Water Treatment

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Investing in chemical cooling water treatment

Precipitation fouling and corrosion create major problems in cooling systems within the process industry. To prevent unexpected shutdowns and conserve water, Assistant Professor Kostas D. Demadis of the Department of Chemistry at University of Crete presents a strategic analysis of the entire chemical treatment process, starting from proper selection of the treatment program, to proper application, to effective monitoring and maintenance of system performance.

ndustrial water systems face several challenges related to formation of sparingly soluble electrolytes, corrosion and biofouling (Cowan and Weintritt, 1976). Cooling water systems, reverse osmosis installations, boiler water systems, oilfield wells, all serving important industries (power generation, municipal water, steam generation, oil and gas production) may suffer from a multitude of water-originating problems.

Utility plants, manufacturing facilities, airconditioning systems are some applications that use "hot" processes for their operations. These processes have to be cooled by using water as the universal cooling medium because it is cost effective and has a high heat capacity (Kemmer, 1988). After cooling water comes in contact with the "hot" process, it needs to be re-cooled for reuse. This cooling is achieved by evaporation in the cooling tower (Tanis, 1987). The end result is concentration of all species found in water until reaching a critical point of "scaling," leading to precipitation, and ultimately to deposition of mineral salts. Species usually associated with these deposits, depending on water chemistry, are calcium carbonate, calcium phosphate(s), silica/metal silicates, etc. Such undesirable deposition issues can be avoided with careful application of chemical water treatment technologies (Figure 1), which can be symbolized with a triangle. The sides of this triangle represent three strategic approaches: (a) scale/deposit inhibition; (b) corrosion control; and (c) microbiological fouling prevention (Demadis, 2003). Prevention of scale formation is greatly preferred by industrial water users to the more costly (and often potentially

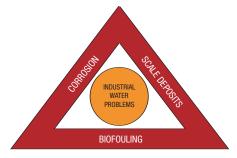


Figure 1. The water treatment "triangle".

hazardous) chemical cleaning (Frenier, 2001) of the adhered scale after deposition occurs. Common examples of scales that require laborious mechanical and potentially dangerous cleaning are silica and silicate salts. Phosphorus-containing compounds and polymeric additives are integral parts of water treatment programs (Demadis, 2004). They function as scale inhibitors by adsorbing onto crystal surfaces of insoluble salts and prevent further crystal growth.

Investing wisely on a chemical water treatment program

In most water treatment programs, other components are often formulated with scale inhibitors. For example, "yellow metal" (copper, admiralty brass) corrosion inhibitors, dispersant polymers and tracers can be components of the same treatment, whereas biocides for microbial control, such as chlorine or bromine, are usually fed separately.

Many factors must be taken into account during the chemical treatment program selection process. Among the most critical ones are the following:

(a) *Water chemistry*. Before selecting a program one needs to know the species present in the "make-up" (or raw) water and the process (recirculating) water. Increasing economical pressures dictate use of low quality water for cooling purposes. This poses severe limitations with regards to achieving high cycles of concentration because fouling becomes a serious concern. Presence of other species in water will dictate the treatment approach. For example, high chloride and sulfate content increase the risk for localized corrosion, therefore measures have to be taken toward protecting the system from corrosion than from deposition.

(b) *Water tendency*. In general, waters can be either corrosive or scaling. "Soft" make-up waters have virtually no scaling potential due to low concentrations of scaling ions, but can be extremely corrosive. "Hard" waters on the other hand pose a scaling/fouling risk that requires treatment. The type of make-up water will dictate the final treatment approach. (c) *Environmental concerns*. Increasing environmental concerns and discharge limitations



have imposed additional challenges in treating process waters. Therefore, the discovery and successful application of chemical additives that have mild environmental impact have been the focus of several researchers (Demadis, 2005).

(d) *Cost considerations.* Chemicals that constitute multi-component treatment programs have a cost associated with them. There are cost-effective programs and more costly ones. Budgetary concerns rather than technological considerations often are responsible for program selection. Either way, one should taking into account the capabilities, limitations, and costs of a variety of chemical treatment programs in order to select the most appropriate that fits the needs of the particular operation.

The success of a chemical treatment program depends largely on whether it is properly applied so it fits the needs of the individual water system.

