Corrosion in Cooling Waters

Treated open & closed loops:

Metallurgies:

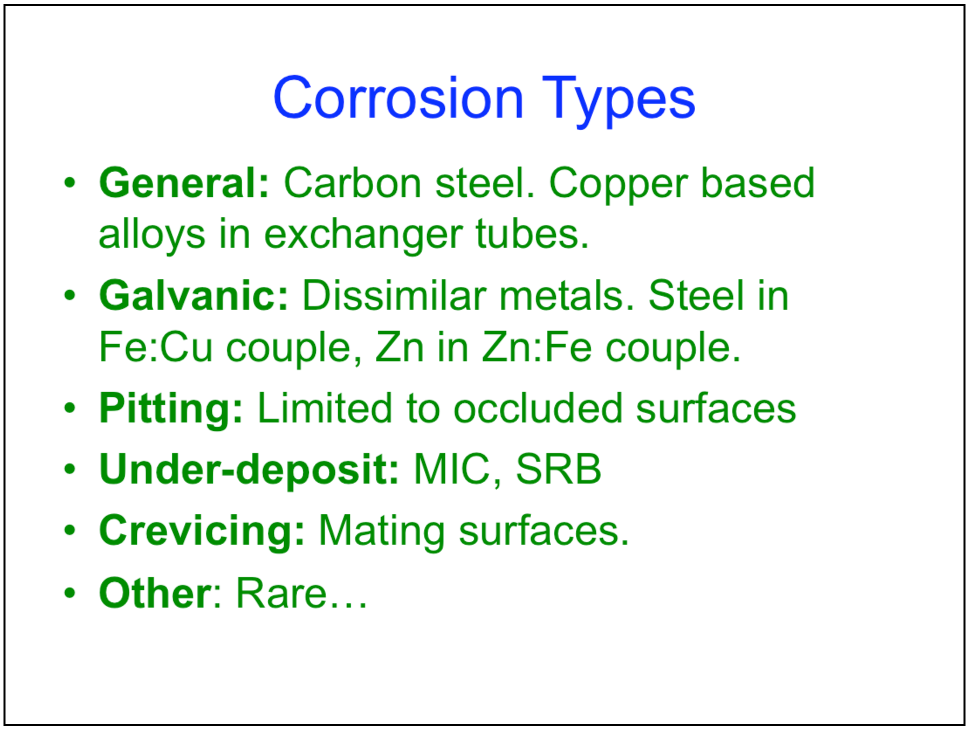
Steel, Copper, Bronzes, Galvanized (zinc), limited Aluminum & low grade (304) stainless

Process:

100 to 10,000uS, pH 6-10, 50C max.

Open to atmosphere.

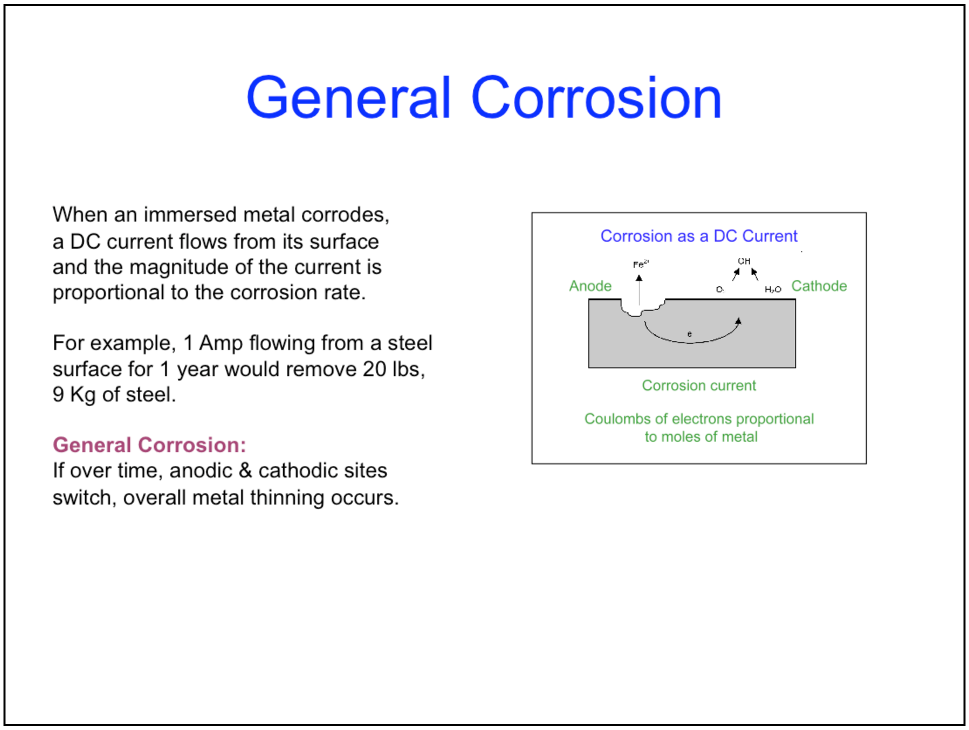
1. Aquatrac series controllers that include corrosion rate monitoring are limited to cooling water streams; the atmospheric loop in cooling towers and the semi-closed, chilled loops between chiller & air handler.
2. We're going to get context from a generalized overview of corrosion in cooling waters, a similar overview on measuring corrosion and then a specifics on Linear Polarization Resistance, the method used in these controller's
3. Cooling water streams are either chemically treated to inhibit corrosion or cycled up to increase the pH and lower corrosion rates.
4. Towers are aerated, conductive streams exposed to eternal sources of biological & inorganic contaminants, which if not modified would corrode steel and copper and under selective conditions remove galvanizing, pit aluminum and stainless.
5. Closed Loops are typically oxygen scavanged and in some cases treated with biocides.
6. Cooling water piping is typically cleaned and passivated post-construction prior to use.



