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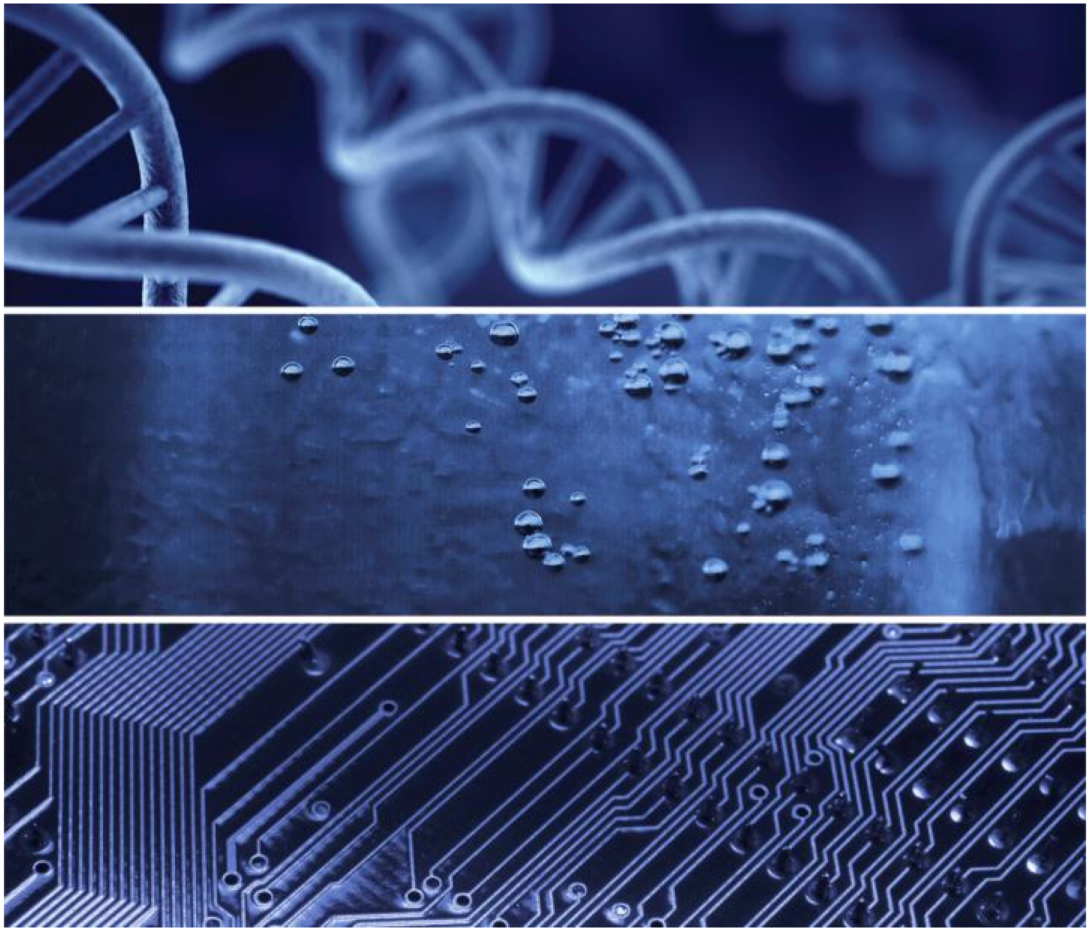

Amine Systems: Corrosion Overview, Impact of Solids on the Corrosion-Fouling Cycle

Laurance Reid Gas Conditioning Conference
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Amine Loop Corrosion

- Carbon steel or alloy corrosion in amine service is a very broad, complex and costly area of plant focus
- Issues include many factors, such as:
  – High operating temperatures
  – Amine type and concentration
  – High rich and lean amine loadings
  – Acid gas type and CO_2 to H_2S ratio in the acid gas
  – Amine solution contaminants including amine degradation products and heat stable salts

Carbon Steel Corrosion and Protective Layers

- Carbon steel in the presence of H_2S forms a weakly adherent protective layer of porous iron sulfide that resists further corrosion. The basic reactions of iron with dissolved H_2S species are:

$$H_2S(aq) + Fe(s) \rightarrow FeS(s) + H_2(g)$$

$$2HS^-(aq) + Fe(s) \rightarrow FeS(s) + H_2(g) + S^=(aq)$$

- In the presence of CO_2, the carbon steel forms a more fragile layer of iron carbonate. The basic reactions of iron with CO_2 are:

$$CO_2(aq) + Fe(s) + H_2O \rightarrow FeCO_3(s) + H_2(g)$$

$$2HCO_3^- + 2Fe(s) \rightarrow 2FeCO_3(s) + H_2(g) + 2e^-$$

Corrosion Mechanisms, Industry Recommendations

- The technical paper provides an overview of corrosion mechanisms and industry recommendations for mitigation for a range of identified issues:
  - Amine solution carbon steel corrosion
  - Wet CO_2 corrosion and wet H_2S corrosion
  - Wet acid gas corrosion due to NH_3 and HCN
  - Stress corrosion cracking (SCC)
  - Hydrogen induced cracking (HIC)
  - Inter-granular corrosion
  - Galvanic corrosion
  - **Erosion-corrosion**
  - **Concentration cell corrosion**

