

# Evaluation of Ammonia "Fixation" Components In Actual Refinery Sour Waters

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Refining Department

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## ABSTRACT

Ammonia fixation is a term used to describe the occurrence of ammonia in stripped sour waters (SSW) that is resistant to removal by means of additional steam. Samples of refinery SSW were analyzed for organic components, oxidized sulfur compounds, and heavy metals to determine the cause of ammonia fixation during stripping. The heavy metals levels measured were too low to be causes of fixation. However, acidic materials were identified that would cause fixation. These acids included thio-sulfuric acid, thiocyanic acid, and weak organic acids. In some SSW, ammonia is synthesized during analysis, resulting in an apparent non-strippable residual ammonia.

Analytical difficulties were encountered in measuring cyanides, ammonia, and sulfides in sour waters. The cyanide measurements often showed free cyanide values exceeding total cyanides. Ammonia measurements yielded high apparent values in some sour waters because ammonia was synthesized during the analysis. Measurement of low sulfide concentrations was hampered by an unknown component in sour water that interfered with the methylene blue test for sulfide. This interference could not be eliminated by sample dilution. The sulfide test also gave highly variable results even when interferences were not a factor.

The amount of ammonia fixation that will occur with a particular sour water can be predicted by a potentiometric titration. Fixation can also be predicted by batch stripping using nitrogen gas until the pH of the stripped water reaches 6.

Laboratory experiments showed that fixed ammonia can be freed by adding caustic to the sour water stripper. The most effective place to add caustic is high in the stripping tower. The amount of caustic required to free fixed ammonia has no effect on sulfide stripping.

Laboratory stripping experiments were used to demonstrate that caustic can substitute for steam in producing a SSW with low levels of ammonia. An economic analysis showed that caustic use is only warranted when very high ammonia removal (> 97%) is required, and that the economic optimum steam and caustic usage would degrade sulfide removal performance.

Laboratory stripping experiments could not be used to study the behavior of cyanides during stripping of actual refinery sour waters.

Cyanide measurements were accurate in artificially prepared sour waters and studies with these artificial sour waters showed that average refinery stripper operation could remove simple cyanide and convert some cyanide to thiocyanate. Metal-complexed cyanide was largely unaffected by stripping.

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## I INTRODUCTION

Since 1971 the American Petroleum Institute has been investigating the problem of stripping-resistant, or fixed, ammonia in sour waters generated by refinery processing operations. Surveys of refinery operations conducted in 1972 indicated that the problem was severe enough to justify a research program to develop improvements in stripping technology and stripper design. The research program has concentrated on identifying the causes of ammonia fixation and on developing new equilibrium data for the  $\text{NH}_3\text{-H}_2\text{S-H}_2\text{O}$  system in order to provide an expanded data base for stripper design.

An experimental study of sour water stripping conducted in 1974 (Bechtel, 1976) concluded that ammonia fixation was probably caused by acidic material in the sour water. No positive identification of the acidic material was made in the 1974 study. In March 1976 an experimental study of ammonia fixation was initiated to answer some questions raised by previous studies and to study stripper operating procedures designed to eliminate ammonia fixation. The five principal objectives of the study were:

- Identify the organic and inorganic compounds present in sour waters which cause ammonia fixation.
- Identify factors in refinery processing operations or feedstocks that may be responsible for ammonia fixation.
- Investigate in the laboratory the suitability of caustic addition and pH control during stripping for eliminating ammonia fixation.
- Identify the cyanide compounds present in refinery sour waters and determine their behavior during stripping.
- Determine if there is any incentive for substituting caustic for steam during stripping of sour waters that do not have high ammonia residuals.

Stripped sour waters from eight refineries were analyzed to determine the composition of refinery sour water. The refineries were chosen to include plants processing California, Middle East, Gulf Coast and Mid-Continent crudes. Sour waters from several of these refineries were stripped in a laboratory scale stripping column to fulfill the other objectives of the program.

## II CONCLUSIONS

### Sour Water Composition and Ammonia Fixation

- (1) In the sour waters examined, ammonia fixation appears to be caused by weak organic acids and acidic oxidized sulfur compounds. Organic acids were an important acidic component of the sour waters studied. Ammonia-metal complexes were not a factor in the sour waters studied.
- (2) The sample of 8 refineries was not large enough to identify the source of the acidic compounds. Neither the organic acids nor the oxidized sulfur compounds could be firmly associated with a particular crude source or crude processing operation.
- (3) The amount of ammonia fixation can be measured in unstripped sour water by batch stripping tests where nitrogen and steam are used to strip ammonia and sulfide, or by acid-base titrations of sulfide-free stripped sour water.
- (4) The distillation procedure for ammonia concentration measurement gave high readings for some sour waters.
- (5) Some ammonia may actually be synthesized during analysis. Ammonia measurement by Nesslerization and any use of distillation pH values greater than 7.4 should be avoided.
- (6) Phenol, cresols, and other aromatics with molecular weights less than 300 constitute a substantial fraction of the organic material found in sour waters.

### Eliminating Ammonia Fixation

- (7) Ammonia fixation can be eliminated by adding caustic to a sour water stripper. The amount of caustic required is the molar equivalent of the fixed ammonia.
- (8) The optimum place to apply caustic to free the fixed ammonia is at the top of the column. Even when 10% excess is added to the top tray, sulfide stripping is not inhibited.

- (9) In terms of ammonia removal efficiency, multiple-point caustic injection is inferior to single-point injection.
- (10) Caustic can be economically substituted for steam during stripping of sour waters with no fixed ammonia. Caustic substitution for steam is optimum when very high ammonia removal efficiencies are required, but the level of ammonia removal at which caustic addition becomes attractive depends on the price of steam relative to caustic. For the sour water studied the following results were obtained:

| <u>Price of Steam</u> | <u>Price of Caustic</u> | <u>Ammonia Removal Efficiency where Caustic Addition Becomes Economically Attractive</u> |
|-----------------------|-------------------------|------------------------------------------------------------------------------------------|
| \$3.00/1000 lb *      | \$0.07/lb               | 97%                                                                                      |
| 0.50/1000 lb          | \$0.11/lb               | 99%                                                                                      |

When fixed ammonia is not present, caustic addition does degrade sulfide removal efficiency.

### Cyanides

- (11) Tentative ASTM methods A and F for measuring cyanide compounds are unsatisfactory for the sour waters used in this investigation.
- (12) Metal-complexed cyanides are by and large unaffected by conditions in a stripping column. A small percentage of these break down to simple cyanide, which is stripped.
- (13) Some  $\text{CN}^-$  was converted to  $\text{SCN}^-$  during cyanide stripping.
- (14) Simple cyanides such as  $\text{HCN}$ ,  $\text{KCN}$ ,  $\text{NaCN}$  appear to be readily stripped under the conditions normally encountered in sour water strippers, even though cyanide stripping experiments with buffered solutions show cyanide stripping is severely impaired at pH 9.

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\* 1000 lb = 454 kg. See page H-2 for factors used to convert English units to metric units.

### Hydrogen Sulfide

- (15) The methylene blue test used for sulfide concentration measurement is not reproducible and it is heavily dependent on analyst technique.

