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HCN distribution in sour water systems

Hydrogen cyanide (HCN) is commonly present in refinery gases. Because of its low volatility and, to some extent, its acidity, it travels through amine and sour water systems in an unusual and, heretofore, poorly understood way. To shine some light on this subject and perhaps develop a worthy solution, a simulation study has been performed with HCN removal being treated on a mass transfer rate basis. This will help develop an understanding of how HCN distributes in the sour water system and where it might form an internal recycle within a tower.

HCN is an insidious contaminant in raw gas from cracked stocks, and has far-reaching effects on amine and sour water system performance and equipment longevity. After hydrocarbon contamination, its presence is probably the primary reason refinery amine and sour water systems suffer from accelerated corrosion and from operability and reliability problems. When HCN enters the amine system, its hydrolysis produces ammonia (NH_3) and formate ($HCOO-$), a heat-stable salt (HSS) anion. Reaction of HCN with oxygen and hydrogen sulfide (H_2S) generates another HSS, thiocyanate ($SCN-$). Accelerated corrosion from the resulting heat-stable salts leads to faster formation of particulate iron sulfide, filter element plugging, fouled equipment, lower capacity and more stable foams. Most of the HCN, however, travels with blown-down ammonia to the sour water stripper (SWS). In this report, mass transfer rate-based simulation is used to study HCN distribution in SWSs in unprecedented detail.

Background. Amine data collected over some 20 years show a consistent pattern over time and unit configuration of the relative amount of HSS anions, mainly HCOO– and SCN– produced from various refinery units. Amine systems treating gases from various sources experience different rates of HSS formation.

Treating gases and liquids for H_2S from delayed cokers have the greatest buildup of amine HSS anions. This is followed by fluid catalytic crackers (FCCs) without gasoil feed hydrotreating, and then by FCCs with feed hydrotreating. Amine systems serving hydrocrackers and hydrotreaters, completely isolated and separate from coking and FCC operations, normally show minimal signs of HSS buildup. This information is shown in **FIG. 1**.

Solvent analyses and investigations at many facilities indicate that HCN is the main contaminant source for producing HSS anions. **TABLE 1** shows the mechanisms for the formation of the most common refinery HSS anions. Data from several refineries have shown that:

- Beginning to treat oxygen containing streams in an amine system that previously had only HCOO– buildup will show a dramatic increase in the rate of thiocyanate accumulation

- Dumping tail gas unit (TGU) amine contaminated with thiosulfate ($S_2O_3^{2-}$) into primary amine systems will cause an immediate increase in the amount of SCN buildup.
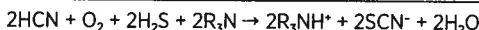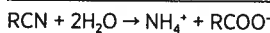
Ammonium polysulfide (APS) is commonly added to wash water systems to aid in the control of cracking and blistering in carbon steel in wet H_2S service. Companies that sell and monitor APS confirm the presence of HCN in these systems.

HCN is a byproduct of cracking the heavier fractions of crude oil in a refinery (either thermally as in a coker, or catalytically as in a FCC). The gasoil (boiling point 750°F/399°C+) and heavier fractions tend to have greater concentrations of nitrogen than the diesel and lighter fractions. Compared to high-pressure hydrotreating and hydrocracking processes, cracking processes that operate at high temperature and low hydrogen partial pressure do not completely convert byproduct molecules like HCN.
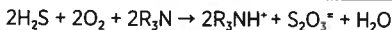
Thus, HCN occurs quite naturally in refineries and has many sources. Some processes are high producers; others do not seem to produce HCN at all. Once it has been produced, HCN finds