Corrosion Types

- **General:** Carbon steel. Copper based alloys in exchanger tubes.
- **Galvanic:** Dissimilar metals. Steel in Fe:Cu couple, Zn in Zn:Fe couple.
- **Pitting:** Limited to occluded surfaces
- **Under-deposit:** MIC, SRB
- **Crevicing:** Mating surfaces.
- **Other**: Rare…

1. Inhibitors targeted on the 2 most common forms of corrosion in cooling waters, General & Galvanic. Dispersants target Pitting & Under-deposit corrosion.
2. General corrosion is the evenly distributed thinning of an immersed metal. It increases with both temperature and the rate at which you can bring reactants (oxygen) and remove reactants (oxides) from the surface.
3. Galvanic corrosion is driven by the solution potentials of the dissimilar metals. The more electro-negative metal becomes the anode & corrodes at a Faradaic rate (proportional to the current discharged from its surface). In addition to 2., the closer the surfaces and the higher the conductivity, the higher the corrosion rate.
4. Pitting is not spontaneous in cooling waters. It needs an an accelerant like high chlorides or temperature or organic deposits. **A pit, once initiated, it's isolated from bulk water chemistry by it's corrosion products.**
5. **M**icrobiologically **I**nduced **C**orrosion, **S**ulfate **R**educing **B**acteria – subsets of pitting.
6. Crevicing: Flange faces, tubesheet/tube interfaces,
7. Rare: Flow related, Stress Corrosion.. Rare, Google NACE Basic Corrosion



General Corrosion

When an immersed metal corrodes, a DC current flows from its surface and the magnitude of the current is proportional to the corrosion rate.

For example, 1 Amp flowing from a steel surface for 1 year would remove 20 lbs, 9 Kg of steel.

