# Should We or Shouldn’t We Continue APS Injection?

An Amine Best Practices Group

Cameo Presentation

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Brimstone Sulfur Symposium 2025

# Amine Best Practices Group

- Industry informal data and practices sharing network
- Representatives from operating companies and former representatives of operating companies
- Discussions involve safety, reliability, and environmental compliance
- No economic or business data discussed
- No guarantees, warranties, or mandates derived from member opinions
- Annual meetings and use of the Data Exchange Network (DEN) to facilitate discussion

# ABPG Technical Discussion Categories

- Amine Treating
- SRU (Sulfur Recovery Unit)
- TGU (Tail Gas Unit)
- SWS  (Sour Water Stripper)
- Lessons Learned

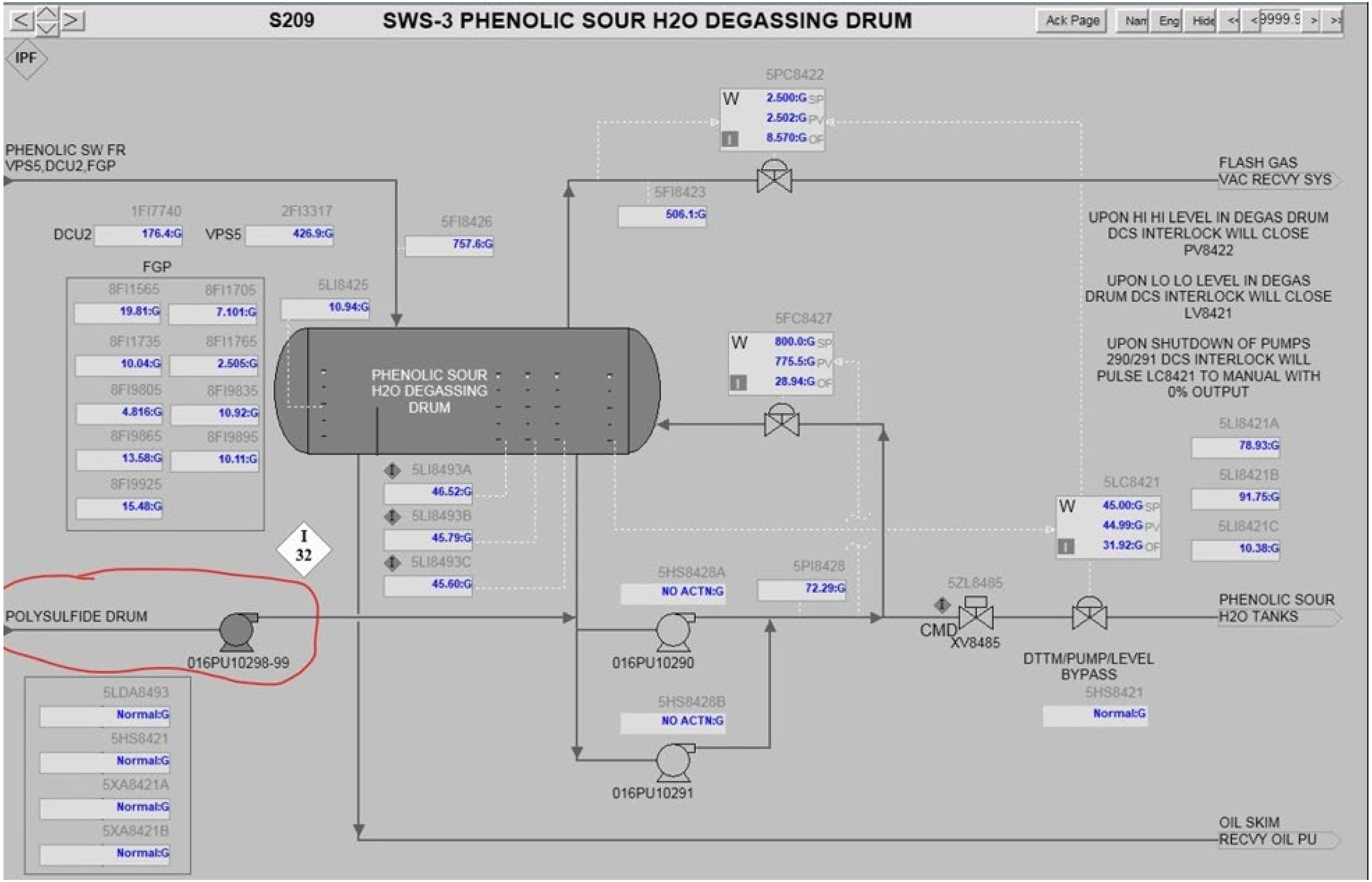
# Posted Question to SWS Category

**Question Id: SWS-064**

**Title:** APS (Ammonium Polysulfide) Injection for Cyanide and SWS Metallurgy

Attachment(s): SWS-064.docx, SWS-064A.jpg, SWS-064B.docx

**[SWS-064]**: A question has been asked by our service provider concerning the discontinuation of our APS injection into our Sour Water feed (see schematic in SWS-064A). I recommend keeping the injection but wanted to ask the group. If you do not have APS injection to treat cyanides, what metallurgy do you have in your SWS OH fin fans, etc. that allows you to not have APS injection. Our fin fans are 316SS, but I'm still recommending to keep the injection due to some history that I have experienced with replacing fin fans in <10 years of operation.



S209
SWS-3 PHENOLIC SOUR H2O DEGASSING DRUM