TABLE 1. Sources of HSS incursion

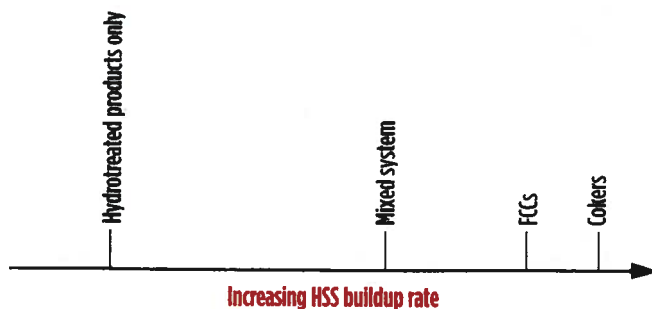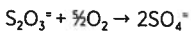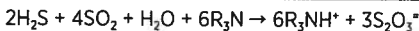| Cyanides from treating cracked stocks, FCCs and cokers |
| --- |
| $RCN + 2H_2O \rightarrow NH_4^+ + RCOO^-$ |
| $NH_4^+ + R_3N \rightarrow R_3NH^+ + NH_3$ |
| $2HCN + O_2 + 2H_2S + 2R_3N \rightarrow 2R_3NH^+ + 2SCN^- + 2H_2O$ |
| **Oxygen incursion, FCCs and vacuum tower offgas** |
| $2H_2S + 2O_2 + 2R_3N \rightarrow 2R_3NH^+ + S_2O_3^= + H_2O$ |
| **SO$_2$ breakthroughs (Claus TGUs)** |
| $2H_2S + 4SO_2 + H_2O + 6R_3N \rightarrow 6R_3NH^+ + 3S_2O_3^=$ |
| $S_2O_3^= + \frac{1}{2}O_2 \rightarrow 2SO_4^=$ |

FIG. 1. Pace of HSS anion formation in refinery amine systems.

its way into the amine system with the H_2S-containing gases. HCN forms in various processes within a refinery; HSSs form in the amine system. Once in the amine system then, various conditions and the presence of other contaminants allow some of the HCN to be converted into HSS anions. The rest of the HCN either goes overhead to the sulfur plant, or it gets blown down with NH_3 and enters the sour water system.

HCN in sour water. A recent case study shows a rather surprising distribution of HCN in a SWS—in this case, a packed tower. **TABLE 2** shows the composition and flow of this typical refinery sour water stream. **FIG. 2** shows the SWS setup, configured to return all overhead vapor condensate to the stripper. The SWS was 5.5 ft in diameter, and we used 33-ft and 48-ft beds of random packing to assess the effect of packed depth on stripped water quality. The overhead pressure was 22 psig, and for this case

study, a reboiler duty of 33 MMBtu/h was selected to achieve 100 ppmw of ammonia in the stripped water. The preheater sent 245°F sour water feed to the top of the column.

With the 33-ft deep bed, the stripped water was simulated to have 100.5 ppmw NH_3 and 12.5 ppmw HCN, with undetectable H_2S. With the 48-ft deep bed, the corresponding performance metrics were 28 ppmw NH_3 and 4.5 ppbw HCN. Of course, in condensing water from the stripper overhead, a lot of the gases already stripped (in Stream 3) are reabsorbed into the condensate (73% of the NH_3, 70% of the HCN, and 51% of the H_2S) and are returned to the stripper. This is unavoidable if the stripped gas is to be further processed for sulfur recovery without overloading the system with water vapor, but it may be worth noting that a lot of energy is expended to strip and restrip the same contaminants repeatedly.

Perhaps the most surprising aspect of HCN in the SWS is its distribution across the column itself. **FIG. 3** (left panel) shows how the concentration of HCN in the water phase changes with vertical position within the packed beds of two different depths. **FIG. 3** (right panel) shows the corresponding temperature profiles. The lower temperature near the top of the column is not
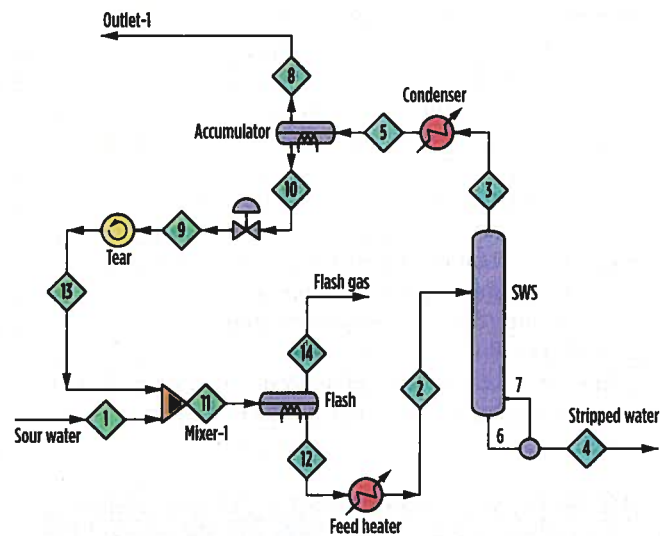

FIG. 2. SWS configuration.

