LABORATORY AND FIELD STUDIES OF LOCALIZED AND GENERAL CORROSION INHIBITING BEHAVIORS OF SILICA IN ZERO LIQUID DISCHARGE (HIGH TDS COOLING WATER) USING REAL TIME CORROSION MONITORING TECHNIQUES

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ABSTRACT

Corrosion rate studies were conducted in the laboratory on high total dissolved solids (TDS), zero liquid discharge (ZLD) cooling water. The cooling water had been treated with silica corrosion inhibitor chemistry in the field operating system. Corrosion rates were measured using real time coupled multi-electrode array sensor technology. The study evaluated both general and localized (pitting) corrosion rates for carbon steel (CS), copper, aluminum, zinc and stainless metals at temperatures ranging from 77 to 190°F (25 to 88°C).

The study confirmed that the silica chemistry provided exceptional corrosion inhibition with very low corrosion rates (i.e., < 0.3 mpy [0.0076 mm/yr] on1008 CS) for mild carbon steel at high TDS and temperature extremes, as well as exceptionally low corrosion rates on other metals evaluated. The laboratory study corroborated field corrosion results, and established this procedure as a potentially efficient means of predicting corrosion inhibitor performance with various metals and water temperatures in field systems with given system water chemistry and inhibitor residuals.

The "Green Chemistry" corrosion inhibitor evaluated was silica (SiO_2) which is controlled at concentrations between 200 mg/L and saturation, typically greater than 300 mg/L as soluble SiO_2, provided through evaporative concentration and conversion of natural silica in the source water.

INTRODUCTION

Most operators are reluctant to try new technologies in their full scale operations fearing failure and disruptions of production. This fear can be overcome if sufficient confidence can be gained from bench or pilot scale investigations. In pursuing the development of silica chemistry as described in this paper, the authors have demonstrated that by using the corrosion monitoring techniques described, the performance at the pilot level matches the performance in full operations.

As more oil and gas plants move to zero liquid discharge (ZLD), they are choosing to use demineralized water as cooling water make-up in order to reduce the amount of blow down to be sent to the evaporator/crystallizer systems. Chemical treatments of such systems are challenging with traditional inhibitor chemistry and therefore the opportunity to consider this proposed silica chemistry becomes very relevant for the industry.

Three main objectives have therefore been met.

- Confidence in transferring pilot data to full operations
- Silica chemistry can prevent corrosion in high TDS waters and
- Silica chemistry qualifies as "green" inhibitor chemistry

Silica Chemistry

Silica has been one of the major scale and fouling problems in many processes that use water. Silica is difficult to deal with because it can assume many low solubility chemical forms, depending on the water chemistry and metal surface temperature conditions. Below about pH 9.0, silica (monomer) has limited solubility (125-180 mg/L as SiO_2 at 77° F) and tends to precipitate as these concentrations are exceeded with the insoluble salts of polyvalent metal ions (hardness) in source waters.

In industrial applications, most scale and corrosion control methods used in evaporative cooling water systems typically rely on the addition of a scale and corrosion inhibitors in combination with controlled blow down wastage of system water to prevent scale and corrosion problems. In this regard, the major scale formation potentials are usually contributed by the quantity of hardness (calcium and magnesium) and silica ions contributed by the source water,

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while the major corrosive potential results from the ionic or electrolytic strength that is concentrated from the source water by evaporation, or by chemicals (such as acid) added to the system water to control hardness deposition.

Treatment methods to reduce corrosion have principally utilized the addition of chemical additives that suppress corrosive reactions occurring at either the anode or the cathode present on the metal surface, or combinations of chemical additives that inhibit reactions at both the anode and cathode. The most commonly applied anodic inhibitors include chromate, molybdate, orthophosphate, nitrite and silicate; whereas the most commonly applied cathodic inhibitors include polyphosphate, zinc, organic phosphates and calcium carbonate.

In view of toxicity and environmental concerns, the use of more effective heavy metal corrosion inhibitors, such as chromate and zinc, have been prohibited and most methods now rely on a balance of the scale formation and corrosive tendencies of the system water which are generally referred to as alkaline treatment approaches. This balance, as applied in such treatment approaches, is defined by control of system water chemistry with indices such as Langelier Saturation Index (LSI) or Ryznar Saturation Index (RSI), and is used in conjunction with combinations of scale and corrosion inhibitor additives to inhibit scale formation and optimize corrosion protection at more limited concentrations of dissolved solids from the source water. These methods however, were still limited by the concentration of silica and potential for silica deposition. Corrosion rates for alkaline approaches are also significantly higher than those previously available with use of heavy metals such as chromate. Since the use of chromate and other toxic heavy metals has been restricted, corrosion protection has generally been limited to optimum ranges of 2 to 5 mpy (or 0.051 to 0.127 mm/yr) for carbon steel when treating typical source water qualities. Source waters that are high in TDS have higher corrosion rates.

Some programs may use the addition of acid to treated systems to control pH and reduce scaling potentials at higher concentrations of source water chemistry. This allows reduced blow down and conservation of water through modification of the concentrated source water, while maintaining balance of the scale formation and corrosive tendencies of the water. While blow down is reduced, this approach has the drawback of being prone to greater risk of scale and/or corrosion consequences with excursions with the acid / pH control system. There is also an overall increase in corrosion potential due to the higher ionic or electrolytic strength of the water that results from addition of acid ions that are concentrated along with ions in the source water. Such corrosion control methods rely on significantly higher chemical additive residuals to offset corrosive tendencies. Silica concentration must still be controlled below solubility limits by system blow down.

Pre-treatment of source water to reduce hardness ions has been used in some systems to control calcium and magnesium scale potentials. Current corrosion protection methods are less effective with softened makeup water due to absence of the corrosion inhibition contributed by calcium carbonate in the source water. These treatment approaches still rely on blow down to control silica residuals at maximum guidelines to avoid silica deposits.

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Accepted practice is to limit the amount of silica in cooling water to about 150 mg/L, expressed as SiO_2. Reportedly, the best technology currently available for control of silica in cooling water is use of various low molecular weight polymers, various organic phosphate chemistries, or their combinations. Even with use of these chemical additives however, silica is still limited to less than 180 mg/L in most system applications. Since many arid areas of the U.S. and other parts of the world may contain from 50-90 mg/L silica in source water, cooling water can only be concentrated to 2 to 3 times such levels before the risk of silica or silicate deposition becomes too great. A method that would enable significant water conservation of typical source waters, re-use of wastewater, and use of either brackish or high silica content source waters for evaporative cooling water systems is of great benefit.