### Organic Analysis

- (16) A simple method for measuring phenol and cresol concentrations in sour waters was developed. The procedure utilizes direct analysis of the sour water sample by high pressure liquid chromatography. This method could be readily adapted to measuring aromatic carboxylic acids.
- (17) XAD<sup>\*</sup> resins can be used to separate the organic compounds in sour water into basic, phenolic and acid fractions. Separations using XAD resins are much sharper and quantitative than separations using solvent extractions.

---

\* Rohm and Haas Company.

### III RECOMMENDATIONS

- (1) Procedures using XAD resins and high-pressure liquid chromatography show promise as a means of separating phenols from organic acids so that the acids in sour water can be identified and measured. Work in this area should be continued.
- (2) Analytical procedures for measuring cyanides in sour waters are inadequate. Ongoing programs to validate cyanide measurement methods should continue.
- (3) Nitrogen compounds that hydrolyze to form ammonia appear to be present in several of the sour waters tested. The compounds could not be identified because they could not be separated from phenolic compounds. Separation procedures using XAD resins should be developed.
- (4) Alternate hydrogen sulfide measurement procedures should be investigated.
- (5) Additional sour waters with high ammonia residuals should be analyzed by titration and batch stripping tests to validate the relationships identified in this study.
- (6) A larger sample of refineries would be required to identify crude or processing operation influences on sour water composition and ammonia fixation. Any future study should analyze sour waters produced by individual processing units rather than the composite sour water from the entire refinery.

#### IV BACKGROUND

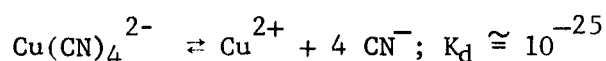
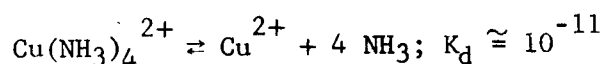
Refinery sour waters contain thousands of parts per million (ppm) of sulfides and ammonia and hundreds of ppm of various organic compounds. Sulfides and ammonia are generated by many process operations and show up in distillation condensates and scrubbing streams. Distillation tower overhead condensate often contains water that entered with the feed or was introduced as a vapor phase diluent. Because of high vapor concentrations and water solubilities, sulfide and ammonia in the feed streams are concentrated in the condensed water. Operations that generate sour condensates include crude distillation and residual vacuum distillations as well as distillations following operations such as coking, gas oil hydrotreating, and cracking. Additional sour waters result from neutralized caustic scrubbing streams that are used to remove sulfide and sulfur compounds as well as phenols from cracked and hydro-treated hydrocarbon streams.

The various sour water streams are collected and steam-stripped to remove sulfide and ammonia. Stripped sour water is amenable to biological treatment and is usually mixed with other aqueous effluents on their way to treatment facilities. The ammonia level in stripped sour water can be a major determinant of whether the treated combined effluent meets discharge requirements.

Sulfide removal from sour water is accomplished readily by stripping. Ammonia removal is a more difficult problem. Laboratory experiments and theoretical calculations have shown that in aqueous solutions of phenol, hydrogen sulfide, and ammonia, almost complete removal of both sulfide and ammonia is possible. Some refineries actually achieve this level of sulfide and ammonia removal. Other refineries achieve good sulfide removals but cannot achieve ammonia bottoms values below 100 ppm. This ammonia often cannot be removed by increasing stripping steam rates. There are a number of possible explanations for this residual or fixed ammonia. In some cases, it can be related to acidic materials that tie up ammonia as  $\text{NH}_4^+$ . Acids containing sulfur and oxygen were implicated in laboratory work conducted for the API by Bechtel Corporation (1976). The Bechtel study also suggested that carboxylic acids such as fatty acids and naphthenic acid were involved, but these compounds were not identified positively by chemical analysis. The current project demonstrated, however, that when acidic compounds are responsible for retention of ammonia, caustic addition to the sour water can reduce or eliminate ammonia residuals.

In some cases, however, it is more difficult to identify the cause of ammonia retention, because pH adjustment does not release all of the ammonia (Dobrzanski and Thompson, 1974). A possible explanation is heavy metals that form complexes with ammonia. Alternatively, ammonia residuals may be apparent only because they are caused by interferences during the analytical procedure.

Metal-ammonia complexes are not strong relative to cyanide complexes as can be seen by considering copper complexes as an example:



Metals form cyanide complexes preferentially and would be available to form ammonia complexes only when the metals are present in excess of the amount required for cyanide complexes.

Interference in analysis of ammonia may be a more plausible explanation than formation of metal complexes. Organic acids, aldehydes, ketones, and amines interfere with the direct Nesslerization test because they react with the reagents. Nesslerization after distillation is subject to the same interferences because some of the volatile compounds can distill over with the ammonia. Ammonia determinations by titration are also subject to positive interference by basic organic nitrogen compounds. Some compounds, such as urea, hydrolyze to form ammonia under the distillation conditions (Hoffman, 1976). A complete understanding of ammonia retention (apparent or real) requires identification of acidic compounds and the various interfering substances.

In cases where ammonia removal can be improved by pH control, the proper place to introduce a base into the stripper has been a point of controversy. Introduction of caustic in the tower top is optimum for ammonia removal since it will increase ammonia volatility in every stripping stage. However, this is the least optimum point for sulfide removal since sulfide volatility is decreased in all stripping stages. It has been suggested that some point in the middle of the column would be a reasonable compromise.

Once an appropriate caustic addition strategy has been established, it seems proper to consider whether adding caustic would permit good stripping of both sulfide and ammonia with less steam than is used in

common practice. The incentive for considering this alternative is the increasing unit cost of steam. Although in the long run caustic price will also rise when steam cost increases, there may be some lag due to market forces, since much caustic is produced as a coproduct of chlorine manufacture. Stripping response will be a complex function of steam rate, caustic addition rate, and the number of equilibrium stages in the column. Sour water organics such as weak acids will also affect stripping response. When adequate computational models are available, the incentive for caustic-steam substitution can be studied without resort to experiment, but experiments are required at present.

Some cyanide compounds are extremely toxic. Their fate during stripping is important if the stripped sour waters are discharged to receiving streams. Free cyanide may not be the most abundant cyanide compound present in sour waters since many metals form strong complexes with cyanide. Metals such as copper catalyze reactions that convert cyanide to cyanate. Because the possibilities for cyanide reactions are numerous, it seems most reasonable to determine how cyanides react under stripping conditions by experiment.

### Fundamentals of Stripping

Since several phases of this investigation involve steam stripping of both refinery and artificial sour waters, it is appropriate to review the fundamentals of stripper operation. A simple stripper of  $N$  equilibrium stages with no reflux can be modeled mathematically by the expression [Smith (1963)].

$$f = \frac{1 - S}{1 - S^{N+1}},$$

where  $f$  is the fraction of a component in the feed that remains in the bottoms.  $S$  is the stripping factor  $K(V/L)$  when  $V$  is the vapor rate, and  $L$  is the liquid rate in the column.  $K$  is the liquid-vapor partition coefficient for the component being considered. This simple model assumes that liquid and vapor rates are constant along with  $K$ .

