Corrosion/Erosion in Sulfur Recovery (Real-Life Examples)

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By: Philip J. Oberbroeckling, P.E.
Consulting Engineer
Process Design & Technology
Houston Refining LP
## Corrosion – Definition
(Webster’s New Collegiate Dictionary)

- **Cor·ro·sion** \(kə-rō-zhən\)
  - **noun**
  - 1 : the action, process, or effect of **corroding**
  - 2 : a product of **corroding**

- **Cor·rode** \(kə-rōd\)
  - **Inflected Form(s):** cor·rod·ed; cor·rod·ing
  - **transitive verb**
  - 1 : to **eat away** by degrees as if by gnawing; especially : to **wear away gradually usually by chemical action** *<the metal was corroded beyond repair>*
  - 2 : to weaken or destroy gradually

## Erosion – Definition
(Webster’s New Collegiate Dictionary)

- **Ero·sion** \(i-ˈrō-zhən\)
  - **noun**
  - 1 a : the action or process of eroding b : the state of being eroded
  - 2 : an instance or product of erosion

- **Erode** \(i-ˈrōd\)
  - **verb**
  - **Inflected Form(s):** erod·ed; erod·ing
  - 1 : to **diminish or destroy by degrees:** a : to **eat** into or away by slow destruction of substance (as by acid, infection, or cancer) b : to wear away by the action of water, wind, or glacial ice *<flooding eroded the hillside>* c : to cause to deteriorate or disappear as if by **eating or wearing away** *<inflation eroding buying power>*
  - 2 : to produce or form by eroding *<glaciers erode U-shaped valleys>* **intransitive verb**
Under Insulation Corrosion: Reflux Return – Valve Body Failure

Insulated carbon steel lines are very susceptible to corrosion activity at transitional pieces and elbows where water collects. These areas must be part of a proper periodic monitoring program.

Condenser/Steam Reheater Leaks: Signs of Failure – Water in Sulfur Run Down

Finding free-standing water in the sulfur rundown is a sure sign of a leak in either the corresponding condenser or steam re heater.
Condenser/Steam Reheater Leaks:
Signs of Failure – Water in SulTrap™

In this example, significant amounts of water were present in the SulTrap™ after being lined up during a restart of the unit from an unscheduled shutdown as a result of loss of plant load. Upon inspection, the corresponding condenser was found to have a significant leak.

Wet H$_2$S Corrosion:
550# Steam Claus Reheater - Tube Failure

Slide 1 of 3: No.1 Reheater was found to have significant metal loss at the tubesheet and numerous tube to tubesheet leaks after cleaning. Suspected failure mechanism is wet H2S attack that may have started with the tube crack shown in the upper right, or a cracked weld at the tube sheet as shown in the lower left. It is suspected that the cracks may have resulted from excess thermal expansion resulting from out of step startup sequencing, where the tubes were being heated up before steam was introduced to the shell side.
Wet H$_2$S Corrosion:
550# Steam Claus Reheater - Tube Failure

Slide 2 of 3: A few of the extracted tubes were found to have excessive deep pitting on the inlet side, most likely due to under deposit corrosion where sulfur impregnated into the metal matrix.

Wet H$_2$S Corrosion:
550# Steam Claus Reheater - Tube Failure

Slide 3 of 3: One of the extracted tubes had through-wall leak at one of the pits. Outer tube corrosion most likely occurred during the unit clearing after the steam was shut off.
Erosive Power of Steam:
550# Steam Claus Reheater – Tubesheet Weld Failure

This set of photos illustrates the erosive power of steam. This 550# Steam Reheater on a Claus Unit started with a pin hole leak in the tube to tubesheet weld. While leaking, the force of the steam near completely washed out the bottom quarter of the tube/tubesheet weld just below the leak. This illustrates what happens on high-pressure Thermal Reactor WHBs as well. Once a leak starts, it is only a matter of time before a significant leak presents itself, forcing a unit shutdown for repair.

