COMBATING HEAT EXCHANGER FOULING AND CORROSION PHENOMENA IN PROCESS WATERS

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ABSTRACT

Fouling is a major barrier for wide use of Compact Heat Exchangers (CHEs) in the process industry. Corrosion processes taking in process water are of critical importance as well. Localized corrosion, for example, is one of the most catastrophic ones, since it can render metal surfaces on the heat exchanger completely useless. Prevention of scale deposits can benefit industrial water users by eliminating (or at least by minimizing) unexpected production shut-downs and by offering substantial savings to the end user through water conservation (especially in arid areas with high water costs). This paper focuses on crystallization fouling and deposition (especially by calcium carbonate) and its mitigation by using various chemical water treatment approaches. Treatment approaches are also presented to fouling and corrosion problems with emphasis to enhanced heat exchanger tubes (internally corrugated), where this problem is commonly observed. A detailed analysis is given on the entire chemical treatment process, starting from proper selection of the treatment program, to proper application, to effective monitoring and maintenance of system performance.

INTRODUCTION

Industrial water systems face several challenges related to formation of sparingly soluble electrolytes (Cowan and Weintritt, 1976). Cooling water systems, in particular, may suffer from a multitude of problems. Utility plants, manufacturing facilities, air-conditioning systems are some applications that use "hot" processes for their operations. These processes have to be cooled. Water is 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). A simplified schematic of the heat exchange process is shown in Figure 1. 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*.

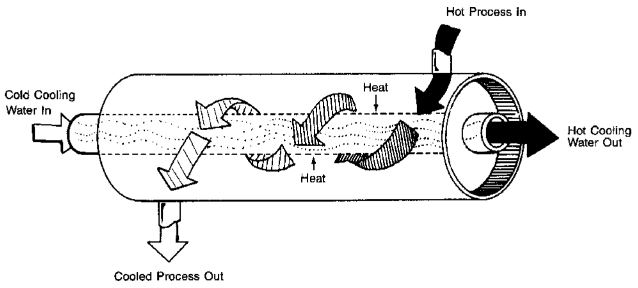

Figure 1. Schematic drawing of the heat exchange process.

Such undesirable deposition issues can be avoided with careful application of chemical water treatment techniques, Figure 2, which can be symbolized with a triangle. The sides of this triangle are scale inhibition, corrosion inhibition and prevention of microbiological fouling (Demadis *et al*., 2000).

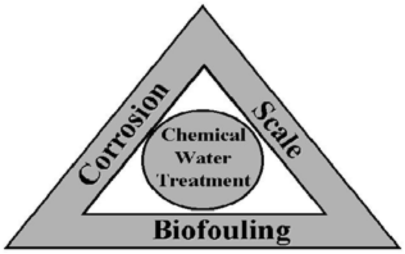

Figure 2. Schematic view of the water treatment "triangle".

Prevention of scale formation is greatly preferred by industrial water users to the more costly (and often potentially hazardous) chemical cleaning (Frenier, 2001; Panchal *et al*., 2000) of the adhered scale, in the aftermath

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of a scaling event. Classic examples of scales that require laborious mechanical and potentially dangerous cleaning are silica and silicate salts. Phosphorus-containing compounds, usually referred to as organic phosphates or phosphonates, are an integral part of a water treatment program (Amjad, 1995). They function as scale inhibitors by adsorbing onto crystal surfaces of insoluble salts and prevent further crystal growth. Schematic structures of some commercial scale inhibitors are shown in Figure 3.

