The Contribution of Chemical Water Treatment in Combating Deposition and Corrosion Phenomena

By: *Kostas D. Demadis**

Corrosion has been defined in many ways. All definitions, although different in expression, have emphasized the changing of the mechanical properties of metals in an undesirable way. ISO 8044 defines corrosion as "Physico-chemical interaction, which is usually of an electrochemical nature, between a metal and its environment, which results in changes in the properties of the metal and which may often lead to impairment of the function of the metal, the environment, or the technical system of which these form a part".

The cost of corrosion has been reported from many studies to be in the order of 1 to 5 % of the Gross National Product of any country. The cost of corrosion for the **Shell Company** has been calculated to be equivalent to $400 million in 1995. These numbers do not include the cost of lost production, shutdowns to make repairs to corroded equipment, etc. **British Petroleum (BP)** has reported that the cost of corrosion is equivalent to 6% of the net asset value of the company. Corrosion cost in the USA electric power industry reaches $10 billion each year, according to the **Electric Power Research Institute (EPRI)**. Also, it has been reported by the EPRI that corrosion is the cause for more than 55% of all unplanned outages and it adds over 10% to the average annual household electricity bill. The impact of corrosion on all branches of industry in almost all countries can be observed. For example, in 1993 it was estimated that 60% of all maintenance costs for the North Sea oil production platforms were related to corrosion either directly or indirectly. A report on inspection results of several offshore production plants showed that corrosion was a factor in 35% of structures, 33% of process systems and 25% of pipelines. Every year, microbiologically influenced corrosion causes well impediment. Removal of defective pipelines required production to cease for at least 5 days. It is, therefore, apparent that corrosion control is of significant economical and technical interest. Corrosion management can be achieved in several ways, one of which is based on corrosion inhibitors. These are chemical additives that delay or (ideally) stop metallic corrosion.

Corrosion inhibitors are effective for the decrease of metal corrosion in nearly neutral conditions by forming weakly soluble compounds with the metal ion existing in the solution, which precipitates on to the surface to form a three-dimensional protective layer. Such inhibitors (often called interphase inhibitors) for cooling water treatment technology, in the last decades, comprised different types of phosphonic acids.

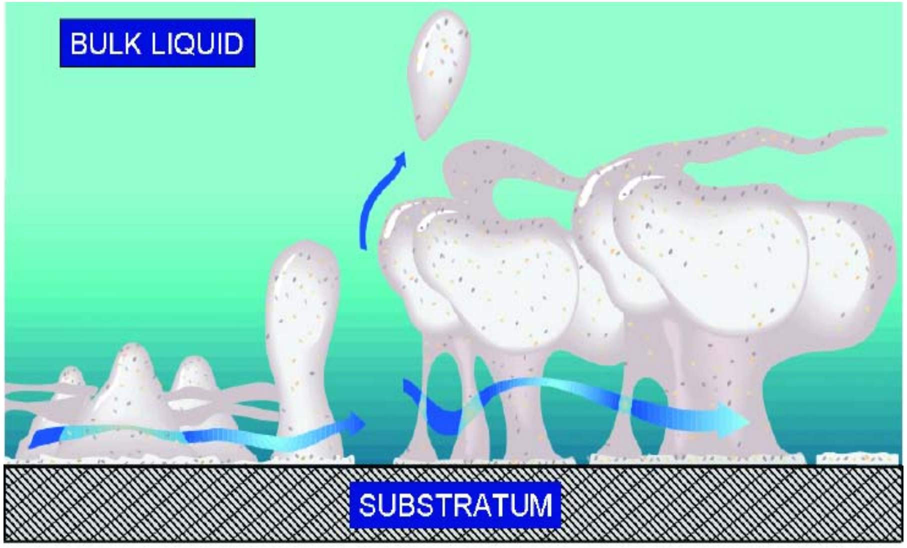
Biofouling

Biological fouling (biofouling) is the undesirable accumulation of micro-organisms, plants and animals on artificial surfaces. This occurs on artificial surfaces submerged in seawater (marine biofouling), such as ship's hulls, seaside piers and sea defences, as well as on other surfaces in continuous contact with water, such as air conditioning systems and water pipes. Organisms that cause biofouling can be subdivided into minute microfoulers and larger macrofoulers. Microfoulers (e.g. sticky biofilms of bacteria) initiate the process by colonizing new surfaces. These, then, allow the larger macrofoulers (e.g. barnacles, limpets and seaweeds) to gain a foothold. Biofouling on ships reduces their speed (due to a reduction in hydrodynamics) and manoeuvrability, causing increased fuel and maintenance costs. On static structures biofouling can enhance the corrosion of metal by seawater, reducing the metal's susceptibility to environmental fracture, and increasing the risk of mechanical failure. Biofouling in air conditioning systems can prevent airflow, reducing cooling efficiency and increasing energy costs. Blooms of algae can block both fresh and salt water filtration systems, and require water pipes to be frequently cleaned to prevent blockage.