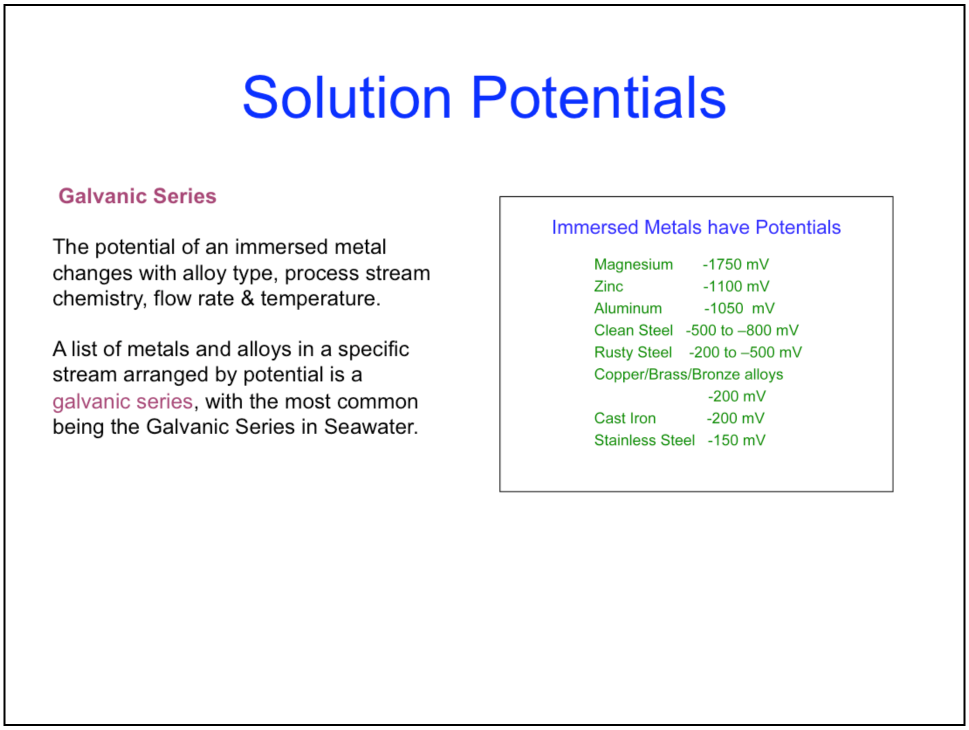
General Corrosion:
If over time, anodic & cathodic sites switch, overall metal thinning occurs.

Corrosion as a DC Current

Corrosion current

Coulombs of electrons proportional to moles of metal

1. We’re most familiar with ‘General Corrosion’ which occurs when metal ions go into solution (becomes oxides, sufides…) at the same rate that electrons transfer between oxidation-corrosion and reduction sites.
2. All aqueous phase corrosion cells have both liquid (ions) & a metallic (electron) paths for charge carriers.
3. Any action, mechanical or chemical that slows the rate of reaction at either oxidation or reduction site, slows the rate of metal loss, the corrosion rate.
4. When we apply water treatment we’re either/or/and controlling the bulk water chemistry to reduce corrosion rates or forming surface films on the anodic or cathodic sites.



Solution Potentials

Galvanic Series

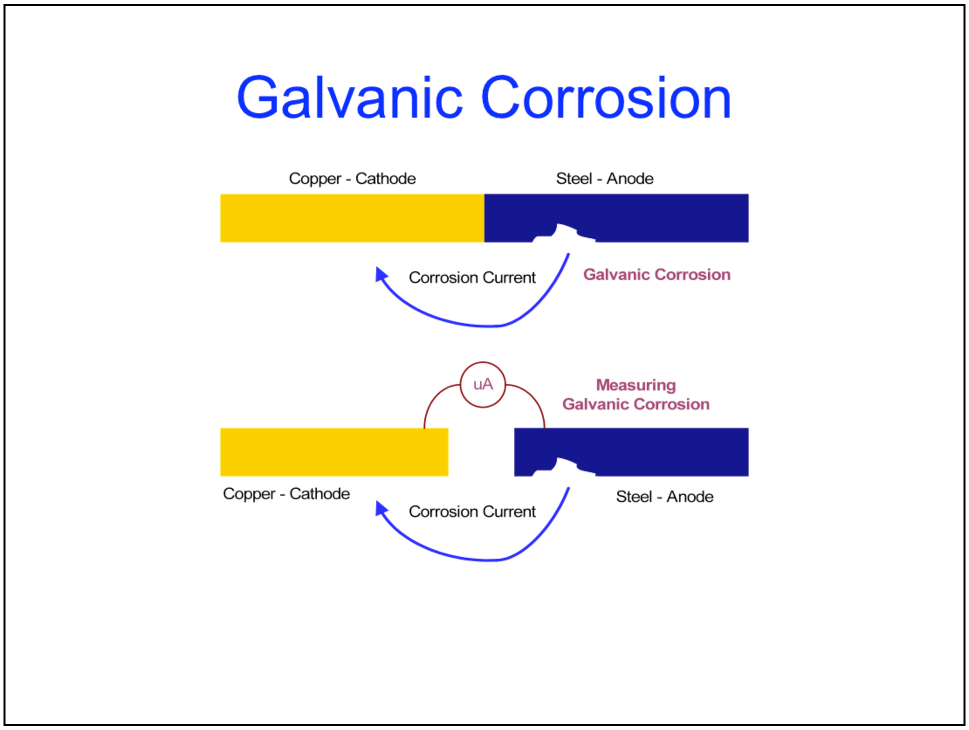
The potential of an immersed metal changes with alloy type, process stream chemistry, flow rate & temperature.