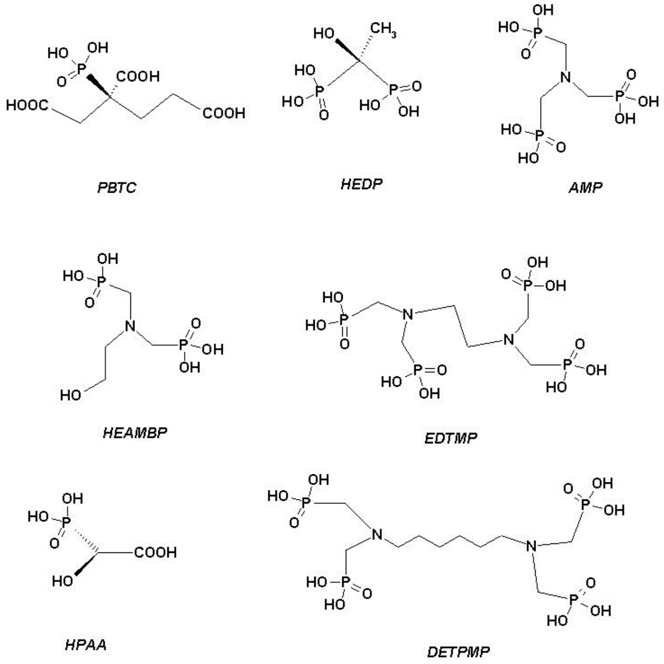


Figure 3. Chemical Structures of some widely used scale inhibitors in their acid forms. The symbol abbreviations are as follows: **PBTC** 2-phosphonobutane-1,2,4-tricarboxylic acid, **HEDP** 1-hydroxyethylidene-1,1-diphosphonic acid, **AMP** amino-*tris*-(methylenephosphonic acid), **HEAMBP** 2-hydroxyethyl-amino-*bis*(methylenephosphonic acid), **EDTMP** ethylene-diamine-*tetrakis*(methylenephosphonic acid), **HPAA** hydroxy-phosphono acetic acid, **DETPMP** hexamethylene-diamine-*tetrakis*(methylenephosphonic acid).

Phosphonate inhibitors usually contain multiple phosphonate groups ($R-PO_3H_2$, R = organic chain), most commonly found in their deprotonated form (pH range of operation 7.0-9.8). These additives perform scale inhibition in minute quantities (parts per million, ppm) and usually work synergistically with dispersant polymers. Aminomethylene phosphonates in particular are used extensively in cooling water treatment programs (Hasson, 1998), oilfied applications (Browning, 1996) and corrosion control (Sastri, 1998). This paper reviews the physicochemical processes involved in fouling and corrosion of heat exchanger surfaces, as well as recommends methodologies to combat such undesirable phenomena. The goal of this report is to update technologists in the water treatment area, both from fundamental (science) and technology (application) perspectives, who seek technical input for systems where the potential of fouling and corrosion presents operational challenges.

EXPERIMENTAL SECTION

Materials

Deionized water was used for all experiments. Materials were obtained from commercial sources. AMP (in acid form, 50 % in water) was obtained from Solutia Inc., $CaCl_2 \cdot 2H_2O$ was from Fischer Scientific. Polymers A and B were proprietary products from Nalco Chemical Company. Polymers **1** and **2** are acrylate/acrylamide/alkylsulfonate terpolymers with different degree of sulfonate groups. **2** has higher number of sulfonate and lower degree of acrylate groups than **2**.

Calcium Carbonate Scale Inhibition Test

Ca^{2+}, Mg^{2+}, and HCO_3^- are expressed as ppm $CaCO_3$, whereas AMP and polymeric additives as ppm actives. Stock solutions of 40,000 ppm of $CaCl_2 \cdot 2H_2O$, $NaHCO_3$ and $MgSO_4 \cdot 7H_2O$ were prepared using de-ionized water. Appropriate amounts of stock solutions were used to achieve final concentrations of Ca^{2+}, Mg^{2+}, and HCO_3^-. In a volumetric flask Ca^{2+}, Mg^{2+} were mixed and then the appropriate amount of inhibitor was added. Finally, the desired amount of $NaHCO_3$ was added and the remaining volume was made up with de-ionized water. Depending on test analysis requirements, the final volume of the test solution was between 100 – 500 mL. The solution was then transferred to an Erlenmeyer flask. The flask was covered and placed in a water bath maintained at 43 ºC under constant stirring. pH 8.8 was maintained by addition 0.1 N NaOH *via* an auto-titrator. After 2 h the flask was removed from the water bath and a sample was filtered through a 0.45 μ filter. Analysis by atomic absorption spectroscopy gave the concentration of "soluble Ca^{2+}". The remaining solution was covered and stored *unstirred* at room temperature. A second set of samples was withdrawn from just below the surface, 24 h after pH was first raised to 8.8. The analytical results of these unfiltered samples yielded "dispersed Ca^{2+}" concentration.

SCALE FORMATION AND DEPOSITION

Mechanism of Scale Formation

Scale usually refers to an intimate mixture of sparingly soluble mineral salts. Formation of calcium carbonate, calcium phosphate, silica, silicate salts, calcium sulfate, corrosion products *etc.* depend on water pH, temperature and water chemistry. Calcium carbonate is the predominant component of the hard and tenacious scale deposited from natural waters, especially in processes involving heat transfer.

The principle factor that promotes calcium carbonate scale formation is concentration of dissolved solids by repeated partial evaporation of the water. Therefore, certain waters that have no scale tendency will eventually become scale-forming when concentrated x times, where x = 2, 3, 4 and even higher. The number x is defined as cycles of concentration. Economic considerations to minimize water use require low blowdown and increased cycles of concentration.