Biofouling also occurs most often during nanofiltration and Reverse Osmosis processes. This is because the membranes cannot be disinfected with chlorine, in order to kill bacteria. Biofouling in nanofiltration or RO membranes is probably the least comprehended contamination that can occur in membrane systems. This can be ascribed to the complex growth of microbiological bacteria. These micro-organisms have damaging, often irreversible effects on these systems. The types of micro-organisms, their growth factors and concentration in a membrane system greatly depend on critical factors, such as temperature, the presence of sunlight, PH, dissolved oxygen concentrations and the presence of organic and inorganic nutrients. Micro-organisms can enter the system through water or air, or both. Aerobic (oxygen-dependent) bacteria usually live in an environment of warm, shallow and sunlit water, with a high dissolved oxygen content, a PH of 6.5 to 8.5 and an abundance of organic and inorganic nutrients. Aerobic bacteria (oxygen-independent), on the other hand, are usually present in closed systems with little to no dissolved oxygen and become active when a sufficient amount of nutrients is present. One of the most abundant types of biofouling originates during pre-treatment of RO systems and in parts of membrane systems that can promote the growth of algae.

Membrane system parts that are exposed to sunlight or contain still water can cause the growth of algae to expand. Another type of biofouling in a membrane system is the attachment of bacteria to the inner walls of pipelines. Corners and dead-ends are locations in a pipeline that bacteria can absorb to. After bacteria have absorbed to a wall, the first parts of a biofilm are formed. The biofilm will increase in size while bacteria keep multiplying and while dead organic matter absorbs to the biofilm structure. Despite the fact that bio films influence the water flow, it still attracts small suspended solids and micro-organisms. Biofilm deposits become a strong, coherent and recalcitrant mass that is very hard to remove. Eventually, parts of the biofilm will be released and spread through the system components, including membranes. When attached to membranes micro-organisms start multiplying using nutrients that are present in the feed water. As a result a biofilm will develop on membranes, encumbering feed water flow through the membrane. This results in a higher pressure, which in turn causes higher system costs and irreparable membrane damage.

Oxidizing and non-oxidizing biocides are commonly used in an attempt to control biofouling in industrial water systems. Many of these programs, however, fail due to the incorrect selection and application of these chemical compounds. Knowledge of the organisms to be eliminated and system hydraulics are important operational parameters in ensuring the successful application of chemical control programs. A further complicating factor is the build up of bacterial resistance to many of these compounds. One way of limiting resistance is the alternation of oxidizing and non-oxidizing biocides at the correct miminum inhibitory concentration and using these in combination with surface active compounds to dislodge any biofilm. A variety of surface monitoring techniques are in use in order to monitor the success of biofouling control programs. Unfortunately, none of these techniques are ideal and results have to be considered very carefully.



Investing on a "Functional" 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.

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) **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 has been the focus of several researchers.

(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 take 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 with 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 the Need for Inhibitor Dosage**:

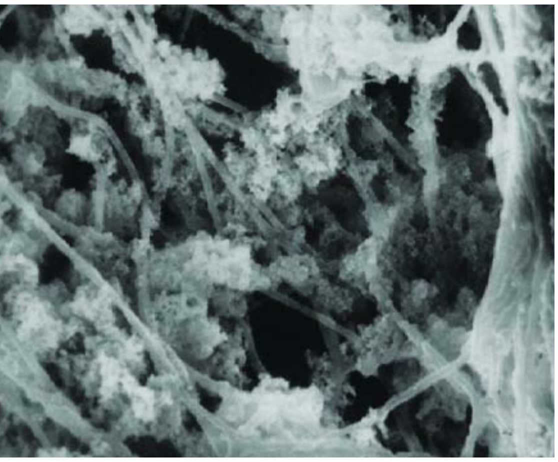
Chemical wastage can be avoided when system operators have knowledge on water chemistry and requirements for active levels. Underfeeding may cause severe scaling and/or corrosion phenomena, and overfeeding wastes chemicals.

(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.