Ack Page
IPF
PHENOLIC SW FR
VPS5,DCU2,FGP
1FI7740
DCU2 176.4:G
2FI3317
VPS5 426.9:G
5FI8426
757.6:G
FGP
8FI1565 19.81:G
8FI1705 7.101:G
8FI1735 10.04:G
8FI1765 2.505:G
8FI9805 4.816:G
8FI9835 10.92:G
8FI9865 13.58:G
8FI9895 10.11:G
8FI9925 15.48:G
5LI8425 10.94:G
PHENOLIC SOUR
H2O DEGASSING
DRUM
5PC8422
W 2.500:G SP
2.502:G PV
8.570:G OP
5FI8423 506.1:G
FLASH GAS
VAC RECVY SYS
UPON HI HI LEVEL IN DEGAS DRUM
DCS INTERLOCK WILL CLOSE
PV8422
UPON LO LO LEVEL IN DEGAS
DRUM DCS INTERLOCK WILL CLOSE
LV8421
UPON SHUTDOWN OF PUMPS
290/291 DCS INTERLOCK WILL
PULSE LC8421 TO MANUAL WITH
0% OUTPUT
5FC8427
W 800.0:G SP
775.5:G PV
28.94:G OP
5LI8421A 78.93:G
5LI8421B 91.75:G
5LI8421C 10.38:G
5LC8421
W 45.00:G SP
44.99:G PV
31.92:G OP
5LI8493A 46.52:G
5LI8493B 45.79:G
5LI8493C 45.60:G
I 32
POLYSULFIDE DRUM
016PU10298-99
5HS8428A NO ACTN:G
5PI8428 72.29:G
5ZL8485
CMD
XV8485
PHENOLIC SOUR
H2O TANKS
016PU10290
DTTM/PUMP/LEVEL
BYPASS
5HS8421 Normal:G
5LDA8493 Normal:G
5HS8421 Normal:G
5XA8421A Normal:G
5XA8421B Normal:G
5HS8428B NO ACTN:G
016PU10291
OIL SKIM
RECVY OIL PU

# What is APS and Why is it used?

- Ammonium Polysulfide $(NH_4)_2S_x$, x=3 or 4 typically
  - Made by dissolving sulfur in ammonium bisulfide solution
- Polysulfide ion is attacked by cyanide ion
  - $(NH_4)_2S_4 + 3CN^- => NH_4^+ + 3\ SCN^- + HS^- + NH_3$
- Polysulfide ion competes with cyanide ion for iron ion in FeS(s)
  - Reducing $Fe(CN)_6^{-4}$ formation helps retain FeS layer protection for carbon steel
  - Reduces problems with hydrogen blistering and cracking in FCC and Coker main fractionator overhead systems and wet gas compressors