The severity of scaling tendency is related to the saturation index (SI), defined as follows:

$$SI = \frac{\left[Ca^{2+}\right]\cdot\left[CO_3^{2-}\right]}{K_{sp}CaCO_3}$$

$[Ca^{2+}]$ and $[CO_3^{2-}]$ are activities of the corresponding free ions and $K_{sp}CaCO_3$ is the conditional solubility product for $CaCO_3$.

Evaporation causes increase in dissolved solids concentration. Moreover, carbon dioxide is "stripped" away due to aeration resulting in pH increase. Therefore, water becomes highly supersaturated with respect to mineral salts. At this highly metastable state, alkaline earth salts (especially calcium carbonate) precipitate. Initial electrostatic interaction of dissolved anions and cations is the genesis of ion pairs that sequentially act as "building blocks". They later assemble to form larger aggregates. This may lead to massive scale deposition onto critical surfaces. The metal surfaces (heat exchangers) are usually very critical pieces of equipment and great care has to be taken so scale deposits on them can be avoided.

Supersaturation is also the driving force for enlargement and growth of these aggregates to a "critical size". Contrary to the smaller-size aggregates, these larger particles do not easily re-dissolve, and therefore serve as growth surfaces for crystal growth. The above process is called homogenous nucleation and refers to particle formation in the bulk of the solution. On the other hand, heterogenous nucleation relates to generation of nuclei onto a surface, *eg*. a metal surface in contact with the supersaturated water (Rieger et al., 1997).

Following a nucleation event (either homogenous or heterogeneous), several growth mechanisms can occur, which involve one or more of the following: (a) crystal growth, that is cation-anion incorporation (*eg*., Ca^{2+} and CO_3^{2-}) directly along certain crystallographic planes of a crystallite (b) particle agglomeration (c) deposit on "hot" metal surfaces (d) biofilm-induced scale growth.

$CaCO_3$ is especially problematic because it possesses "inverse solubility" (less soluble at higher temperatures). It tends to accumulate and deposit onto critical "hot" metallic surfaces (*eg*. heat exchanger tube walls), where "skin" temperatures are considerably higher that "bulk" water temperatures. $CaCO_3$ tends to form tenacious scale that strongly adheres to heat transfer surfaces. Chemical cleaning by acids or chelants involves a corrosive procedure and results in operations downtime.

Scale Inhibition and Dispersion

There are four basic approaches for $CaCO_3$ scale control: (a) maintenance of low operational pH (b) use of sequestrants (c) maintenance of low cycles of concentration, and (d) use of scale inhibitors. Use of acid is an effective way to prevent calcium carbonate formation by maintaining a low pH. However, it raises concerns due to its hazardous nature and the potential of accelerating metal corrosion. The use of sequestering agents is too costly for open recirculating water applications. Maintaining low cycles of concentration leads to costly water waste. Scale inhibitor use is a widely accepted practice and involves addition of minute amounts of scale inhibitors in the recirculating water. These additives contain phosphonate and/or carboxylate groups, and can be monomeric or polymeric (Figure 3). They function at threshold levels, since the [Ca]:[inhibitor] concentration ratio is extremely high. It is believed that they perform "threshold inhibition" by a surface adsorption mechanism involving Langmuir adsorption. Adsorption onto the $CaCO_3$ crystal surface(s) causes inhibition (or delay) of crystal growth at the very early stages. Other changes induced by the presence of inhibitor include modification of crystal morphology as shown in Figure 4, for the case of $CaCO_3$.

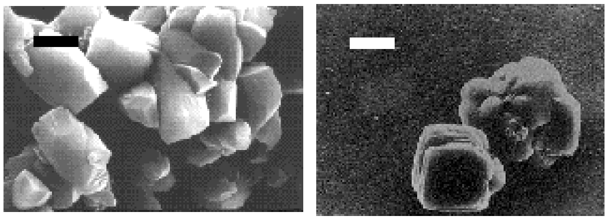


Figure 4. $CaCO_3$ precipitates from solutions containing no additives (left) and polyacrylate polymer (right). Bar = 20 μ.

The Scale Inhibition Test was used to investigate the effect of AMP (Figure 3) as $CaCO_3$ inhibitor at high Ca^{2+} and CO_3^{2-} levels, as well as high temperatures and pH (see Table 1). The experiments were run at 43 ºC. Bulk water temperatures in the range 40-50 ºC are commonly found in industrial applications. The synergism between AMP and certain dispersant polymers was also investigated.