TABLE 2. Refinery sour water	
Temperature, °F	100
Pressure, psig	9
Flow, bpd (gpm)	16,500 (480)
Composition, ppmw	
CO_2	50
H_2S	8,000
HCN	300
NH_3	4,500
Thiocyanate	36
Chloride	9
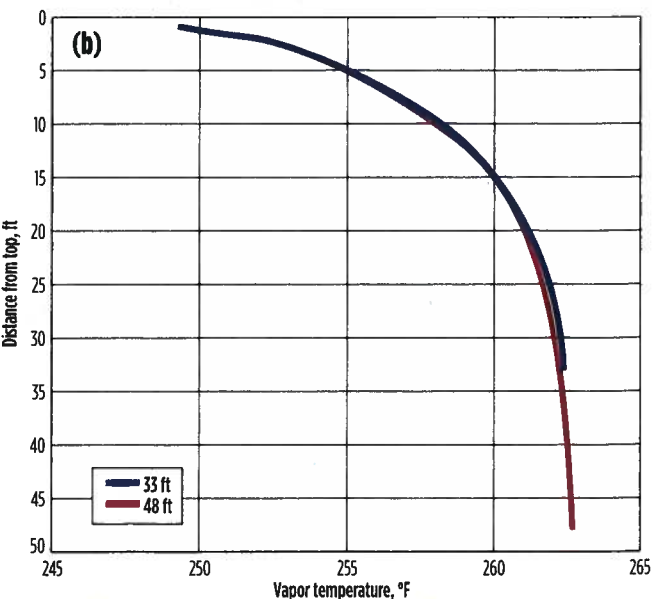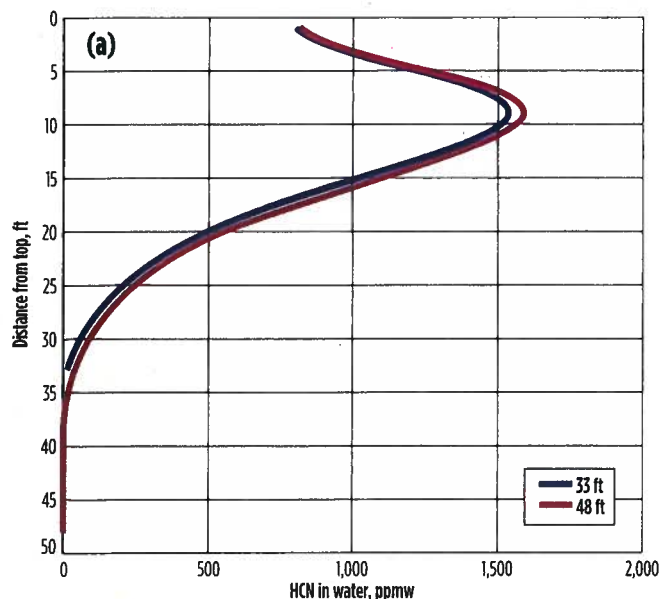
FIG. 3. Profiles of HCN in water, and of vapor temperature.

caused by sour water that is being fed too cold—in fact, the sour water enters the column with the liquid just above its bubble point with 0.3% vapor. The bubble point is a function of the composition of the water with respect to the volatile acid gases and NH_3.[1] On the other hand, temperature also affects HCN solubility in water. As a result, the temperature profile has a profound effect on the HCN profile in the stripper. HCN that was removed from the water in the reboiler and in the bottom part of the column is partially reabsorbed near the top of the column where the temperature is 14°F to 15°F colder.

Although the original sour water in this theoretical study contained only 300 ppmw HCN, water entering the top of the column contained 875 ppmw because of HCN reabsorption into the returned condensate. Peak concentrations in the tower are simulated to be about 1,530 ppmw and 1,580 ppmw HCN

