Acid Coolers – Selection, Operation and Maintenance for Maximum Reliability
Sulphuric Acid Coolers - Historical

- Historically serpentine coil acid coolers used
- Anodically protected SS acid coolers introduced by Chemetics (CIL) in 1970
- Vast majority of serpentine coil coolers replaced in 1970-80
- Very reliable - Many original coolers still in use today.
Anodically Protected Sulphuric Acid Coolers

Reference Electrode connection

Main Cathodes
ANOTROL®
Anodic Protection System

- Controls corrosion from HOT H₂SO₄ within cooler
- by creating an environment whereby the corrosion product exists as a protective oxide film which limits further corrosion.
Typical Polarisation Curve
Stainless Steel In $H_2SO_4$
Reference Electrode

Mounted in coupling on cooler shell measures the Anodic Potential

Two electrodes, one adjacent to each acid nozzle are normally used
Main Cathode

Location of Baffles

Un-perforated sections provide electrical insulation between Cathode & baffles

Tube Sheet
Anodically Protected Acid Coolers

Pros
- Small footprint vs. serpentine coil
- Low maintenance
- Low operator intervention
- Relatively low cost

Cons
- Does not like rapidly fluctuating operating conditions of %H$_2$SO$_4$ or acid/tubewall temperature
- Too reliable leading to operator complacency and lack of understanding on what to do in case of issues
Anodically Protected Acid Coolers

- 1600+ AP Coolers supplied by Chemetics (CIL) since 1970
- Well constructed units regularly last longer than 30 years with minimal maintenance and care

37 year old acid cooler

- Failures on old as well as new units have become more common in the past 5 years (30+ significant issues this year alone)
- Failure causes are many but are all inter-related and are avoidable through attentive care, regular maintenance inspections and training
Anodically Protected Acid Coolers

Current state of many worldwide sulphuric acid plants

- Most built in 1960s through 80s
- Most have staffing issues – retirement, lack of experience
- Equipment (acid coolers, boilers, superheaters, economizers, piping, etc…) is old and can fail/leak at any time
- Consequences of failure on one piece of equipment and ripple effects on others not understood fully by operators – leads to slow and inappropriate responses to failures
- Instruments (T, P, pH, conductivity, etc…) often not present, not calibrated or not adequately paid attention to
- Maintenance inspections often not done on standard items like strainers, pumps, valves, etc…
Causes of Failure of Anodically Protected Acid Coolers

1. Water Side
2. Repair Issues - leading to repetitive leaks/failures
3. Over Design in Original Installation
4. Acid Side
5. Electrical/Anodic Protection

- 80%+ of issues leading to leaks are water side!
Water Side Issues

- Plugging of Tubes

Seawater Cooler
Water side plugging – Strainer failure – River Water
Waterside Fouling

- Design water velocity is not being maintained. (Bypassing water, Pump issues, Plugged strainer, Valve issues, etc…)
- Chemical treatment program out of balance.
- Biocide program ineffective
- Contamination from other cooling source
Chloride Stress Corrosion Cracking and Pitting

Stress Corrosion Cracking of Stainless Steel will happen when all 3 of the following factors are present:

- Material is under Stress
- High metal temperature
- High local concentration of Chlorides
Chloride Stress Corrosion Cracking and Pitting

- Typically occurs at >750 ppm chlorides in the water provided to the cooler (make up water should be < 150 ppm Chlorides)

Chloride pitting in bore of extracted tube
Chloride SCC and Pitting

- Low water flow, high water side fouling with chloride pitting

Product Cooler Water Outlet Silica Fouling (prior to cleaning)

Chloride Pitting on the Product Cooler Water Outlet Tubesheet after Silica and Rust Deposits Removed
Waterside Corrosion

• Increased tube wall temperature does the following:
  - Increases rate of chloride SCC/pitting
  - Increases rate of corrosion on acid side
  - Increases stresses due to differential thermal expansion
Waterside Corrosion