To address these problems, methods for controlling deposition and fouling of silica or silicate salts on surfaces in evaporative cooling water systems have been derived and include:

1)   Inhibiting precipitation of the material from the cooling water;
2)   Maintaining an aqueous chemical environment that supports transformation and stability of increased residuals of soluble silica species;
3)   Producing a non-adherent form of silica precipitants in the bulk water.

Prior limitations with silica deposition have prevented exploration of silica chemistry, particularly at higher concentrations, as a potential corrosion inhibitor. Since current methods inhibit corrosion and scale formation primarily through water wastage or acidification, there is a need for inhibition methods that will permit discharge reduction that are cost-effective and environmentally friendly. Processes that would likely benefit from such methods would include evaporative cooling towers, evaporative coolers, cooling lakes or ponds, and indirect cooling of enclosed or secondary cooling and heating loops.

Currently disclosed silica chemistry and methods for preventing fouling of surfaces with silica or silicates now provides opportunity for application of corrosion inhibition methods that use silica concentrated from natural source waters, and enables silica to be used as a non-toxic and environmentally friendly corrosion inhibitor.

Silica Corrosion Inhibitor

Recent U.S. patents[1] disclose methods for controlling silica and silicate fouling problems while concurrently controlling the corrosion of system metallurgy in evaporative cooling systems with high concentrations of dissolved solids (high ionic strength). The corrosiveness of various source waters is generally a function of the concentration of corrosive ions (such as chloride and sulfate) and electrolytic (ionic) strength that are concentrated in evaporative systems that cool heat transfer surfaces. Accordingly, varying source water quality will impact system corrosion, and determines the required level of protection needed from a corrosion inhibiting mechanism.

Silica chemistry can be applied to provide significantly greater corrosion protection for system metals that encounter very high concentrations of corrosive ions or electrolytic strength. Since this technology will permit cooling system operation at much greater concentrations of

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corrosive ions (high TDS) without consequence of corrosion to system metals, significant water conservation benefit is provided for both the applicant and environmental conservation. Field testing and lab studies have confirmed that silica chemistry can control corrosion of mild steel, copper, stainless steel, aluminum, zinc, galvanized steel and various alloys of such metals at very low levels, in particular with high evaporative concentrations of corrosive ions contained in source water (increased electrolytic potential or ionic strength). Prior methods have not enabled pursuit of water conservation at higher TDS concentration levels, due to ineffective corrosion protection or prohibitive cost of pretreatment and inhibitor application. The cost for pretreatment with methods such as ion exchange to remove multivalent ions is much lower than the cost of using additional makeup water for blow down and associated disposal with current inhibitor methods.

This silica inhibitor method is directed to the removal of polyvalent metal (PVM) ions from the source water, control of specified method chemistry residuals in the evaporative cooling system to prevent deposition of PVM silicate or silica scales on system surfaces, and preventing PVM interference with corrosion inhibiting mechanisms of silica on system metallurgy. Silica and silicate scaling problems occur in cooling systems when silica residuals exceed solubility, following concentration of silica contained in source water. These deposits can be controlled by removing PVM ions (calcium and magnesium being the most prevalent ions) from the makeup source water using simple pretreatment methods such as ion exchange or chemical precipitation. The pretreatment method should reduce the total PVM ions in the makeup water to less than 10% of the makeup silica residual (mg/L SiO_2), as determined from an initial assessment of the source water. Preferably, the total PVM ions will be reduced to less than 2% of the makeup silica residual to permit higher silica concentration and water conservation.

Monovalent metal (MVM) ion residual is controlled above the soluble silica residual in the system, and preferably is in the concentration range of 0.1 N to 0.2 N total MVM ions[2,3,4]. Such control may be provided by concentration of the pre-treated makeup in the evaporative cooling system or supplemental feed of MVM ions (salts or alkalinity chemicals) directly to the system. In some applications, control of MVM ion concentration at greater than 0.3 N is desired to enable corrosion protection at reduced silica concentrations.

Alkalinity is then controlled (as quantified by relation to pH) at 7.0 pH or higher [2, 3], with a pH of 9.0 or higher being more highly preferred in some applications along with control of soluble silica at residual concentrations at saturation solubility, preferably with control at residuals in some applications exceeding 300 mg/L as SiO_2. Optimum alkalinity and silica residual concentrations may generally be attained by evaporation and concentration of pre-treated source water in the cooling system with elimination or reduction of blow down.

Specifics of inhibitor mechanisms and film formation chemistry are not addressed in this discussion due to the scope of this topic, and will be addressed in future publications. By establishing and controlling saturated soluble silica residuals in equilibrium with amorphous silica (illustrated in Fig. 1), the method is believed to promote formation of a non porous silica surface barrier on all polyvalent metal surfaces. Numerous references cited [2-15] indicate the

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probable silica polymerization and surface chemistry behavior (film formation) of related silica applications believed to function in this method of silica corrosion inhibition.

This combination of pre-treatment and system chemistry control steps, when applied in evaporative cooling systems where bulk water temperature [2, 4, 11, 14] and water contacting heat transfer surfaces exceeds source water temperature, provides highly effective residuals of silica corrosion inhibitor and protective film mechanisms. Further, this water chemistry environment permits transformation[2] of natural monomeric and low molecular weight silica contained in source water to stable residuals of corrosion inhibiting silica structures that provide exceptional corrosion protection of cooling system metals.

EXPERIMENTAL PROCEEDURES AND DISCUSSION

Laboratory Studies

The study was conducted with cooling water taken from a system that has operated with zero liquid discharge for three years while treated with the silica inhibitor method. Field corrosion results and system chemistry results over this period of operation are described in the next section. Analysis of the study water sample determined the key chemical parameters at approximately 50000 TDS, 9000 mg/L chloride, pH 10 and 450 mg/L silica (soluble SiO_2). Non inhibited control testing was conducted with simulated seawater (3%wt sea salt [approximately 30000 TDS] solution) at neutral pH. Temperature of water and metal surface were continuously monitored and thermostatically controlled at target level. Water evaporated during high temperature studies was replaced with distilled water to maintain original concentration of sample chemistry.

Coupled multi-electrode array sensors [16] were used to measure corrosion rates of mild carbon steel (Type 1008 -- UNS G10080), Copper (CDA 110-UNS C11000), Aluminum (Type 1100, UNS A91100), pure zinc, and stainless steel (Type 316L--UNS S31603) in both the silica-inhibited and the non-inhibited sea salt waters. In a coupled multielectrode sensor, there are multiple miniature electrodes made of materials identical to the component of interest. Statistically, some of the electrodes have the properties that are close to the anodic sites and others have the properties that are close to the cathodic sites of the corroding metal. The resulting electrical currents are measured. The localized corrosion rate is calculated using the current from the most anodic electrode, and the general corrosion rate is calculated using the average anodic currents from all the electrodes in the array [17]. The multi-electrode array sensor probes were made of 1-mm diameter wires of these metals and each has 16 electrodes. During the study, these probes were immersed in the test solutions and connected to a nanoCorr S-50[*] multi-electrode corrosion analyzer which gives both localized and general corrosion rates on real time. The corrosion analyzer was also connected to a temperature probe, an oxidation/reduction potential (ORP) probe, and a saturated Ag/AgCl reference electrode, all of which immersed in the same test solution.

