2 ppmw.

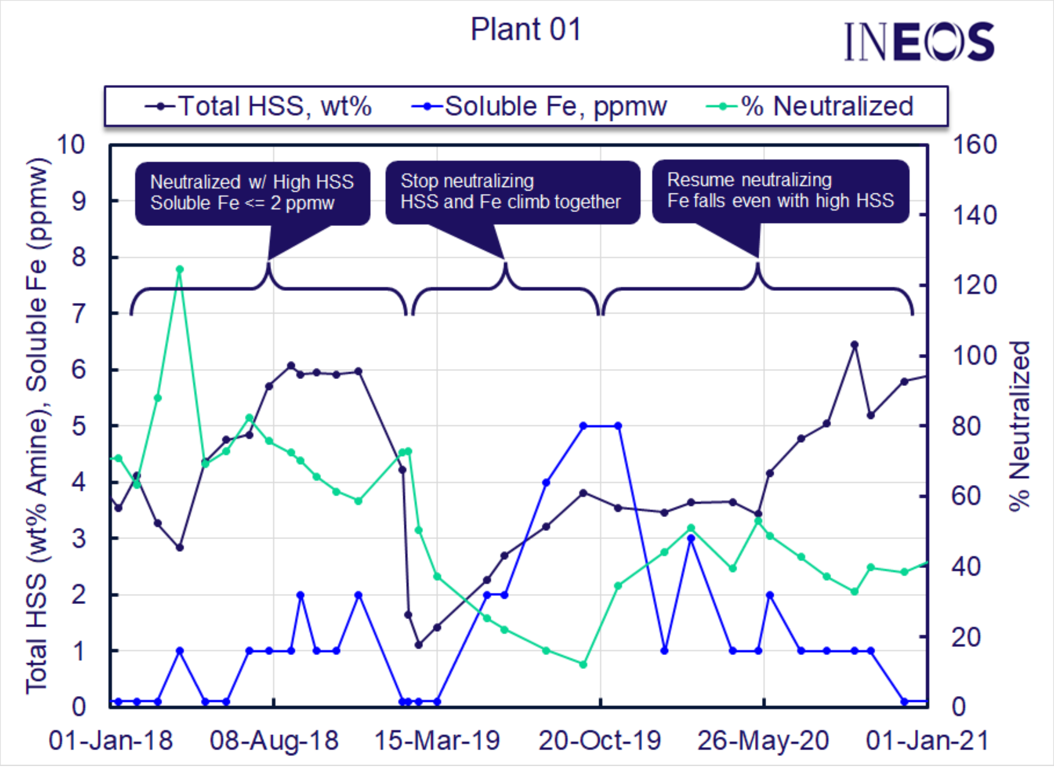


Figure 8 - Plant #1. Neutralization leads to lower soluble iron.

Plant Data: Plant #3 – Neutralization leads to less corrosion and longer filter life (anecdotal)

In this H_2S and CO_2 system, the plant reported experiencing corrosion failures and frequent filter changes. They added NaOH to reach 7000 ppmw Na^+ and 100% neutralized (Figure 9). The plant reported fewer corrosion issues and longer filter life. There was a noticeable increase in lean loading (Figure 10), but soluble metals did not have a clear response (Figure 9).

This rather inconclusive example was included in the paper to represent a typical real-world case: plant personnel report a benefit for neutralizing, but supporting data are thin.