A sour water stripper has approximately constant  $L$  and  $V$  when stripper feed is preheated, with  $L$  being the feed rate and  $V$  the steam rate, but  $K$  need not be constant, principally because ionic equilibrium between the species  $H_2S - HS^-$ ,  $NH_3 - NH_4^+$ , and  $H^+$  affects vapor pressure.

In the case of ammonia, we express ammonia liquid-vapor equilibrium by

$$y_{\text{NH}_3} = K'_{\text{NH}_3} x_{\text{NH}_3} \quad (2)$$

where  $x$  and  $y$  are mole fractions of  $\text{NH}_3$  in the liquid and vapor phases and  $K'_{\text{NH}_3}$  is the liquid-vapor partition coefficient.  $K'_{\text{NH}_3}$  is a constant that is only a weak function of  $\text{NH}_3$  concentration.  $\text{NH}_3$  is in equilibrium with  $\text{NH}_4^+$ , and the relative amounts of the two species are determined by the ionic equilibrium constant  $k_N$ :

$$k_N = \frac{[\text{NH}_4^+]}{[\text{NH}_3] [\text{H}^+]} \quad (3)$$

where  $[\text{H}^+]$  is the hydrogen ion concentration. Because of this equilibrium, Equation (2) can be rewritten as

$$y_{\text{NH}_3} = K'_{\text{NH}_3} \left[ \frac{1}{1 + k_N [\text{H}^+]} \right] x_N \quad (4)$$

If we identify  $K'_{\text{NH}_3} / (1 + k_N [\text{H}^+])$  as  $K_N$ , Equation (4) becomes

$$y_N = K_N x_N \quad (5)$$

where  $y_N$  and  $x_N$  represent the mole fraction of the sum of both ammonia species,  $\text{NH}_3$  and  $\text{NH}_4^+$ . This sum is measurable as ammonia nitrogen ( $\text{NH}_3\text{-N}$ ). In Equation (5), liquid-vapor equilibrium has been redefined in terms of the concentrations measured by the analytical procedures normally used in a laboratory. Relationship (2) or (5) holds even when other ionic species are present in the system.\* The only impact of these other species is to change  $k_N$  by ionic strength effects. For ammonia, it is  $K_N$ , the liquid-vapor partition coefficient for ammonia nitrogen (which is a strong-function of only pH) that becomes the appropriate partition coefficient to use in the stripping factor,  $S$ .

\* Chemical reactions with carbonate and bicarbonate to form urea and carbamide are neglected in this development.

In a similar manner, we can include the pH effects on the partitioning of sulfide between liquid and vapor by including the equilibrium between sulfide species,  $k_S = [H^+] [HS^-] / [H_2S]$ . This gives

$$y_S = K'_{H_2S} \left( \frac{[H^+]}{k_S + [H^+]} \right) x_S \quad (6)$$

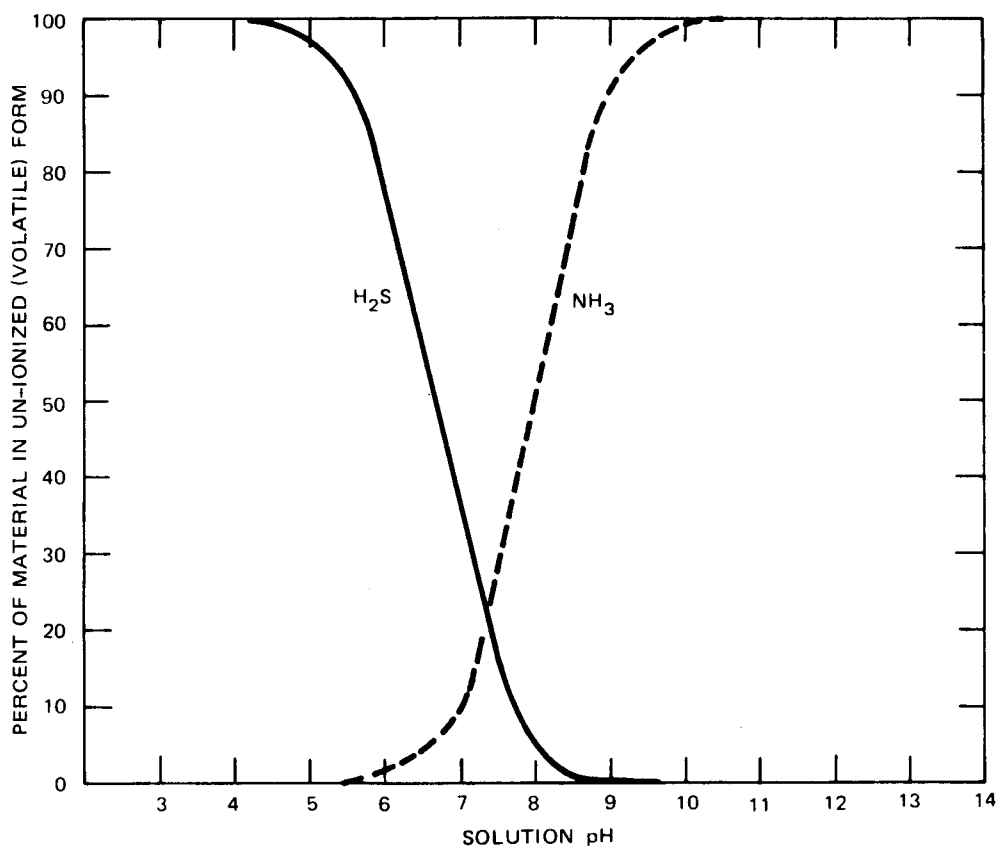
and

$$y_S = K_S x_S \quad , \quad (7)$$

where  $y_S$  and  $x_S$  represent the mole fraction of the sum of the species  $HS^-$  and  $H_2S$ , identified as sulfide sulfur ( $H_2S-S$ ).  $K_S$  is a function of pH and describes sulfide vapor-liquid equilibrium in terms of the variable measured by analytical techniques. It is the appropriate partition coefficient to use in a stripping factor  $S$  for sulfide sulfur.