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[*] Trade name of Corr Instruments, LLC, San Antonio, Texas, USA

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Discussion of Laboratory Results

Carbon Steel. Figure 2a shows both the general and localized (maximum pitting rate) corrosion rates for carbon steel (Type1008) at temperatures from 77 to 190°F (25 to 88°C). The data displayed is condensed to permit illustration of the effect of various temperatures evaluated, as well as brief periods of limited film destabilization when each of the temperature adjustments was made. Upon immersion of the probe (freshly polished to 400 grit) in the test solution at 77° F, the corrosion rates were initially high (4 mpy for the maximum localized corrosion rate and 1 mpy for the general corrosion rate). The corrosion rates decreased rapidly in the first 2 hours (to <1.5 mpy for maximum localized corrosion rate and <0.2 mpy for general corrosion rate) as the protection film on the sensing electrode surface was formed. At the end of the 4 day test at room temperature, the corrosion rates stabilized (to <0.1 mpy for maximum localized corrosion rate and <0.02 mpy for general corrosion rate). Upon subsequent step changes in temperature, the corrosion rate was high initially, but decreased rapidly as new equilibrium was reached on the sensing electrode surfaces. Approximately 10 hours after the step change from 160 to 190° F, the maximum localized corrosion rate was 1.9 mpy and the general corrosion rate was 0.2 mpy.

Figure 2b shows the oxidation/reduction potential (ORP) measured on the platinum electrode, corrosion potential of the carbon steel multi-electrode array probe, and the temperature during the tests. Initially, the corrosion potential of the freshly polished carbon steel probe was low (-0.5 V [Ag/AgCl] and close to that of the carbon steel probe in air-saturated seawater [17] (-0.6 V [Ag/AgCl]), indicating that the carbon steel electrodes on the probe were active. However, the corrosion potential became more positive and stabilized at -0.25 V (Ag/AgCl) in approximately 3 days, indicating that the electrodes on the probe were passivated by the silica film. The ORP did not change significantly during the test.

The carbon steel corrosion rates were exceptionally low for such high TDS water, and in particular at the higher temperature extremes evaluated. Such levels of protection would indicate opportunity for consideration for use of carbon steel in high temperature and high TDS conditions that would normally require use of stainless or other specialty materials of construction.

Stainless Steel. Figure 3 shows both the general and localized (maximum pitting) corrosion rates for stainless steel (Type 316L) and temperatures evaluated during the test. At room temperature, the stabilized rates of the Type 316L stainless steel were extremely low (<0.005 mpy for the maximum localized corrosion rate and 0.0015 mpy for the general corrosion rate). Similarly to the carbon steel, the corrosion rates of the stainless steel increased for a short time during temperature transitions, but decreased and stabilized several hours after the temperature changes. The maximum localized corrosion rate of the Type 316L was less than 0.013 mpy at 190° F.

Aluminum. Figure 4 shows both the general and maximum localized (maximum pitting) corrosion rates for aluminum (Type 1100) and the temperatures during the test. At 134°F, the

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stabilized rates of the Type 1100 aluminum were 0.09 mpy for the maximum localized corrosion and 0.02 mpy for general corrosion, repectively. Seven hours after the temperature was maintained at 190°F, the corrosion rates of the Type 1100 aluminum were 0.37 mpy for the maximum localized corrosion rate and 0.06 mpy for the general corrosion rate. The temperature was then reduced from 190°F to 77°F, where both the maximum localized and the general corrosion rate dropped below 0.006 mpy.

Corrosion Rates in Control Solution. Control studies with simulated seawater (Figures 5 and 6) showed maximum localized corrosion rates of 50 mpy for Type 1008 carbon steel, 20 mpy for Type 1100 aluminum and 0.04 mpy for Type 316L stainless steel at only room temperature. Higher corrosion rates would be expected at higher temperatures. Figure 7 provides a visual comparison of carbon steel and a stainless steel probes after exposure in simulated seawater at room temperature for 3 weeks versus a carbon steel probe after exposure in silica inhibited water at temperatures up to 190°F for one week. Table 1 summarizes and compares laboratory data for the silica inhibited high TDS water for various metals and temperatures, and sea salt control study data. The silica inhibited studies verify the corrosion rates and inhibitor performance found in field studies discussed below.

Field Studies

Analytical tests were performed on samples from cooling tower systems treated with the silica chemistry method to demonstrate efficacy in transforming source water monomeric and low molecular weight silica, and controlling the stability of soluble silica and other silica particles at increased concentrations.   Two samples were obtained from different operating time frames for each of the following: 1) pre-treated make-up source water; 2) the resultant treated system water; and 3) tower sump insoluble accumulations. Corrosion rate studies were also conducted with weight loss test specimens via ASTM Standards G4-01 Standard Guide for Conducting Corrosion Tests in Field Applications and G1-03 Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens.

Discussion of Field Results

Water Analyses. Cooling tower and makeup water analytical tests in two cooling tower system chemistries (Table 2 and Table 3) illustrate the effectiveness of the method in maintaining higher levels of soluble silica in the cooling tower system. Soluble silica residuals were at 306 and 382 mg/L in these tower samples at the respective 9.6 and 10.0 pH levels. The lower chemical concentration ratios (CR) for silica in these tower samples, as compared to the higher evaporative concentration residuals for other soluble chemistry (chloride, alkalinity, conductivity), indicate that some of the excess silica may be precipitating as non-adherent material, and accumulating in the tower basin. However, a significant proportion of the silica expected to concentrate from the source water would not be detected by the analytical procedure since condensation and adsorption growth into large colloidal particles does not permit detection of the original concentration of low molecular weight soluble silica. However, limited precipitation of amorphous silica is confirmed by the ratio of amorphous silica found in the tower basin deposit analyses. System heat exchange surfaces were free of silica or other deposits.

