

**MANGANESE-DEPENDENT CORROSION IN THE
ELECTRIC UTILITY INDUSTRY**

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ABSTRACT

Manganese dioxide is deposited by chemical and biological oxidation of dissolved manganese that occurs naturally in surface and groundwaters throughout the United States. In industrial cooling systems, manganese scales degrade heat exchanger performance and are commonly held to promote corrosion due to formation of underdeposit conditions. The direct galvanic action of manganese dioxide in the corrosion process is less well recognized and can promote severe localized attack. The present paper reviews the chemical and biological origins of manganese deposition and discusses mechanisms of manganese-related corrosion. A case history of surface condenser corrosion at a steam electric utility is presented and chemical methods used to control manganese fouling at this site are described. The performance of the chemical program at the end of one year is reviewed.

INTRODUCTION

Fouling by manganese deposition has been a concern in pipelines and waterworks throughout the 20th century¹ and very likely has impacted water supplies since antiquity. Reports implicating manganese in pipeline corrosion however, have only begun to appear with frequency since the 1960's². Beginning about the same time, incidents of stainless steel corrosion due to exposure to natural waters began to appear and a corrosive electrochemical phenomenon known as Ennoblement became recognized³. These observations were linked recently when it was demonstrated that manganese-oxidizing bacteria could engender the electrochemical effects of Ennoblement⁴ and induce pitting corrosion⁵. Widespread reports of Ennoblement - in marine, estuarine, and freshwaters worldwide - together with collected accounts implicating manganese in the corrosion of stainless steel and copper alloys^{4,6-8} combine to form a solid indictment of manganese as a contributing factor in corrosion processes.

Manganese deposition in cooling water circuits degrades corrosion resistance, lowers heat exchanger efficiency, and reduces biocide performance. These effects incur significant costs to the electric power industry through increased fuel consumption, more frequent and extensive cleanups, higher chemical treatment costs, and in some cases, significant capital costs for component replacement. Concerns over manganese fouling are less universal than those related to calcium, silica, or iron due to the often low or undetectable levels of manganese in cooling water supplies. However, many surface and groundwaters throughout the United States carry manganese levels that pose a significant fouling threat. The corrosive impact of manganese deposition in systems relying on these waters can lead to condenser retubing and replacement expenses that far exceed costs associated with the more common mineral scalants.

MECHANISM OF MANGANESE-DEPENDENT CORROSION

Manganese dioxide is a water insoluble, oxidizing material that serves a variety of technological applications including use as the cathode in alkaline-zinc batteries. In industrial water systems, manganese dioxide promotes pitting and crevice corrosion through a combination of electrochemical effects caused by galvanic coupling between MnO_2 deposits and the underlying metallic surface [hereafter the formula MnO_2 denotes a mixture of manganic oxides often found in industrial and natural deposits]. The effect of the galvanic action is to shift the metal corrosion potential (E_{corr}) in the positive or noble direction fostering passive film breakdown and localized corrosion. The term Ennoblement refers to this positive shift in potential without implying that the metal has gained corrosion resistance. Galvanic effects caused by MnO_2 are similar to those caused by other oxidizing species in the environment eg. ferric ions or hypochlorous acid, however the solid phase conductivity of MnO_2 enables current to be drawn extensively from the deposit without mass transfer restrictions, yielding a large cathodic capacity.

MnO_2 deposition shifts E_{corr} towards a threshold value beyond which pitting corrosion can develop. This critical threshold - the pitting potential (E_{pit}) - is dependent on alloy composition, weldment quality, temperature, pH, and anion concentration among other factors; and consequently the exact relationship between E_{corr} and E_{pit} must be determined empirically for each system. Under certain conditions, the shift in E_{corr} caused by MnO_2 deposition can exceed E_{pit} , causing localized breakdown of protective surface oxides that become nucleation sites for active metal dissolution. Metal ion hydrolysis then acidifies the nucleation site and attracts charge-neutralizing counter-ions (eg. chloride, sulfate) that further disrupt the oxide structure. Left unimpeded, these self-sustaining processes quickly lead to stable pitting corrosion.