A list of metals and alloys in a specific stream arranged by potential is a galvanic series, with the most common being the Galvanic Series in Seawater.

Immersed Metals have Potentials

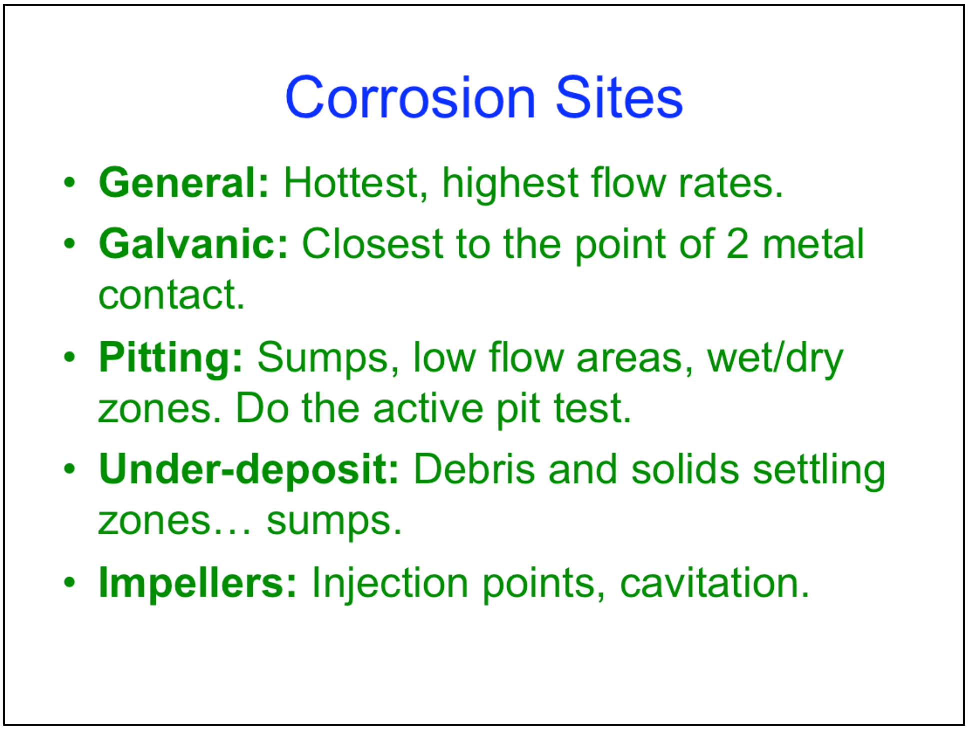
Magnesium	-1750 mV
Zinc	-1100 mV
Aluminum	-1050 mV
Clean Steel	-500 to –800 mV
Rusty Steel	-200 to –500 mV
Copper/Brass/Bronze alloys	-200 mV
Cast Iron	-200 mV
Stainless Steel	-150 mV

1. Extending the electrical analogy of corrosion… Solution Potentials
2. Perhaps one of the most familiar solution potentials to us, is the ORP sensor. It’s the solution potential of Pt with respect to an Ag/AgCl reference electrode. As oxidant levels increase, so does the solution potential, ORP.
3. If you connect any 2 different metals or alloys & immerse them, the more negative becomes the anode & corrodes, the other becomes the cathode & does not corrode (gross generalization!)
4. This is why we put Magnesium anodes in freshwater headboxes (bell ends) & Zinc in hot or higher conductivity stream headboxes or Aluminum in seawater headboxes. The anode corrodes & the steel headbox does not.