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Turbidity Analyses. Although the exact mechanism of action of the process is not completely understood, the method reduces the turbidity of the treated water, which demonstrates effective soluble silica stabilization and control of amorphous silica deposition. Methods that produce treated water of less than eight (8) nephelometric turbidity units (NTU) are considered improvements over typical evaporative cooling system residuals of insoluble particle suspensions or dispersions content. Turbidity measurements (Table 4) performed on samples taken from the cooling systems, before and after filtration through a 0.45-micron filter, illustrate effective silica inhibition in the treated water. The turbidity levels are well below typical cooling tower systems, in particular at such high evaporative concentration ratios (CR), and indicate the method provides controlled non-adherent precipitation of excess silica and other insoluble materials entering the system. Clean heat exchanger surfaces have confirmed that the method silica precipitation is non-adherent. The precipitated silica forms are contained in the cooling tower sump. However, the volume of precipitant and scrubbed accumulations in the tower sump were no greater than previous treatment methods due to reduction of insoluble PVM salt precipitates by pretreatment removal.

Deposit Analyses. Microscopic and chemical analysis of deposit samples from accumulated residue in the tower basin of a system treated by present methodology are shown in Table 5 and Table 6. Both analyses illustrate a significant ratio of amorphous silica and silica materials in the deposit. The major proportion of this silica is the probable result of silica adsorption or reaction with insoluble precipitates of PVM ions as introduced and concentrated in the tower water, or amorphous silica precipitation with attainment of elevated MVM ion concentrations. Visual inspections of heat transfer equipment in the system have confirmed that it has remained free of silica and other scale deposits. System heat transfer efficiencies were also maintained at minimum fouling factor levels.

Corrosion Rate Measurements. Data in Table 7 illustrate the effectiveness of the method in inhibiting corrosion of mild steel and copper evaluated by weight loss coupons in the system. No pitting was observed on coupon surfaces. Equipment and exchanger tube surface inspections have confirmed excellent corrosion protection. Comparable corrosion rates for mild steel in this water quality with prior treatment methods were optimally in the range of 2 to 5 mpy.

RESULTS SUMMARY

Corrosion inhibition performance was excellent for all metals and temperatures evaluated with the silica inhibitor. The silica inhibitor rapidly reduced both general and localized corrosion rates detected by coupled multi-electrode array sensor probes. Laboratory study results confirmed field results obtained with established ASTM corrosion measurement methods and equipment inspection.

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CONCLUSIONS

Current laboratory procedures typically rely on synthesis of water chemistry, inhibitor residuals, and heat transfer surfaces in the lab that require extensive investment in controls, evaporative simulation and technical oversight to provide reasonable prediction of field performance. This study demonstrated use and testing of pre-established system water chemistry (concentrated by evaporation) to evaluate temperature effects that simulate given operating cooling water conditions. The study objective was to verify that this procedure can be used to facilitate efficient modeling and prediction of corrosion inhibitor behavior that will meet desired performance and environmental objectives in field applications.

The laboratory study indicates this procedure can provide an excellent means of predicting field corrosion inhibitor performance for given water chemistry and inhibitor conditions. The laboratory procedure and real time on line feedback provide an efficient means for evaluating various metals and temperatures that can guide potential modification of cooling system heat transfer equipment metallurgy, cooling system materials of construction and operating water temperatures. Such prediction will enable economical and performance desirable optimization in existing systems or new construction design.

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Table 1
The Effect of Silica and Temperature
On Corrosion Rates in High TDS Waters

Metals	Inhibitor Solution	Temp (°F)	Temp (°C)	General (mpy)	Max Loc (mpy)
CS 1008	Sea Salt	77	25	-	60
CS 1008	Silica	77	25	0.02	0.1
CS 1008	Silica	130	55	0.1	0.2
CS 1008	Silica	160	71	0.2	0.4
CS 1008	Silica	190	88	0.2	1.9
SS 316 L	Sea Salt	77	25	-	0.04
SS 316 L	Silica	77	25	< 0.0015	< 0.005
SS 316 L	Silica	130	55	< 0.01	< 0.01
SS 316 L	Silica	160	71	< 0.01	< 0.01
SS 316 L	Silica	190	88	< 0.01	0.013
AL 1100	Sea Salt	77	25	-	20
AL 1100	Silica	77	25	< 0.05	< 0.1
AL 1100	Silica	130	55	0.002	0.009
AL 1100	Silica	160	71	< 0.05	0.2
AL 1100	Silica	190	88	< 0.060	0.37
Zn	Sea Salt	77	25	8	80
ZN	Silica	77	25	< 0.05	< 0.01
ZN	Silica	130	55	< 0.2	0.4
ZN	Silica	160	71	-	2.0
CU 110*	Sea Salt	77	25	-	0.4
CU 110	Silica	77	25	< 0.05	< 0.2
CU 110	Silica	130	55	< 1.0	3.0
CU 110	Silica	160	71	-	4.0

*from reference (17)

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Table 2
Cooling Tower No. 1
Makeup & Tower Chemistry Concentration Ratios (CR)

Cooling Tower No. 1 - Makeup & Tower Chemistry Concentration Ratios (CR)			
SAMPLE / TESTS	Tower	Makeup (soft)	CR
Conductivity, μmhos	33,950	412	82.4
pH	10.01	8.23	-
Turbidity, NTU Neat	3	0.08	-
Copper, mg/L Cu	ND	ND	-
Zinc, mg/L	ND	ND	-
Silica, mg/L SiO_2	382	9.5	40.2
Calcium, mg/L $CaCO_3$	16.0	0.20	-
Magnesium, mg/L $CaCO_3$	3.33	0.05	-
Iron, mg/L Fe	ND	ND	-
Aluminum, mg/L Al	ND	ND	-
Phos, mg/L PO_4	ND	ND	-
Chloride, mg/L	6040	80	75.5
Tot. Alkalinity, mg/L	13200	156	84.6
ND = Not Detectable; CR = Concentration Ratio			

Table 3
Cooling Tower No. 2
Makeup & Tower Chemistry Concentration Ratios (CR)

Cooling Tower No. 2 - Makeup & Tower Chemistry Concentration Ratios (CR)			
SAMPLE / TESTS	Tower	Makeup (soft)	CR
Conductivity, μmhos	66,700	829	80
pH	9.61	7.5	-
Turbidity, NTU Neat	4	0.08	-
NTU Filtered (0.45μ)	2	-	-
Zinc, mg/L	ND	ND	-
Silica, mg/L SiO_2	306.4	11	28
Calcium, mg/L $CaCO_3$	21.5	0.20	-
Magnesium, mg/L $CaCO_3$	0.65	0.05	-
Iron, mg/L Fe	ND	ND	-
Aluminum, mg/L Al	ND	ND	-
Phos, mg/L PO_4	ND	ND	-
ND = Not Detectable; CR = Concentration Ratio			

Table 4
Tower Water Turbidity Analyses

Tower Water Turbidity Analyses		
Sample No. 1:	(Turbidity, NTU)	Neat, 4 NTU; Filtered, 2 NTU
Sample No. 2:	(Turbidity, NTU)	Neat, 3 NTU