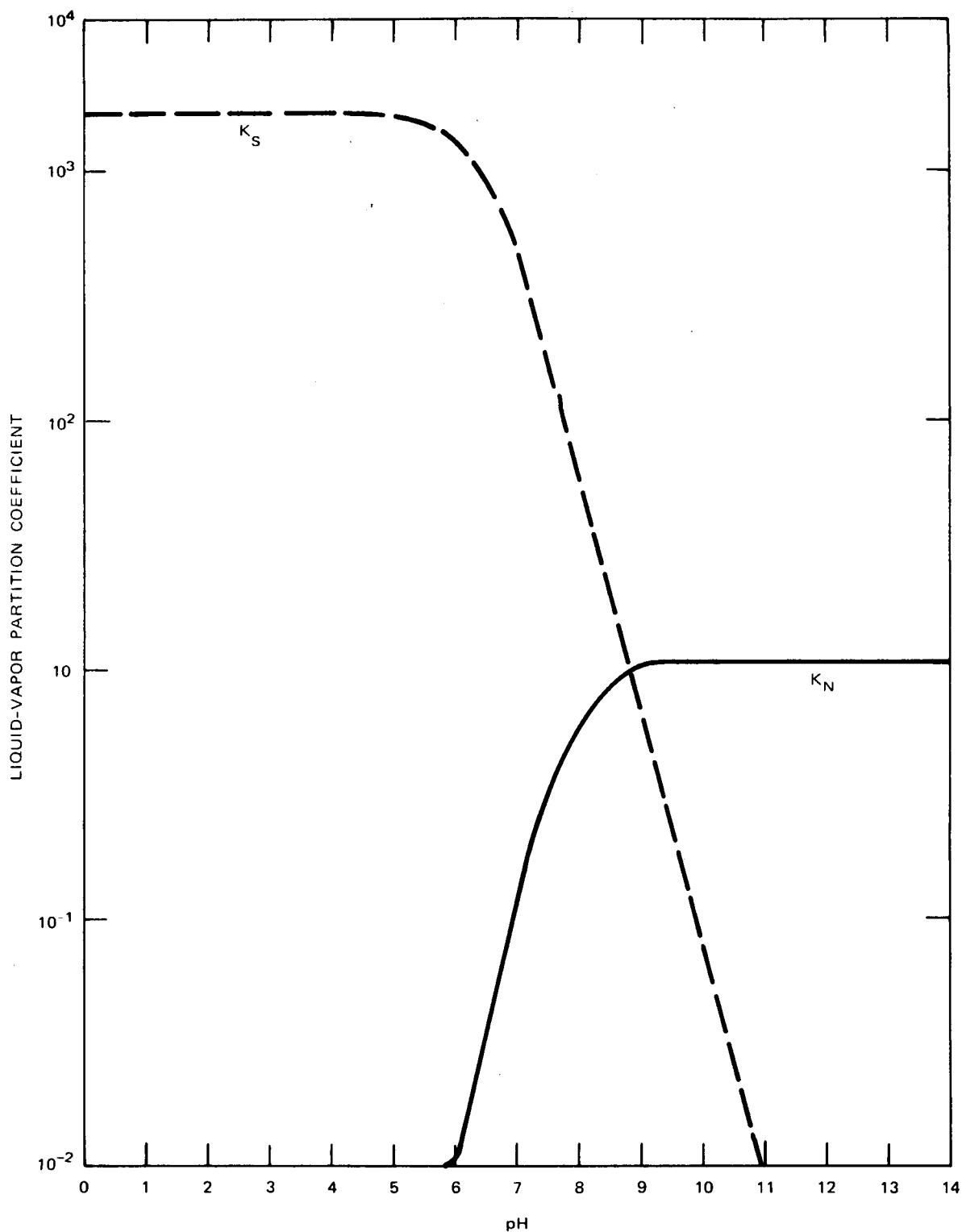
Figure 1 illustrates the effect of pH on the ionic equilibrium of  $H_2S$  and  $NH_3$ . When this behavior is combined with Henry's Law constants (Wilson, 1976), for both species, the result is Figure 2. These plots show liquid-vapor partition coefficients  $K_N$  and  $K_S$  over the entire pH range at a temperature of  $100^\circ C$ . Figure 2 shows that  $H_2S-S$  and  $NH_3-N$  are both volatile over the pH range 6 to 11. Below pH 6, only  $H_2S-S$  is volatile; above pH 11, only  $NH_3-N$  is volatile. In the pH range where both are volatile,  $H_2S-S$  is the more volatile from pH 6 to pH 9, and  $NH_3-N$  is the more volatile above pH 9. It is important to note that  $NH_3-N$  has a constant  $K_N$  for all pH values above 10.

Both Figures 1 and 2 are shown in terms of the pH at conditions in the tower. These figures would look different if pH at  $25^\circ C$  were used because of the way temperature effects  $K_N$ ,  $K_S$ , and  $K_W$ , where  $K_W$  is the equilibrium constant for the reaction  $H_2O \rightleftharpoons H^+ + OH^-$ . When a solution of  $H_2S$  and  $NH_3$  at  $100^\circ C$  is cooled, the concentration of  $H^+$  decreases as the temperature falls. The pH of the solution increases. The magnitude of this pH effect depends on the concentrations of  $H_2S$  and  $NH_3$  present and in general is larger when concentrations are large. Thus at concentrations typical of sour water feed, the pH at  $25^\circ C$  could be almost 2 units higher than the pH at  $100^\circ C$ . For stripped sour water with low concentrations of  $NH_3$  and  $H_2S$ , the change in pH with temperature would be small.



SA-5015-18

FIGURE 1 AMMONIA AND SULFIDE IONIZATION AS A FUNCTION OF SOLUTION pH AT 100°C (WILSON, 1976)



SA-5015-22

FIGURE 2 LIQUID-VAPOR PARTITION COEFFICIENTS FOR AMMONIA-NITROGEN AND SULFIDE-SULFUR AS A FUNCTION OF pH AT 100°C AND 1 ATMOSPHERE TOTAL PRESSURE

The result of the pH behavior of  $K_N$  and  $K_S$  (illustrated in Figure 2) is that any sour water containing only ammonia, sulfide, and compounds that do not effect pH would leave a stripper at a pH of about 9, regardless of feed ammonia and sulfide composition. This pH of 9 will be referred to often in the rest of this report. It is important to realize that this pH is dependent on the choice of equilibrium and Henry's Law constants. It is also a function of stripper temperature. An actual stripper may converge to a different pH, but this difference does not affect the principles involved. A feed containing a molar excess of sulfide would start out acidic. Under this condition of  $K_S > K_N$ , the feed would lose a higher percentage of its sulfide than its ammonia on each stripping stage. As the feed progressed down the stripping column, it would become more basic until it approached a pH of about 9 where  $K_S = K_N$ , and it would lose the same percentage of both components on each stripping stage below this point in the column. This equal percentage loss would keep concentration ratios, and thus pH, constant during the rest of the feed's passage through the stripper.

A feed that starts with an excess of ammonia would lose ammonia more rapidly than sulfide and approach a constant pH of 9 from the basic side. In cases where steam rates are high, excess sulfide or ammonia might be lost quite rapidly and for most of the stripper  $K_S = K_N = \text{constant}$ . Equation (1) could be used to give an approximate model of stripping behavior. From Figure 2 we see that at pH 9,  $K_S = K_N = 10$ . For a stripper using 1.5 lb of steam per gallon of tower feed,  $S \cong 2$  and

$$f = \frac{1}{2^{N+1} - 1} ,$$

The presence of species that have an effect on solution pH can influence the operation of a stripper in a number of ways. Except for cases where these materials are present in large amounts, we would expect the effect to be strong only in the bottom of the column where their relative molar quantities are high. Consider, for example, a sour water feed of 10,000 ppm  $H_2S$  and 7,500 ppm  $NH_3$ , which has a pH of about 9 (Beychok, 1967). The concentrations are equivalent to 294 meq/l  $H_2S-S$  and 441 meq/l  $NH_3-N$ . If this sour water also contained 500 ppm TOC from benzoic acid (733 mg/l benzoic acid), the acid would represent only 6 meq/l, or less than 2% of the  $H_2S-S$  equivalents present. Under these circumstances, the benzoic acid would have only a very small effect on pH and hence the volatility of ammonia or sulfide in the top of the column. Toward the bottom of the column, however, after most of the sulfide and ammonia have been stripped, the benzoic acid could

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\* 1.5 lb/gal = 179.7 kg/m<sup>3</sup>. See p. H-2 for conversion of English units to metric units.

represent an important ionizable species. The column bottoms would be acidic, rather than having a pH of near 9 as expected. It can be shown that when the moles of ammonia nitrogen present are equal to the moles of benzoic acid present, the pH of the solution falls below 6. From Figure 2 it can be seen that under these circumstances ammonia is no longer volatile; it has been fixed.