Galvanic Corrosion

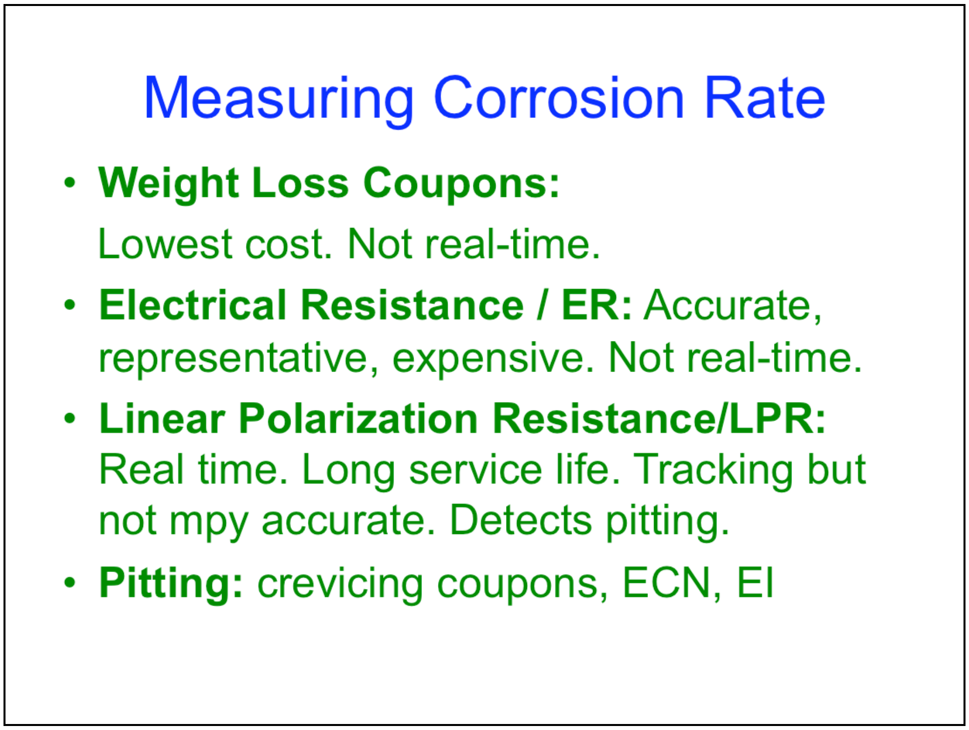
1. When dissimilar metals are connected & immersed, a ‘Galvanic Corrosion’ cell forms.
2. Circulating water systems are inevitably mixed metal & metallurgies & we add chemicals or remove oxygen to reduce the anodic and/or cathodic corrosion rates.
3. We don’t have an ionic ammeter, but if we separate the two metal surfaces & measure the electron current that flowing between them, we have a measure of the galvanic corrosion rate.
4. Measuring galvanic corrosion rate in this way makes assumptions about the dominant corrosion reaction, the area ratios of the anode & cathode…. Like any corrosion rate measurement, it’s useful to measure relative, not absolute metal loss rates.
5. **Aside:** Its likely apparent why you never coat the anode of a corrosion cell (a headbox) without installing sacrificial anodes No coating is perfect & the worst case is one pinhole. A large adjacent cathode (tubesheet) & a very small anode (pinhole) will perforate in weeks.



Corrosion Sites

- **General:** Hottest, highest flow rates.
- **Galvanic:** Closest to the point of 2 metal contact.
- **Pitting:** Sumps, low flow areas, wet/dry zones. Do the active pit test.
- **Under-deposit:** Debris and solids settling zones… sumps.
- **Impellers:** Injection points, cavitation.

1. Corrosion may be a combination of types and due to both initiating and accelerating causes.
2. General: Transfer piping & exchanger tubing. Galvanized sumps in locations where pH is adjusted for cycles or bleach-chorine conversion.
3. Galvanic: Tube sheets / Galvanized, partially immersed structural steel / Soldered-Brazed joints in air handlers with faulted scavanging.
4. Pitting: Structural Aluminum in high chloride waters / Steel or Galvanized debris loaded sumps. Failure to passivate on commissioning. Knock the top off the pit & note the color gradation (Fe:black/red/orange/white) to white metal at bottom…that's an active pit…. A distressing array of oxidation states & pH.
5. Under Deposit: immersed or intermittently immersed debris blocked or slimed surfaces.
6. Impellers: Bronze common in cooling water re-circ. Where is the bleach/oxidant or in the extreme, acid fed for general corrosion. Pitted impellers are typically flow related. Look for leaking seals.
7. Rare: Crevicing / weld line attack / stress crqcking more common in process applications.