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Table 5
Microscopically Analyzed / Polarized Light Microscopy

MICROSCOPICAL ANALYSIS - POLARIZED LIGHT MICROSCOPY
DEPOSIT DESIGNATION: Cooling Tower Basin Deposit

% ESTIMATED	CONSTITUENTS
>30	**Amorphous silica**, including assorted diatoms, probably including amorphous magnesium silicate; calcium carbonate (calcite)
1-2	Assorted clay material including feldspar; hydrated iron oxide; carbonaceous material
<1	Silicon dioxide (quartz); assorted plant fibers; unidentified material including possibly aluminum oxide (corundum)

Table 6
Chemical Analysis / Dried Basin Deposit Sample

CHEMICAL ANALYSIS – DRIED SAMPLE
DEPOSIT DESIGNATION: Cooling Tower Basin Deposit

% ESTIMATED	CONSTITUENTS
12.1	CaO
8.5	MgO
5.2	Fe_3O_4
3.7	Fe_2O_3
<0.5	Al_2O_3
13.2	Carbonate, CO_2
51.1	**SiO_2**
5.7	Loss on Ignition

Most probable combinations: **Silica ~54%**, Calcium Carbonate ~32%, Oxides of Iron ~9%, Mg and Al Oxides ~5%.

Table 7
Cooling Tower Corrosion Test Data

CORROSION TEST DATA		
Specimen Type	Mild Steel	Copper
Test location	Tower Loop	Tower loop
Exposure period	62 Days	62 Days
Corrosion Rate (mpy)	0.2	< 0.1

