

## APPLICATION NOTE

### Cooling Water Quality

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#### Discussion

Good water quality (physical, chemical and biological characteristics) is essential to maintaining the integrity of the SunSource™ sputtering source and its components. Failure to provide high quality cooling water and maintain a well-designed cooling water system will likely result in galvanic corrosion, physical erosion, flow restrictions, reduced heat transfer, attack of solder joints in copper plumbing and transmission of power down the cooling water lines among other issues. Generally, these problems manifest themselves nearly immediately, resulting in the need to replace parts and costly, unnecessary maintenance. Some guidelines follow. **Pay attention to them.** It is strongly recommended that the user consult with qualified, professional experts in water quality analysis and treatment when experiencing problems like galvanic corrosion.

Water quality varies very significantly regionally and internationally. Water from our Boulder, CO plant generally requires little or no treatment. Water from our San Diego, CA facility needs more pH and water hardness control. Please note this and use common sense and some research about your local water conditions before acting on any of the information in this application note. It's meant to be informative, not completely comprehensive.

#### Cooling Water System Materials of Construction

Dissimilar metals and alloys have different electrode potentials. When they come into contact a galvanic couple is set up, one metal acting as an anode and the other as a cathode. Mil Standard 889B and the US Army Missile Command Report RS-TR-67-11 "Practical Galvanic Series" characterize the probability of this occurring. Report RS-TR-67-11 assigns material characteristic rankings from 1 through 92. The metal with the lower number will most likely act as the anode and will corrode preferentially, although the water quality (electrolyte) can change this. The closer two materials are ranked, the less likely galvanic corrosion will occur. Potential metals exposed to the cooling water system in the sputtering source include Brass (46), Ni plated Brass (51), C110 Copper (55), Molybdenum (58) and Stainless Steel (71). In order, these are the magnet assembly cover, water fittings, cathode body, target backing plate(s) and magnet module plate. As a matter of practical consequence, these materials are very closely matched and do not intrinsically promote galvanic corrosion due to having highly dissimilar electrode potentials.

It's **very likely** that galvanic corrosion will occur if materials other than brass, stainless steel, molybdenum, copper, elastomers, appropriate plastics and PTFE are present in the cooling water system. It **WILL** occur in any event if the cooling water has not been properly treated according to the needs of the local conditions. Ignore paying attention to the cooling water system at your peril. Money spent honestly assessing and understanding the quality and condition of your cooling water system is money well-spent. It will improve the reliability of every component that is water-cooled and significantly reduce cost of ownership.

## Common Factors Influencing Water Quality

- Suspended Particulates
- PH
- Hardness
- Microbiological Growth
- Dissolved Air

## Indicators of Poor Water Quality

- “Slime” buildup on molybdenum or copper backing plate
- Black film buildup
- Scale buildup
- Pitting of stainless steel and molybdenum target backing plates
- Pitting of directly water cooled targets
- Physical erosion of the copper cathode body and target backing plate, particularly adjacent to the water fittings
- Nickel plating on brass water fittings degraded and galvanic corrosion of brass occurs
- Pitt corrosion of stainless steel water fittings
- “Dark” buildup within polyethylene water lines
- Inability to apply desired power level to sputtering source (maximum possible power level decreases over time)

## Understanding the Variables

### Galvanic Corrosion



Degradation of magnet module stainless steel plate caused by a combination of physical erosion (center location of water inlet/outlet) and galvanic corrosion (areas just adjacent to the cooling water channels (different electrical potentials resulting from copper cathode body (not shown) and stainless steel magnet module component in direct contact. Galvanic corrosion caused by stainless steel screws (attached to brass top cover (cannot be seen) is evident.

Galvanic corrosion is caused by the process of electrolysis. Simply put, this is the passage of a direct electric current through an ionic substance (cooling water with some amount of dissolved material causing it to be more or less electrically conductive), resulting in a chemical reaction between the anode and cathode (dissimilar materials). A sputtering source connected to a power supply perfectly fits this definition.

From Mil Std-889B: “Coupled dissimilar metals may exhibit different responses in the electrolyte solution because of pH changes. A metal which is the anode in a neutral or acidic solution may become the cathode if the solution is made basic.” In plain English – the pH (combined with hardness) can have dramatically different effects depending upon water quality and hardness.

More from Mil Std-889B: “Oxygen dissolved in the electrolyte solution can act to depolarize the cathode by oxidizing adsorbed hydrogen. In some cases, oxygen may be necessary for oxidation of the anode. Available oxygen and the rate of its diffusion therefore can increase galvanic current.....Agitation or movement of the solution will increase the reaction rate.” In translation – dissolved air (bubbles) in the cooling water can be a problem. By design, the water flow through the source is turbulent to aid in more efficient thermal transfer. Lots more contact with the backing plate surface with a fluid medium rich in oxygen.