# ABPG Response Summary-Mixed Opinions

- No APS use makes titanium and/or hastelloy tubes in SWS overhead cooler a must (3 respondents)
- Cyanide ion concentration is reduced by hydrolysis to ammonium formate in both amine and SWS systems (1 respondent)
- Overhead condensers are more susceptible to cyanides than pump around loop SWS, since the cyanide and $NH_4HS$ can be absorbed into first water then condenses in the finfan tubes and then are diluted farther down the tube length as more water is condensed. (1 respondent)
- We don’t use APS and we have to use SS, Ti, or Hastelloy anyway (5 respondents)

# SWS Overhead Cooler Corrosion Considerations

- Carbon Steel Corrosion Rates
  - Modeled by N. Hatcher and A. Keller from JIP (Joint Industry Program) on Rich amine and Sour Water corrosion studies (Brimstone 2008)
  - Corrosion rate, mpy = $K_o e^{\{-(aV+b)/RT\}}[(aH_2S)^n(aHS^-)^p + c]$
  - Ko = Arrhenius pre-exponential factor
  - a, b, n, c and p = fitting coefficients
  - $aH_2S$ = molal activity of dissolved $H_2S$ in solution = f (T, composition)
  - $aHS^-$ = molal activity of dissolved bisulfide ion in solution = f (T, composition)
  - R = ideal gas constant
  - T = absolute temperature
  - V = fluid velocity

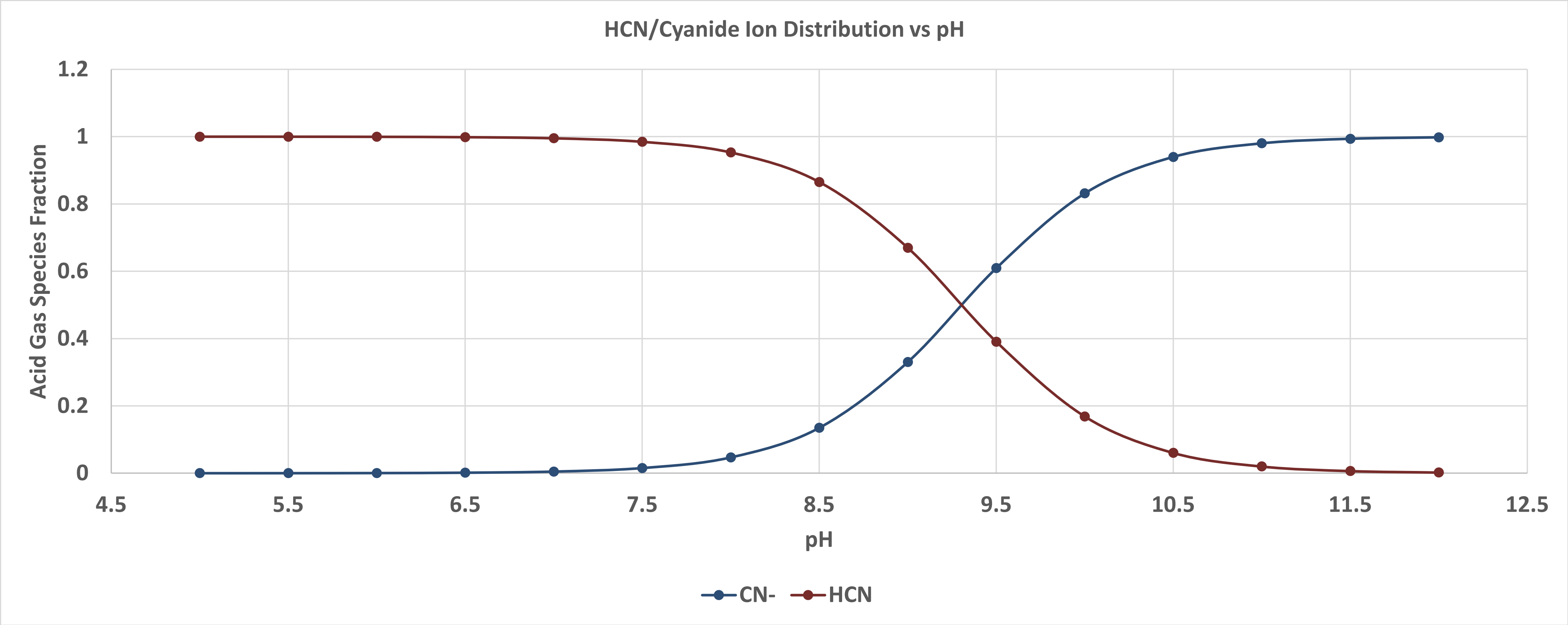
# SWS CS Corrosion Example (Keller et. al. Brimstone 2008)