for the 33- and 48-ft beds, respectively. These are some five times the concentration in the original sour water feed. The corresponding HCN level in the vapor is 825 ppmv. These elevated concentrations have a much higher tendency to corrode steel, so this may go some way towards explaining the need for expensive upgraded metallurgy in the SWS overhead system. As can be seen from the figure, HCN stripping is far poorer than one might have expected, even accounting for the higher HCN content of the column feed. In the case of the 33-ft bed, the bulge occupies the top half of the column, rendering half the column ineffective for HCN removal. When the bed depth is increased to 48 ft, the HCN bulge profile and peak value remain virtually identical. Increasing the bed depth by 15 ft has allowed the HCN profile to become what it might have been expected to be without the bulge. Other conditions being the same, HCN
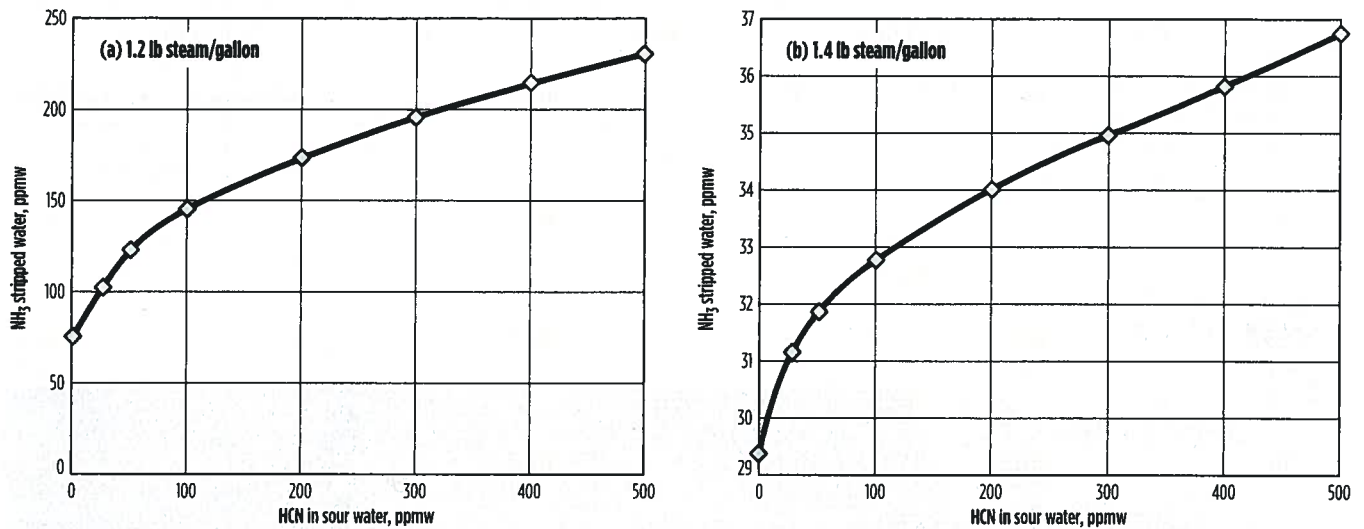

FIG. 4. Effect of sour water HCN level on residual NH_3 in treated water.
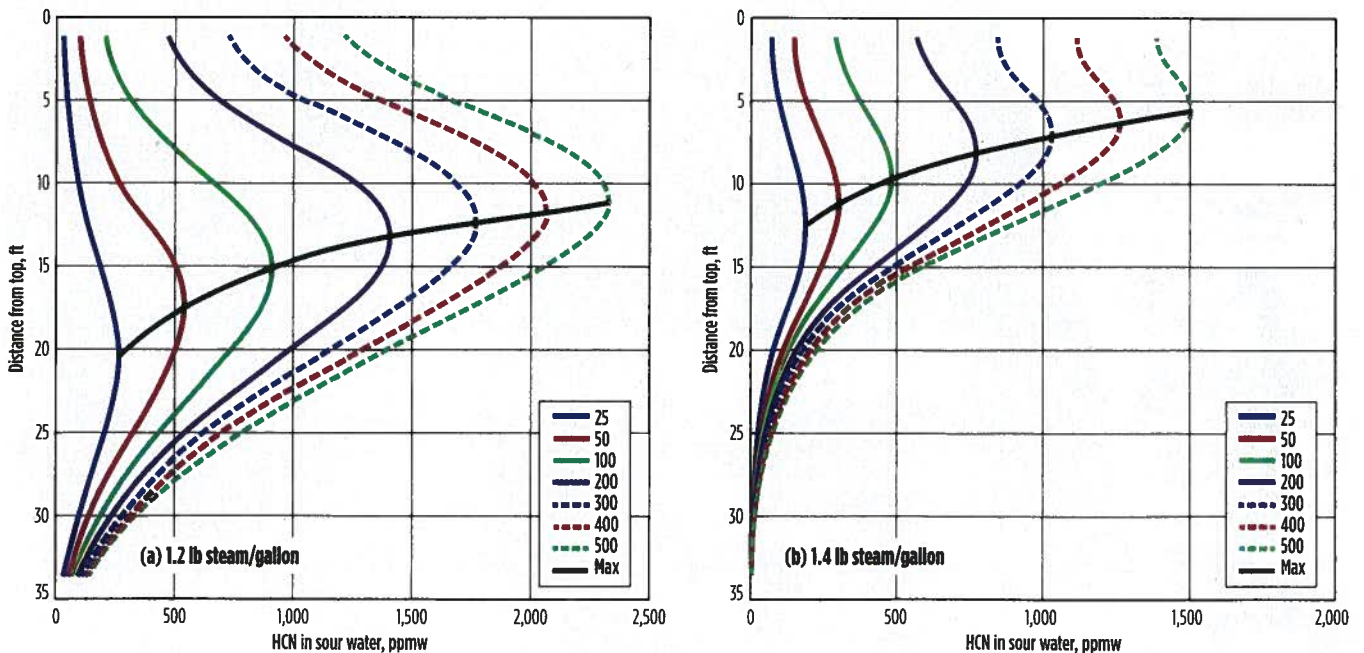