Proper Monitoring

To ensure satisfactory performance of the treatment program, operators



are required to perform several physiochemical 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 the use of properly calibrated and functioning online instruments:** Water chemistry tests performed on-site also offer great benefits. By monitoring DCycles (Cycles based on a non-scaling ion and Cycles based on scaling ion, eg. calcium), loss of soluble species can be determined. Theoretically, DCycles 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 high hardness. Dispersant polymers can be consumed due to adsorption onto surfaces and oxidizing biocides to oxidize treatment chemicals. Therefore, monitoring of critical treatment actives is necessary to ensure performance, and be able to indicate a problem in its genesis.

(e) **pH control by the 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.

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

A Comment on "Green Additives" and Environmental Concerns

The environmental regulations affect scale and corrosion inhibitor usage and their impact to the aqueous environment. A classic example is chromate, which was once the corrosion inhibitor of choice for once through or recirculating cooling tower. It has been completely banned once its bad health effects were revealed.

Use of phosphate and heavy metals such as, molybdate, zinc for scale or corrosion control has also come under great scrutiny. Some geographic locations have completely banned and others have greatly reduced their discharge limits.

Discharge of chloramines is a limiting factor for the use of a low-cost combination of amine-based scale or corrosion inhibitors and chlorine as a biocide. Use of toxic biocides is being replaced with non-toxic bio-dispersants.

Emphasis has shifted from the control of micro-organisms in suspension (planktonic) to biofilm formation on surfaces (sessile). In the development of new inhibitor chemistries, all the aforementioned factors must be considered carefully.

Discovery and commercialization of chemical additive technologies that meet all the above requirements is a difficult task.

In today's world, an ideal inhibitor must be able to perform under the most severe conditions, cost-effective, compatible with all other treatment components, and environmentally friendly, preferably biodegradable. This definition is applicable to scale, deposit, and corrosion inhibitors, as well as to biocides. ■

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لقد جرى تعريف التآكل بطرق متعددة، جميعها أكّدت على حدوث تغيّر في المزايا الميكانيكية للمعادن بطريقة غير محبّذة وبالتالي أدت إلى حدوث التآكل. عرفت ISO 8044 التآكل على أنه تفاعل فيزيائي كيميائي ذات طبيعة كيميائية كهربائية يأخذ مكانه بين المعدن والبيئة المحيطة به ويؤدي إلى تغيّر مزاياه وحدوث خلل وظائفي فيه وفي الجهاز المعتمد عليه.

أظهرت دراسات أن كلفة معالجة التآكل تَعدّ بين واحد إلى خمسة بالمئة من إجمالي الإنتاج الوطني لكل دولة. فعلى سبيل المثال كلّف التآكل شركة Shell حوالي ٤٠٠ مليون دولار أميركي في العام ١٩٩٥. وهذه الأرقام لا تتضمن تكلفة توقف عمليات الإنتاج أثناء عملية معالجة الآلات التي طرأ عليها التآكل. أما شركة British Petroleum فتقدّر تكلفة معالجة التآكل فيها بحوالي ٦٪ من مجمل أصول الشركة السنوية، فيما تصل هذه الكلفة حتى ١٠ مليار دولار في صناعة الطاقة الكهربائية في أميركا، التي تقول التقارير بأن أكثر من ٥٥٪ من حالات انقطاع التيار الكهربائي فيها سببها التآكل. في العام ١٩٩٣ قدرت كلفة عمليات الصيانة وإعادة التأهيل من التآكل عند منصة استخراج البترول في البحر الشمالي بحوالي ٦٠٪ من إجمالي تكاليف أعمال الصيانة. بالإضافة إلى ذلك أظهر تقرير تناول العديد من المصانع الإنتاجية أن التآكل سبب في ٣٥٪ من الخلل الحاصل في البنى و٣٣٪ من ذلك الحاصل في الأجهزة و٢٥٪ من ذلك الحاصل في الأنابيب. إن إزالة التآكل من خطوط الأنابيب يستلزم حوالي ٥ أيام تتوقف أثنائها عمليات الإنتاج. وهذا ما يظهر أن التحكّم بالتآكل له فوائد اقتصادية وتقنية هائلة.

التحكّم بالتآكل يتم عبر تحقيقه باتباع وسائل متعددة منها استخراج موانع التآكل والتي هي عبارة عن مواد كيميائية تؤخر أو توقف حدوث التآكل في المعادن. يتناول هذا المقال طرق منع التآكل المختلفة التي تستند على معالجة المياه بإستخدام المواد الكيميائية.

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