If a basic material like sodium hydroxide is present in small amounts, it also would not affect the pH in the top of the column. Near the bottom of the column, however, where ammonia and sulfide concentrations are low, the basic material would be an important component of the sour water and would cause the pH to raise above the level of 9. If sufficient base were present to raise the column pH above 11, sulfide would become nonvolatile or fixed.

It is important to notice that the point in the column where ammonia and sulfide levels become low enough to permit small amounts of acids and bases to affect the pH is strongly dependent on the steam rate. With high steam rates, low ammonia and sulfide levels will be achieved high in the column. With low steam rates, acids and bases will only be able to affect the pH near the column bottom.

## V ANALYTICAL PROCEDURES

This section discusses the analyses of sulfide, ammonia, and cyanide, which significantly affected the results of this study. The routine analytical methods, including those of heavy metals and alkaline earth elements, all sulfur compounds, and nitrogen compounds, are included in Appendix A.

### Sulfide Determination

Sulfides proved to be the most difficult sulfur compounds to measure. Preliminary analyses using sour waters indicated that the methylene blue procedure described in Standard Methods (American Public Health Association, 1976) was reproducible and accurate. Known amounts of sulfide added to sour waters could be quantitatively recovered. Measurements of sulfide levels in refinery stripped sour waters were made by adding the color reagents to diluted samples. Later in the project it was found that measurements of low sulfide concentrations in laboratory stripped sour waters could not be made by direct addition of the color reagents to diluted samples. At low sulfide levels (10 ppm), some organic material in the sour water interferes with proper color development. At times it looked as though the methylene blue dye was being adsorbed by colloidal organic material that was present in our samples.

On the basis of this finding, we suspect that our measurements on refinery stripped samples may have underestimated the sulfide levels. The procedure that evolved for laboratory stripped samples entailed precipitation of the sulfide with cadmium hydroxide to separate the sulfide from the interference. Cadmium sulfide was removed from the sample by centrifugation.

Even with interferences removed, the method is not entirely satisfactory because it is too dependent on analyst technique. The timing of reagent addition and the amount of agitation used while adding reagents has a profound effect on the ultimate color development.

On the basis of duplicate analysis of laboratory stripped bottoms, we estimate that when concentrations were around 5 ppm the reproducibility was  $\pm 1$  ppm. At 100 ppm the reproducibility was  $\pm 16$  ppm.

For every stripping run the sulfide level in the feed was measured. Feed levels were on the order of 3000 ppm and our reproducibility was  $\pm 10\%$ .

The details of the method are described in Appendix A.

#### Ammonia Determinations

Ammonia was measured with an ammonia ion-specific electrode (Orion Research, Ammonia Electrode 95-10). All determinations with this electrode require that the solution measured be adjusted to a pH  $> 11$  to convert all ammonia to the un-ionized form. Various experiments were conducted to determine what sample pretreatment was required to achieve accurate and precise measurements with the electrode, and to compare electrode results with alternate ammonia measurement procedures.

The major interferences claimed for the ammonia electrode<sup>\*</sup> are

- Mercury ions that form strong complexes with ammonia
- Volatile organic amines
- Wetting agents such as organic acids and phenols.

The first interference could not be a problem because no mercury was detected in any of the sour waters used in this study. Volatile amines are a very unlikely interference in stripped sour waters, although they may be present in the unstripped sour waters. The major interference of concern was organic acids and phenols, components that would be present in both stripped and unstripped sour water.

Table 1 contains a summary of a series of tests used to determine the suitability of various procedures using the Orion ammonia electrode. The table shows that with actual refinery-stripped sour water, the results of spike recoveries vary.

The following procedures were investigated:

- (1) Direct determinations using an Orion model 95-10 ammonia electrode, including some measurements made after removal of organic acids and phenols by ether extraction.
- (2) Ammonia electrode determinations of condensate collected from a sample buffered to pH 9.5 during distillation. This method is described in an EPA manual (1976). Phenols as a class are not very volatile at any pH. Organic acids are essentially non-volatile at pH 9.5. Therefore, the distillate or condensate would not contain either of these materials.

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\* Instruction Manual, Ammonia Electrode 95-10, Orion Research.

Table 1

## AMMONIA DETERMINATIONS WITH THE AMMONIA ELECTRODE--SPIKE RECOVERIES

| Ammonia Addition<br>to 25 cc of Refinery A<br>Stripped Bottoms<br>Diluted to 100 cc<br>with Water and<br>Dechlorinating Agent | mg/l NH <sub>3</sub> -N in Diluted Sample       |                                                              |      |                                                                                      |
|-------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|--------------------------------------------------------------|------|--------------------------------------------------------------------------------------|
|                                                                                                                               | Direct Measurement                              |                                                              |      | Measurement with<br>Ammonia Electrode<br>after Distillation at<br>pH 9.5      pH >11 |
|                                                                                                                               | Direct Measurement<br>with Ammonia<br>Electrode | with Ammonia<br>Electrode<br>After Organic<br>Acids Removed* |      |                                                                                      |
| + 0 mg/l NH <sub>3</sub> -N                                                                                                   | 3                                               | 4                                                            | 6    | 13                                                                                   |
|                                                                                                                               | 3                                               | 4                                                            | 6    |                                                                                      |
| + 10 mg/l NH <sub>3</sub> -N                                                                                                  | 13                                              |                                                              | 16   |                                                                                      |
|                                                                                                                               | 13                                              |                                                              | 15.5 |                                                                                      |
| + 20 mg/l NH <sub>3</sub> -N                                                                                                  | 22                                              | 22                                                           | 23.5 |                                                                                      |
|                                                                                                                               | 23                                              | 23                                                           | 25   |                                                                                      |
| + 30 mg/l NH <sub>3</sub> -N                                                                                                  | 32                                              |                                                              |      |                                                                                      |
| + 40 mg/l NH <sub>3</sub> -N                                                                                                  | 41                                              | 39                                                           | 41   |                                                                                      |
|                                                                                                                               |                                                 | 41                                                           | 42.5 |                                                                                      |

\* Multiple extraction with ether under acidic conditions.

- (3) Ammonia electrode determinations of condensate collected from a sample adjusted to pH > 11 before distillation.

