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Passivation in cooling water circuits

Passivation—the formation of a corrosion-resistant oxide on a clean metal surface—is the key to optimizing system reliability on the waterside of heat exchangers. Most plant personnel are aware of the risks of corrosion. However, they are not aware of the importance of passivation.

Passivation primer. During passivation, metal oxides convert from a porous, nonprotective form to a tight, adherent, protective form. For carbon steel, the nonprotective oxide, iron hydroxide (FeOH) converts to a moderately protective oxide, hematite (Fe_2O_3) to the most protective form, magnetite (Fe_3O_4). Under the right conditions, this conversion reaction is spontaneous. But it is not necessarily a fast reaction. Optimizing the kinetics of the passivation reaction requires optimizing water chemistry and operating conditions.

The optimal conditions for carbon steel passivation are: low dissolved oxygen concentration in the water, high temperature and high pH. In cooling water circuits, passivation is not spontaneous because cooling water is oxygenated ($7 \text{ mg/l} < O_2 < 13 \text{ mg/l}$) at ambient or moderate temperatures—70°F–100°F (15°C–38°C)—and neutral to mildly alkaline pH ($6.5 < \text{pH} < 9$). High-alloy steels, admiralty and other copper alloys, form highly protective oxides more rapidly than carbon steel and under a wider range of conditions. However, high concentrations of chlorides and sulfates in the cooling water will compromise the passivation process, thus resulting in an oxide that is not protective against corrosion.

Passivation decisions. Passivation of newly fabricated carbon steel heat exchangers is so important that it should be a non-negotiable part of start-up. Plants may choose to conduct passivation procedures by isolating a single heat exchanger or circulating chemicals in the entire cooling water circuit, depending on the number of new heat exchangers or the number of new tubes.

Pre-cleaning procedures are also non-negotiable since passivation procedures are only effective on clean metal surfaces. New heat exchangers may have residual metal-working fluids from the manufacturing process or an oil-based coating to protect against corrosion during shipping and storage. Passivation of cooling water circuits following a turnaround will reduce the risk of under-deposit corrosion from solubalized iron oxides formed during idle periods due to stagnant water and/or exposure of water-wetted carbon steel surfaces to air.

Does passivation matter? A refinery installed two new carbon steel heat exchangers in a key unit. The plant had wrapped the heat exchangers in plastic and stored them outside, in the laydown yard, for one year. Plant personnel installed and commissioned these two exchangers without implementing any pre-cleaning or pre-passivation procedures. The cooling water exceeded the recommended maximum concentration of iron during start up. Both exchangers failed within one year of commissioning. The root cause for the failure was under-deposit corrosion from deposits that formed from in-situ corrosion during commissioning.

Procedures. There are several key issues for the design of pre-cleaning and passivation procedures:

- Most plants hire a contractor to conduct the pre-cleaning and passivation processes. Yet, plant personnel are responsible for confirming the optimal procedures.
- Heating the chemical solutions will accelerate the cleaning and passivation processes, reducing the project time by as much as 50%. However, there should be minimal or no heat load from the process until the passivation process is complete.
- Plant personnel may choose to treat the spent cleaning solutions in their wastewater plant to avoid offsite disposal costs.
- Plant personnel should never *reuse* spent pre-cleaning solution for the passivation process. There is a large risk of re-deposition of the contaminants removed during the pre-cleaning process.
- Passivation and commissioning should immediately follow the pre-cleaning process to eliminate any corrosion that will occur on clean steel surfaces in idled, drained or stagnant cooling water systems.
- **Under no circumstances should plant personnel initiate passivation procedures until the iron concentration is less than 3 ppm.** High iron concentrations indicate inadequate flushing and/or insufficient control of corrosion.
- Typical control parameters for pre-cleaning are: pH, temperature, foam and soluble iron concentration[1]
- Storage of new heat exchangers requires special considerations to minimize in-situ corrosion.

In summary. Proper pre-cleaning and passivation procedures do increase the reliability of heat exchangers and should be a mandatory part of start up procedures. Ideally, plants will create and validate internal procedures for pre-cleaning and passivation procedures based on industry standards, experience and site-specific limitations. **HP**

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