According to results in Table 2, AMP is an effective $CaCO_3$ scale inhibitor. It maintains 400 ppm (of 800 ppm) of soluble calcium at high supersaturation and temperature (run 1). Furthermore, its performance is assisted by the dispersant properties of polymers 1 and 2. At Ca^{2+}/HCO_3^- of 800/800 $CaCO_3$ inhibition is assisted by both polymers 1 and 2. The blend AMP/polymer 1 achieves 64 % inhibition (run 4) and the blend AMP/polymer 2 is more effective with 74 % inhibition (run 5). At lower supersaturations (Ca^{2+}/HCO_3^- of 700/700) the blend with polymer 2 performs better than the one with polymer 1, 82 % inhibition for the former (run 3) *vs.* 75 % for the latter (run 2). At higher supersaturations however, (Ca^{2+}/HCO_3^- of 900/900) the performance of both blends is about the same ~ 60 % (runs 6 and 7).

Table 1. Scale Inhibition Test Conditions.

Run	**Ca^{2+} (ppm)**	**HCO_3^- (ppm)**	**Mg^{2+} (ppm)**	**AMP (ppm)**	**polymer (ppm)**
0	800	800	200	0	0
1	800	800	200	30	0
2	700	700	200	30	30 of 1
3	700	700	200	30	30 of 2
4	800	800	200	30	30 of 1
5	800	800	200	30	30 of 2
6	900	900	200	30	30 of 1
7	900	900	200	30	30 of 2

Table 2. Scale Inhibition Test Results.

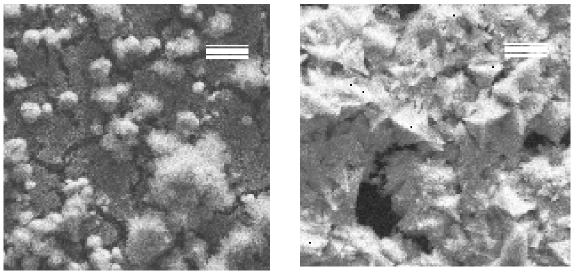
Run	**Soluble Ca^{2+} (ppm, 2h)**	**% Inhibition (2h)**	**Dispersed Ca^{2+} (ppm, 24h)**	**% Dispersion (24h)**
0	5	< 1	0	0
1	409	51	354	44
2	522	75	692	99
3	572	82	715	102
4	510	64	716	90
5	596	74	726	91
6	557	62	734	82
7	553	61	757	84

The dispersant properties of polymers 1 and 2 seem to be very similar based on measurements of dispersed Ca^{2+} (Table 2). Both blends achieve quantitative dispersion of $CaCO_3$ at Ca^{2+}/HCO_3^- levels of 700/700 (runs 2 and 3). At higher stress conditions (Ca^{2+}/HCO_3^- of 800/800) the dispersion performance is still high at ~ 90 % (runs 4 and 5), but drops to ~ 80 % at $CaCO_3$ of 900/900 (runs 6 and 7).

An additional point of interest is the way AMP (together with the polymers) affects crystal and particle morphology of the resulting $CaCO_3$ scales. In order to examine the effect more carefully, samples of those $CaCO_3$ deposits were analyzed by Scanning Electron Microscopy. The SEM images are given in Figure 5.

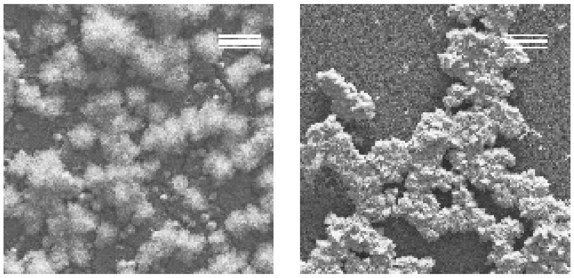
Upon examination of the morphology of $CaCO_3$ scale deposits, it becomes evident that there are obvious differences. $CaCO_3$ solids that precipitate from solutions containing AMP and polymer 1 (Figure 5, left column) are largely amorphous (non-crystalline) spheres and have little tendency to “stick” to each other. Their approximate size is 6 μ. On the other hand, $CaCO_3$ crystals from AMP and polymer 2 solutions (Figure 5, left column) have well-defined crystalline morphology, and, apparently, tend to agglomerate to larger aggregates. Their size is ~ 10 μ.

Both polymers 1 and 2 show virtually the same good synergistic effects with AMP scale inhibition. However, polymer 1 causes the precipitated $CaCO_3$ to form amorphous (and, consequently, more easily removed) scale, whereas polymer 2 allows formation of larger agglomerates composed of crystalline microparticles.