Measuring Corrosion Rate

- **Weight Loss Coupons:** Lowest cost. Not real-time.
- **Electrical Resistance / ER:** Accurate, representative, expensive. Not real-time.
- **Linear Polarization Resistance/LPR:** Real time. Long service life. Tracking but not mpy accurate. Detects pitting.
- **Pitting:** crevicing coupons, ECN, EI

1. **Weight Loss:** Both steel and tube metallurgy (Copper, 90:10 CuNi, Admiralty(bronze)) installed for 30 to 90 days. Weight difference converted to an mpy (mils/year) corrosion rate. Pitting fails method.
2. **ER:** Not usually used in cooling waters. Measure increase in electrical resistance of wire or wafer element as corrosion thins. Trades resolution for useable sensor life. Disposed after use.
3. **LPR:** Commonly used in process & cooling waters. Multiple vendors with Aquatrac only water treatment controller mfg. Long sensor life in cooling towers. Replacement tips low cost. Alarms on pitting but cannot measure pitting rate.
4. **Measuring Pitting:** Not done in cooling streams. Difficult for coupon to simulate the pitting conditions. **E**lectro**C**hemical **N**oise: both current and potential noise measured & corrosion mechanism inferred – not used as an on-line method in cooling waters.. Google it along with Electrochemical Impedance.
5. **Limits**: It's common to locate sensor to get the desired commercial result (downstream from inhibitor or pot feeder…. Coolest water..).

All of these methods only measure **General Corrosion** and all are limited in that they only approximate immersed surfaces (ECN claims to the contrary).

LPR: Sensor & Method

- **Sensor:**

  2 cylindrical pins, nominally 5mmx32mm of the same, target metallurgy.
- **Method:** 2 minute cycle

1. Polarize 10mV, measure current.
2. Polarize 0mV, measure current.
3. Polarize -10mV, measure current.
4. Calculate Corrosion Rate.

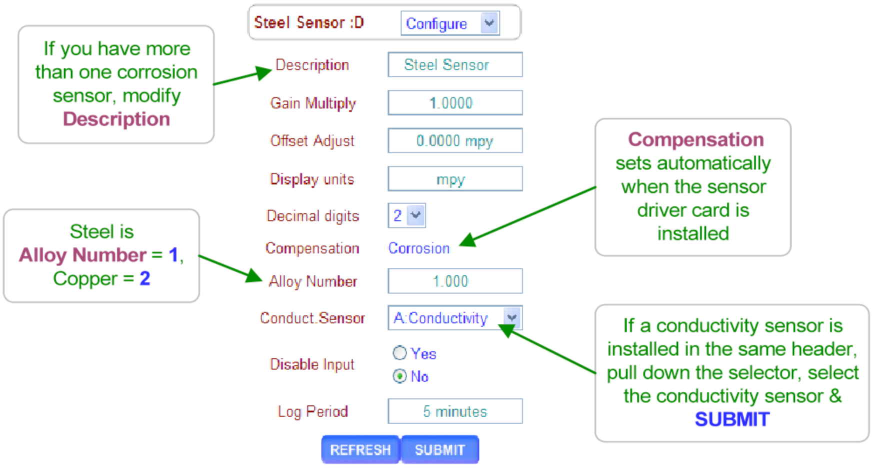
1. **Installation:** 3” NPT ‘T’. Tips face upstream although direction doesn’t make any difference in cooling water streams.
2. **Method:** Assumes linear Tafel slope either side of the corrosion potential. Uses Faraday equivalent (assumes an oxidation valence change) to convert current to weight loss (assumes nominal sensor tip dimensions). Steel @ 9.1 Kg/AmpYear.
3. **Real Time:** Corrosion rate updates every 120 seconds. You can see the immediate effect of feeding bleach or acid, flow/no flow, temperature shift, aeration…
4. **Accuracy:** Typically 50% to 200% of LPR. If you want mpy, use weight loss coupons. If you want to see the immediate effect of a process change on mpy, use LPR.
5. **Pitting, Polarize 0mV:** If both tips at the same potential, measures nominally 0mV. Larger mV indicates one of the tips pitted & sets the controller pitting alarm. Cannot measure pit current (to calculate a pitting rate) since this current flow is local only to one tip, from the bottom of the pit the the adjacent surface.
6. This is a generalization of the actual measurement. The corrosion rate card sequences. The controller synchronizes with the card and samples the card voltage.