FIG. 5. Effect of sour water HCN level on HCN profiles and on the position and size of the composition bulge.

can be stripped to very low levels but only by using more bed depth. The reason for the deeper bed requirement is the presence of a very significant bulge and, consequently, a very large, non-functional section of packed bed in the column.

Higher HCN levels in the sour water cause higher residual NH_3 in the treated water. In **FIG. 4,** this is shown in the left and right panels, which, respectively, correspond to 1.2 lb and 1.4 lb of 50-psig saturated steam per gallon of water treated. The high-performance random packing was 33.5 ft deep. At the lower steam consumption rate, the effect of HCN is significant, but at the higher, more-typical rate of 1.4 lb/gal, the effect is somewhat more marginal.

FIG. 5 shows how the HCN levels in the raw water affect the HCN profiles in the SWS. The size of the peak, of course, increases with the HCN content of the raw water. Furthermore, the peak occurs higher in the stripper, the higher is the HCN content of the original sour water. Higher steam rates push the bulge further up the tower and reduce its size; nevertheless, the bulge still exists even at this higher steam rate, and a sizeable portion of the stripper is completely ineffective in terms of what might have been expected had the existence of the composition bulge not been known.

Wrap up. The discovery that HCN accumulates internally within a SWS has been reported here for the first time. The use of mass transfer rate-based simulation has allowed this significant internal recycle of HCN to be quantified in unprecedented detail. The discovery of this recycle may go some way toward explaining observed tower corrosion rates in existing plants and may permit better informed material selection decisions to be made for plants still in the design phase. We speculate that such a distribution of HCN probably always occurs in both amine regenerators and SWSs because the mechanism by which it forms is through the connection between solubility, vapor pressure, and local temperature, and this exists in both types of units. **HP**
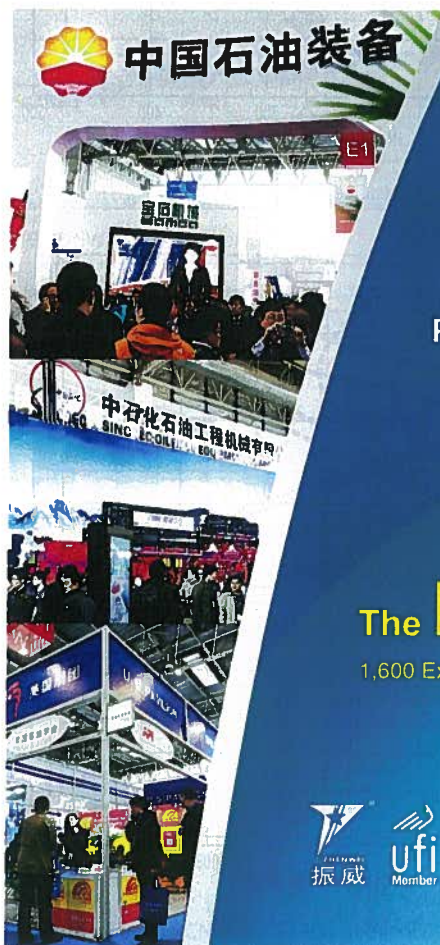
NOTE
[1] Bubble point is the temperature at which the vapor pressure over the solution is equal to the system pressure. It is greatly affected by the presence of volatile, dissolved components in the water.

RALPH WEILAND founded Optimized Gas Treating in 1992 and has been active in Canada, Australia and the US in basic and applied research in gas treating since 1965. He also spent 10 years in tray R&D with Koch-Glitsch LP, Dallas, Texas. He has bachelor's, master's and Ph.D. degrees in chemical engineering from the University of Toronto.

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CLAY JONES is the principal technical development engineer with Optimized Gas Treating. He has a bachelor of science degree from McNeese State University and a master's degree from the University of New Mexico. Before starting his current job in 2012, Mr. Jones spent 11 years with ConocoPhillips in sulfur plant and amine unit operations.