The tendency for pits to self-propagate is offset by polarization effects arising during pit nucleation, that shift E_{corr} in the negative direction. This cathodic polarization reflects the requirement for balanced net anodic and cathodic rates on the metal surface. As pitting stimulates the anodic rate, the metal potential shifts negatively to accelerate the cathodic reaction until a new balance is reached. The negative shift also slows the anodic rate however, and below a critical threshold known as the protection potential (E_{prot}), the anodic rate is insufficient to maintain the acidic, corrosive pitting environment; and pitting terminates. The cathodic activity of MnO_2 inhibits cathodic polarization, enabling pits to remain active. The net effect of elevated potential and increased cathodic activity is to stimulate pit nucleation and prevent repassivation.

Underdeposit and crevice corrosion is promoted in a similar way, again with the MnO_2 cathode serving to elevate E_{corr} and inhibit cathodic polarization. In addition, the high cathodic efficiency diminishes solution IR drops which otherwise tend to diminish overvoltages and limit oxide damage.

MnO₂ deposition on stainless steel under oxic, neutral conditions gradually shifts E_{corr} from values near -100 mV_{SCE} to limiting potentials between +300 and +400 mV_{SCE} as illustrated in Figure 1 [all potentials reference the saturated calomel electrode, SCE]. The limiting potential is indicative of the surface redox reaction shown in equation 1, which fixes the metal potential at the potential of the reversible manganese dioxide half-cell⁹. These potentials can exceed E_{pit} for waters containing chloride levels as low as 100 ppm and are well above E_{prot} for 300 series stainless steels.

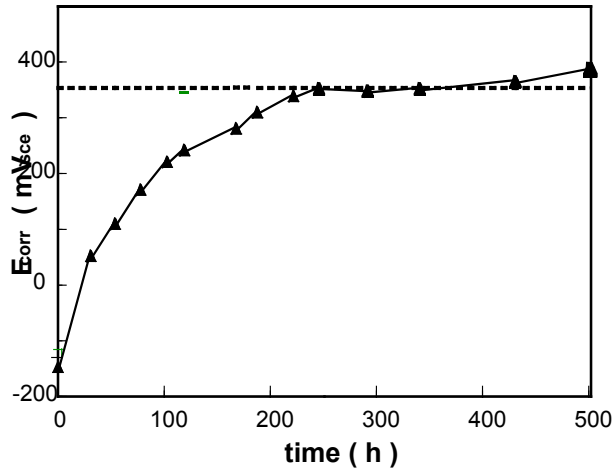


Figure 1. Characteristic E_{corr} vs. time curve for stainless steel exposed *in-situ* to neutral, oxic, natural water. Horizontal dashed line indicates the half-cell potential according to equation 1.

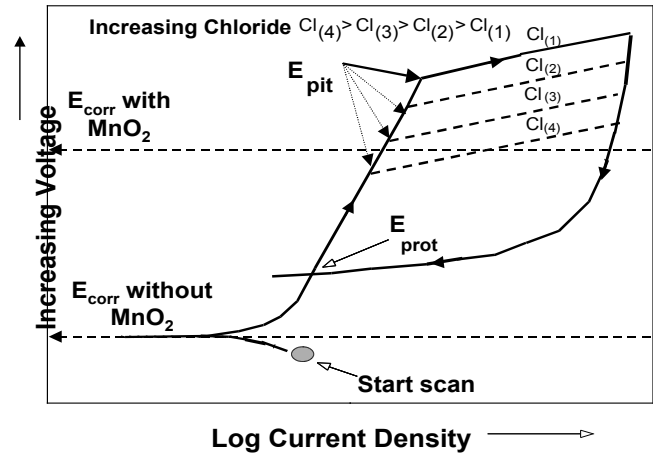


Figure 2. Schematic electrochemical pitting scan illustrating the relationship between E_{corr}, E_{pit} and E_{prot} and the effects of MnO₂ and chloride ion.