(a) *Target cycles of concentration*. Certain areas have challenging make-up waters; others have very high water costs. Make-up water quality and cost will dictate the concentration cycles.
(b) *Definition of need for inhibitor dosage*. Chemical wastage can be avoided when system operators have knowledge on water chemistry and requirements for actives levels. Underfeeding may cause severe scaling and/or corrosion phenomena, and overfeeding wastes chemicals.

(c) *Mechanical engineering integrity*. Chemical feed pumps have to be properly functioning at all times, serviced frequently and checked periodically. This ensures that chemical feed is uninterrupted and at proper levels.

To ensure satisfactory performance of the treatment program, operators are required to perform several physicochemical measurements either in the field or in the laboratory to provide proper monitoring. These are useful indicators on whether a certain >>

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CHEMICAL WATER TREATMENT PROGRAM SELECTION PROCESS

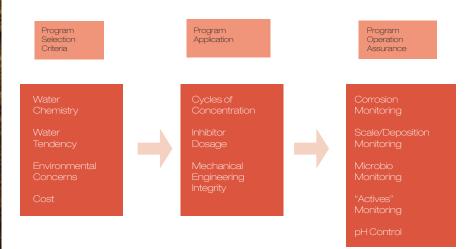


Figure 2. Chemical water treatment: from program selection to application to assurance.

component of the program is failing, or whether the program is performing according to initial goals.

Corrosion monitoring can be done on-line with commercially available corrosion monitors. An important point is that these need to be maintained properly, calibrated frequently and the measurements have to be complemented by observations based on corrosion coupons. Monitoring of underdeposit corrosion is vital in systems with history of severe deposition problems.

Scale monitoring can be accomplished by use of properly calibrated and functioning on-line instruments. Water chemistry tests performed on-site also offer great benefits. By monitoring ▲Cycles (Cycles based on a non-scaling ion – Cycles based on scaling ion, eg. calcium), loss of soluble species can be determined. Theoretically, ▲Cycles should be zero. A small increase is a warning sign, whereas a "split" of 1 or higher indicates active precipitation and deposition.

Microbiological growth monitoring in bulk water may be useful, however it can also be deceiving, since it does not take into account biofilm growth, a critical phenomenon that can have direct effects on heat transfer. Usually maintenance of a low biocide residual that is monitored carefully will ensure process waters free of major problems.

Monitoring of critical chemical treatment actives is necessary, ensures performance, and can indicate a problem in its genesis (Hale et al., 1999). Water treatment chemicals can degrade over time, or be depleted due to precipitation. Occasionally, scale inhibitors precipitate as calcium salts because of overfeeding or because of high hardness. Dispersant polymers can be consumed due to adsorption onto surfaces and oxidizing biocides to oxidize treatment chemicals.

Control of pH by use of acid is not uncommon. Failure to control pH can result in pH upsets. These can cause corrosion rates to dramatically increase, thus endangering the integrity of the system.

Monitoring the efficiency of a heat exchanger ensures proper system performance. If the efficiency is lower than specified, then cleaning (chemical or mechanical) may be needed to restore system performance.

The above strategic and holistic approach is represented schematically in Figure 2.

Author's Note

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References

Cowan, J.C., Weintritt, D.J., 1976, Water-Formed Scale Deposits, Gulf Publishing Co., Houston, TX, U.S.A. Demadis, K.D. and Katarachia, S.D. Metal-Phosphonate Chemistry: Preparation, Crystal Structure of Calcium-Amino-tris-Methylene Phosphonate and CaCO3 Inhibition, Phosphorus, Sulfur, Silicon, 2004, 179, 627. Demadis, K.D., Combating Heat Exchanger Fouling and Corrosion Phenomena in Process Waters, in Compact Heat Exchangers and Enhancement Technology for the Process Industries; Editor: Shah, R.K, Begell House Inc.; New York: 2003, p. 483.

Demadis, K.D. et al., Inorganic Foulants in Membrane Systems: Chemical Control Strategies and the Contribution of "Green Chemistry", Desalination 2005, 179, 281.

Frenier, W.W., Technology for Chemical Cleaning of Industrial Equipment, NACE Press, Houston, Texas, 2001. Hale, E.R., Hoots, J.E., Nicolich, S.N., 1999, Tracers track down water problems, Power Engineering, September, p. 21.

Kemmer, F.N., 1988, The Nalco Water Handbook, McGraw-Hill Company, New York. Tanis, J.N., 1987, Procedures of Industrial Water Treatment, Ltan Inc., Ridgefield, CT.