- Broad documentation exists on the first seven issues
- Today's presentation focuses on discussing the last two issues

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Erosion-Corrosion

- Erosion-corrosion – caused by:
  - High amine solution velocities creating shear stress on solid surfaces
  - Solution turbulence
  - Impingement of amine and gas on metal surfaces
  - Removal of the protective FeS or $FeCO_3$ layer exposing fresh iron
    - Released sulfides and/or carbonates solids act as scouring agents
    - Localized corrosion rates increase
  - Presence of heat stable salts (HSS) weakening FeS lattice, enabling more severe erosion-corrosion vs. systems with low HSS
  - ‘Dirty’ amine solutions containing abrasive suspended particulates

Erosion-Corrosion: Amine Solution Velocities

- Maximum amine solution velocities are recommended to minimize erosion-corrosion
- Various recommendations are seen from different sources:
  - Jones et al:
    - General: CS, lean amine — <2.1-3 m/sec (7-10 ft/sec)
    - General: CS, rich amine — <0.9-1.5 m/sec(3-5 ft/sec)
  - API RP 945 (R2008), "Avoid Environmental Cracking in Amine Units, 3rd Edition":
    - CS piping, lean & rich: — <1.8 m/sec (6 ft/sec)
  - Campbell:
    - General, CS, rich or lean amine: — <0.9 m/sec (3 ft/sec)
- Note: Flashing of the dissolved gas in the amine:
  - Can lead to enormous increase in the velocity of the resulting two phase flow
  - Greatly increases scouring potential and reducing component life
- **While some maximum amine velocity recommendations comment on the benefits of cleaner amine, none quantify the impact of solids**

Corrosion: Commercially Available Predictive Models

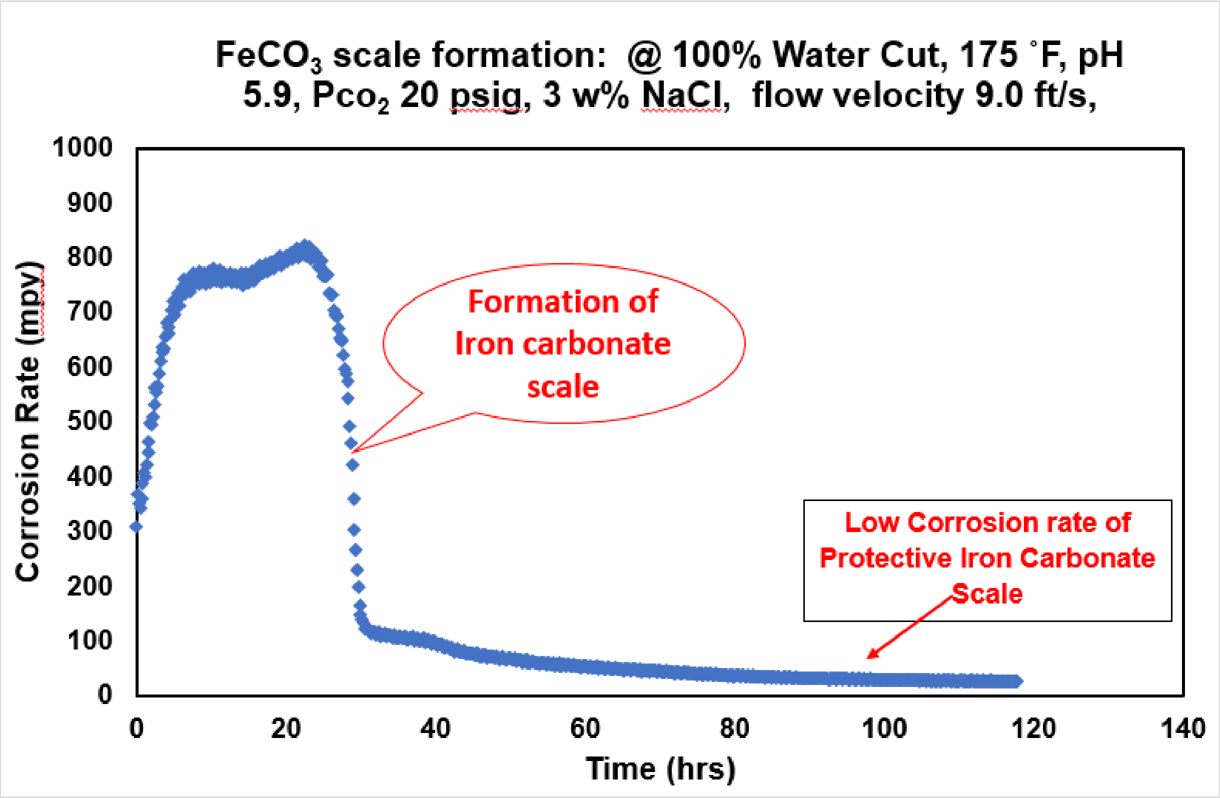
- Predictive corrosion modelling software now available from various suppliers
  - Incorporate detailed chemistry and hydraulics-based corrosion rate data from public and proprietary sources
  - Many corrosion mechanisms and industry recommendations are included
  - Detailed analysis of many parameters is available, such as:

    Bisulfide ion (HS^-), free dissolved H_2S, bicarbonate ion (HCO_3^-), free dissolved CO_2
  - Fluid velocity, temperature, HSS, metallurgy data on a wide range of materials including CS, 304L and 316L SS, 2205,2507, 825 and C-276 alloys
- **In general, software shows a strong correlation between model and measured rates of corrosion**
- **None at this time appear to account for variations in solids levels within the recirculating solution**

Corrosion Rates: Carbon Steel vs. Iron Carbonate

- Research by Nassef et al, Erosion/Corrosion Research Center, U. Tulsa:

Iron Carbonate Scale Formation



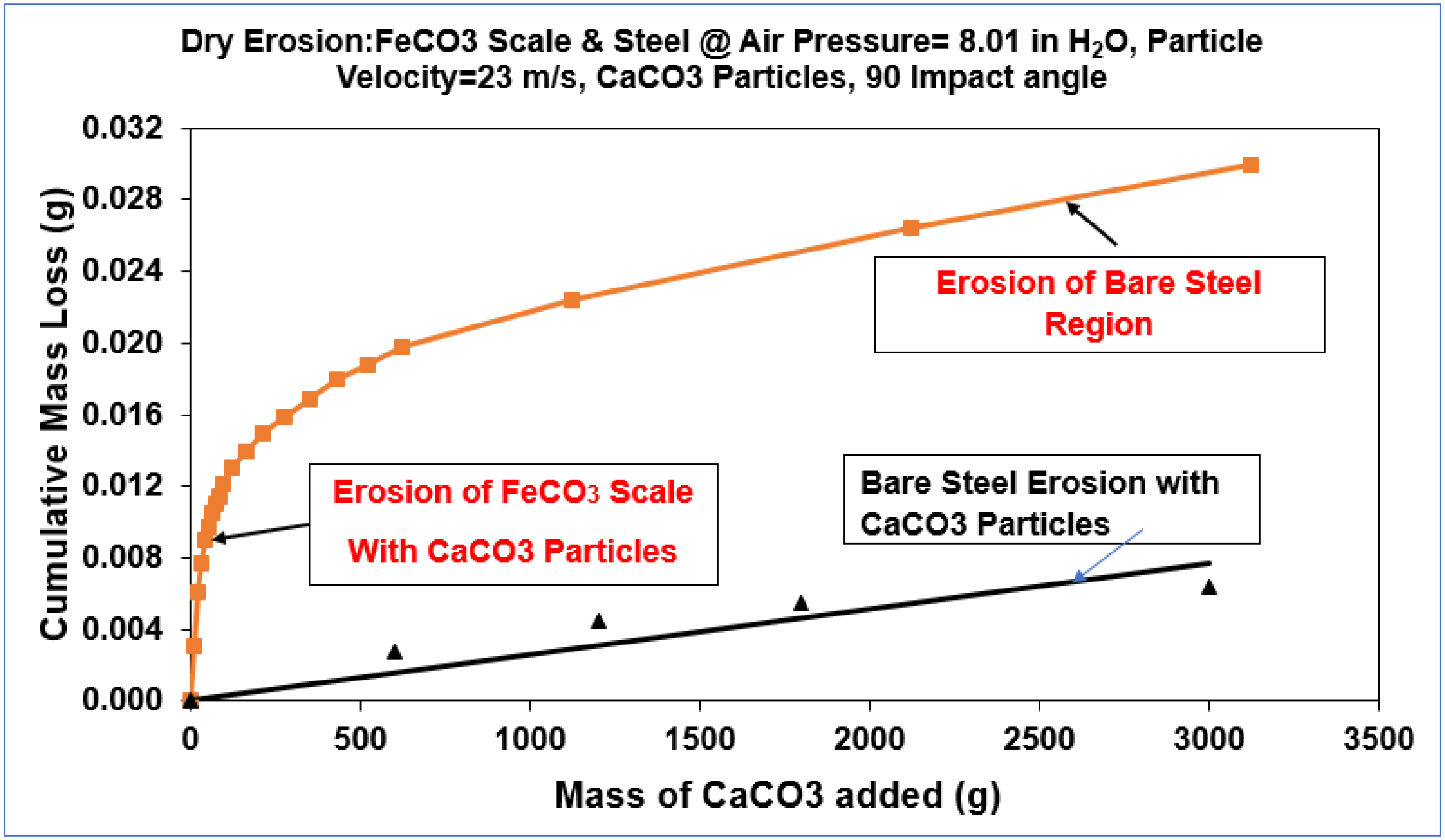
Courtesy University of Tulsa

Carbon steel exhibits high corrosion rate until an iron carbonate layer is formed

Erosion-Corrosion: Impact of Solids

- Research by Nassef et al, Erosion/Corrosion Research Center, U. Tulsa:

Dry Erosion – $FeCO_3$ Scale vs. Steel



Courtesy University of Tulsa

Erosion-Corrosion: Impact of Solids

- Research by Nassef et al, Erosion/Corrosion Research Center, U. Tulsa:
- Dry conditions, 150 µm sand, 250 µm calcium carbonate ($CaCO_3$) particles

a) Test 1 - impact on 1080 CS at 23 m/sec:

- Showed linear response to erosion vs. solids load
- No erosion at zero solids loading
- Higher erosion rate with the heavier sand than the $CaCO_3$

b) Test 2 - impact on 1080 CS with iron carbonate layer on the surface, 20 m/sec:

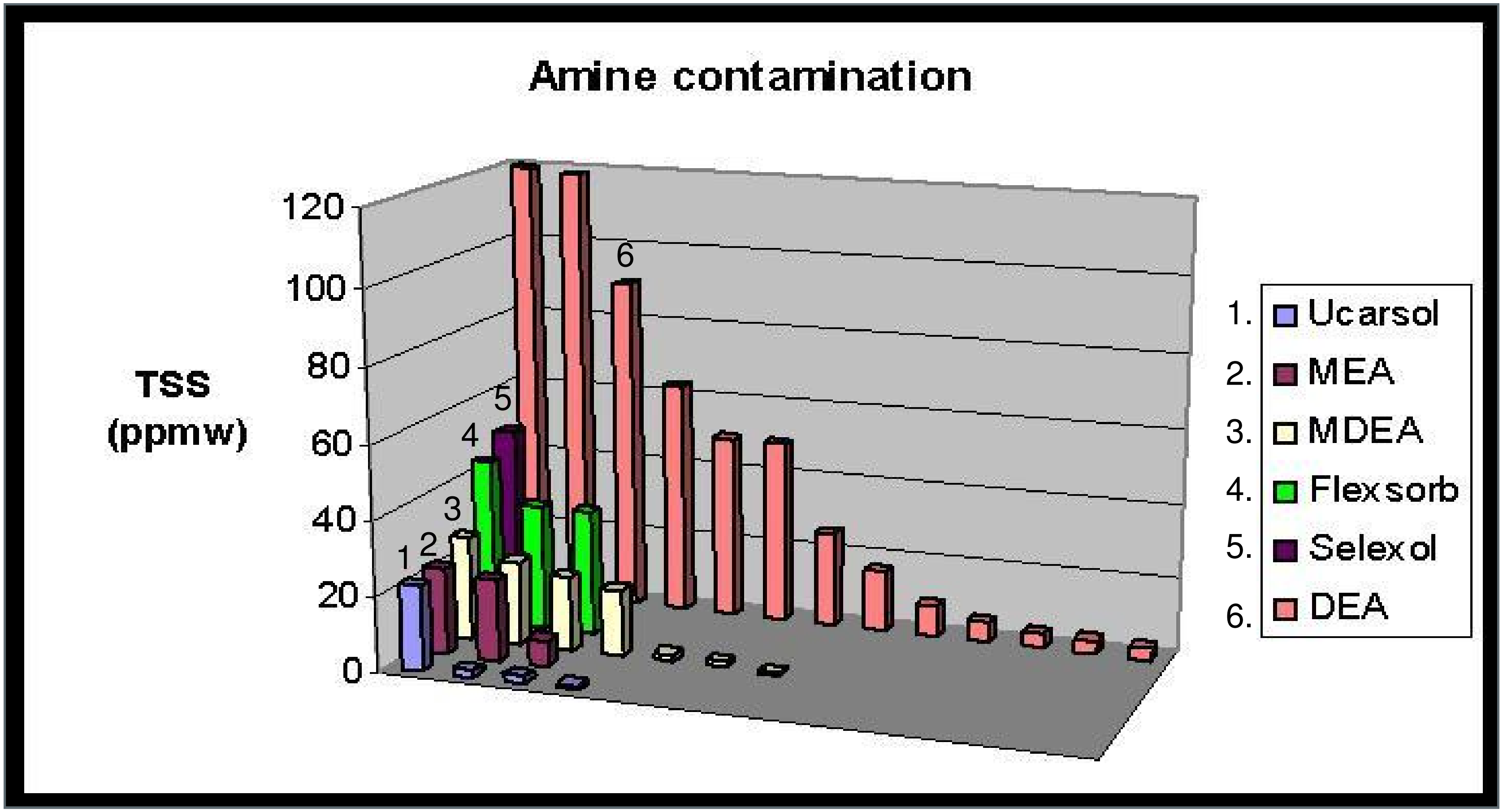
- Zero to $mass_1$: More rapid vs. test 1, linear response to erosion vs. solids load
- $Mass_1$ to $Mass_2$: Rate of material loss decreased with increasing solids load
- $Mass_2$ to $mass_3$: Rate of material lowered to rate of test 1, and linear