MnO₂ that is present in combination with other aggressive factors such as oxygen-depleted underdeposit conditions, high chloride level, or poor weldment quality, markedly increases the risk of pitting. Figure 2 illustrates the relationship between E_{corr}, E_{pit}, and E_{prot} as determined using a schematic corrosion pitting scan. Arrows in the figure denote the direction of polarization. The sharp increase in current density on the forward sweep indicates pit initiation. Higher current density on the reverse sweep indicates that pits do not repassivate until the potential decreases to E_{prot}, which lies well below E_{pit}. Dashed horizontal lines indicate E_{corr} for stainless steel in the presence and absence of MnO₂. The effect of MnO₂ and increasing chloride is to shift E_{pit} below E_{corr}, enabling pits to develop. At chloride levels found in many natural waters, MnO₂ will sustain E_{corr} above E_{prot}, allowing nucleated pits to remain active. Under moderately aggressive conditions encountered in cycled cooling water, MnO₂ deposition can shift E_{corr} above E_{pit} to initiate pitting.

MNO₂ DEPOSITION PROCESSES

Biological Oxidation

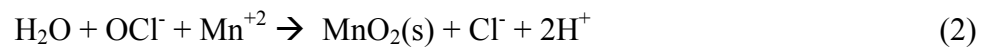
Dissolved manganese is oxidized to insoluble MnO₂ by a wide range of naturally occurring microorganisms in surface and groundwaters worldwide. Wellwater piping often develops dense iron and manganese encrustations as *Gallionella*, *Leptothrix*, *Siderocapsa* and other bacterial species catalyze oxidation of dissolved iron and manganese released from confined aquifers that are penetrated by the surface wells. Extracellular microbial reactions scavenge manganese in a highly efficient

manner, enabling waters containing as little as 20 ppb manganese to deposit visible MnO₂ deposits within a few days¹⁰. Surface waters including lakes, ponds, rivers, and stagnant basins also harbor these and other bacteria that take part in the complex redox cycle of manganese. Sulfate-reducing bacteria and manganese-oxidizing bacteria coexist within narrow redox gradients in stagnant waters or shallow sediments and create seasonal shifts in the manganese concentration of overlying waters. These shifts can strongly impact the risk of deposit formation within cooling water systems that rely on these waters. Manganese-depositing biofilms that become inoculated with sulfate-reducing bacteria pose a severe risk of corrosion due to the concerted effect of strongly oxidizing MnO₂ deposits adjacent to regions of low redox potential caused by sulfide production.

Manganese-oxidizing bacteria readily colonize vegetation, rocks, wood, metal and other submerged surfaces to create mucoid biofilms. MnO₂ deposition within biofilms on metal substrata places the oxidizing material and metal in close proximity, enabling galvanic coupling that promotes corrosion.

Chemical Oxidation

MnO₂ is formed by the reaction of manganese with chlorine or other halogens according to equation 2.



Oxidizing microbicides such as peroxide and ozone also react with manganese to produce MnO₂.

Figure 3 shows the time course of manganese(II) and free halogen concentration in a solution initially containing 0.35 ppm manganese(II) and 1.5 ppm combined free chlorine/bromine residual, carried out in synthetic cooling water (40 ppm Ca, 63 ppm total alkalinity (both as CaCO₃), pH 8.15.) The effect of a chemical treatment to inhibit manganese oxidation is also shown. Figure 4 shows additional manganese-chlorine reaction under conditions described in the section - Methods of Manganese Control.