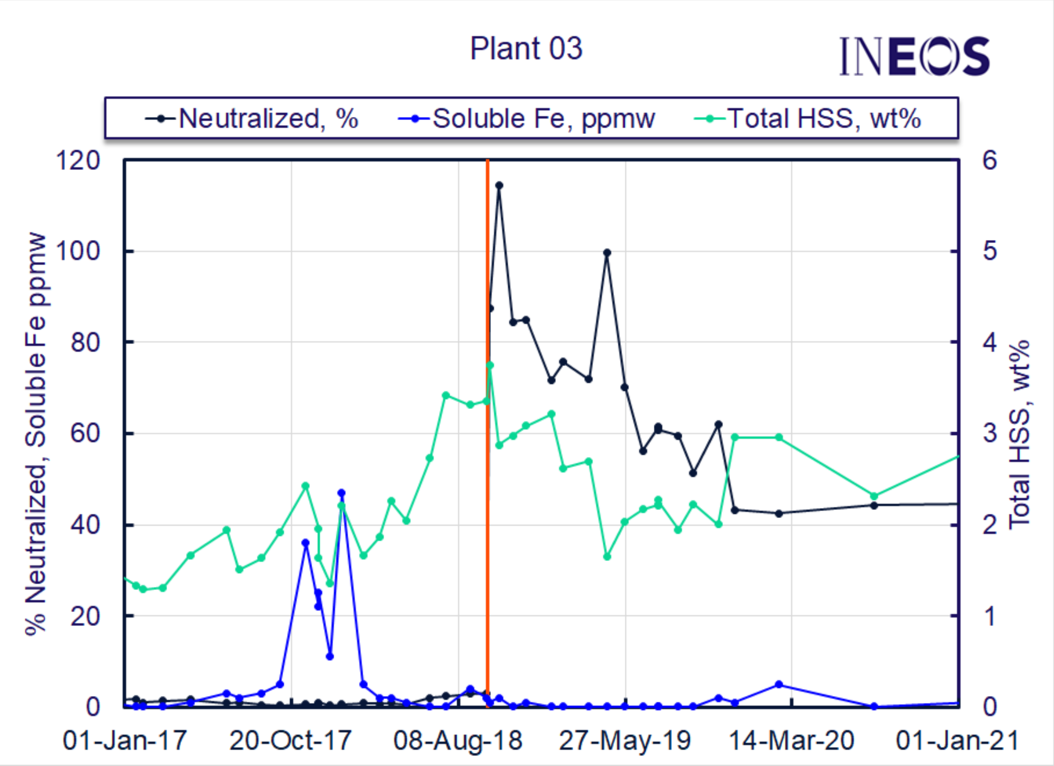


Figure 9 - Plant #3, % neutralized, Soluble Fe, Total HSS trend.

