



# The CONTACTOR™

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## Heat Stable Salts I: Jargon

In amine systems attached to refineries, Heat Stable Salts (HSSs) tend to accumulate in the amine solvent. They readily chelate iron and so accelerate corrosion. Corrosion is intimately tied to assessing tolerable levels of HSSs. At some level of HSS the cost of amine replacement must be borne and there are always costs associated with changing particulates filtration media, shutting down prematurely to repair, clean or replace equipment and piping, or to reduce gas throughput forced by plugging or foam stabilization. HSS levels can be controlled or managed by a number of methods, but each carries its own operating and sometimes capital costs. How the *level* of a HSS can affect the treating performance of an amine unit is much less well known.

Even small concentrations of HSS can significantly affect absorber and regenerator performance. In certain situations, such as the tail gas section of an SRU, HSSs can actually be beneficial. In other cases, however, HSSs affect treating performance negatively. With respect to H<sub>2</sub>S removal, the way a given amine contactor is pinched will determine whether HSSs help or hurt treating.

To benefit from HSSs, an absorber must be lean-end pinched (performance controlled by lean loading) with the HSS acting as a stripping promoter. For a given application, there will be a “sweet spot” in the treating, which can only be revealed through process modeling with a truly fundamental rate-based model (ProTreat®) that uses the correct chemistry. Figure 1 illustrates this “sweet spot” for a given application.

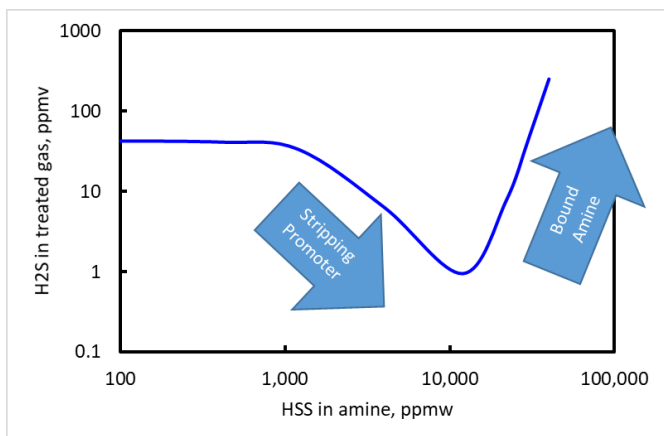


Figure 1: Representative HSS Effects on H<sub>2</sub>S Treating

Heat Stable Salts is such a broad ranging topic and one with such profound economic and operational impact that it's impossible to cover it adequately in a two-page Contactor. What follows is a brief synopsis of part of a much [more in-depth study](#). We will be satisfied with providing some definitions that might help clarify some common misunderstandings, a general understanding of how HSSs interact with amines, and how they affect corrosivity and amine treating performance.

### Definitions

Considerable confusion exists in the industry about the difference between heat stable salts and amine degradation products as well as how the contaminants are reported. Much of this confusion has resulted from analytical methods that do not directly measure the parameter of interest, and widespread propagation of jargon.

*HSSs are not amine degradation products.* As their name implies, they are salts which cannot be thermally reversed to their original components. They are permanent species that do not respond chemically to the application of heat, e.g., by a reboiler. They are salts that in aqueous solution dissociate into a hydrogen ion (H<sup>+</sup>) and an anion characteristic of the particular salt (e.g., acetate, thiocyanate, etc.)

### HSAS

The term “HSAS” or “heat stable amine salt” refers to the amount of protonated amine, expressed as AmH<sup>+</sup> that results from a titration measurement. We will use the example of an aqueous 30 mass% DEA solution where 10% of the DEA is bound with a heat stable salt anion. A simplified calculation assumes that H<sup>+</sup> comes from an external acid source, not water, so the mass of water doesn't change. The amount of protonated DEA (DEA-H<sup>+</sup>) can be expressed as (Table 2):

- $(0.02853 \text{ gmol } \text{DEA-H}^+ / 4.171 \text{ gmol total}) \times 100 = 0.6841 \text{ mole\% in solution,}$
- $(3.029 \text{ g } \text{DEA-H}^+ / 100.029 \text{ g total}) \times 100 = 3.028\% \text{ mass in solution,}$
- Or 3% of the **total amine** in solution

By convention, industry uses the definition of 3.028% wt HSAS (heat stable amine salt). An alternative way of reporting this

might be to say that we have 27%wt free DEA, 3%wt bound DEA (expressed as DEA, not DEA-H+) and 30%wt total DEA in solution.

Regenerable Free Base (RFB) is another term used for the free amine (27%wt) in this example. Only RFB (or free amine) can react with acid gases.