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Species In Equilibrium with Amorphous Silica
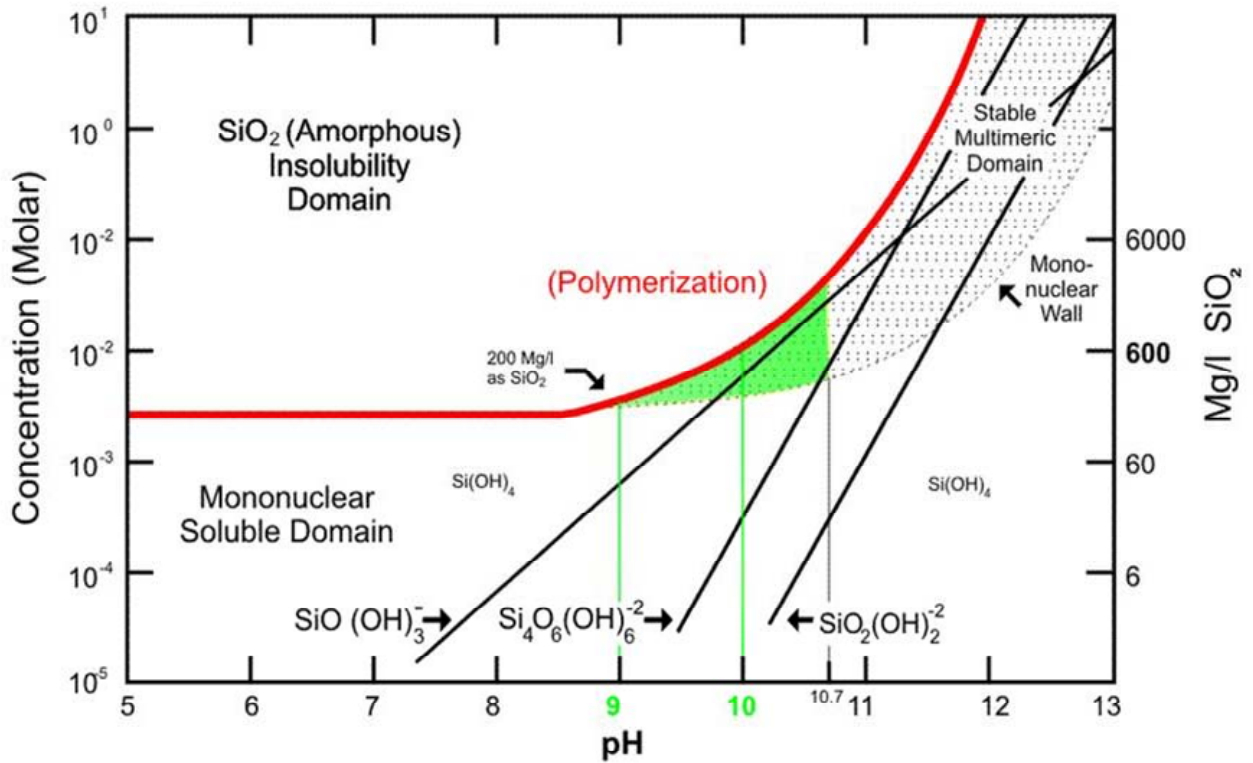
Figure 1 - Relationship between soluble, insoluble (amorphous) and stable multimeric (polymeric) silica species at varying pH and concentration in absence of polyvalent metal ions.
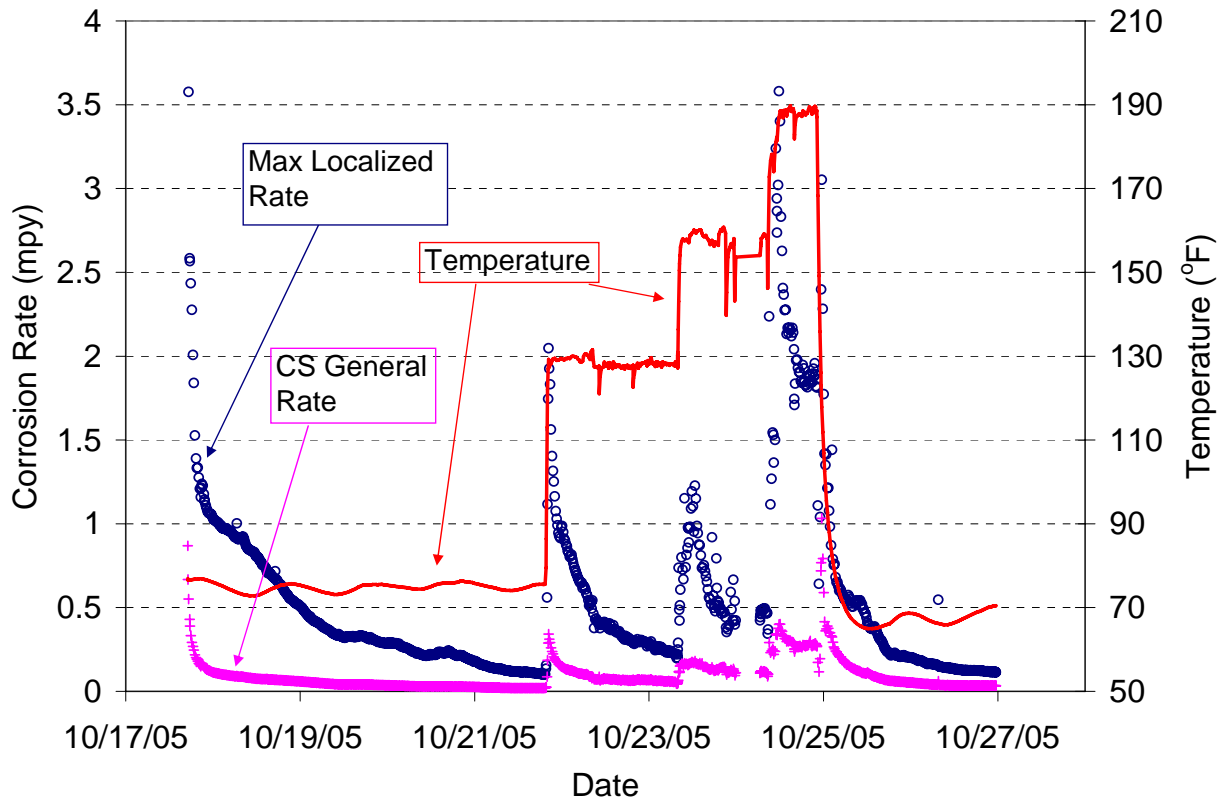
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Figure 2a - **Maximum localized and general corrosion