Damaging Power of Steam:
600# Steam Claus WHB – Tubesheet Weld Failures

This is a photo of the leaks seen during a post shutdown hydrotest of a 600# steam thermal reactor WHB. The high pressure steam disintegrates the insertable ferrules leaving the tubesheet further exposed to extreme high temperatures and sulfide attack. Once a leak starts, it is only a short period of time until the unit requires a shutdown for repair.
High Temperature Sulfide Attack: Claus Waste Heat Boiler Tubesheet Leaks

The metal loss on the tube to tubesheet welds observed on this Claus Unit Thermal Reactor WHB tubesheet are caused high temperature sulfide corrosion. This resulted from poor hot-gas protection from the casted-ferrule tubesheet insulating wall due to shrinkage separation of the casted material from the ferrules. The shrinkage led to gaps around the ferrules and ferrule breakage as shown in the upper right photo. This tubesheet insulation wall has since been upgraded to the two-piece hex-head insertable ferrules, which provide far greater insulating and hot-gas by-pass protection.

Wet Sulfur Corrosion: Sulfur Condenser – Tube Failure (External View)

Slide 1 of 2: Post cleaning external view of extracted tubes from a leaking No.1 Condenser. The tubes were found to have two through-wall leaks after cleaning.
Slide 2 of 2: Post cleaning internal view of extracted tubes revealed significant pitting. It was determined that the pitting resulted from cold acid attack from wetted sulfur impregnated in the metal matrix. During shutdowns, the condenser becomes cold enough for moisture to condense in the tubes, which will cause the residual impregnated sulfur to become acidic. The investigation found that during the last couple of shutdowns on the unit, the condensers were left to go cold without soda ash neutralization hydro-blasting, which is a critical maintenance activity necessary to prevent this type of failure.
Wet Sulfur/Wet H₂S Corrosion: Sulfur Tank – Wall Coil/Tank Wall Failure

This is a wall coil inside a sulfur storage tank that developed a leak at the ~30 ft mark. The acidity caused by the coil leak eventually resulted in a wall-plate failure at the ~25ft mark. The wall surfaces at this level in the tank were not aluminized (only the top 15ft and roof were aluminized. The tank was constructed and commissioned in late 1995. It is not clear when the coil began leaking, however, the first signs of wall failure occurred in early 1998. Resolution = 1) remove the wall coils – the Houston area climate and proper insulation have deemed that the floor coils provide sufficient heat load; 2) aluminize the wall surface all the way to the floor – aluminum is not susceptible to acid attack and flame-spraying costs have become very economical.
Wet Sulfur/Wet H₂S Corrosion: Sulfur Rundown Look Box Failure

Severely corroded carbon steel sulfur look boxes showed signs of corrosion after less than one year of operation. The look boxes were replaced with 316L stainless steel during the unit’s first turnaround and show no signs of corrosion after ten years of service.

Wet H₂S Corrosion: Sulfur Pit Eductor Failure

The gun barrel and chamber of this steam ejector for a sulfur pit eductor system fabricated of carbon steel illustrate the point that components in this highly corrosive service must be fabricated of corrosion-resistant materials. Note the gun tip that is fabricated with stainless steel showed no signs of corrosion.
Wet H₂S Corrosion:
Sulfur Tank – Roof Damage

These photos show significant roof damage on a sulfur tank that was encountered during a turnaround. This tank prior to this shutdown did not have aluminized coating on the walls and roof. Within its 27-year service, it required major plate replacements every time it was taken out of service. After full restoration for this outage, the walls and roof were flame sprayed with aluminum to ~10 mils in thickness to prevent future corrosion.

Wet H₂S Corrosion:
Acid Gas Feed Control Valve – Seat Loss

SWS Acid Gas feed control valve showing body corrosion/erosion on the backside of the butterfly – note that the valve did not have any leak-by or flow control problems because the seating surface had not yet been damaged. This valve was in service for only five years.
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Wet H\textsubscript{2}S Corrosion:
Claus Unit Rupture Disk – Premature Relief

Slide 1 of 2: This is a 316L stainless steel rupture disk installed on the No. 1 Condenser Outlet of a Claus Unit with the discharge routed to a sulfur pit. This is a view of the outlet side (pit side) of the rupture disk. Because of piping issues, the rupture disk seat sits in a section of pipe that does not free drain; pooled liquid accumulates and sits up against the rupture disk; creating a wet H2S environment which attacked the stainless steel. The metallurgy of the rupture disk has been upgraded to Hastelloy.