**Table 2: HSAS Simplified Calculation — 10% Reacted**

Component	MW	Start Solution		Reacted		End Solution	
		g	gmol	g	gmol	g	gmol
DEA	105.14	30	0.2853	-3.000	-0.02853	27.000	0.25680
DEA-H <sup>+</sup>	106.15	0	0	3.029	0.02853	3.029	0.02853
H <sub>2</sub> O	18.015	70	3.8857	0	0	70	3.8857
Total		100	4.1710	0.0288	0	100.029	4.1710

This simplified calculation ignores the mass concentration of the particular anion involved. If we had added hydrochloric acid to the solution, the total weight of the solution before and after reaction would be different than if we had added an equivalent charge of phosphoric acid (-3 charge for phosphate anion vs. -1 charge for chloride, not to mention the anions also have different ionic weights). So not all HSS are equal.

Table 3 puts several of the commonly measured HSS anions in amine solutions onto a relative molar charge basis for the equal weights in solution. Using Table 3, 1000 ppmw of phosphate would bind 1.0/0.5533 = 1.87 times the amount of amine that 1000 ppmw acetate would. Both charge and molecular weight of the HSS anion are important in assessing how much amine is protonated or bound with the HSS. Even though chloride has a -1 charge, it ties up more amine than sulfate because of its relatively low molecular weight!!

**Table 3: Relative Molar Charge of Various HSS Anions for Same Weight Concentration (Complete dissociation)**

HSS Anion	MW	Charge	Relative
Phosphate (PO <sub>4</sub> <sup>-3</sup> )	98.004	-3	1.0000
Chloride (Cl <sup>-</sup> )	35.453	-1	0.9214
Oxalate (C <sub>2</sub> O <sub>4</sub> <sup>=</sup> )	88.019	-2	0.7423
Formate (HCOO <sup>-</sup> )	45.017	-1	0.7257
Sulfate (SO <sub>4</sub> <sup>=</sup> )	96.061	-2	0.6802
Thiosulfate (S <sub>2</sub> O <sub>3</sub> <sup>=</sup> )	112.127	-2	0.5827
Thiocyanate (SCN <sup>-</sup> )	58.083	-1	0.5624
Acetate (CH <sub>3</sub> COO <sup>-</sup> )	59.044	-1	0.5533
Propionate (C <sub>2</sub> H <sub>5</sub> COO <sup>-</sup> )	74.078	-1	0.4410
Glycolate (C <sub>2</sub> H <sub>3</sub> O <sub>3</sub> <sup>-</sup> )	75.044	-1	0.4353
Sulfite (SO <sub>3</sub> <sup>-</sup> )	80.062	-1	0.4080
Butyrate (C <sub>3</sub> H <sub>7</sub> COO <sup>-</sup> )	87.099	-1	0.3751
Lactate (C <sub>3</sub> H <sub>5</sub> O <sub>3</sub> <sup>-</sup> )	89.071	-1	0.3668

Amine solution analyses are nearly always reported on a weight basis, but reactions are molecular, so Table 3 in terms of molar charge may be useful in understanding the relative power of a given HSS. A word of caution though: Table 3 does not reflect that the different acids have different acidity and de-

pending upon the solution pH, the acid may or may not be fully dissociated.

Industry guidelines have been established for the control of heat stable salts with the primary objectives being safe, reliable, and cost-effective operations. These guidelines were developed some time ago, but there is some disagreement between the various amine suppliers and even amongst the providers of amine reclamation services as to what the safe levels of heat stable salts are. Table 4 summarizes the three main sets of guidelines that are referenced most often in industry.

**Table 4: HSS Control Guidelines**

Anion	Reference by Industry (ppmw)	Reclaiming Service #1 (ppmw)	Reclaiming Service #2 (ppmw)
Formate	1,000	7,000	N/A
Acetate	1,000	1,000	N/A
Chloride	1,000	500	N/A
Oxalate	500	1,000	N/A
Sulfate	500	N/A	N/A
Thiosulfate	10,000	10,000	N/A
Thiocyanate	10,000	10,000	N/A
Total HSS anions	Target 1-2%wt (3%wt max) R.O.T. < 5-10% of amine alkalinity	< 1.2%wt -or- < 8% capacity	< 0.8 – 1.0 %wt
Strong Cations, %wt	Not covered	<1.5%wt and <100% neutralized	< 2000–3000 ppmw

These guidelines relate to corrosion in amine systems and the effect of various HSSs. We hasten to add however, that they apply to systems containing CO<sub>2</sub>. The presence of H<sub>2</sub>S can completely change the complexion of corrosion because H<sub>2</sub>S can passivate metals (especially iron) making them a lot less susceptible to corrosion by dissolved acid gases. Whether the system treats H<sub>2</sub>S is vitally important—some of these guidelines fall apart in H<sub>2</sub>S-only systems. Recent work has quantified the effects of HSS levels on corrosion acceleration in H<sub>2</sub>S bearing MDEA<sup>†</sup>.

To learn more about this and other aspects of gas treating, plan to attend one of our training seminars. For details visit [ogtr.com/training](http://ogtr.com/training).

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<sup>†</sup> Laboratory Study of the Effect of Heat Stable Salts on Steel Corrosion Rates, Malkiewich, R.J., Parajuli, S., Chinchilla, M.A., Waite, S., NACE Corrosion 2014 Conference, San Antonio, TX