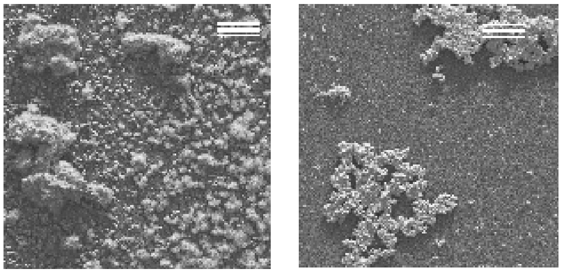
polymer 1
Bar = 20 μ

polymer 2
Bar = 20 μ



polymer 1
Bar = 40 μ

polymer 2
Bar = 40 μ



polymer 1
Bar = 100 μ

polymer 2
Bar = 100 μ

Figure 5. $CaCO_3$ precipitates from solutions containing AMP and polymers A or B as additives. Bar = 20 μm

Dispersion Mechanisms

It is important to recognize that the dispersion process consists of three steps and to separately consider each step in order to understand the various factors involved. The three steps discussed below are distinctively different but overlapping from a practical perspective:

(1) *Wetting of the suspended solid.* The wetting process depends on particle surface characteristics, dispersion medium, and the stabilizer. Non-ionic polymers have been used as surfactants. Standard surfactants, although capable of wetting suspended solids, may cause severe foaming problems. It should be noted that not all dispersants exhibit good wetting/surfactant properties.

(2) *De-agglomeration of the large particles.* Before each primary particle is available to the wetting liquid aggregates must break down completely. This may require considerable mechanical energy. Several factors are involved in achieving the primary particle state including type of cluster (agglomerate or large particle), bonds between particles in the cluster, wetting characteristics, *etc*.

(3) *Stabilization of the primary particles.* It is generally accepted that most fouling materials in cooling waters are (slightly) negatively charged. Addition of *anionic* dispersant polymers to process waters is effective because they cause increase in surface charges. Therefore, the prevent agglomeration and particle growth by keeping particles separated, dispersed, or stabilized.

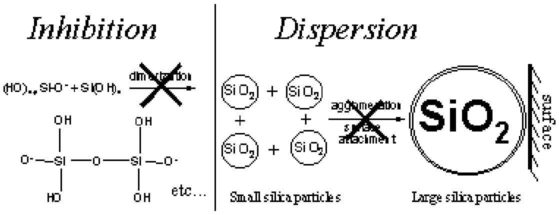
As shown in the experiments above, combination of scale inhibitors and dispersant polymers is advantageous for treating $CaCO_3$ scale. Each component plays an important role during the scale control process: the scale inhibitor prevents crystal growth and, in the event that crystallites form, the dispersant polymer keeps those primary particles stabilized and prevents them from depositing on critical surfaces.

Silica Scale Formation and Inhibition

Silica scale formation is a serious problem in cooling waters with high dissolved silica content, used in industrial applications (Sheikholeslami, 1999). As such, it deserves special note. Silica and/or magnesium silicate deposition limit industrial water users to low cycles of operation. In certain areas of the world, such as the Pacific Rim, Latin America, Texas, New Mexico, South Europe and others, waters used for industrial cooling applications contain high amounts of silica (50 – 100 ppm, as SiO_2). Silica solubility has been measured to be 150 – 180 ppm, depending on the dissolved species and temperature. This imposes severe limits to water users and forces them to either (a) operate at very low cycles of concentration, thus consuming enormous amounts of water, or (b) use chemical water treatment techniques in order to prevent silica scale formation and deposition. It is worth-noting that silica and/or silicate deposits are particularly difficult to remove once they form. Harsh chemical cleaning (with hydrofluoric acid) or mechanical removal, are usually required (Midkiff and Foyt, 1978).

Silica scale formation is favored at pH < 8.5, whereas magnesium silicate scale forms at pH > 8.5 (in waters with high Mg^{2+} levels). Silica has "normal" solubility, in contrast with the "inverse" solubility of magnesium silicate. The formation of the former is favored in as temperature increases, while the formation of the latter is more pronounced at higher temperatures. When silicate ion polymerizes, it forms a plethora of structural motifs: rings of various sizes, cross-linked polymeric chains of different molecular weights, oligomeric structures, *etc.* (Iler, 1979). The resulting "silica scale" is a complex and amorphous product (colloidal silica), which in fact is a complicated mixture of numerous components, linked randomly through Si-O-Si bonds.

Silica scale prevention can be achieved principally in three ways: (1) by silica removal from make-up water by "hot-lime softening" (precipitation with $Mg(OH)_2$ or $MgCl_2$, followed by filtration), (2) by inhibition (retardation or elimination of colloidal silica formation), and (3) by dispersion (elimination of surface attachment of "larger" silica colloids). Inhibition stops silica polymerization at early stages, whereas dispersion prevents growth of larger particles and their attachment to surfaces. These are shown schematically in Figure 6.