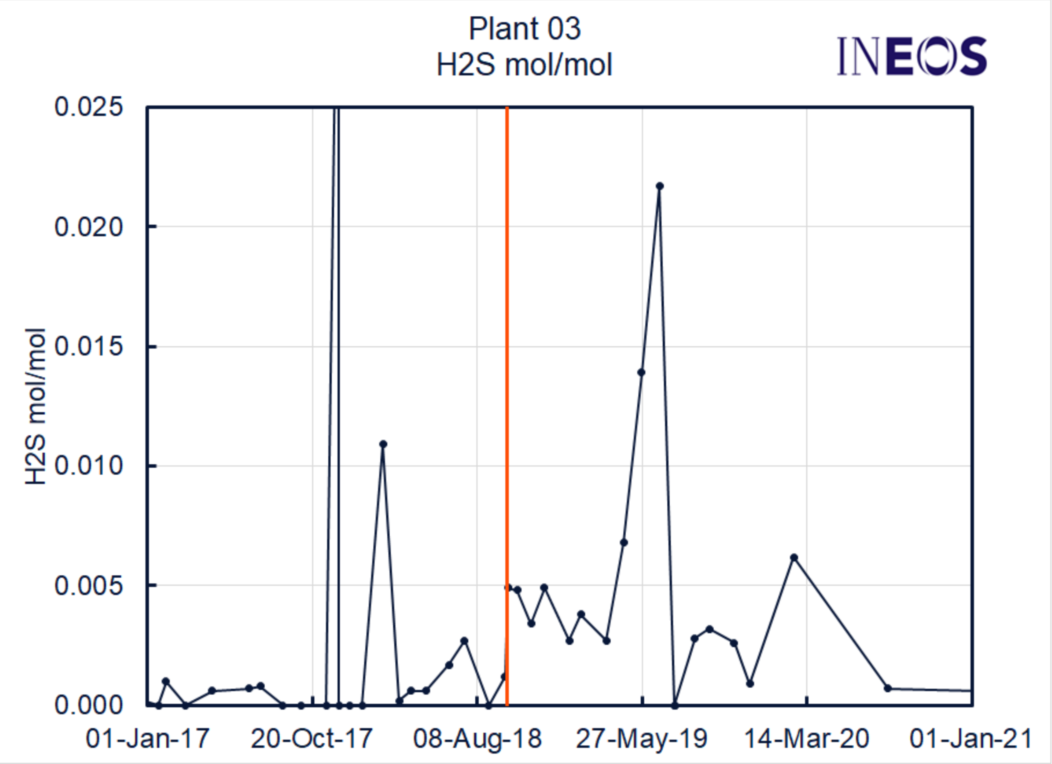


Figure 10 - Plant #3. Lean loading trend.

Part 4 – Effects of adding too much NaOH

Simulation study

If some neutralization is good, is more better? Not usually. Figure 11 shows our HSS chart for the 34% MDEA system with 5000 ppmw acetate, extended to 120% of neutralization. Eventually the HSAS drops to zero, meaning that no amine is 'bound' as HSAS.

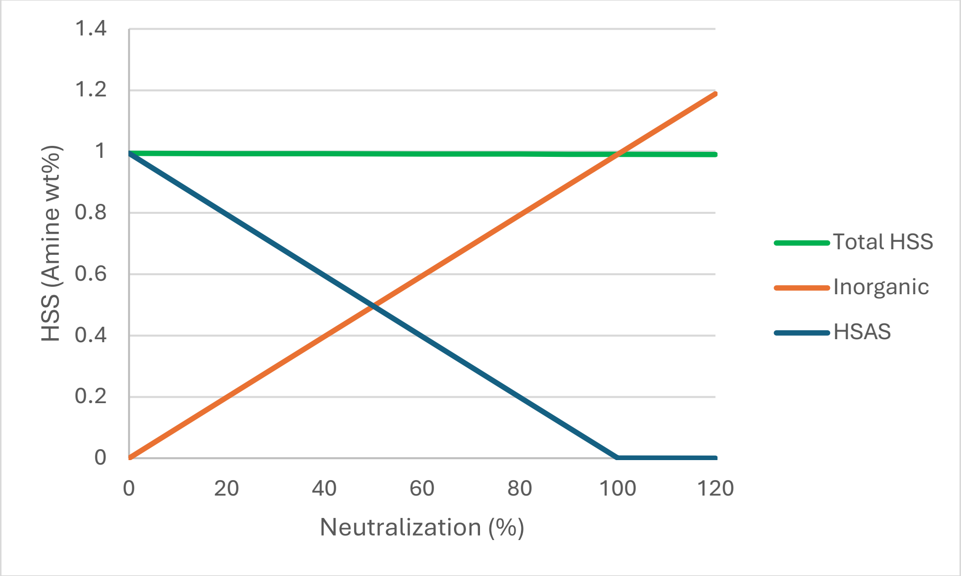


Figure 11 - Effect of Over-neutralization

Figure 12 explores what is going on with the chemistry for a lower H_2S loading solution. As we continue to increase % neutralization, the solution pH continues to rise and ultimately the ionic strength also begins to rise as more [OH^-] ions are present. These effects would be expected to correlate with increasing conductivity and will directionally increase the risk of alkaline stress corrosion cracking. While the amine is technically 'unbound' from the HSS at 100% neutralized, the $MDEAH^+$ does not completely disappear, even at 120% neutralization, due to the presence of the HS^- and OH^-.