Double entries in Table 1 represent duplicate determinations from the same sample. The duplicate determinations suggest that the precision of the technique is  $\pm 1$  ppm.

The data show that at sample ammonia levels below 30 ppm, good spike recoveries are obtained when determinations are made with the ammonia electrode in the condensate collected during distillation at pH 9.5. The good spike recoveries indicate that if the total amount of ammonia introduced into the distillation apparatus is carefully restricted, pH 9.5 is adequate to give 100% ammonia recovery. For the unspiked sample, determinations were made in condensate obtained from distillation at pH 9.5 and pH 11. Recovery is complete at pH 9.5, and reproducibility is  $\pm 1$  ppm. The 6 ppm increase in ammonia seen when the distillation pH is adjusted from 9.5 to 11 indicates that free ammonia is generated from some nitrogen-containing material present in the stripped sour water.

The data also show that good spike recoveries are obtained when the ammonia electrode is used directly in the sample without distillation. There is no apparent effect of concentration on spike recoveries.

Comparison of the results obtained after extraction of organic acids, phenols, and other organic compounds with results obtained from untreated samples indicates that with this particular stripped sour water, organic acids do not interfere with the performance of the ammonia electrode.

In summary, the data in Table 1 suggest that:

- (1) Spike recoveries in sour water indicate that direct determinations with the ammonia electrode without distillation are accurate.
- (2) Distillation pretreatment is unnecessary and is harmful. Certainly, distillation at pH greater than 9.5 must be avoided. Standard methods (1976) emphasize the use of pH of 7.4 to reduce interferences.
- (3) Organic acids and phenols did not interfere with determinations made with the ammonia electrode.

EPA-approved methods for ammonia determination do not permit using the ammonia electrode except after distillation. Therefore, additional studies using several stripped sour waters were conducted to determine the effects of distillation. In addition, ammonia electrode determinations were compared to Nesslerization results. The data are shown in Table 2.

Table 2

DETERMINATION OF THE EFFECT OF DISTILLATION PRETREATMENT  
AND DIFFERENT FINISHES ON AMMONIA MEASUREMENTS  
(ppm)

| Refinery Sample    | Procedure                                               | Sample Number   |                    |                      |                    |
|--------------------|---------------------------------------------------------|-----------------|--------------------|----------------------|--------------------|
|                    |                                                         | A1              | A2                 | F1                   | G1                 |
| TKN                |                                                         | 192             | 242                | 197                  | 52                 |
| NH <sub>3</sub> -N | Direct determination<br>with ammonia electrode          | 14              | 11                 | 90                   | 26                 |
| NH <sub>3</sub> -N | EPA distillation at pH 9.5;<br>Ammonia electrode finish | 24              | 30,26 <sup>*</sup> | 88,86 <sup>*</sup>   | 30,30 <sup>*</sup> |
|                    | Nessler Finish                                          | --              | 33,28 <sup>*</sup> | 112,109 <sup>*</sup> | 40,35 <sup>*</sup> |
|                    | TKN finish                                              | --              | --                 | 90,85 <sup>*</sup>   | 34,30 <sup>*</sup> |
| NH <sub>3</sub> -N | Distillation at pH 11;<br>Ammonia electrode finish      | --              | 53,51 <sup>*</sup> | --                   | --                 |
|                    | Nessler finish                                          | 56 <sup>†</sup> | 55,50 <sup>*</sup> | --                   | --                 |

\* Duplicate determinations of the same sample.

† Analysis supplied by refinery.

Multiple entries are from duplicate determinations. Analysis of the duplicates suggest that the reproducibility of our analysis was  $\pm 2$  ppm for this series of tests.

For samples F1 and G1 and ammonia concentration in the condensate from the EPA-approved distillation at pH 9.5 was measured by ammonia electrode, Nesslerization, and total Kjeldahl nitrogen (TKN).

- (1) The agreement between the TKN and electrode methods is strong evidence that the electrode is accurately measuring ammonia concentration in the condensate.
- (2) The agreement between the TKN and electrode methods indicates that samples F1 and G1 contain no volatile amines to interfere with electrode determinations.
- (3) Nesslerization is a poor choice for ammonia measurements in sour waters. For both samples F1 and G1, the Nesslerization result is high, probably because of interference from organics such as ketones, aldehydes, or phenols.

Assuming that the electrode and TKN finishes are both correct, the ammonia concentrations determined after distillation for F1 and G1 are  $87 \pm 2$  and  $31 \pm 2$ , respectively. The results can be summarized as follows:

|                                                                   | <u>F1</u>  | <u>G1</u>  |
|-------------------------------------------------------------------|------------|------------|
| NH <sub>3</sub> -N direct determination<br>with ammonia electrode | 90 $\pm$ 2 | 26 $\pm$ 2 |
| NH <sub>3</sub> -N determination after<br>distillation at pH 9.5  | 87 $\pm$ 2 | 31 $\pm$ 2 |

The differences (for samples F1 and G1) between determinations with and without distillation are not significant. Two inferences were drawn from this result.

- (1) It is another confirmation of the accuracy of direct measurements of ammonia with the electrode without distillation pretreatment.
- (2) It shows that distillation of these two samples at pH 9.5 does not generate ammonia.

It is important to compare the results for samples A1 and A2 with those for F1 and G1. If direct electrode determinations of ammonia in samples A1 and A2 (and F1 and G1 as well) are correct, the results in Table 2 show that free ammonia is being generated by the EPA distillation procedure for sample A1 and A2 but not for sample F1 and G1. Note the increase in ammonia generation when the pH is raised from 9.5 to 11.

It is also interesting to note that Nesslerization determinations after distillation agree with electrode determinations after distillation for samples A1 and A2. This is a sharp contrast to the results obtained with samples F1 and G1.

We feel that the conclusions to be drawn from these comparison studies are:

- (1) Nesslerization should not be used to measure ammonia in sour waters.
- (2) With some sour waters, the EPA distillation at pH 9.5 generates free ammonia, thus causing overestimation of ammonia concentrations.
- (3) An ammonia measurement using a distillation at pH > 9.5 should not be used.
- (4) Direct determination of ammonia with an ammonia electrode gives an accurate measurement of concentration for the sour waters.

Even though direct electrode determinations were the preferred technique for this study, electrode determinations after distillation at a pH of 9.5 were chosen as the method for the bulk of the experimental work in order to produce results that would be consistent with future regulatory procedures.