rates of a carbon steel multi-electrode array probe and temperature during the test in high silica water.** (Note: mm/yr= mpy/39.4)
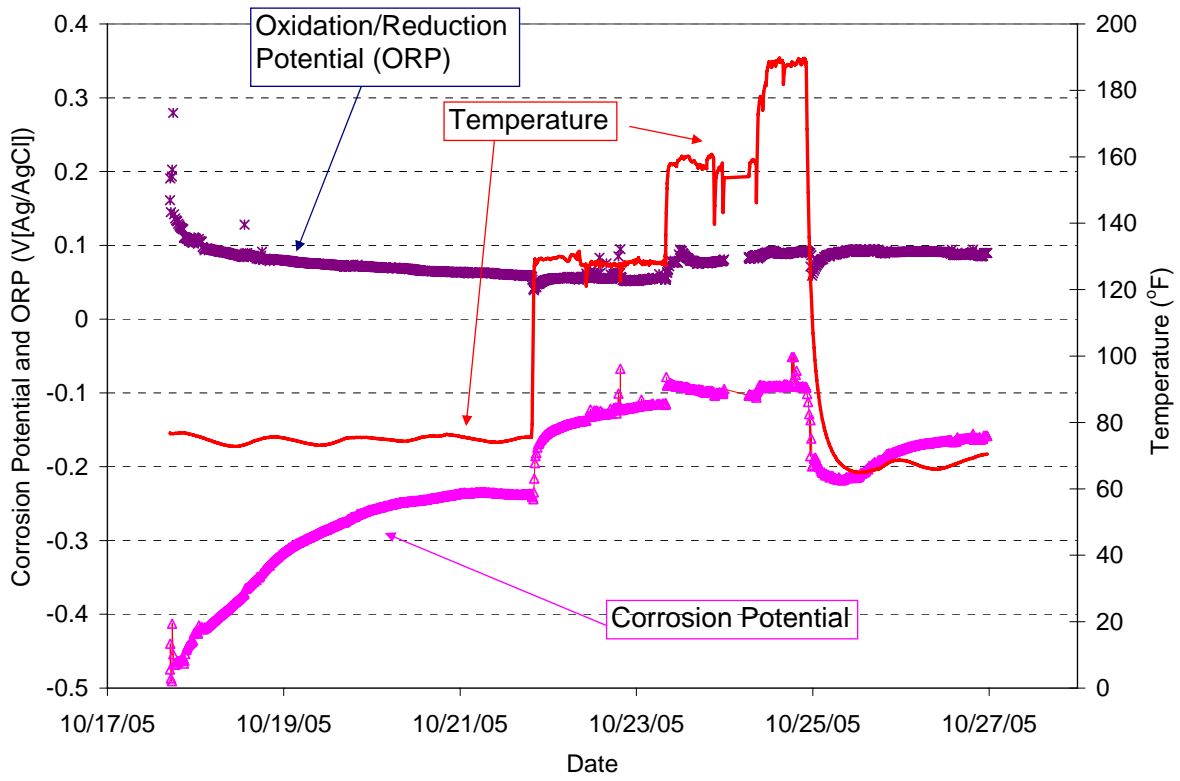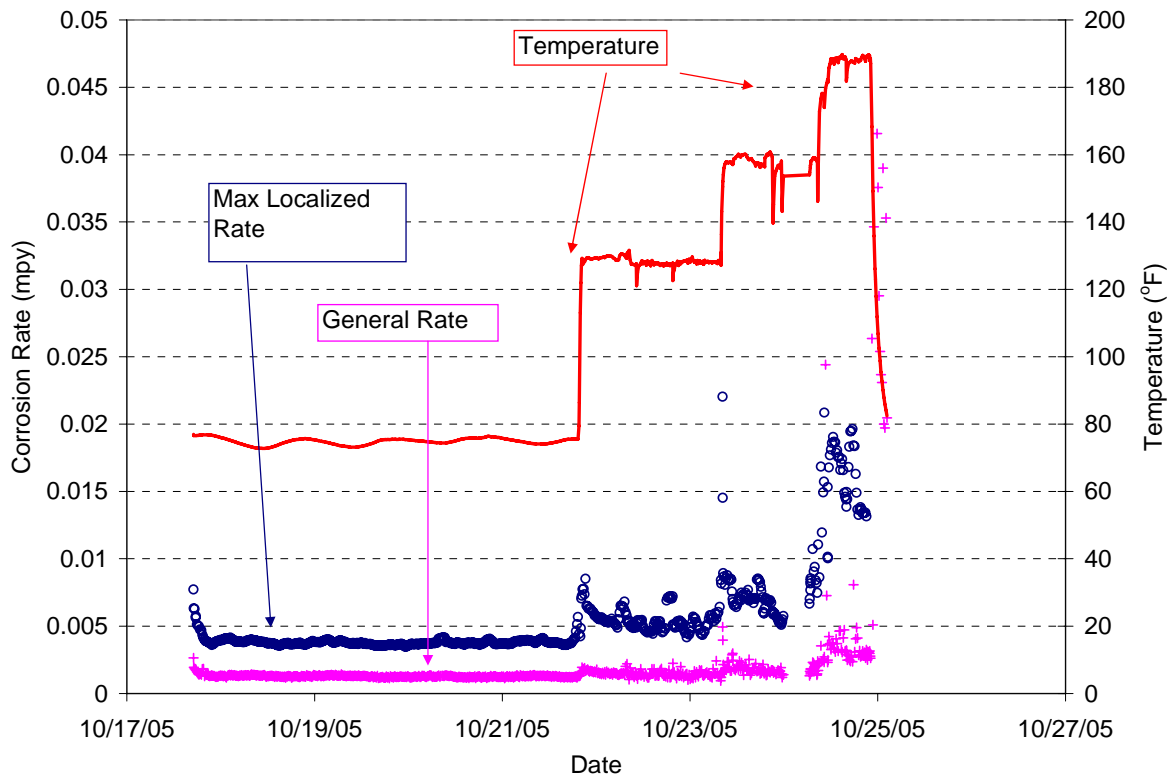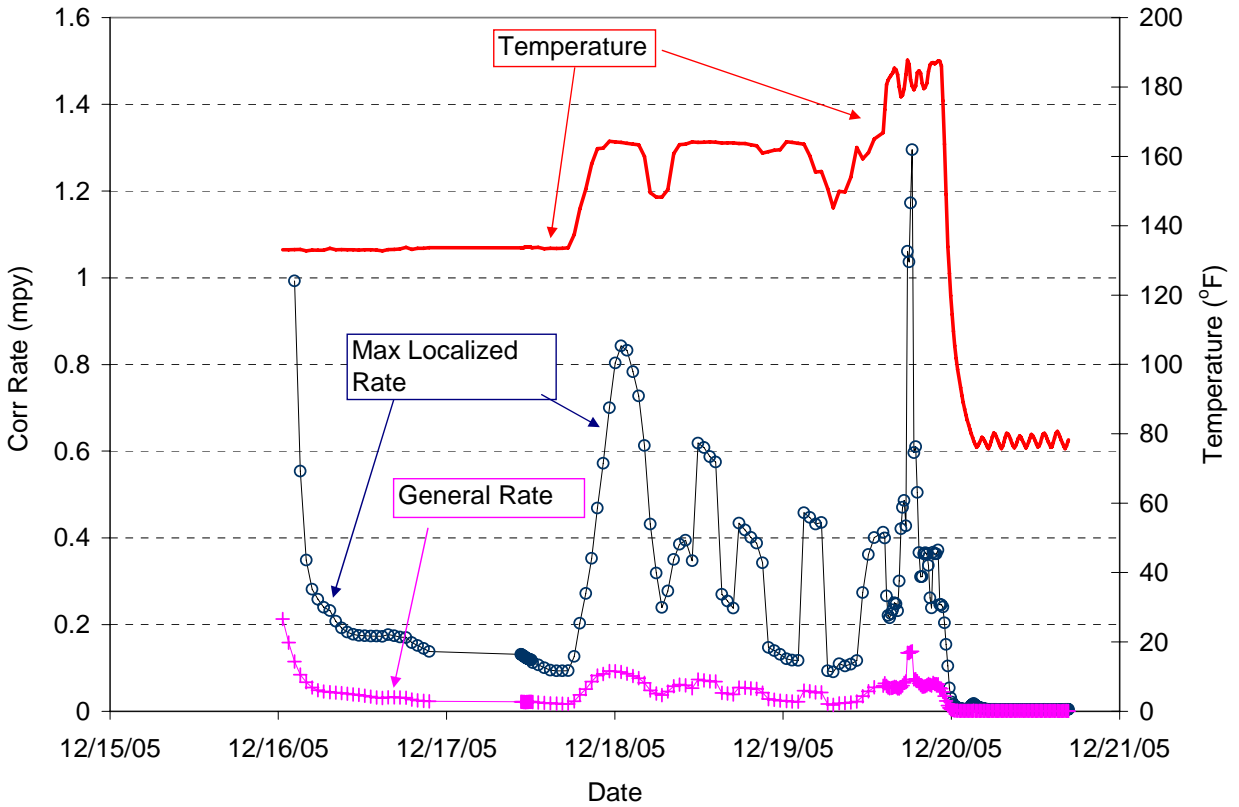
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**Figure 2b -** Oxidation/reduction potential, corrosion potential of carbon steel multi-electrode array probe, and temperature during the test in high silica water.