### **Water Purity**

**DO NOT** use de-ionized (“DI”), distilled or reverse osmosis water, as they will promote corrosion of the copper body as well as the magnet plate. **Conditioned (treated)** city or well water in recirculation water systems is best.

Reverse osmosis water is so chemically unstable and acidic that in many countries national plumbing codes restrict water that has been filtered by reverse osmosis from being introduced into copper pipes due to its corrosiveness on the copper. It also corrodes all the other metals exposed to it.

DI water, by design, promotes aggressive ion-exchange – thus corrosion. That’s why it’s used in aqueous cleaning systems for semi-conductors and precision optics. It’s expensive to produce and absolutely counterproductive.

### **Hard Water (Mineral Content) and pH**

Water hardness is determined by the concentration of multivalent cations in the water (primarily  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ). In nearly every instance, calcium and magnesium sulfates and/or chlorides cannot be removed by distilling (“boiling”) because they become more soluble as the temperature increases. Water softeners or ion exchange columns easily remove these impurities.

Hard water causes deposits (“scale”) that clog the water lines (typically calcium carbonate, magnesium hydroxide and calcium sulfite). Their appearance is usually “off-white.”

Hard water (presence of ions in the electrolyte – aka cooling water) leads to galvanic corrosion. It’s the precise mixture of minerals dissolved in the water, together with the pH and temperature that determines water hardness. pH is a major consideration with regard to closed-loop recirculation systems with dissimilar metals. Should the pH and corrosion inhibition doses be incorrect in a closed-loop recirculation system, galvanic corrosion will be accelerated.

Water hardness influences pH levels.

## pH Level



Galvanic corrosion of molybdenum target backing plate caused by ion exchange due to poor water quality.

pH is the measure of dissolved hydrogen ions. Pure water has a pH close to 7 (neutral – neither acidic or alkaline). Levels below 7 are acidic and higher levels are alkaline. Levels up to 8 can be used, depending upon the local water conditions. If the water is too acidic, it will corrode metals, cause **etching and corrosion**. If the water is too alkaline, it can cause **scaling**. The necessary pH level is closely tied to the local water hardness conditions.

We recommend the use of a pH Controller and Pump that automatically monitors and maintains this level in closed-loop recirculation systems when the water levels are replenished. Otherwise, cooling water quality will degrade over time.

## Particulates

Physical erosion caused by suspended particulates and galvanic corrosion (“slime”) of molybdenum backing plate due to acidic pH



Particles within the 0.5 to 2.0 (or larger) micron size can have a “sandblasting” effect. 1 micron filters (at a minimum) should be installed on the water inlet lines to eliminate these particles. **The filters need to be maintained (!)** for them to remain effective.

In systems with significant amounts of buildup, it may be necessary to first flush the system with polymer solutions specific to the corrosion products present in the system prior to filling it with properly treated water. Flushing the system in this manner helps precipitate material in solution so that it can be filtered out and removed. This process may have to be repeated several times.

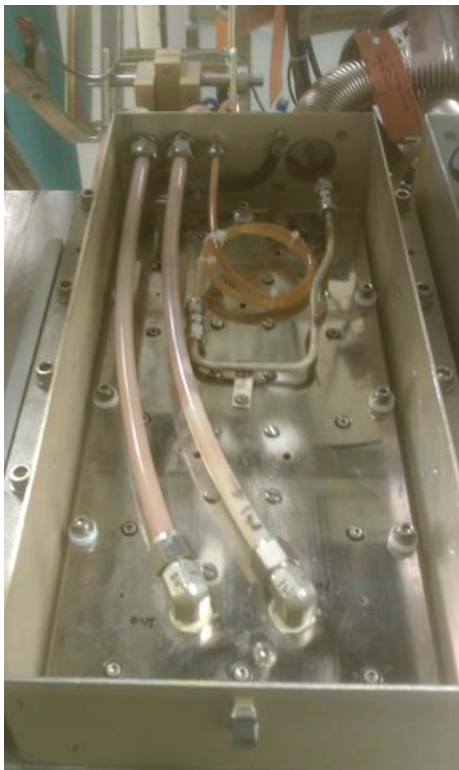
## Air Bubbles



The effect of dissolved oxygen (“air bubbles”) has been described above in “Galvanic Corrosion.” **Additionally, air bubbles present in the cooling water can have the same “sandblasting” effect that physical particles induce.**

Physical erosion in copper cathode body caused by suspended particulates and/or air bubbles in cooling water system

## Microbiological “Stuff”



The presence of biological growth (“biofilm”) will result in undesired chemical reactions and likely the promotion of unwanted galvanic corrosion. It’s worse than just having “green slime” in the cooling water system.