- **Extrapolations:**
  - **Clean fluids at very low velocity will not cause significant erosion of carbon steel or iron carbonate surfaces**
  - **Increasing solids levels increases rates of carbon steel or $FeCO_3$ corrosion**
  - **$FeCO_3$ erodes much more quickly than carbon steel**

The Corrosion-Fouling Cycle

- Expands erosion-corrosion concepts by looking at the variable of amine solids loading on the iron sulfide and iron carbonate layers
- Good protective layers should be building up in most amine systems
  - If maximum flow recommendations have been met
  - Unless severe acid gas breakout is causing localized high velocity conditions,
- Pall's site experience shows this is often NOT the case
  - Many sites have high corrosion rates and ineffective filtration so that solids levels are high - in the tens to hundreds of ppm
  - Filter life is short due to the high rate of new solids generation in the loop
- **Our experience shows that if amine solids levels reduce to the 1-5 ppm range, filter life will greatly extend due to the significant reduction in new solids generation throughout the system**
- **The rationale is that the erosive effects of the high velocity solids has been removed, allowing the protective iron sulfide or iron carbonate layer to re-establish, reducing the corrosion rate**

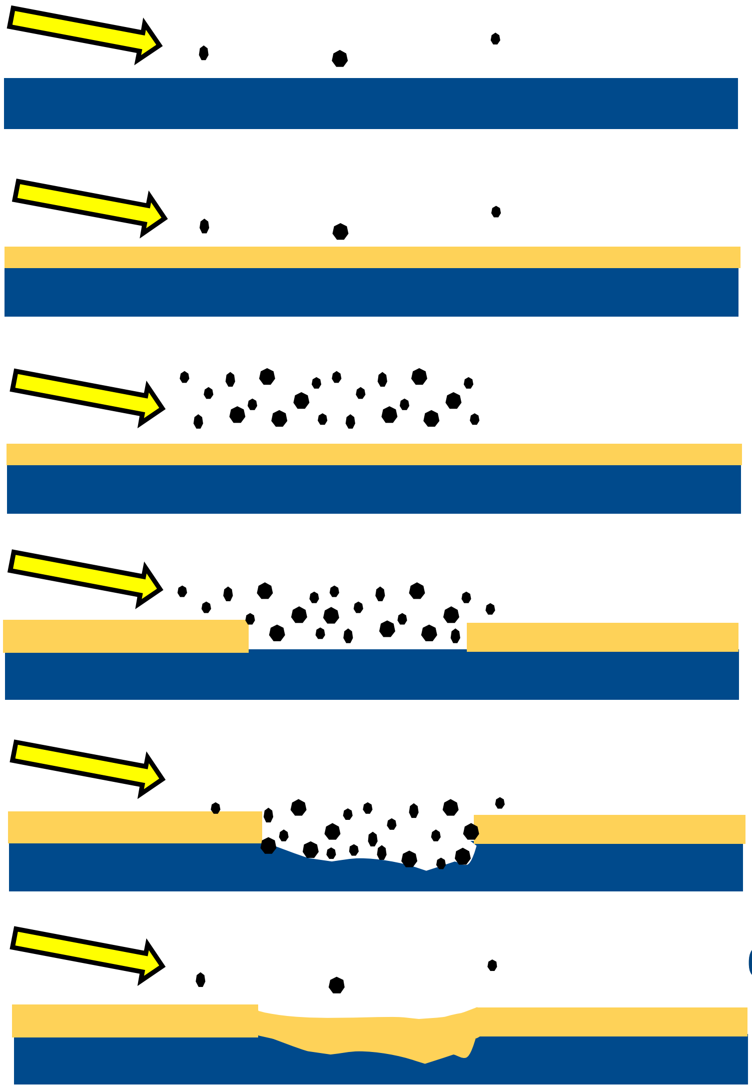
Measured Amine Loop Solids Loadings



Amine Solution Total Suspended Solids (TSS) Measurements (Pall Corporation)