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Figure 3 - **Maximum localized and general corrosion rates of a Type 316L stainless steel multi-electrode array probe and temperature during the test in high silica water.** (Note: mm/yr= mpy/39.4)

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Figure 4 - **Maximum localized and general corrosion rates of a Type 1100 aluminum multi-electrode array probe and temperature during the test in high silica water.** (Note: mm/yr = mpy/39.4)

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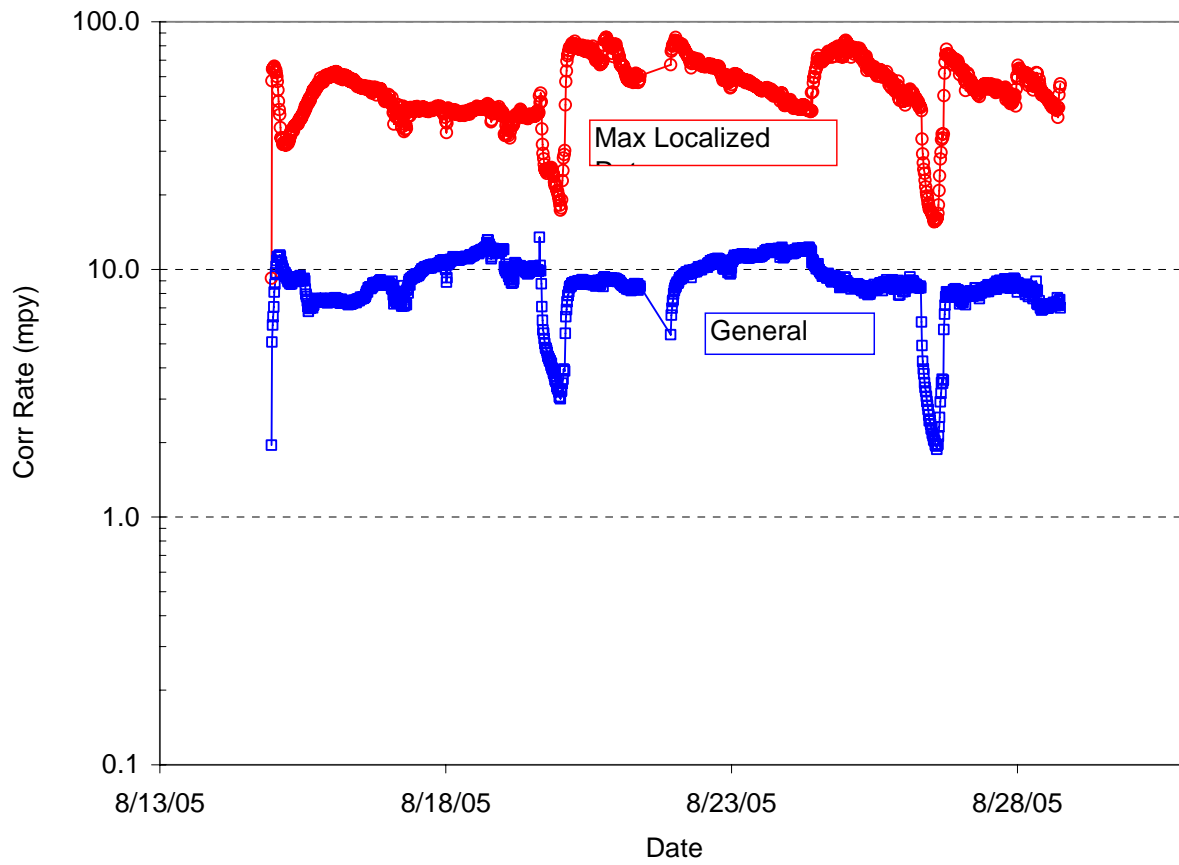
Figure 5 - **Maximum localized and general corrosion rates of a Type 1008 carbon steel multi-electrode array probe in simulated seawater at room temperature.** (Note: mm/yr = mpy/39.4)
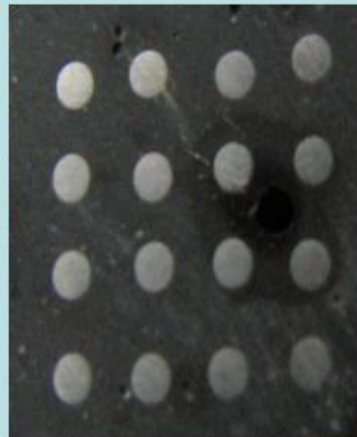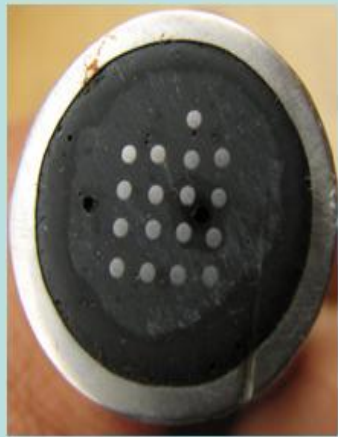
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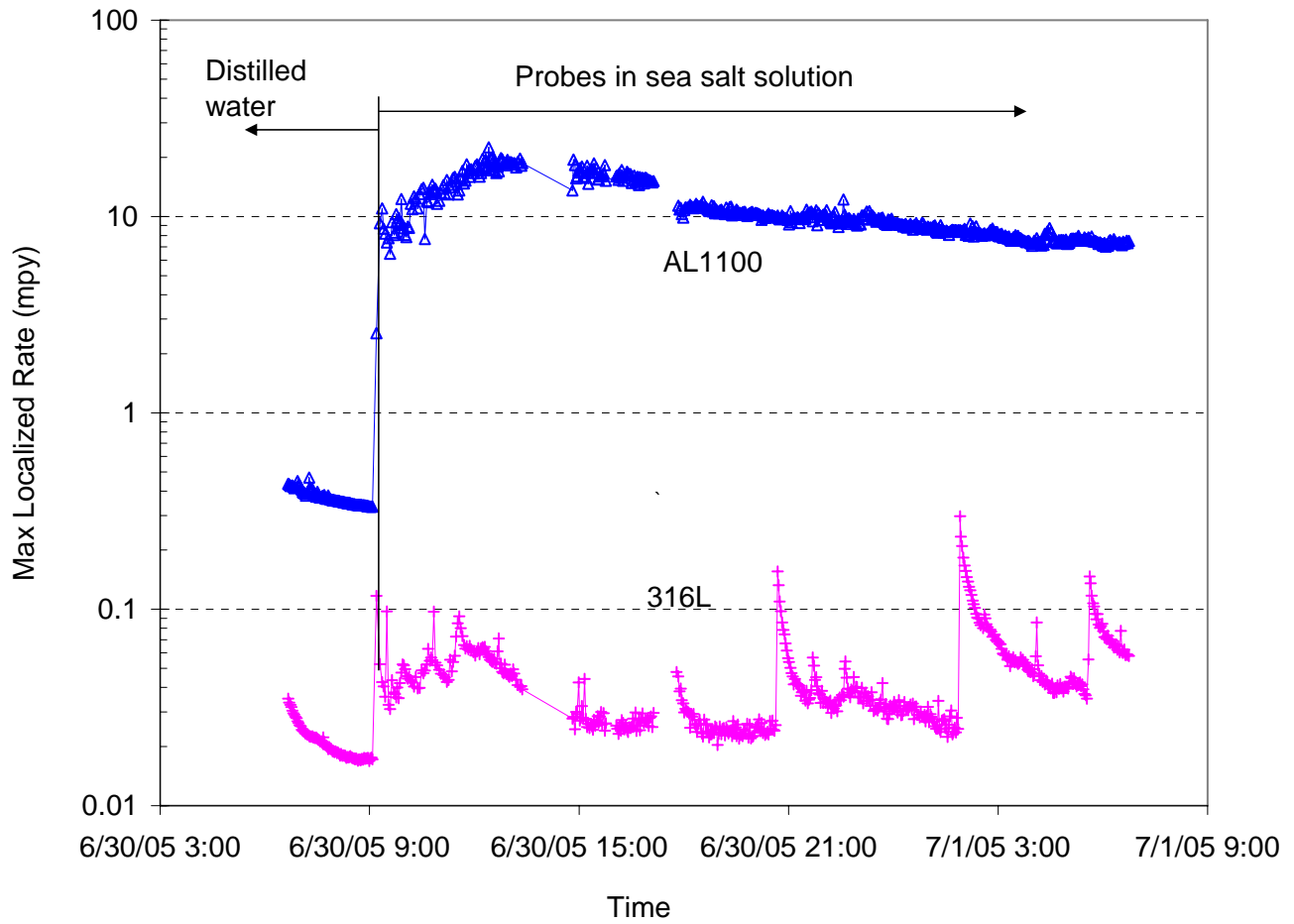
Figure 6 - **Maximum localized corrosion rates of a Type 1100 aluminum and a Type 316L stainless steel multi-electrode array probes in distilled water and simulated seawater at room temperature.** (Note: mm/yr = mpy/39.4)

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Figure 7 - Comparison of Post Test Probe Appearance