Biofilms act as thermal insulators, substantially reducing cooling efficiency and heat transfer.

Biofilm usually results in a substantial corrosion rate increase due to formation of anaerobic areas under the biofilm. This creates galvanic corrosion and forms metabolic products such as hydrogen sulfide which attack the metals in the cooling water system.

A formalized biocide treatment program should be implemented.

“Green Slime” buildup in old MRC Sputtering System Cooling Lines. They should be white opaque. Power is being conducted down the cooling water lines resulting in lower applied power levels to the sputtering source and increased corrosion of all the metal components in the entire cooling water system.



## Recommended Additives

Azoles are ringed organic molecules that are used as corrosion inhibitors for copper in recirculating cooling water systems. Azoles bond with copper ions at the metal surface to form a protective layer that inhibits oxidation. They also work to reduce soluble copper in the cooling water. We recommend the use of **halogen resistant** azoles (minimum 10 ppm for copper and brass protection). Halogens (commonly used chlorine and more generally recommended bromine) degrade the effectiveness of azoles, reducing their effectiveness in preventing corrosion.

The silica level should be kept at a minimum of 30 ppm to protect the molybdenum and stainless steel parts.

Both of these treatments form protective layers on the surface of the affected parts. We recommend the use of water treatments with the appropriate combination of biocide and corrosion inhibitor for the local water conditions.

The water treatment(s) should be polymer-free. They absorb many times their size in water and when present in sufficient concentrations can restrict water flow.

A pH buffer monitoring and treatment system is strongly recommended.

Avoid ethylene glycol based additives (“Dowtherm”, etc.) due to the possibility of water contamination of the vacuum system. Practically speaking, this contamination is impossible to remove at a molecular level once the vacuum chamber is contaminated.

## Typical Problems



**Low pH can lead to increased corrosion and deposition from soluble materials precipitating out of solution, potentially restricting water flow and heat transfer.**



**Pit corrosion of directly water cooled 6061 Al target and re-deposited material from corrosion of brass from magnet module assembly**



**Zinc plating on steel water fitting acts as sacrificial anode when exposed to untreated, water with improper pH-water hardness balance. Without proper water treatment, removed from other surfaces (cathode body) will likely redeposit on exposed steel, increasing galvanic corrosion of the water fitting.**



**Re-deposited corrosion byproducts shown wiped away along top edge and corners of molybdenum target backing plate. Note significant pit corrosion adjacent to o-ring sealing surface, potentially compromising it's integrity.**

## COOLING WATER RECOMMENDATIONS

Water Hardness (Measures Primarily Calcium & Magnesium Content)	Maximum pH Value (Allowable Values Vary According to Water Hardness)
8° dH / 142 ppm – “Hard Water”	7.8
6° dH / 107 ppm – “Moderately Hard Water”	8.1
4° dH / 71 ppm – “Soft Water”	8.3
Common Chemical and Biological Parameters (Not Intended to be All-Inclusive – Just the Main Culprits Nearly Universally Encountered)	Maximum Limits
Carbonic Acid	No detectable amounts allowed
Ammonia	No detectable amounts allowed
Nitrite	< 1mg/l (< 1 ppm)
Iron	< 0.3 mg/l (< 3 ppm)
Manganese	< 0.05 mg/l (< 0.05 ppm)
Sulfate	< 250 mg/l (< 250 ppm)
Chloride	< 250 mg/l (< 250 ppm)
Chemical Oxygen Demand (indication of organic components in the water)	< 40 mg/l (< 40.04 ppm)
Ozone	No detectable amounts allowed
Hydrogen Peroxide (Organic byproduct of oxidation metabolism)	No detectable amounts allowed
Peracids (indication of organic activity)	No detectable amounts allowed
Aerobic Bacteria	< 1000 cells/ml
Anaerobic Bacteria (film forming – leads to under deposit corrosion and general system fouling)	< 50 cells/ml
Sulfate Reducing Agents	No detectable amounts allowed
Additives (Consult Local, Professional Water Treatment Firm!)	
Polymer-Free Inhibitor Containing Silica & Halogen Resistant Azole  (Chlorine and Bromine used in halogen-based biocides attack the protective films formed by azoles, resulting in a loss of corrosion protection)	Silica > 30 ppm minimum (steel & molybdenum protection).  Azole > 10 ppm minimum (brass & copper protection)
Biocide (must be used only in conjunction with above referenced polymer-free inhibitor – NOT alone)	Free Halogen < 0.15 mg/l (< 0.15 ppm)

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