- 50 gpm sour water in 2 inch sch. 80 pipe with 0.125 in corrosion allowance

| Ammonia wt% | Wt% $H_2S$ | Temperature, F | Predicted mil/yr | Predicted life, yrs |
|---|---|---|---|---|
| 1.0 | 2.0 | 110 | 5.5 | 22.9 |
| 3.0 | 6.0 | 110 | 18.3 | 6.8 |
| | | | | |
| 1.0 | 2.0 | 180 | 14 | 8.9 |
| 3.0 | 6.0 | 180 | 66.8 | 1.9 |

- CS never appropriate for this service whether $CN^-$ present or not!

# The Cyanide Divide-Is APS Effective?




**Typical sour water conditions mean more HCN than CN-. Consuming CN- will simply make more CN-**

# Cyanide in SWS OVHD Water-Simulation With no Reactions

- Water feed is 1 wt% ammonia, 1.8 wt% $H_2S$, 100 ppmw HCN
  - pH is 8.0, HCN is about 95% of the total cyanide, so $CN^-$ is 5 ppmw
- Reflux is 9.1 wt% ammonia, 7.2% $H_2S$, 816 ppmw HCN
  - pH is 8.3, HCN is about 84% of the total cyanide, so $CN^-$ is about 130 ppmw
- Adding APS in this feed would not significantly change the cyanide ion content of the feed water as the pH is too low to allow effective conversion of HCN to $CN^-$
- Adding APS in the feed would not likely impact the concentration effect in the reflux as the HCN would get stripped

# Cyanide Containing Solutions-Can We Measure Cyanide Accurately?

- HCN/Cyanide containing solutions are very unstable to air/$H_2S$ and somewhat unstable to water
- HCN reacts with $H_2S$ and oxygen to form thiocyanate ions:
  - $2\ HCN + O_2 + 2\ H_2S + 2\ NH_3 \Rightarrow 2\ NH_4^+ + 2\ SCN^- + 2\ H_2O$
- HCN reacts with water to form formate ions and ammonia:
  - $HCN + 2\ H_2O \Rightarrow NH_4^+ + HCOO^-$

# Sampling Interferences Aid in Understanding HCN in SWS

- If a solution contains thiocyanate ion, it likely means HCN was dissolved but reacted with oxygen and $H_2S$
- Thiocyanate ion paired with amine or ammonia should behave as heat stable salts. The amine/$SCN^-$ or ammonia/$SCN^-$ ion pair must leave with the stripper bottoms product
  - Any thiocyanate ion in the feed, if related to HCN in the feed water, should disappear in the bottoms showing the HCN was stripped
  - Any thiocyanate in the bottoms can be assumed to be HCN that was converted in the sour water collection/storage/stripping