- *Inhibition* maintains silica soluble
- *Dispersion* prevents silica particles from forming larger agglomerates and depositing onto critical surfaces

Figure 6. Mechanisms for silica inhibition and dispersion.

CORROSION PHENOMENA

The corrosion of metals is a fundamental academic, industrial and economic concern that has received considerable amount of attention. Failures of critical metal surfaces due to corrosion are not uncommon in industrial water systems, especially on carbon steel, a material commonly used in heat exchanger tubes (Herro and Port, 1993). From an electrochemical point of view, corrosion can be envisioned as the oxidation of metals. Figure 7 shows schematically the electrochemical cell for the corrosion of metallic iron to iron oxides/hydroxides. This process is accompanied by the reduction of oxygen to hydroxyl ion.

Use of corrosion inhibitors is a widespread method for protection against corrosion (Sastri, 1998). They act by adsorption on the metal surface forming a thin protective film. Other corrosion inhibitors, such as PO_4^{3-}, form a calcium phosphate thin layer by controlled precipitation with Ca^{2+}. The most important properties for compounds to be efficient inhibitors are:

(a) ability to form a stable, compact barrier film,
(b) high adsorption energy for the metal surface,
(c) stability towards oxidizing biocides (*vide infra*),
(d) inertness towards other treatment additives.

An interesting form of corrosion that has been observed in internally riffled copper condenser tubes is the so-called "ants'–nest" or formicary corrosion (Notoya, 1997). This form of corrosion has its roots in the presence of small amounts of carboxylic acids, which are believed to be degradation products of chemicals used during the manufacturing process. Upon storage, these acids start copper corrosion that proliferates *via* an autocatalytic mechanism. The end result is premature tube failure.

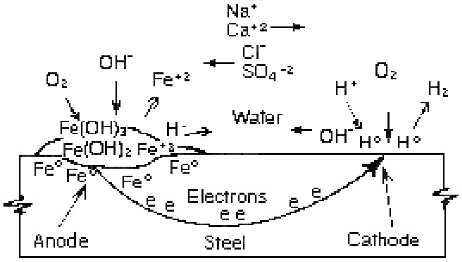


Figure 7. The electrochemical cell for the corrosion of iron.

Combating this type of corrosion involves a multitude of important factors. Tubes must be thoroughly cleaned from those lubricating oils. When installed and during start-up they need to be passivated (there are commercial products for this purpose). During operation, a treatment program must be used that contains a copper corrosion inhibitor (Fiaud, 1995). Common copper and admiralty brass corrosion inhibitors are triazoles (Metikos-Hukovic *et al*., 2000). Presence of suspended matter may lead to fouling and this, in turn, may result in underdeposit corrosion. Therefore, a dispersant polymer must be used as well.

MICROBIOLOGICAL FOULING

Microorganisms are abundant in industrial water, where a multitude of nutrients can exist. These can proliferate rapidly and cause enormous problems if not treated properly. Uncontrolled microbiological growth results in fouling of heat exchanger tubes (see Figure 8), thus interfering with fluid flow and the heat exchange process. Often surfaces colonized by microorganisms can act as sites for deposition of mineral salts.

Control of these organisms is based on biocides. These are chemical additives that interfere with the cell life of the organism, ultimately leading to death. Biocides are oxidizing and non-oxidizing. Chlorine, bromine, sodium hypochlorite, chlorine dioxide, and BCDMH (1-bromo-3-chloro-5,5-dimethyl-hydantoin) are among the most commonly used oxidizing biocides. Glutaraldehyde and isothiazolones are examples of non-oxidizing biocides.

Biocide Application and Stability of Scale Inhibitors

Although the primary criterion for potentially successful scale control is inhibition performance, secondary concerns are important as well. One of the most significant ones is scale inhibitor stability toward oxidizing biocides. As mentioned above, one of the most common microbiological treatments is chlorine. Due to its strong oxidizing power, chlorine is effective but, unfortunately, can degrade scale inhibitors present in the water treatment program. As a result, chlorine-resistant technologies find widespread acceptance and popularity.

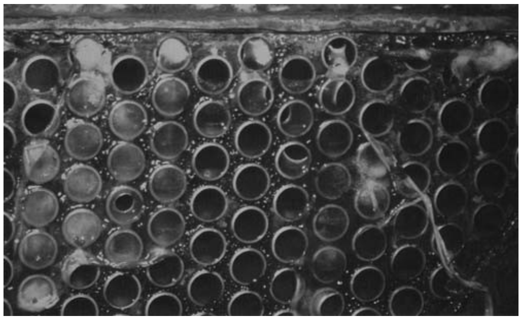


Figure 8. Microbiological growth on heat exchanger tubes.