Wet H\textsubscript{2}S Corrosion:
Claus Unit Rupture Disk – Premature Relief

Slide 2 of 2: Process side of the rupture disk was subject to sulfur pooling, but it is believed that this had no cause in the premature failure.
Wet $H_2S$ Corrosion: Amine Regenerator – Upper Section

This is an example of wall corrosion seen in an amine regenerator on a primary amine system servicing primarily HDS units. This system also often sees high levels of NH3 in the regenerator overhead. When the regenerators were replaced, the upper sections of the towers were cladded with 316 L stainless steel.
Wet H$_2$S Corrosion and Possible Chloride Attack: Sour Water Stripper – Top Tray Loss

This is what is left from a top section (above the chimney tray) 316L Stainless Steel tray in a Sour Water Stripper designed with an internal reflux system. The top five trays all fabricated of 316L SS suffered 80% metal loss after nine years of operation. Additionally, the tower vessel wall with 316L SS cladding will require weld overlay repair during its next turnaround. Analysis of the sour water did detect trace levels of chlorides. The internal reflux design makes for a very wet acid gas environment in the top section of the tower, which is corrosive even to stainless steel. Adding trace chlorides significantly increases the difficulty of maintaining mechanical integrity of these trays and this section of the tower. Ironically, the SWS did not suffer any stripping performance problems even up to the last days of operation before this turnaround occurred.
Effect of Heat Stable Salts and Acid Gas Loading of Rich Amine on Carbon Steel Corrosion Rates

For velocities >5 fps multiply corrosion rate by 2.0

For operating temps >220° F multiply corrosion rates by 2.0

Corrosion impact of elevated HSS in amine

High HSS Aggravated Corrosion: Amine Regenerator Kettle Reboiler

Slide 1 of 2: This leak was experienced on a carbon steel kettle reboiler shell for a TGU amine regenerator. The leak occurred just past the baffle plate which keeps the tubes liquid covered (spill back section).
High HSS Aggravated Corrosion: 
Amine Regenerator Kettle Reboiler

Slide 2 of 2: The failure occurred just past the weir on the drain side of the kettle. As can be seen in the left photo, the “washed” out area was quite large and concentrated near the bottom, indicating that the corrosion may have been aggravated by an erosion accelerating factor. The accelerated corrosion mechanism was determined to be from a high heat stable salts (6-8%) event resulting from a significant tail gas unit upset.
Excessive H$_2$S Flashing:
Amine Regenerator Thermal-siphon Reboiler

Tail Gas Unit Regenerator thermal siphon reboiler. This reboiler was retubed and returned to service in June 2000. The reboiler was in service for 16 months then required shutdown due to excessive leaking - 193 tubes (6.4%) were leaking. Numerous other tubes in addition to the leaking ones had extensive metal loss at the tube sheet, as shown in the upper left photo. Root cause is attributed to extensive H2S flashing. Long-term resolution = 316SS tubes that are strength welded to a carbon steel tube sheet in a carbon steel shell. Keeping the shell and tube sheet in carbon steel avoids significant reboiler modifications that would be required for a different grow factor associated with an all stainless steel reboiler.

Cavitation Erosion:
800 psig BFW Control Valve (let down to 50 psig)

High Pressure (800 psi+) Boiler Feed Water minimum flow Control Valve that let down to ~50 psi system suffered significant cavitation erosion.
Wet Steam: Claus Unit Air Blower – 550# Steam Turbine Driver

Slide 1 of 7: This Claus Unit air blower driver is a steam turbine of the Curtis design type. It consists of two rotating rows of blades with a stationary reversing section between the rows. As steam enters the turbine it passes across a nozzle block. The nozzle block directs the steam on the first row of rotating blades. The steam then passes across the reversing section to the second row of rotating blades. Steam entering the turbine at design conditions will exit the turbine above the saturation point (no moisture). The design conditions for the steam supply to the turbine are 520 psi at 700 F (218 F of superheat). The design exhaust condition is 55 psi. Local instrumentation indicates that the steam supply to the turbine is entering at saturated conditions at 560 psi. As the steam passes across the first row of blades, it is reaching a lower energy state and condensing. The water droplets in the inlet steam and the condensate are carried through the turbine, impacting the lower alloy components and causing corrosion/erosion.