# Coker Fractionator and Wet Gas Compression Water Samples-Site 1

( ppm as ug / g )

| ions in ug/ml | Sour Water Samples at the Unit | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| NAME | Coker PIF water | Quench tank water | Recontact drum sour water | Interstage drum sour water | Frac ohd sour water | Frac ohd sour water | Settling drum sour water | Settling drum sour water |
| Date | 30-Oct | 30-Oct | 30-Oct | 30-Oct | 30-Oct | 30-Oct | 30-Oct | 30-Oct |
| Sodium | 202 | 40 | 0 | 0 | 0 | 0 | 5 | 1 |
| | | | | | | | | |
| Formate | 0 | 0 | 50 | 71 | 52 | 76 | 2 | 4 |
| Acetate | 13 | 8 | 449 | 516 | 493 | 680 | 11 | 8 |
| Chloride | 132 | 126 | 25 | 21 | 25 | 46 | 44 | 13 |
| Sulfate | 434 | 404 | 104 | 71 | 61 | 54 | 24 | 22 |
| Sulfite | 0 | 0 | 428 | 285 | 106 | 122 | 0 | 11 |
| Thiosulfate | 35 | 88 | 1,232 | 766 | 546 | 523 | 472 | 427 |
| Thiocyanate | **0** | **0** | **1,062** | **856** | **374** | **351** | **19** | **119** |
| Sulfide | 0 | 0 | 3,458 | 5,359 | 4,597 | 5,512 | 0 | 220 |
| Oxalate | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Phosphate | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| MMEA | 14 | 6 | 7 | 8 | 13 | 22 | 1 | 0 |
| Ammonium | 28 | 20 | 3,103 | 3,380 | 2,988 | 3,297 | 113 | 233 |
| MEA | 0 | 0 | 7 | 4 | 12 | 32 | 0 | 0 |
| DEA | 26 | 0 | 55 | 54 | 40 | 45 | 0 | 0 |
| MDEA | 0 | 0 | 18 | 16 | 20 | 28 | 0 | 0 |
| DIPA | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

Indicates HCN (Formate)

Indicates HCN (Thiocyanate)

# Sour Water Feed and Bottoms Samples From Site 2 (Includes Coker Sour Water)

| NAME | Date | Chloride | Sulfite | Sulfate | Oxalate | P-PO4 | S2O3= | SCN- |
|---|---|---|---|---|---|---|---|---|
| T-131 Feed from D1901 | 11-Apr | 19 | 130 | 52 | <1 | <1 | 59 | 15 |
| T-131 Water | 11-Apr | 30 | 196 | 42 | <1 | <1 | 76 | 21 |
| T-73 Feed from D600 | 11-Apr | 131 | 839 | 797 | <1 | <1 | 617 | 5 |
| T-73 Water | 11-Apr | 195 | 948 | 947 | <1 | <1 | 720 | 6 |
| No1 SWS Btms | 11-Apr | 151 | 11 | <1 | <1 | <1 | <1 | <1 |
| No 2 SWS Btms | 11-Apr | 154 | 4 | <1 | <1 | <1 | <1 | <1 |
| No 3 SWS Btms | 11-Apr | 18 | <1 | <1 | <1 | <1 | <1 | <1 |
| No 5 SWS Btms | 11-Apr | 17 | <1 | 2 | <1 | 2 | <1 | 5 |

Notice much lower thiocyanate numbers in SWS feed. This may indicate that dissolved HCN had been hydrolyzing during transport, separation, and storage. The bottoms samples with no SCN- indicate that any HCN that was in the feed was stripped.

# Conclusions

- APS (Ammonium Polysulfide) addition at the 3-phase separator in the original question not likely to have an impact on cyanide ion in SWS reflux
  - There may not be much HCN left after the water sits in the feed tank due to hydrolysis
  - APS will not significantly impact HCN or cyanide concentration in the reflux due to equilibrium distribution
  - CS is unacceptable for SWS overhead condensers and piping due to high $HS^-$ concentration
  - Choice of metallurgy should only be to handle extremely high $H_2S$ concentration water in SWS overhead systems