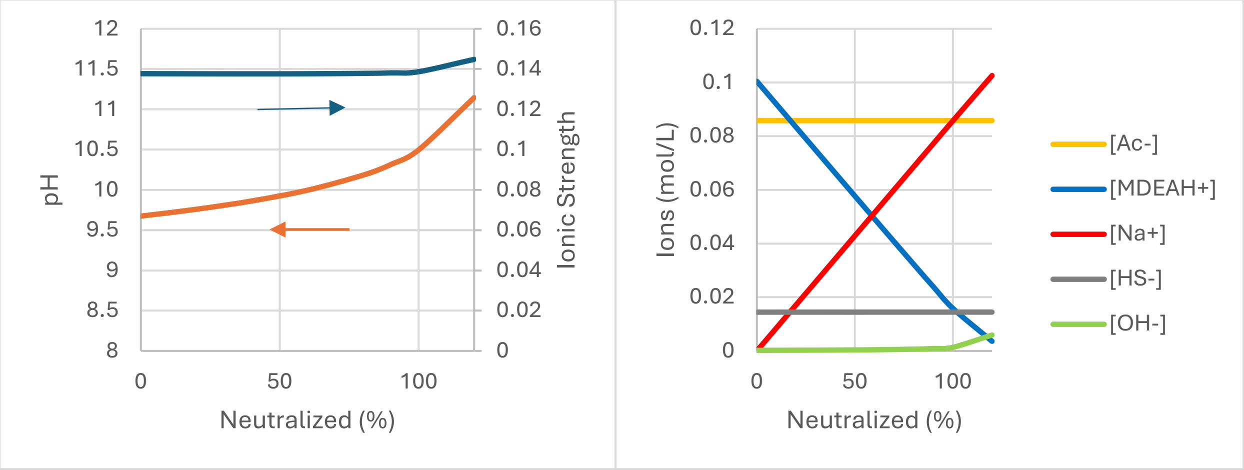


Figure 12 - Over-neutralizing simulation study

In the case of a more highly loaded solution, over-neutralization does not change the ionic character of the system substantially. The HS^- dominates relative to the acetate, so neutralization only increases the pH by 0.1 and the ionic strength remains essentially unchanged.

Increased lean loading, potential for plugging

With respect to lean loading and potential for plugging, the trends which were explained above in Part 3 are extended even further when too much NaOH is added. As the solvent approaches and exceeds 100% neutralized, the impact on lean loading becomes more pronounced. As the amount of excess NaOH increases, it begins to irreversibly trap H_2S in solution as NaHS, which – thanks to the common ion effect and Equation 12 – also affects the ability of the solvent to pick up additional H_2S. Therefore, there is a further increased risk of more H_2S slip through the absorber and inability to reliably hit treating targets. Note that the impact on treated gas is not always observed, depending on the operating regime of each amine contactor. The effect on lean loading is shown in the plant data example below.

Figure 13 shows the simulated impact of over-neutralization on lean loading and treated gas H_2S in a typical TGU. At roughly 85% neutralization, the lean loading has returned to the level for the case without HSS. Above this point, continued neutralization leads to further increases in lean loading and H_2S in treated gas.