This blower is one of three, where two are always in operation. During this turbine’s last inspection in 2007, some erosion of the wheels were observed. The turbine was shut down on May 26, 2009 due to excessive vibration. A few weeks weeks prior to the failure, vibration in the bearings were checked and determined to be within acceptable limits.
Wet Steam:
Turbine Failure – Blade Erosion

Slide 2 of 7: This is showing the wheel erosion that was observed. As the erosion creates clearance between blades and spacers, these parts wear against each other.

Wet Steam:
Turbine Failure – Blade and Shroud Band Damage

Slide 3 of 7: This is a top view of an area with a section of the shroud band and a blade missing. The blade is supported at the end opposite of the root by a tenon connection. As the root area loosens, it contributes to the tenon connection loosening.

As the blades pass the steam nozzles, they vibrate in the slot and the blades are subject to high-cycle fatigue. After many cycles of operation, the blades lose the fit in the wheel and shroud band. Eventually the shroud band and blade break.
Wet Steam:
Turbine Failure – Blade Wear

Slide 4 of 7: This photo shows the blade wear that was experienced in this turbine. As the erosion creates clearance between blades and spacers, these parts wear against each other. Significant wear is on the blade anchor due to this relative movement.

Wet Steam:
Turbine Failure – Blade Anchor Fracturing

Slide 5 of 7: This shows one of the blades with complete anchor failure.
Wet Steam:
Turbine Failure – Blade Anchor Fracturing

Further investigation revealed that the blade anchors were undergoing a stress cracking failure mechanism in addition to the standard water droplet erosion that would normally be expected with this quality of steam.

Wet Steam:
Turbine Failure – Blade Anchor Crack (380X Magnification)

High-level magnification of the stress cracks revealed that residue was present in the crack structures. Definitive analysis of the deposits was not possible due the small quantity available, but it was determined that the material was basic and had caustic characteristics possibly from the BFW treatment chemicals. This clearly indicated that corrosion stress cracking played a significant role in the failure mechanism for this critical turbine driver.
Types of Hydrogen Damage in Carbon Steel

These illustrate the various failure mechanisms of hydrogen, with the fourth illustration showing the difference of sulfide-stress cracking.

Hydrogen Permeation Mechanism

This diagram shows how atomic hydrogen penetrates into the metal matrix.
Hydrogen Blister Formation

Atomic hydrogen that penetrates through the metal wall into a micro-void area can result in the atoms recombined to H2. The resultant build-up of hydrogen gas in the metal matrix forms a gas pocket by separating the metal, resulting in a “hydrogen blister”.

Automated Ultrasonic (A-UT) Scans

- Automated ultrasonic scans detect and document defects in the base material by providing a 3-D image of the defect:
  - A-Scan = Single dimension detection of a defect
  - B-Scan = cross-sectional, longitudinal view of the defect
  - C-Scan = topographical image showing the position and depth of the defect
  - D-Scan = cross-sectional axial view of the defect

Illustration of the automated ultrasonic scanning process and the scan information that can be obtained.
Hydrogen Blistering:
HDS Recycle Hydrogen Amine Contactor (725 psig)

Slide 1 of 3: Scan of this HDS recycle hydrogen amine contactor that operates at 735 psig showed metal hydrogen blistering near the bottom of the contactor.

Hydrogen Blistering:
HDS Recycle Hydrogen Amine Contactor (725 psig)

Slide 2 of 3: Detailed scan information highlighting the large 15" X 12" metal hydrogen blister near the bottom of the contactor that was found.
Hydrogen Blistering:
HDS Recycle Hydrogen Amine Contactor (725 psig)

Resultant blister delaminated the metal of the vessel wall

Slide 3 of 3: The resultant large blister in the carbon steel amine contactor was an area 15" X 12" in size in the bottom section of the tower. Along with large amounts of smaller blistering, this warranted a complete replacement of an 8’ segment of the tower shell and the tower bottom head.
Concrete Sulfate Attack
Sulfur Pit Wall Erosion

