Purging Condensate to Remove Heat Stable Salts

In the April issue of The Contactor™ we discussed the use of condenser blowdown to remove accumulated components from an amine system. From time to time one hears the recommendation to remove heat stable salts the same way—blow them down at the overhead condenser by purging condensate. Sensible?

Everything that enters an overhead condenser should get there as part of the vapor. In other words, all the components entering the condenser should be volatiles. As the name implies, heat stable salts are salts or ions derived from salts. As such they are absolutely nonvolatile—they have zero vapor pressure. So the question immediately arises: how did they get into the condenser? There are two possible sources:

**Entrained Liquid**

In the absence of wash or reflux trays, if HSSs are found in the reflux water from an amine OH condenser, they probably got there by a (hopefully) small amount of top-tray liquid being entrained into the vapor. Towers should always have a demisting pad in the head space at the top of the column, so one of the first questions is whether the mist pad is intact and has been correctly selected for the service it is in. Mist pads do not correct for bad tray design and they’re not perfect. But they can be sized to remove entrained droplets down to below 5 micron size.

Sprays from trays are typically in the range 2–1,000 microns and demisting pads are quite efficient down to about 5 micron droplet size. Capacity should not be an issue in eliminating mist from tower overheads simply because a correctly designed tray will not show high entrainment rates. If it does, there is either foaming of the design is poor. Incidentally, a common mistake made even by reputable tray designers is to use the same tray design in the wash section as in the stripping section. Liquid rates in the wash section are one or two orders-of-magnitude lower than in the stripping section which is conducive to promoting sprays with conventional valve trays especially if the downcomers are dynamically sealed.

If entrainment is the source of HSSs in condensate from an overhead condenser, its concentration should not increase over time because the condensate is continually being returned to the tower from which it came and at the same rate. There is no mechanism that would allow it to accumulate in the condensing section of the tower. Blowdown is only effective in dealing with substances that accumulate in the system. If HSSs are not entering the amine system, then they are being formed within the system. In that case, any accumulation is caused by continual formation from volatile components already in the gas entering the amine treating unit. In short, they are being formed within the amine system and as long as that continues they will indeed accumulate. But will they reach the condenser? Not necessarily, because HSSs themselves are nonvolatiles—they have no way to get there, unless they are...

**Formed in the Condenser**

Hydrogen cyanide, alkyl cyanides, sulfur dioxide, and hydrogen sulfide are ingredients which in various combinations are capable of forming such HSSs as thiocyanate (SCN⁻), thiosulfate (S₂O₃²⁻), and sulfate (SO₄²⁻) ions. An overhead condenser and the upper reaches of an amine regenerator are wonderful places to form these components because HCN accumulates there in fairly high concentrations. As discussed elsewhere†, HCN will hydrolyze to form ammonium and acetate ions:

\[
HCN + 2H₂O → NH₄⁺ + COOH⁻
\]

With oxygen, H₂S and ammonia, HCN will form thiocyanate:

\[
2HCN + O₂ + 2H₂S + 2NH₃ → 2NH₄⁺ + 2SCN⁻ + 2H₂O
\]

Other reactions include thiosulfate and sulfate formation:

\[
2H₂S + 2O₂ + 2R₁R₂R₃N → 2R₁R₂R₃NH⁺ + S₂O₃²⁻ + H₂O
\]

\[
2H₂S + 4SO₂ + H₂O + 2R₁R₂R₃ \rightarrow 6R₁R₂R₃NH⁺ + 3S₂O₃²⁻
\]

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\[ \text{II} \]

\[ S_2O_3^+ + \frac{5}{2}O_2 \rightarrow 2SO_4^= \]

Being noncondensible, any oxygen that has found its way into the system and has dissolved in the solvent will reach and possibly accumulate in the overhead condenser high point. Likewise, HCN, SO₂, NH₃, and H₂S are all at high concentrations in the condenser so this is likely where the HSSs thiosulfate, thiocyanate, and sulfate will most readily form.

If they form in the condenser, condenser blowdown will remove and control them and the reactants from which they form. However, if HSSs form elsewhere in the amine system, they should never reach the condenser. If they do there is another problem, quite likely excessive carryover of entrainment from trays that are operating too close to jet flood or from trays that are foaming. The canary in the mine is amine.

Condenser condensate containing a significant level of amine is a red flag for foaming and tray flooding. In this case, blowing down condensate is the wrong approach to a long-term solution for a HSS problem because blowdown generates increased, expensive, amine losses. Better to attack the problem’s root cause(s).

If condensate is mostly amine free but contains HSSs, blowdown is probably the simplest solution to controlling salt levels in the system. And to prevent the accumulation of HSSs in the rest of the system by returning it to the regenerator in reflux water, one may need to blow down a large fraction of the condensate.

The complication with all of this is that the end operator usually doesn’t have the analytical tools onsite to distinguish between amine and ammonia in the reflux water, nor can he tell whether the thiosulfate and sulfate in the reflux water came originally from HCN or it was generated \text{in the sample} from H₂S that was oxidized by the air in the sample bottle or by air exposure in the lab (see The Contactor, Vol 12, No 2). In a refinery amine unit, there is almost guaranteed to be ammonia and H₂S in the reflux water. Purging the reflux reduces the concentrations of both. Because there is less H₂S in the reflux sample to oxidize to thiosulfate, the operator gets the impression that purging reflux reduces HSS. Perhaps the only way to distinguish whether purging is helping to reduce HSS is to look at the HSS accumulation rate in the main amine system inventory, take controlled purging steps over days and weeks of operation, and engage a qualified lab.

Advice to blow down condensate to control HSS levels in an amine system should be taken with a grain of salt until one has examined the facts closely and listened for the canary.

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