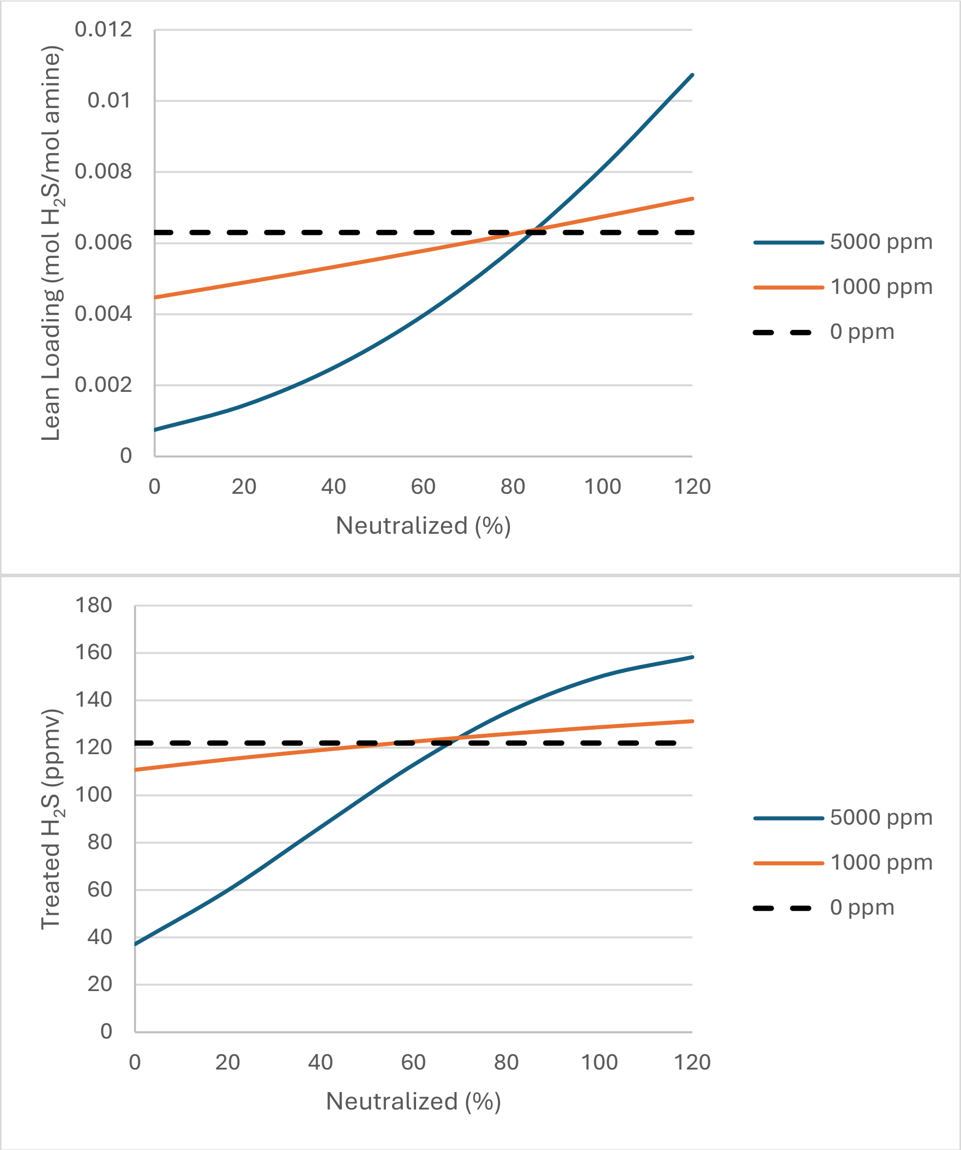


Figure 13 Effect of over-neutralization on treating performance (fixed reboiler duty) in a TGU

Potential risks of plugging also increase if a system is neutralized beyond 100%. Precipitates could include sodium salts (e.g., $NaHCO_3$, Na_2CO_3), iron salts (e.g., $FeCO_3$), or corrosion products like FeS which may tend to sluff off during neutralization [2]. INEOS has direct experience with a refinery which over-neutralized to > 7000 ppmw Na and > 100% HSAS neutralized. This plant experienced severe plugging in their carbon bed which took considerable effort to clean out.

Plant Data: Plant #4 – Over-neutralization leads to higher lean loadings

This refinery ARU had unintentional Na^+ and K^+ incursion (Figure 14) leading to > 100% neutralized solvent. The issue was eventually resolved. Soluble metals were low during the entire time. There was a clear correlation between over-neutralizing and higher lean loadings (Figure 15).