Tube wall Temperature

Acid

Cooling Water

Heat Flux
Waterside corrosion

- Chlorides concentrate in waterside scale – accelerated SCC and pitting when waterside fouling present
- When leaks form and acid flows into the water and chlorides present can become activated (ie. become HCl) increasing corrosion rate
Waterside Corrosion

- Plugged tube leads to high wall temperature, acid or water side corrosion, acid leak into tube, weak acid flow out of tube, recirculation eddies bring weak acid to neighbouring tubes on tubesheet. Weld fails and then tube pops out. Damage to surrounding tubes. Damage propagates if not noticed.
Repair to corroded area – Blocked tube failure slow pick up. pH meter ignored for extended period (days). Heavy local corrosion. Area repair required (19 tubes lost).
Water Side Issues

Methods to minimize waterside issues
1) Use a water strainer (max mesh size 50% of tube diameter)

316L S.S wire mesh with 5/16” [8mm] max opening
[Use 254 SMO for Seawater]
Water Side Issues

2) Select appropriate materials of construction for chloride content and temperature of water and acid
   - < 750 ppm chlorides (except BFWH) – 316L
   - Seawater, Brackish Water – CIRAMET
   - Demin Water – Duplex SS, 316L

3) Minimize fouling build up
   - Maintain or exceed design tube water velocity
   - Do not EVER bypass water – if temperature control of acid to the tower is required, BYPASS ACID, NOT WATER
Water Side Issues

4) Actively monitor for acid leaks
   Detection methods are:
   - water pH Meter - Local weak acid in tubes = local accelerated corrosion
   - Reduction in required water addition to the acid
   - Conductivity meter

5) Minimize future acid leaks by monitoring
   - Water temperature rise
   - Water pressure differential across cooler
   - ANOTROL system amps

ANY step change in any of these readings is bad no matter how small
Water sampling system for pH measurement

Perforated S.S. Tube across Pipe centerline with two rows of 5/16” diameter holes on 1½” centers.

Use 254SMO or equivalent material for Seawater.

Locate sampling point reasonable distance away from cooler discharge and after elbows to ensure good mixing.

Weekly addition of acid to test response of pH monitoring system

pH probe
Acid Side Issues

Factors Affecting Corrosion of Stainless Steel in $H_2SO_4$

- Temperature
- Acid Concentration
- Acid Velocity
Acid Side Issues

- Line showing 0.001” (25 µm) Corrosion/yr or less – Exponential increase in corrosion rate as one moves further above the line – Use acid inlet temperature as ref.

Fig. 4.1

Temperature, °C

% H₂SO₄

SAFE REGION FOR NORMAL OPERATION OF ACID COOLER USING ANODIC PROTECTION
Acid Side Issues

Anodic Passivation

Shape and Values of Passivation Curve will vary dependent on Acid Concentration & Temperature
Acid Side Issues

Different Acid Concentration

Current
Acid Side Issues

Different Metal Temperature

Current
Acid Side Issues

- Changes in % H2SO4, particularly towards weaker acid make it difficult, or possibly impossible to establish (or maintain) a stable passive film on the wetted surface of the cooler
- Significant increases in acid temperature will also be detrimental to the anodic film

The AP System will increase amps and alarm telling the operator immediately when a weak acid event is occurring!

Piping, pumps, tanks, towers, distributors, etc… all similarly detrimentally affected by weak and/or high temperature acid
Acid Side Issues

Causes of weak or high temperature acid to cooler:

- Erratic control of water addition to acid
- Defective strength analysis equipment which controls water addition
- Accidental water addition (stuck valve) during shut down
- Dilution of circulating acid by moisture absorption during start up (plant being dried out)
- Acid cooler tube failure
- Steam system (boiler, economizer, superheater) leaks
- Shut down drains acid – moisture from atmosphere creates weak acid at low point of cooler
- Weak acid run off from tower during extended shutdowns
Acid Side Issues