Inhibitor degradation by oxidizing biocides is undesirable for several important reasons: (a) the system is depleted from inhibitor leading to poor scale control (b) orthophosphate is one of the by-products of decomposition of phosphorous-containing inhibitors and may lead to calcium phosphate(s) scale (c) the biocide's oxidizing power is "consumed" in decomposing the inhibitor and not to limit biological growth, resulting in poor microbiological control. These problems can be minimized by use of halogen stabilizers or more halogen-resistant scale inhibitors, or an appropriate biocide-inhibitor combination.

The severity and importance of oxidizer attack on treatment chemicals depends on system conditions, type of oxidizer, and nature of the chemical additive. Laboratory testing showed that degradation of inhibitors depends on factors such as pH, [Ca^{2+}], impurities, temperature, as well as the oxidizer itself (Johnson *et al*., 1987).

Chlorine is less costly *per* mole oxidant, but bromine, at pH 8-9, is more effective for any given oxidant dosage. Hypobromous acid has a higher pK_a than hypochlorous acid. This allows a higher percentage of the bromine biocide to be present in the more active acid form, while chlorine is predominantly in the less active ionized form.

While phosphonates are, in general, more prone to oxidation than carboxylates, it is an oversimplification to say that all phosphonates are unstable in the presence of oxidizers. PBTC is very resistant to oxidation. HEDP is quite resistant to chlorine, but readily attacked by bromine. AMP on the other hand, is readily attacked by chlorine, but to a lesser extent by bromine. These observations are in excellent agreement with the results of Berg *et al*., who used High Performance Liquid Chromatography (HPLC) to study decomposition of various inhibitors by bromine. This indicates that when chlorine is used as the biocide in a system, AMP is not a wise choice for scale inhibitor because it is rapidly degraded by chlorine. PBTC or a (less expensive) PBTC/HEDP blend would be a good choice. Indeed, such programs have been successful for many years.

With bromine as the biocide, PBTC or a PBTC/AMP blend would be the best choice.

Some system operators use cationic biocides (*eg.* quaternary ammonium biocides). Although these are very effective, they may interfere with other treatment (anionic) chemicals by reacting with them and causing precipitation. This phenomenon causes depletion of biocide and other additives, *eg.* dispersant polymer or scale inhibitor.

INVESTING WISELY ON A CHEMICAL WATER TREATMENT PROGRAM

In 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.

Proper program selection

Many factors have to 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) ***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 and limitations, as well as costs of a variety of chemical treatment programs in order to select the most appropriate that fits the needs of the particular operation.

Proper program application

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.

Proper monitoring

To ensure satisfactory performance of the treatment program, operators are required to perform several physicochemical measurements either in the field or in the laboratory. These are useful indicators on whether a certain component of the program is failing, or whether the program is performing according to initial goals.

(a) ***Corrosion monitoring.*** This 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.

(b) ***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 ΔCycles (Cycles based on a non-scaling ion – Cycles based on scaling ion, *eg.* calcium), loss of soluble species can be determined. Theoretically, ΔCycles should be zero. A small increase is a warning sign, whereas a "split" of 1 or higher indicates active precipitation and deposition.

(c) ***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.

(d) ***"Actives" monitoring.*** Water treatment chemicals can be degrade over time, or depleted due to precipitation. Occasionally, scale inhibitors precipitate as calcium salts because of overfeeding or because of very high calcium levels. Dispersant polymers can be consumed due to adsorption onto surfaces. Oxidizing biocides can be consumed not to control biological growth, but to oxidize treatment chemicals. Therefore, monitoring of critical treatment actives becomes very significant, ensures performance, and can indicate a problem in its genesis (Hale *et al*., 1999).

(e) ***pH control.*** A large portion of open recirculating water systems use acid to control pH. Failure to control pH can result in pH upsets. These can cause corrosion rates to dramatically increase, thus endangering the integrity of the system.