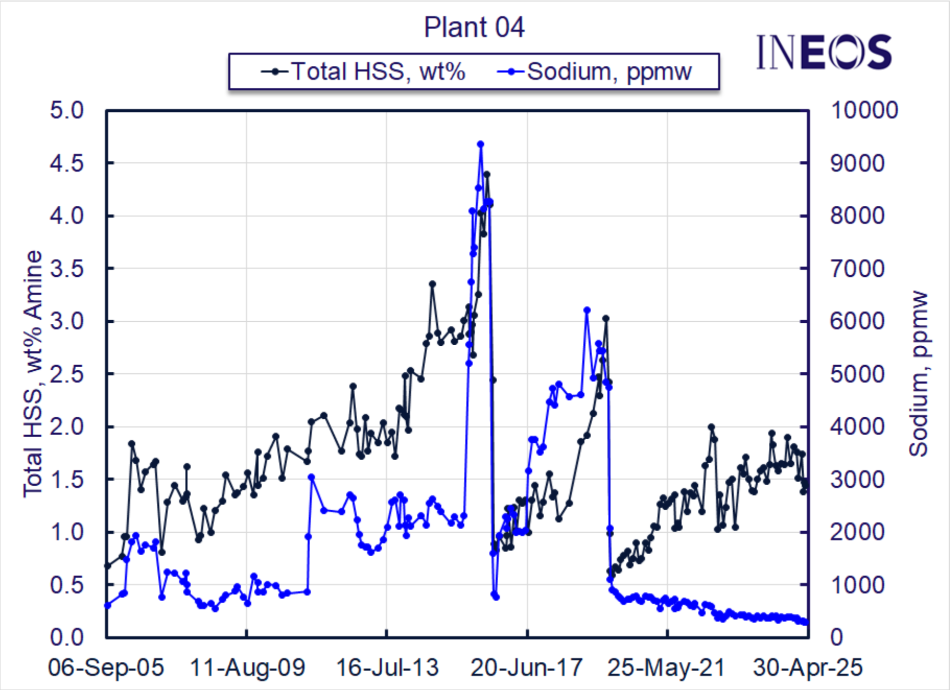


Figure 14 - Plant #4. Total HSS and Sodium trend. HSS accumulated relatively steadily and were periodically reclaimed. Sodium incursion was unintentional and was eventually eliminated.

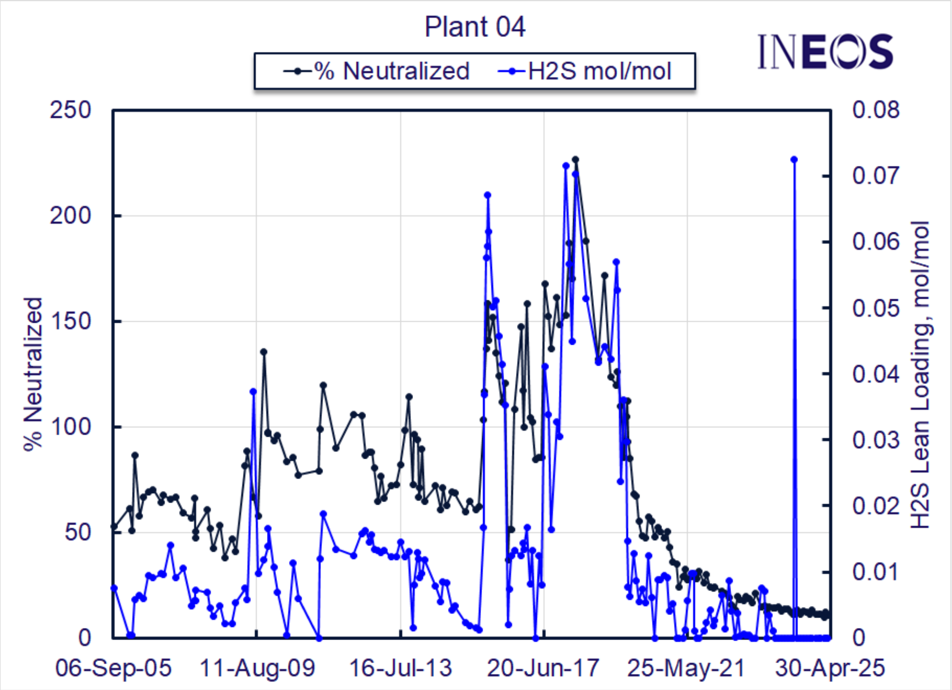


Figure 15 - Plant #4. HSAS % neutralized and H_2S Lean Loading trends. The correlation between % neutralized and H_2S Lean Loading is apparent.