#### Cyanide Determinations

Total cyanide was measured using tentative ASTM Method A, and free cyanide was measured using tentative ASTM Method F. The validity of the procedures used in this study to measure cyanide is questionable. Free cyanide measurements sometimes gave higher results than a total cyanide measurement. Experiments to check the accuracy and precision of Method F (ASTM), which is purported to measure free cyanides, were performed in refinery sample A2 and in distilled water. The averages of duplicate measurements are shown in Table 3. The reproducibility was

Table 3

EXPERIMENTS TO DETERMINE ACCURACY  
OF CYANIDE MEASUREMENTS

| Feed                                                     | CN <sup>-</sup> (Method F) <sup>*</sup><br>(ppm) |
|----------------------------------------------------------|--------------------------------------------------|
| Refinery sample A2                                       | 10.75                                            |
| Refinery sample A2 + 50 ppm CN <sup>-</sup>              | 55.00                                            |
| Refinery sample A2 + 50 ppm CN <sup>-</sup><br>from KSCN | 10.15                                            |
| Distilled water + 0.5 ppm CN <sup>-</sup><br>from KCN    | 0.5                                              |
| Distilled water + 1.0 ppm CN <sup>-</sup><br>from KCN    | 1.0                                              |

\* ASTM Method F is purported to measure only CN<sup>-</sup> in solution. Metal-complexed cyanides and thiocyanate are not supposed to be detected by this procedure.

on the order of one percent. The accuracy, as determined from spike recoveries of added cyanide both in the distilled water and the sour water, appears excellent. The data also show that added thiocyanate does not interfere with the cyanide analysis.

In contrast to the above, cyanide measurements on eight sour water samples obtained from various refineries were generally unsatisfactory. These results are summarized in Table 4. The determinations for samples C1 through G1 were duplicated and showed good reproducibility, with measurements differing from the mean by no more than five percent. However, for refinery samples A2, C1, F1, and G1, the free cyanide determination exceeds the total cyanide determination by a significant amount, perhaps a result of some unknown interferences. It appears that we can measure cyanides reproducibly and accurately in distilled water but not in actual refinery samples.

Table 4

CYANIDE DETERMINATIONS IN REFINERY  
STRIPPED SOUR WATERS

| Refinery<br>Sample | Total Cyanide<br>(ASTM Method A) *<br>(ppm) | Free Cyanide †<br>(ASTM Method F)<br>(ppm) |
|--------------------|---------------------------------------------|--------------------------------------------|
| A1                 | 18.1                                        | 5.5                                        |
| A2                 | 0.6                                         | 10.7                                       |
| B1                 | 0.15                                        | 0.02                                       |
| C1                 | 0.51<br>0.50                                | 2.34<br>2.21                               |
| D1                 | 4.62<br>4.87                                | 4.44<br>4.87                               |
| E1                 | 10.17<br>10.37                              | 0.06<br>0.06                               |
| F1                 | 1.37<br>1.37                                | 9.83<br>9.75                               |
| G1                 | 0.02<br>0.02                                | 1.19<br>1.19                               |

\* Tentative ASTM Method A measures  $\text{CN}^-$  and most metal-complexed cyanide and is not supposed to measure thiocyanate.

† Tentative ASTM Method F measures  $\text{CN}^-$  only and is not supposed to measure thiocyanate.

## VI ANALYSIS OF REFINERY SOUR WATERS

Eight refineries with different crude slates and different refinery operations feeding the sour water strippers were sampled. Most of the stripped sour waters were collected under nitrogen and air-mailed to SRI International, where they were placed in a refrigerator at 4°C until analyzed. The samples were in transit from 2 to 5 days. Several refinery samples were collected by SRI staff and transported to our facilities on the same day.

Refinery A was sampled three times. The second sample was taken because the first had an unexpectedly low pH (the refinery adds caustic to the stripper). The third sample was acquired during the bench scale stripping phase of the program. Refinery B's sample also yielded a pH that was too low, but it was not resampled because it contained very low levels of the materials of interest to this study.

### Nitrogen and Sulfur Compounds

Table 5 summarizes the results obtained from the eight refineries. The analysis on sample H1 is incomplete because it arrived late in the program. For all refineries except A and B, the two ammonia determinations (direct measurement with ammonia electrode and measurement after distillation) gave comparable results. Ammonia and TKN determinations were close in value, indicating that most of the nitrogen in these sour waters is ammonia. Only one, refinery A, stands out as having an excess of non-ammonia nitrogen. This refinery also shows significant generation of ammonia during the distillation part of the ammonia determination. Refinery A stripped sour water shows 14 ppm  $\text{NH}_3\text{-N}$  without distillation, 24 ppm  $\text{NH}_3\text{-N}$  after distillation at pH 9.5 (Table 5), and 52 ppm  $\text{NH}_3\text{-N}$  after distillation at pH 11 (Table 2).

All of the refineries except B and G show significant amounts of sulfur that is not sulfide. This can be seen by comparing the total sulfur measurements with the sulfide measurements. For Refineries A, C, and E, this extra sulfur is principally in the form of thiosulfate. Although the analysis for Refinery H is incomplete, the sulfur balance suggests that, with this refinery also, the non-sulfide sulfur is in the form of thiosulfate. Thiosulfate will behave as a strong acid. Therefore, thiosulfate is a more logical choice for the remaining sulfur in the sour water from Refinery H than is free sulfur, which is neutral.

Table 5

STRIPPED SOUR WATERS: ANALYSIS OF NITROGEN AND SULFUR SPECIES  
(ppm)

| Refinery Sample                  | A1                   | A2   | B1   | C1       | D1     | E1       | F1                    | G1     | H1  |
|----------------------------------|----------------------|------|------|----------|--------|----------|-----------------------|--------|-----|
| pH                               | 5.0                  | 9.5  | 4.0  | 8.6      | 9.0    | 10.2     | 8.5                   | 8.4    | 6.3 |
| TKN <sup>*</sup>                 | 192                  | 242  | 6    | 208      | 80     | 1080     | 197                   | 52     | 82  |
| NH <sub>3</sub> -N               |                      |      |      |          |        |          |                       |        |     |
| After distillation <sup>†</sup>  | 24                   | 28   | 14   | 157      | 30     | 1075     | 87(110) <sup>**</sup> | 30(38) | 60  |
| Direct <sup>‡</sup>              | 14                   | 11   | 5    | 140      | 22     | 1000     | 90                    | 26     | 60  |
| Total sulfur                     | 89[97] <sup>††</sup> | ND   | 0    | 297[231] | 45[49] | 229[276] | 137[87]               | 5.5    | 115 |
| H <sub>2</sub> S-S               | <1                   | ND   | ND   | 41       | <1     | 116      | 13                    | <1     | <1  |
| SCN-S                            | ND                   | ND   | ND   | 60       | 23     | 52       | 29                    | <0.1   | 4   |
| S <sub>2</sub> O <sub>3</sub> -S | 92                   | ND   | ND   | 77       | 17     | 109      | 33                    | <2     | ND  |
| SO <sub>2</sub> -S               | 5                    | ND   | ND   | 1.6      | 1.5    | 2.1      | 12                    | <1     | ND  |
| Free sulfur-S                    | ND                   | ND   | ND   | 52       | 6.4    | <5       | <5                    | <5     | ND  |
| Cyanide <sup>§</sup>             |                      |      |      |          |        |          |                       |        |     |
| Free                             | 5.5                  | 10.7 | 0.02 | 2.25     | 4.5    | 0.06     | 9.79                  | 1.19   |     |
| Total                            | 18                   | 0.6  | 0.15 | 0.51     | 4.7    | 10.2     | 1.37                  | 0.02   |     |

Note: ND = Not determined.

\* Total Kjeldahl Nitrogen.

<sup>†</sup> Ammonia measured with ammonia electrode in distillate using EPA approved distillation method at pH 9.5.