TSS levels of 20 ppmw or more seen in 58% of the samples

The Corrosion-Fouling Cycle – Iron Sulfide Example



1. New, clean CS surface. Minimal particulate. Corrosion is rapid until an iron sulfide layer forms
2. Protective FeS layer has formed, reducing corrosion rate. Minimal particulate
3. System solids loading increasing due to inadequate filtration. FeS layer is at risk of being eroded away from high velocity particulate
4. FeS layer eroded away, exposing bare CS to the amine solution. Localized corrosion begins, adding new solids
5. Heavy localized corrosion from bare metal exposure, continued high solids generation. Corrosion-fouling cycle well-established
6. **High efficiency filtration has reduced TSS into the 1-5 ppm range. Erosion reduction has allowed the iron sulfide layer to re-establish. Corrosion is reduced, filter life is extended**

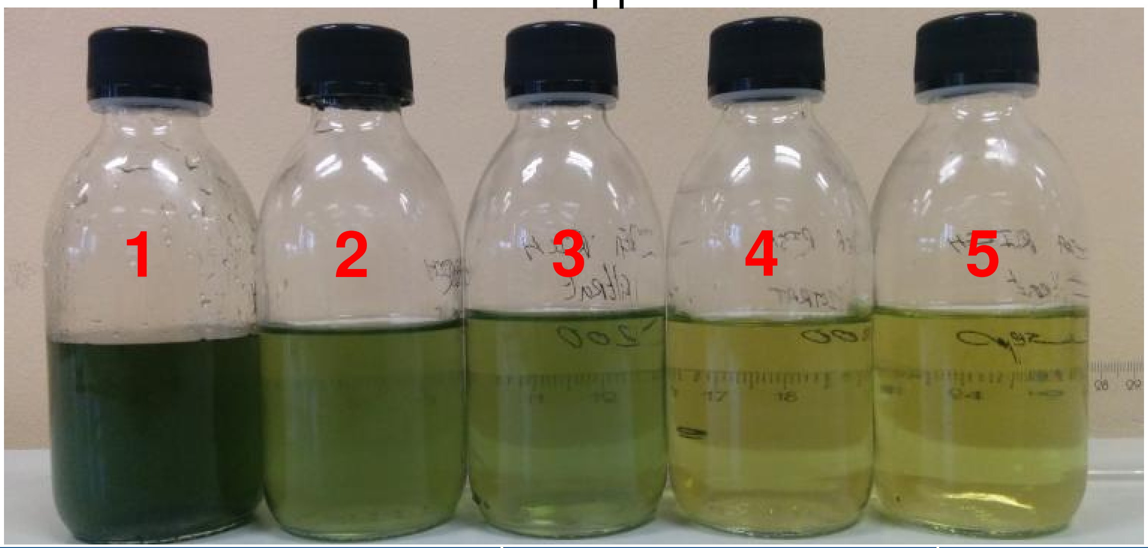
Carbon Steel | Iron Sulfide | Amine Flow | High Velocity, Erosive Particulate

Mitigation of Corrosion-Fouling Cycle Corrosion

- **Bring solids levels in the amine down to the 1-5 ppmw range** to permit the iron sulfide or iron oxide layer to re-establish
  - Conversion to high efficiency particulate filters with either an absolute or Beta rating is recommended to effectively achieve the high efficiency removal
    - **A rating of 10 micron absolute/Beta 5000 is our standard recommendation to achieve 1-5 ppmw solids in the amine loop**
    - Sometimes finer filtration will be required.
  - Expect high filter utilization rate during the clean-up period
  - Life will start to extend as the solids level reaches the 1-5 ppmw range
  - Life will further extend as the protective layer re-establishes on internal surfaces over a period of weeks or months, reducing the rate of solids generation
  - Short term installation of a mobile filter skid will accelerate the clean up period and breaking of an existing corrosion-fouling cycle
  - Once the amine loop is in a healthy state, properly sized high efficiency filters typically exhibit one or more months service life
- **At this point the corrosion-fouling cycle has been broken, with localized corrosion from this issue significantly reduced**

High Efficiency Filtration and Coalescing

- What does amine with a TSS of 1-5 ppmw look like?