Conclusion

Neutralization is not a panacea for all problems related to heat stable salts, but it continues to be practiced in industry with positive results. It would also be most advised for systems that are well-monitored with personnel who know their systems and the phenomenon of acid-base chemistry and its ramifications.

Benefits of Neutralization:

1. Restores amine's capacity for acid gas pickup.
2. Lowers corrosion rate (not unanimously agreed).
3. Can extend time until purge or reclaim is needed.
4. Low cost, quick to implement, uses materials that are often on-site already.

Potential drawbacks of Neutralization:

1. Total HSS level does not change. HSS anions are not removed.
2. Injecting too much or too quickly can lead to plugging and increased risk of alkaline Stress Corrosion Cracking.
3. System now has Inorganic HSS to deal with.
4. Can increase lean loading which can sometimes hurt acid gas pickup (this is not unique to neutralization – it can happen with purge and reclaim too.)

Appendix – Reporting Conventions

Industrial amine solutions will typically contain water, amine, acid gas, and ionic contaminants called Heat Stable Salts (HSSs). The ionic contaminants typically include both anions (e.g., formate, acetate, etc) and cations (e.g., sodium and potassium). In order to effectively communicate information about stream compositions, there are several terms in common use, which are defined as follows:

HSS anions, ppmw – anion contaminants such as acetate, formate, etc are reported in their true concentration as they exist in the amine solution. In other words, lb anion / lb solution * 1,000,000 ppmw.

HSS cations, ppmw – similar to HSS anions, cation contaminants such as sodium and potassium are reported in their true concentration as they exist in the amine solution. In other words, lb cation / lb solution * 1,000,000 ppmw.

Total HSS, wt% - This value represents the wt% amine which could be neutralized by the sum total of HSS anions. First the concentration of each HSS anion is converted to molar charge equivalents. The sum of the molar charge equivalents for all HSS anions is equal to the number of molar equivalents of amine that the HSS anions could neutralize. This molar amount of amine is expressed as wt% amine.

Inorganic HSS, wt% - This value represents the wt% amine that would provide the same number of molar charge equivalents as the HSS cations in solution (Na^+ and K^+). This molar amount of amine is expressed as wt% amine.

Heat Stable Amine Salts (HSAS), wt% - This value represents the wt% amine which could be neutralized by the HSS Anions after taking credit for the Inorganic HSS. HSAS is calculated as the difference between Total HSS and Inorganic HSS.

HSAS = Total HSS – Inorganic HSS

In the event that Inorganic HSS is larger than Total HSS, as in a solution which has been "over neutralized," the HSAS value is capped at a minimum value of 0 wt%. HSAS is expressed as wt% amine. HSAS is equivalent to *Bound Amine*.

% Neutralized – This value represents what fraction of the Total HSS anions could be neutralized by Inorganic HSS cations.

% Neutralized = Inorganic HSS / Total HSS * 100%

When a solution is 0% neutralized, there is no Na^+ or K^+ present, Inorganic HSS = 0 wt%, and Total HSS = HSAS. When a solution is 100% neutralized, the molar equivalent charge of Na^+ and K^+ perfectly balances the molar equivalent charges of all HSS anions, in this instance, Total HSS = Inorganic HSS and HSAS = 0 wt%. The solution is said to be *over neutralized* when it is >100% neutralized, i.e., when there are more molar equivalents of Inorganic HSS cations than the total molar equivalents of all HSS anions.

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