LPR: Operational Issues

- **Alloy#:**
  Copper =2.00, 90/10 Cupro-Nickel = 1.80, Zinc = 1.29, Admiralty = 1.67
- **Conductivity Compensation:**
  Use controller conductivity sensor.
- **Ground Loops:**
  Sensor DC isolated.
- **Verify Measure:**
  10K ohm resistor = 0.5 mpy for Steel

1. **Alloy#:** The rate at which a DC current converts a metal to its oxide normalized to carbon steel. The controller uses the Alloy# to convert the measured current to mpy for each alloy. Stainless & Aluminum not shown since they pit before general corrosion in cooling waters
2. **Conductivity:** If more than 5mV drop across the solution, the controller alarms. LPR usable above 100-200uS. Since LPR is a relative measure and most towers control their conductivity, it's not really necessary to conductivity compensate. More applicable in streams which vary in conductivity
3. **Ground Loops:** We're measuring DC current in the micro-nano amp range so we can't have any path back to controller common. Measured current must only flow between the sensor tips. (Not back thru the pH solution ground or conductivity sensor)
4. **Verify Measure:** Copper corrosion rates in cooling towers typically <0.5mpy & steel typically <1mpy, so a method that verifies to 0.5mpy works. Same method gives you 0.25mpy if Alloy# set for copper.
5. **Cabling:** 2 conductor, unshielded. Up to 60 meters. Not in common conduit with AC power. Low impedance signal not sensitive to noise.

Corrosion : Configure



Steel Sensor :D

Description	Steel Sensor
Gain Multiply	1.0000
Offset Adjust	0.0000 mpy
Display units	mpy
Decimal digits	2
Compensation	Corrosion
Alloy Number	1.000
Conduct.Sensor	A:Conductivity
Disable Input	○ Yes ● No
Log Period	5 minutes

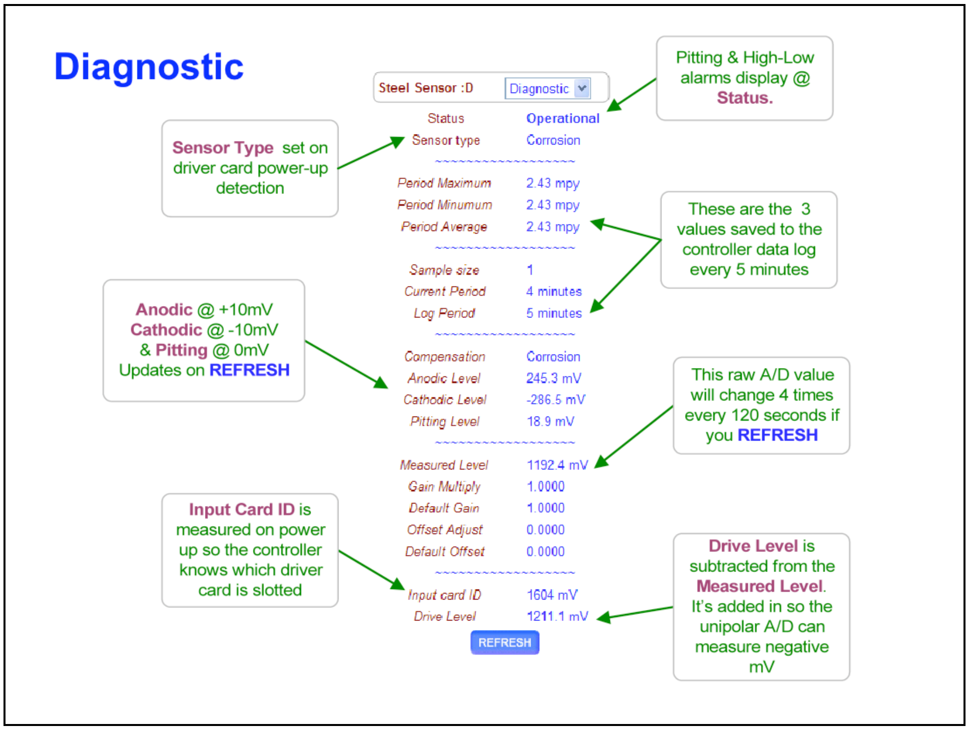
If you have more than one corrosion sensor, modify **Description**

Steel is **Alloy Number** = **1**, Copper = **2**

Compensation sets automatically when the sensor driver card is installed

If a conductivity sensor is installed in the same header, pull down the selector, select the conductivity sensor & **SUBMIT**

