Azole Testing: It’s in the best interest of anyone who operates a chiller plant.

Overview
Azoles are used by most water treatment suppliers in their formulations of corrosion inhibitor blends designed for open condenser water systems, such as chiller cooling. It is well known that azoles are the popular choice for protecting yellow metals in such systems, but they also protect mild steel by virtue of their ability to chelate soluble copper. Chelation simply means that when soluble copper and azole react together, the end product does not precipitate as an insoluble copper-azole complex – it remains soluble and able to be removed from the system by bleed. Without chelation, soluble copper seeks a galvanic “home” and mild steel is plentiful and available! The copper readily films on the steel creating a galvanic cell, and the mild steel becomes the “sacrificial anode” leading to rapid iron wastage both as general metal loss and more seriously, pitting at an accelerated rate.

Why is azole testing so important?
Most copper bearing alloys are located at the heart of a chiller plant, in the chiller itself. Corrosion coupon results are only a relative indication of “water chemistry health”, because they do not take into account the condenser tube bundle skin temperatures. Premature chiller replacement is a very costly proposition and azole testing can ensure that this equipment is adequately protected.

What assurances do you have when it comes to protecting copper tube bundles?
Well, most suppliers generally formulate cooling system inhibitors with azole. When fed correctly at the stoichiometric dose rate, they are designed to supply enough azole to the recirculating water to protect all copper metallurgy in the system. Copper is relatively corrosion resistant (Melbourne water is slightly corrosive at street level) and a little azole goes a long way. However, chelation of soluble copper requires a reserve of azole to be available over and above base metal protection!

When should you test for azole?
You should test for azole in open recirculating cooling systems which include chillers. Never assume that a particular product contains the proper amount of azole even for the yellow metal inhibition required, let alone for chelation of soluble copper!
Please note that a lot of suppliers have “one size fits all” products when it comes to a geographic area. Special plant problems, like high mild steel corrosion rates including pitting especially, need “designer chemistry” not commodity product approaches.

The Do’s and Don’ts of copper AND mild steel corrosion control:
- Don’t assume that enough azole is in a particular formulation to meet every condition.
- Don’t rely on copper corrosion coupons as an indication that results are good.
- Do run copper tests and identify the demand for azole.
- Do make sure azole residuals in the recirculating water exceed base metal protection demand by 0.5 – to 1.5 mg/l.
- Do add on at least another 2.0 mg/l for chelation.
- Do routinely test for confirmation of the required residual for both base metal and chelation requirement.
- Do feed supplemental azole as needed.
- Don’t use azole containing inhibitor to provide the chelate demand – pH excursions may result.
- Do use ORP to control oxidizing biocides. Excess oxidant can destroy protective azole films.
- Do use special precautions when wet storing copper tube bundles.
More Information on Protection of Copper and Copper Containing Alloys

Most steel inhibitors have some positive inhibiting effects on copper-base alloys. However, system upsets, such as pH excursions and process leaks, can dissolve copper into the cooling water where it can interfere with steel protection. *Copper concentrations as low as 0.1 mg/L can deposit on steel surfaces, accelerating localized attack.* Ancillary inhibitors, used at specified dosages, can be very effective in controlling corrosion of copper-base alloys and preventing galvanic deposition or dissolved copper onto ferrous metals.

Three specific azole inhibitors in popular use are:

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<th>INHIBITOR TYPE</th>
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<th>CHEMISTRY</th>
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<tr>
<td>Mercaptobenzothiazole</td>
<td>MBT</td>
<td>Forms an adherent protective film on metal oxide surfaces. The inhibitor reacts with the metal surface forming a chemisorbed barrier. The initial corrosion product of Cu(^+) ions reacts with the MBT molecule to form a 3-dimensional complex of Cu (1) MBT. Rate of film growth is rapid reaching a self-limiting thickness within a short space of time. MBT is susceptible to oxidizing agents (air, chlorine, ultraviolet light from sunlight) which can degrade the molecule into a sulphide having no inhibiting properties. This only occurs with MBT in solution, not the complex on the metal surface. This inhibitor should not be used in systems containing continuous chlorination. MBT functions by effectively inhibiting Cupric ions from depositing onto more active metals such as steel and aluminum, by reacting in a 1:2 molar ratio. In the absence of complicating factors, such as copper concentrations exceeding 0.1 mg/L in the cooling water or a chlorine residual, the concentrations of MBT required for good copper inhibition is approximately 4 mg/L.</td>
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<td>Benzotriazole</td>
<td>BZT</td>
<td>BZT and TT function similarly as MBT. Azoles are classified as cathodic inhibitors because they absorb at the cathodes interfering with the oxygen reduction reaction. These molecules are more resistant to oxidation than MBT. In the presence of chlorine, 1-chlorotolytriazole is formed which has minimal inhibiting properties. However, on dissipation of residual chlorine, the chloro-compounds revert back to the active azole. Chlorination does not affect the integrity of the complex on the metal surface. The azoles can deactivate soluble copper in cooling water systems and prevent its deposition onto steel and other active metals. A 2:1 molar ratio has been found to be effective.</td>
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<td>Tolytriazole</td>
<td>TT</td>
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**Azole Application**

The concentration of azoles necessary for copper inhibition is approximately 1 to 2 mg/L in the absence of any residual chlorine. The optimum practice is to pretreat the system with 2 to 3 times normal concentration for 1 to 2 days, then control at the maintenance dosage. Under chlorination conditions, the azole should be fed after the dissipation of residual chlorine. If continuous chlorination is practiced and cannot be changed to intermittent practice, the level of treatment should be increased to **4 to 5 mg/L**. In the presence of continuous chlorination, overall copper corrosion protection will be less than with intermittent chlorination.

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Steve Powell is a Chemical Engineer specializing in industrial water treatment processes. He has held senior research and sales/marketing positions in multinational water treatment and speciality chemical companies operating within Australian and he brings considerable practical experience to address clients risk management security. Based in Melbourne he is currently Independent Monitoring Consultants (IMC) Victoria/South Australia Account Manager.

Steve says, "IMC is aware of all of the impairments to quality service and servicing. As a privately owned Australian company providing quality services since 1992, IMC was the first to introduce fully independent sampling and testing to help clients manage the control of Legionella, system corrosion, Risk Management, Audits, indoor air quality, OH&S and duty of care obligations. These securities are all important to international hotel chains, major shopping centres, hospitals, and key Property Managers and Owners. IMC was the first major microbiological laboratory in Malaysia. It was also the first to be accredited by Standards Malaysia for both sampling and testing of environmental waters, indoor air quality, and food. IMC technical expertise and proficiency has been perfected during the past 20 years through our national and international experience. With a combined total of more than 150 years of water treatment knowledge and experience in our senior staff IMC is the perfect partner."