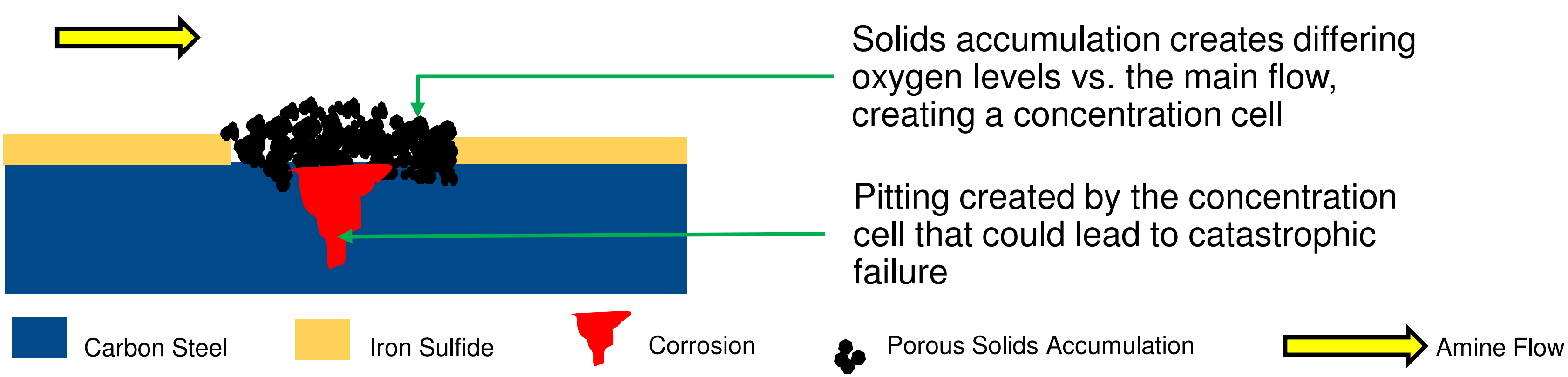


Sample	Description	TSS	Remarks
1	Unfiltered	>> 5 ppmw	Green/black, cloudy
2	40 µm, β = 5000	2 ppmw	Green, cloudy
3	20 µm, β = 5000	< 1 ppmw	Green, partially cloudy
4	10 µm, β = 5000	< 1 ppmw	Pale yellow, clear
5	10 µm, β = 5000 & L/L coalescer	< 1 ppmw	Pale yellow, clear

- **Target is a clear, pale yellow, 'apple juice or straw-colored' liquid**

Concentration Cell Corrosion

- Experience has shown that amine plant corrosion is often highly localized, frequently seen in areas of solids accumulation
- Localized pitting is often the result of concentration cell corrosion:
  - Solids settle out in low flow velocity areas around the loop such as lean-rich exchanger, reboiler, regenerator and contactor trays
  - As solids accumulate, they form a porous mass containing aqueous amine solution with differing oxygen levels vs. the main amine solution flowing around it
  - The differing chemistry creates a concentration cell, corroding away the metal in a deep, narrow pit that is difficult to identify and can lead to catastrophic failure
  - **The application of high efficiency filters and full flow or high percentage slip stream filtration will remove solids before they have the chance to settle out and initiate concentration cell corrosion**



Mitigation of Concentration Cell Corrosion

- Goal is to rapidly remove solids generated in or entering the amine loop, reducing settling in low velocity zones
- **Use of full flow filtration or >50% slip stream with high efficiency 10 micron absolute/Beta 5000 rated filters is recommended** to remove solids within the first or second pass around the loop
- **Placement of 100% full flow filters on the rich amine upstream of the lean/rich exchanger is the <u>ideal</u> choice for a number of reasons**:
  - Protect the lean-rich exchanger from solids from dirty sour gas
  - Remove precipitated iron sulfide solids that can exist in solution in lean amine and precipitate out in rich amine
  - Protect the regenerator and reboiler from solids accumulation:
    - Leading to regenerator hot spots
    - Causing formation of amine degradation products
    - Increasing corrosion rates

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Mitigation of Concentration Cell Corrosion

- **As a long term improvement, install a high efficiency liquid/gas (LG) coalescer upstream of the absorber.** Numerous benefits will be seen:
  - Minimized amine loop fouling from influent solids
  - Extended filter service life
  - Multi-year coalescer service life in most cases, as most removed solids will be swept away with the coalesced and drained liquids
  - Reduced foaming through removal of hydrocarbon liquids
  - Reduced corrosion via removal of heat stable salt precursors:
    - Formic, thiocyanic and other organic acids
    - Enter the amine system and form HSS that further contribute to potential corrosion issues
- **Proper application of high efficiency filtration and LG coalescing can greatly reduce solids accumulation in the amine loop and the potential for solids-related concentration cell corrosion**