- Tube corroded at bottom tubesheet of vertical acid cooler – acid not fully drained leading to local weak acid corrosion
Acid Side Issues

Methods to minimize acid side issues
1) Use a SARAMET acid strainer (max mesh size 30% of tube spacing)
Acid Side Issues

2) Minimize fouling of acid side use low silica make-up water

3) Minimize acid side corrosion by monitoring:
   - Acid Inlet temperature
   - Acid strength
   - Cathode current (Amps) used in anodic protection system
   - Control and reference potential
   - Water pH and/or conductivity

ANY step change in any of these readings means something bad is happening even if change is relatively small
Acid Side Issues

4) Minimize rate of acid side corrosion by
   - Minimizing tubewall temperatures
   - Minimizing normal fluctuations in acid strength and temperature during plant operation – leads to increased Amps and a forced corrosion event to maintain the anodic film
   - Immediately reacting to step changes in key instruments - ie. Shut down

<0.001”/yr corrosion rate for 0.065” thickness tubes = 30+ years operation relatively problem free
Corrosion is expected, rapid weak acid corrosion is potentially dangerous and avoidable
Electrical Issues

• **Electrical Problems:**
  - Cathodes
  - Reference Electrodes
  - Field Wiring
  - System Setup
Electrical Issues

- Cathodes – Consumable parts – 1 to 10 year life depending on acid strength and temperature – must be present
- <10 mm diameter indicates cathode should be replaced
Electrical Issues

- Transpassivity occurs when the potential is allowed to increase beyond the passive range.
- In the Transpassive Range the anodic film becomes soluble in the acid and corrosion rate increases rapidly.
- Weak or high T acid or incorrect C/PS operation can lead to transpassivity.
Electrical Issues

- Pin cathode on acid inlet nozzle. Weak acid in area led to local transpassivity. SCH 40 nozzle reduced to paper thin.
Electrical Issues

Methods to minimize electrical issues

1) Always observe alarms! Alarms mean the cooler is corroding. Always resolve why there is/was an alarm. NEVER silence an alarm and keep operational.

2) Ensure cathode in good shape. Always have a spare for each cooler on site.

3) Ensure electrodes are operating correctly. Watch for step changes in signal.

4) NEVER change set points without consulting with manufacturer.
Electrical Issues

5) Periodically confirm correct CP/S operation. Watch for step changes.

6) Keep all panels closed and clean. Water/dust ingress will damage unit.

7) Periodically check out field wiring and replace as required.
Repair Issues

Common types of repairs are:

- Cleaning
- Tube plugging
- Inspection/replacement of electrical components
Repair Issues

Methods of Tube Cleaning:

- Restore design water velocity.
- Lower pH of Cooling Water.
- Use “mild” Chemical Cleaning.
  Never use HCl or Chlorinated Chemicals
- Hydroblast Tubes.
Repair Issues

Hydroblasting of Tubes – Recommended method

- Use “self propelled” hydroblast nozzle to remove internal scale or deposits in tubes.
- Pressure must be > 5,000 psi (350 bar) to remove deposits.
- Hard scales may require pressures up to 10,000 psi.
Repair Issues

Methods of Measurement of Corrosion.

• Visual inspection & measurement
• Iris or Eddy Current Testing
Repair Issues

Methods of Tube Plugging:

- Expanded plug – Recommended when tube ends are round and clean. Fast. No neutralization required.
- Welded Plugs
Repair Issues

Scheme for shellside cleaning or neutralization MUST be done to get good weld

Steam

S 11

Soda Ash or Caustic Soda Solution at 70°C
Repair Issues

Neutralize shell and perhaps tube side

Clean & dry tube end

Insert Plug

TIG weld with Alloy 20 wire.

Use extreme caution not to damage adjacent welds.

Dye penetrant check weld.