Concrete sulfur pits constructed with conventional grades of concrete can suffer severe deterioration and erosion due to sulfate attack as present in this mid-1970’s constructed sulfur pit. The erosion in this corner had consumed nearly 80% of the wall thickness impacting the integrity of the unit’s foundation. To repair the pit, eroded areas had new rebar tied into place, were filled with sulfate resistant concrete and a new six inch sulfate resistant concrete wall was pour in the entire pit.
Slide 1 of 2: This photo shows a failure sign that something has gone very wrong in the Converter Bed that corresponds to this SulTrap™. A unit shutdown is soon and certain (if not immediate) when this failure sign appears.
Claus Unit Converter “Fillet” Failure and Catalyst Bed Erosion

Slide 2 of 2: Photos 1-3 show the failure of the screen edge seal (“fillet”) that resulted in the collapse of the catalyst bed in this Claus Unit converter. It is suspected that the “fillet” experienced heat-related expansion that caused it to crack and separate from the wall; then erosion forced catalyst behind it where the grating was open to the converter bottom. As catalyst continued to move past the grating and screen and fill the converter bottom, it eventually made its way through the converter outlet into the condenser and out to the sulfur rundown.

Photo 4 shows the significantly reinforced new “fillet” that was installed to resolve this issue. As each of the Refinery’s Claus Units enter into their next turnarounds, the new converter “fillet” design will be installed.
Corrosion/Erosion: High Pressure Rich Amine Pipe (1300 psig)

This is a pipe section fabricated of carbon steel from the rich amine release line off of a recycle hydrogen contactor operating at 1300 psig. The mole loading of the rich amine is typically 0.4 to 0.45 mol/mol and the line velocity is typically 6.7 ft/s. This line is experiencing corrosion/erosion rates 4 times greater than accepted normal loss rate of 10 MPY. The line was upgraded to 316L stainless steel.
Ammonium Salts

- Heavier and more sour crudes tend to have higher concentrations of bound nitrogen
- Bound nitrogen is removed during hydrotreating:
  - Producing ammonia
  - Higher severities to produce low sulfur gasoline and ULSD are typically ensuring removal of the bound nitrogen
  - Denitrification of FCCU feeds to improve cracking yields has been a growing trend
  - Disposition of the bound nitrogen plays a large role in where ammonium salt problems will occur
- Ammonia reacts with H2S to form ammonium salts which are removed with wash water and processed in the SWS
- Ammonium salt (ammonium bisulfide) readily forms in the present of H2S when below 160ºF (71ºC):
  \[ \text{H}_2\text{S(g)} + \text{NH}_3(g) \rightleftharpoons \text{NH}_4\text{SH(s)} \]
- Ammonium salt is removed by adding wash water – the salts have high solubility in water: \[ \text{NH}_4\text{SH(s)} \rightleftharpoons \text{NH}_4(aq) + \text{SH(aq)} \]
- Ammonium salt solutions can cause severe corrosion
- Trace amounts of ammonia slip through the wash water systems and are absorbed in the amine at the contactor
- Ammonia concentrates in the overhead system of the amine regenerator leading to high ammonium salt concentrations in the tower reflux and acid gas

Corrosion/Erosion (Ammonium Salts):
HDS Stripper OVHD Pipe (~100 psig)

This is a pipe section fabricated of carbon steel from the downstream side of an HDS stripper overhead condenser operating at ~100 psig and ~130ºF. Amongst other contributing factors, ammonium salt concentration played a large role in the corrosion/erosion mechanism that lead to this failure. When high amounts of ammonium salt are present, particular attention needs to be given to the flow velocities, materials of construction and water injection rates to ensure piping reliability will be maintained.
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About the Author:

Philip Oberbroeckling, P.E., is a Consulting Engineer for LyondellBasell providing sulfur recovery and refining technical support to the Houston, Texas and Berre, France Refineries. Over Philip’s 21 years of service in the refining industry, he has held numerous engineering and management positions in Process, HSSE and Operations including 5-year tenure as the Operations Superintendent of the Houston Refinery 1000 LT/D Sulfur Recovery Complex. Philip has a Chemical Engineering degree from Iowa State University and is a registered Professional Engineer in Montana and Texas. Philip has authored 34 conference papers and presentations on sulfur recovery and refining topics. Philip is a member of the Sulfur Recovery Symposium Technical Advisory Committee and Chairman of the Environmental and Safety Committee.