<sup>‡</sup> Ammonia measured with ammonia electrode directly in sample.

<sup>§</sup> Free cyanide measured using tentative ASTM method F. Total cyanide measured using tentative ASTM method A.

\*\* ( ) indicates Nessler finish

<sup>††</sup> [ ] indicates total from individual determinations.

The presence of these oxidized sulfur compounds indicates that the sour waters have been exposed to oxygen (Chen, 1971, 1972). Exposure during sampling was minimal, so we feel that the oxygen exposure occurred in the refineries, either from oxygen in the crude or exposure to air in the sour water system. The significance of the oxidized sulfur with respect to the ammonia levels in the sour water will be discussed in Section VII.

The cyanide measurements have been discussed previously in Section V, the only inference that can be drawn from them is that cyanides were present in most of the sour waters sampled.

#### Heavy Metals and Alkali Earth Elements

The results of metal analysis are shown in Table 6. The levels of heavy metals in all of the refinery sour waters are low enough to eliminate ammonia-metal complexes as a cause for ammonia fixation.

#### Organic Analysis of Stripped Sour Waters

The objective of this phase of the project was to identify the organic compounds responsible for high residual ammonia in stripped sour water. We based our investigation on two general mechanisms that could lead to residual ammonia:

- (1) Protonation of dissolved ammonia by weak organic acids, thereby reducing the ammonia vapor pressure.
- (2) Presence of compounds in the stripped water that decompose to yield ammonia under the conditions of the ammonia test.

The ability of weak acids to neutralize ammonia depends on the  $pK_a$  of the acid. Representative  $pK_a$  values of selected acids are given in Table 7. Since the  $pK_a$  of ammonia (actually the  $pK$  of the conjugate acid of ammonia, the ammonium ion  $NH_4^+$ ) is 9.25, both aliphatic and aromatic acids will protonate one mole of ammonia for every mole of acid. However, phenols are weaker acids and in a solution containing 1 equivalent of phenol and 1 equivalent of ammonia, only about 32% of the ammonia will be protonated. Thus, the reduction in the vapor pressure of the ammonia will not be large, and phenols should not significantly increase the residual ammonia.

Table 6

## STRIPPED SOUR WATERS: INORGANIC ANALYSIS

| Refinery Sample                              | A1     | B1   | C1     | D1     | E1     | F1     | G1    | H1 |
|----------------------------------------------|--------|------|--------|--------|--------|--------|-------|----|
| Nonvolatile total solids<br>(residual) (ppm) | 1263   | < 10 | 191    | 313    | 20     | 59     | 13    | ND |
| Composition of residual* (%)                 |        |      |        |        |        |        |       |    |
| Na                                           | 40     | ND   | 7.5    | 35     | 25     | 40     | 20    | ND |
| Fe                                           | 0.5    |      | 1      | 0.75   | 0.2    | 1      | 1     |    |
| Ca                                           | 0.12   |      | 4      | 2.5    | 1.25   | 0.85   | 20    |    |
| Si                                           | 0.07   |      | 12.5   | 0.85   | 12     | 3      | 6     |    |
| Mg                                           | 0.025  |      | 25     | 1      | 0.5    | 0.15   | 2.5   |    |
| Al                                           | 0.02   |      | 0.07   | 0.07   | 0.08   | 0.4    | 0.25  |    |
| Ni                                           | 0.015  |      | 0.005  | 0.02   | 0.75   | 0.008  | 0.01  |    |
| Ba                                           | 0.003  |      | --     | --     | 0.004  | --     | --    |    |
| Cu                                           | 0.002  |      | 0.025  | 0.025  | 6      | 0.06   | 0.035 |    |
| Cr                                           | 0.001  |      | 0.04   | 0.02   | 0.006  | 0.01   | 0.015 |    |
| B                                            | <0.01  |      | 0.75   | 0.12   | 2      | 0.015  | 0.15  |    |
| Mn                                           | <0.001 |      | 0.04   | 0.007  | 0.06   | 0.05   | 0.07  |    |
| Pb                                           | <0.005 |      | <0.005 | <0.005 | <0.005 | <0.005 | 0.01  |    |
| K                                            | <0.5   |      | 2      | 2.5    | 1.5    | 1      | 2     |    |
| Sr                                           | <0.01  |      | 0.15   | 0.04   | 0.008  | 0.015  | 0.02  |    |
| Metals in unfiltered sample                  |        |      |        |        |        |        |       |    |
| Na (ppm)                                     | 500    | 1.3  | 11     | 92     | 2.5    | 18     | 2.5   | ND |
| Fe (ppm)                                     | 6.3    | 0.0  | 0.0    | 1.4    | 0.0    | 0.0    | 0.0   |    |
| K (ppm)                                      | 2.2    | <1.0 | 2      | 1.5    | 0.2    | 0.5    | 0.3   |    |
| Ca (ppm)                                     | 2.0    | 1.6  | 15     | 5.0    | 0.2    | 0.5    | 2.3   |    |
| Mg (ppm)                                     | ND     | ND   | 21     | 1.4    | 0.1    | <0.05  | 0.6   |    |
| Cu (ppm)                                     | ND     | ND   | ND     | ND     | 1.4    | ND     | ND    |    |
| Ni (ppm)                                     | ND     | ND   | ND     | ND     | 0.0    | ND     | ND    |    |

Note: ND = Not determined.

\* Semiquantitative spectrographic reported as oxide.

Table 7

pK<sub>a</sub> VALUES OF SELECTED ACIDS AT ROOM TEMPERATURE

| <u>Compound</u>   | <u>pK<sub>a</sub></u> |
|-------------------|-----------------------|
| Acetic acid       | 4.75                  |
| Propionic acid    | 4.87                  |
| Hexanoic acid     | 4.88                  |
| Benzoic acid      | 4.19                  |
| 1-Naphthoic acid  | 3.70                  |
| 2-Naphthoic acid  | 4.17                  |
| Phenol            | 9.89                  |
| <u>o</u> -Cresol  | 10.20                 |
| <u>m</u> -Cresol  | 10.01                 |
| <u>p</u> -Cresol  | 10.17                 |
| Resorcinol        | 9.81                  |
| Hydrogen sulfide  | 6.9                   |
| Thiocyanic acid   | 4.0                   |
| Sulfurous acid    | 7.2                   |
| Thiosulfuric acid | 1.7                   |

Sources: Handbook of Chemistry and Physics, 54th Ed.  
Page (1953)

Our initial intention was to identify and quantify as many specific weak organic acids as possible in several stripped sour waters. However, we found that the organic material in the test samples was mainly phenolics, which made the analysis of organic acids very difficult within the allotted time and funds. Several attempts to identify organic acids were unsuccessful.

We were able, however, to measure the total concentration of weak acids (organic and inorganic) in the stripped sour waters by potentiometric titration. The inorganic acids were identified chemically, and the organic acids were back-calculated by difference. We also used the technique of gel permeation chromatography to measure the molecular weight distribution of the aromatic organic compounds in the stripped sour waters. The results obtained with both these measurement techniques are summarized below.