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

CONCLUSIONS-PERSPECTIVES

Cooling water accounts for most of the water used in industrial applications. Many cooling systems conserve water by operating under conditions of high mineral salt supersaturation, particularly $CaCO_3$, one of the most abundant scaling salts. Inhibitors are required to prevent scale (Vanderpool, 1997; Demadis 2002). Cooling water systems are complex and dynamic, and each is operated to achieve unique performance goals. Effective cooling water treatment is a complex and challenging process. It is a multi-faceted task that requires control of three major factors: scale, microbiological growth and corrosion. Success of any water treatment program depends on its versatility, proper application and control of variables. Wise selection and combination of inhibitors and dispersants allows the water chemist/system operator to develop high-performing, cost-effective formulations to minimize both scale and corrosion at high cycles and with any biocide program. A well-performing chemical treatment program ensures, if selected, applied, and monitored properly, elimination of down-time and uninterrupted operation.

REFERENCES

Amjad, Z. Ed., 1995, *Mineral Scale Formation and Inhibition,* Plenum Press, New York.

Bartholomew, R.D., 1998, Bromine-based biocides for cooling water systems: a literature review, *International Water Conference,* pp. 523-552.

Berg, D., Vanderpool, D. Rubin, D., 1987, Ion chromatographic analysis of organophosphonates in cooling water, *International Water Conference,* pp. 56-66.

Browning, F.H. and Fogler, H.S., 1996, Fundamental study of the dissolution of calcium phosphonates from porous media, *AIChE Journal*, Vol. 42, 2883-2896.

Cowan, J.C., Weintritt, D.J., 1976, *Water-Formed Scale Deposits*, Gulf Publishing Co., Houston, TX, U.S.A.

Demadis, K.D. *et al.,* 2000, Rational development of new cooling water chemical treatment programs for scale and microbial control, in *Advances in Crystal Growth Inhibition Technologies*; Amjad, Z., Ed., Plenum Press, New York, Chapter 16, p. 215-231.

Demadis, K.D., 2002, Calcium-Phosphonate Chemistry: Preparation, Crystal Structure of Calcium-Amino-*tris*-Methylene Phosphonate and $CaCO_3$ Inhibition, *Phosphorus, Sulfur, Silicon*, Vol. 177, p. 2371-2394.

Dillion, C.P., 1986, *Corrosion control in Chemical Process Industries*, McGraw Hill, New York.

Fiaud, C., 1995, Inhibition of copper corrosion. The complementary role of oxides and corrosion inhibitors. *8th European Symposium on Corrosion Inhibitors, Ann. Univ. Ferrara, Sez. 5 Suppl. 1995*, Vol. 2, 929-949.

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.

Hasson, D., Semiat, R., Bramson, D., Busch, M., Limoni-Relis, B., 1998, Suppression of $CaCO_3$ scale deposition by anti-scalants, *Desalination*, Vol. 118, pp. 285-296.

Hero, H.M., Port, R.D., 1993, The Nalco guide to cooling water system failure analysis, McGraw-Hill Company, New York.

Iler, R.K., 1979, The chemistry of silica (solubility, polymerization, colloid and surface properties and biochemistry), Wiley-Interscience, New York.

Johnson, D.A., Fulks, K.E., Meier, D.A., 1987, Factors influencing the decomposition of HEDP by chlorine, *Materials Performance*, Vol. 26, pp. 24-29.

Kemmer, F.N., 1988, *The Nalco Water Handbook*, McGraw-Hill Company, New York.

Metikos-Hukovic, M. Babic, R., Paic, I., 2000, Copper corrosion at various pH values with and without the inhibitor. *J. Appl. Electrochem.* Vol. 30, pp. 617-624.

Midkiff, W.S., Foyt, H.P., 1978, Scale removal and prevention in high silica cooling waters, *Materials Performance*, Vol. 17*,* pp. 17-23.

Notoya, T., 1997, Localized "ant's nest" corrosion in copper tubes, Proceedings of "Corrosion Prevention", Paper 002, pp. 1-8.

Panchal, C.B., Watkinson, A.P., Bott, T.R., 2000, Fouling mitigation: challenges and opportunities, *Heat Transfer Eng.* Vol. 21, pp. 1-2.

Rieger, J.; Hadicke, E.; Rau, I.U.; Boeckh, D., 1997, A Rational Approach to the Mechanisms of Incrustation

Inhibition by Polymeric Additives, *Tenside Surf. Det.*, Vol. 6, pp. 430-436.

Sastri, V.S., 1998, *Corrosion inhibitors: principles and applications*, Wiley-Intercience, New York.

Sheikholeslami, R.; Tan, S., 1999, Effects of water quality on silica fouling of desalination plants, *Desalination*, Vol. 126, pp. 267-280.

Tanis, J.N., 1987, *Procedures of Industrial Water Treatment*, Ltan Inc., Ridgefield, CT.

Vanderpool, D., 1997, New $CaCO_3$ scale inhibitors: Understanding complexation constants as a tool for finding improved performance, *International Water Conference,* pp. 383-407.