Pressure test vessel.
Repair Issues

- Shell not neutralized. Acid drawn into weld leading to weld cracking. Weld leaked. Repeat numerous times. Pressure tests typically not done. Small leaks propagated and damaged neighbouring tubes.

Typical Appearance of Historical Tube Plugging
Repair Issues

By far largest source of acid cooler failures is waterside issues followed by poor repairs

- Do it once. Do it right. Do not skip steps. Procedures are available upon request.
- Coolers will all eventually leak. Corrosion can be controlled, not stopped.
- Welded plugs require neutralizing of shell and perhaps tube side. Welds will fail if not neutralized.
- Pressure test is very highly recommended after each repair. Small leaks are easy to fix but hard to find. Failure to find them will lead to further shutdowns and more extensive repairs.
- Electrical checkout recommended regularly.
Over Design Issues

Clients often specify design characteristics that could lead to a loss in functionality of the plant. Common specifications:

- Increased water (and acid) side fouling factor
- Safety factor in design
- Increased water temperature
- Lower acid temperature

All above lead to a larger surface area acid cooler.
Over Design Issues

Example client request:
- Fouling factor of 0.00036 m$^2$K/W (vs. normal 0.00026)
- 10% additional over design with maximum water and minimum acid temperatures

Result
- 85% safety factor over clean case at maximum operating conditions. In winter unit well over 100% over required area. Acid will be over cooled leading to reduced tower performance.

What will the client likely do to make the plant work?
- Bypass water (as acid bypass likely too small) leading to water side fouling, increased wall temp. and increased corrosion rate.

Bigger is not better.
SARAMET, Sx, ZECOR (Silicon SS) Acid Coolers

Silicon SS acid coolers are a viable alternative to anodically protected units. How do their issues compare?

- Water side? – Same. Austenitic SS. Not to be used on seawater or high chloride water.

PREN (Chloride Pitting Resistance Equivalent Number).
-Zecor (UNS S3881500) – 18
-SARAMET 23 – 18
-Sx (UNS S32615) – 21
-SARAMET 35 – 21.5
-316L – 24
-2205 Duplex SS – 33
-CIRAMET - 46
SARAMET, Sx, ZECOR (Silicon SS) Acid Coolers

- Acid side? – Better resistance to rapid changes in acid strength or temperature.
- Electrical? – N/A
- Over design? – Same.
- Repair? – Techniques same.
  a) Welding much more difficult. Specially trained/certified welders available for repairs?
  b) Materials significantly harder – Mechanical plug design needs to be different – cracking issue?
SARAMET, Sx, ZECOR (Silicon SS) Acid Coolers

- Cost? – Material 3.5 to 4 times as expensive as 316L. Prohibitive cost on most cooler sizes.
SARAMET, Sx, ZECOR (Silicon SS) Acid Coolers

- Diagnostic ability of weak acid event –
  - AP Cooler – Anodic protection quickly increases amps and alarms – immediate feedback
  - Si-SS Cooler – No change, no alarm

Weak acid events usually result in high temperature, weak acid. This will damage all equipment that touches this acid including the Si-SS acid cooler. Additional concern of hydrogen generation.

Ensure you design your plant controls to ensure quick diagnosis of a weak acid event no matter what type of cooler selected!
Unequalled Experience

Kazakhmys, Balkhash Copper
Summary

- Water Side Issues
- Acid Side Issues
- Electrical/Anodic Protection Issues
- Repair Issues - leading to repetitive leaks/failures
- Over Design in Original Installation

Can all lead to premature failure of an acid cooler.

- A well designed, built, specified, and operated acid cooler can provide 30+ years of reliable service.
Summary

- Acid coolers are not the squeaky wheel but when they do squeak, immediately pay attention. Something bad is happening somewhere in the plant.

- Plants are getting older so just because something has not happened in the past does not mean it cannot happen in the future. Pay close attention to your instruments and watch for step changes. Respond quickly.

- Fix it once, fix it right when a leak does occur.
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