1. Up to 4 corrosion rates can be installed in an Aegis & 14 in an M10 MultiFlex. Both single and dual corrosion rate driver cards available.
2. Plug & Play: Here’s what you’ll see after you’ve turned OFF the power, installed the corrosion rate driver card and turned ON the Aegis. This is a dual card with corrosion rate sensors on inputs ‘**C**’ &’**D**’.
3. Default Alloy# is Carbon Steel. Modify Alloy# for your sensor tips.
4. Don’t calibrate this sensor to avoid tail-chasing obscuring trends.. You’re watching for a relative change in mpy, knowing that the absolute number is the result of many assumptions & in the context of the application, representative only.
5. The Aquatrac corrosion rate sensor is non-metallic & designed for use in cooling towers & closed loops. You can however use a more rugged sensor tip holder for process applications (See Rohrback and Metal Samples) and wire the 2 wires from the tips to the Aquatrac driver. (Other vendor’s holders will have multiple wires but use the same sensor tips. Some have hot entry hardware & isolation valves)



Diagnostic

```
Steel Sensor :D      Diagnostic
        Status          Operational
     Sensor type        Corrosion
          ~~~~~~~~~~~~~~~~~~~~
  Period Maximum        2.43 mpy
  Period Minumum        2.43 mpy
  Period Average        2.43 mpy
          ~~~~~~~~~~~~~~~~~~~~
     Sample size        1
  Current Period        4 minutes
      Log Period        5 minutes
          ~~~~~~~~~~~~~~~~~~~~
    Compensation        Corrosion
    Anodic Level        245.3 mV
  Cathodic Level        -286.5 mV
   Pitting Level        18.9 mV
          ~~~~~~~~~~~~~~~~~~~~
  Measured Level        1192.4 mV
   Gain Multiply        1.0000
    Default Gain        1.0000
   Offset Adjust        0.0000
  Default Offset        0.0000
          ~~~~~~~~~~~~~~~~~~~~
   Input card ID        1604 mV
     Drive Level        1211.1 mV
```

Pitting & High-Low alarms display @ **Status.**

Sensor Type set on driver card power-up detection

These are the 3 values saved to the controller data log every 5 minutes

Anodic @ +10mV
Cathodic @ -10mV
& **Pitting** @ 0mV
Updates on **REFRESH**

This raw A/D value will change 4 times every 120 seconds if you **REFRESH**

Input Card ID is measured on power up so the controller knows which driver card is slotted

Drive Level is subtracted from the **Measured Level**. It's added in so the unipolar A/D can measure negative mV

1. **Diagnostic** is where to start if you have an unexpectedly low or high corrosion rate. If you have a pitting alarm, inspect the tips and change if visibly pitted. If the rate's high, look for a process upset or operational cause like failure to feed corrosion inhibitor. If low, look for fouling or coating of the sensor, oil leaks from the fan drive bearing, air borne organic contamination…
2. **More Diagnostic** Download the controller log and use Trackster to plot operational parameters like ORP & bleach pump run time versus corrosion rate. Ditto temperature, pH, Acid pump run time, flowswitch state, make-up volume…. An upset is the reason this sensor was installed, let's find the cause.
3. **Status** will display 'Low Conductivity' if more than 5mV of the 10mV driving voltage drops across the cooling water. The conductivity where this alarm occurs is a function of both the corrosion current and the water conductivity (V = I x R).
4. **Application Trick:** If you have a Galvanic corrosion problem & are assessing remedial measures, you can use tips of the target alloys (one copper & one steel, for example). You'll get pitting alarms but the reported corrosion rate will be a measure of the galvanic current flow. Galvanic cell driving voltages are usually much more than 10mV so the LPR drive voltage will have minimal effect. A ZRA is the correct way to test galvanic cells, but in its absence….

Mercifully short PowerPoint presentation

Sources:

NACE: Basic Corrosion Course @ www.nace.org.

Aegis_Tech.doc, Section 7.7, driver card.

Rohrback @ www.rohrbackcosasco.com

Metal Samples @ www.alspi.com/corrosion.htm

1. If interested in Corrosion but don’t know much, take the NACE Basic course. Well taught (usually) thorough introduction and you get a great book.
2. The Aegis_Tech manual has all the driver specifics & a lot of other stuff not usually of interest to end users (that stuff’s in Aegis_User & Aegis_Browser).
3. I know you have EU vendors & sources for this stuff because I used to compete against them when in this business, but that was a while ago so here are some U.S. links.
4. Aquatrac buys its LPR sensor tips from Pacific Sensor (no web site). Excellent prices & good delivery. If you start using a lot, buy direct from them. Get contact info from Aquatrac.
5. Happy trails (Roy Rogers) May your sombrero cast a shadow that makes positive identification difficult /ed.