Case Studies

- With corrosion being such a complex subject, it is difficult to analyze many corrosion parameters in isolation
- To support the mitigation steps being recommended, we are presenting a sampling of gas plant and refinery amine systems that have seen:
  - Low overall corrosion rates as demonstrated by high levels of plant productivity and plant reliability, achieved without the need for excessive corrosion-related component maintenance or replacement.
  - Demonstrated long filter service life validating that the rate of solids generation and therefore corrosion in the amine loop, is well under control

Case Study – Gas Plant – New Installation

- Past Lessons Learned used to finalize precise specifications
- Faultless Right First Time Start Up (FRFTSU) principle - avoid delays in plant stabilization from fluid contamination
- Equipment supplied for fluid cleanliness control
  - High efficiency feed gas LG Coalescers
  - High efficiency style lean solvent filtration
    99.98% removal, Beta ratio 5000
- Measured total suspended solids (TSS): <3 ppmw

High Efficiency L/G Coalescers

High Efficiency High Flow Concept Filters

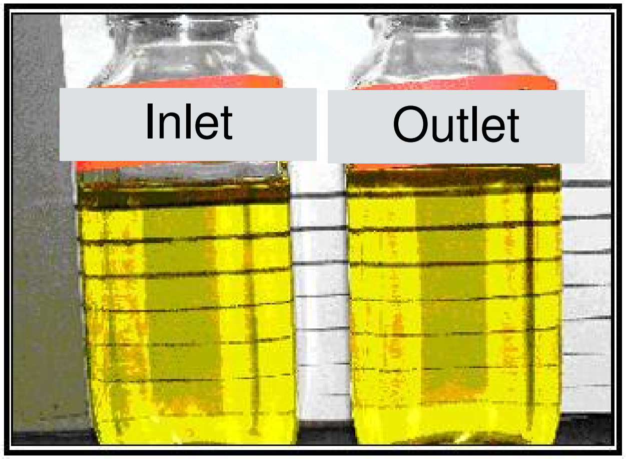
Trouble-free operation. Above design capacity since start-up.

At design, gas at $2.50/MMBTU: > $2 M/day gas production value

Filter life averaging 6-12 months

Case Study – Refinery AGRU Filter Upgrade

- TSS averaged 25 ppm more than 10 years ago
- System upgraded to full flow style filtration, 10 micron $\beta = 5000$
- TSS reduced to 1-5 ppmw range, usually around 1 ppmw
- Amine water to apple juice colored, clear, inlet and outlet



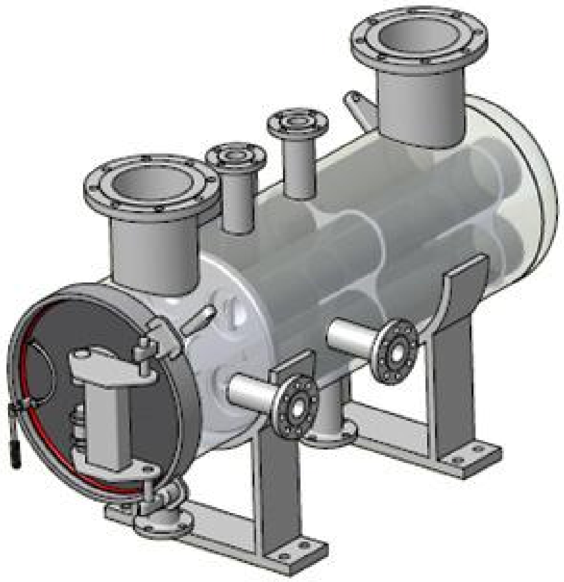
Photograph of inlet and out samples when using rich side 10 micron $\beta = 5000$ filtration

No system corrosion or fouling issues

Average filter service life: 4 – 8 weeks

Case Study – Refinery – Long Term Upgrade

- Installation of high efficiency 10 micron β = 5000 high flow style filters
- 100% rich amine filtration
- Since 2010, TSS levels average 1 – 5 ppmw



Example of a horizontal high flow style filter housing

High efficiency, high flow style filter element

6"OD x 40, 60 or 80" long

No system corrosion or fouling issues

Rich side filter life: 8 weeks on average

Summary

Amine system corrosion is a very complex subject due to the number of variables at work. Recommendations to reduce amine system corrosion are:

- **Implement best practice, by applying industry guidelines:**
  - **Referenced in this presentation and related paper**
  - **Body of historic research available**
  - **Available through amine suppliers**
  - **Provided by corrosion consultants**
- **Consider use of amine system corrosion prediction software for new construction, ongoing monitoring or upset analysis**
- **Implement and maintain low amine loop total suspended solids levels:**
  - **1 – 5 ppmw, ideally 1 ppmw**
  - **Best ensures formation and maintenance of the protective iron sulfide and iron carbonate layers on carbon steel surfaces**
  - **Minimizes erosion-corrosion and concentration cell corrosion issues**
  - **Reduces scheduled and unscheduled OPEX expenditures**