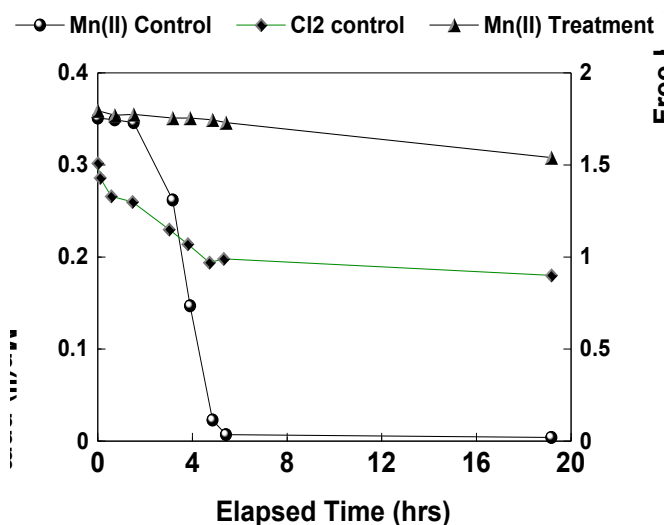


Figure 3. Mn (II) and free halogen versus time. Chemical treatment with polymer-phosphonate additive strongly inhibits manganese oxidation.

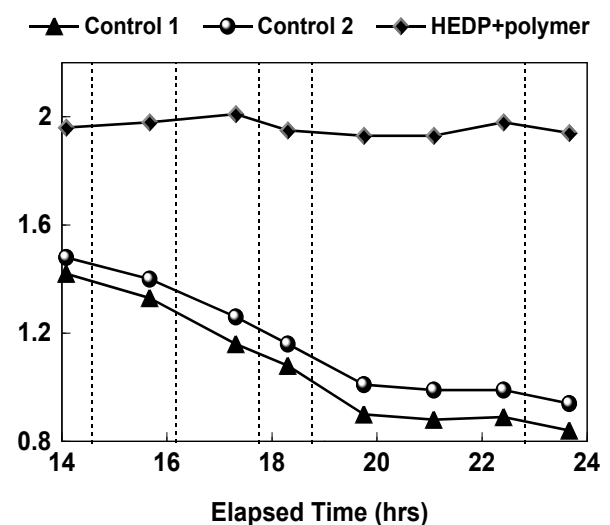
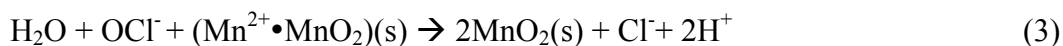


Figure 4. Mn (II) stabilization by HEDP-polymer treatment. At times indicated by vertical lines, halogen was added to give 0.2 ppm free residual.

The Mn (II) control curve in figure 3 shows a slow initial decrease in manganese over the first two hours of reaction, followed by a rapid drop that continues until nearly all manganese(II) is consumed by hour six. Halogen levels show a similar reaction trend. This behavior reflects catalysis of manganese(II) oxidation on the MnO₂ surface according to equation 3 and indicates that once manganese is adsorbed onto the MnO₂ surface it reacts much more rapidly with halogen than does manganese in solution¹¹.



The autocatalytic reaction of manganese(II) with chlorine has important consequences for MnO₂ deposition and for passive metal corrosion. Thin MnO₂ films formed on tube walls serve as an active surface to "seed" further chemical MnO₂ deposition, enabling rapid deposit build-up under conditions that might not otherwise support chemical manganese oxidation. Efficient microbial processes that initiate MnO₂ fouling from waters with low manganese content may thus enable *chemical* MnO₂ fouling in these waters. Chlorine, used for microbial control, is consumed by reaction with manganese(II) on the tube wall deposits, lowering the concentration available for control of sessile organisms. The surface accumulation of microorganisms and MnO₂ produces an ideal environment for underdeposit corrosion and for the growth of acid-producing and sulfate-reducing bacteria. Normally corrosive effects of sulfate-reducing bacteria are intensified by the MnO₂ deposits which shift E_{corr} above E_{pit} or E_{prot}. Moreover, halogen demand exerted by manganese oxidation increases chloride levels near the tube walls, aggravating solution corrosivity.

GEOGRAPHIC SCOPE

Manganese is the third most abundant transition element in the earth's crust, appearing in the form of numerous silicate, oxide, and carbonate minerals that comprise approximately 0.1% of crustal rock¹². Geological weathering of these minerals introduces colloidal manganese into surface and groundwaters where chemical and biologically mediated processes solubilize and further mobilize the material. Reducing conditions in confined, oxygen-depleted aquifers enable high levels of dissolved manganese to exist in equilibrium with surrounding manganese minerals. When these aquifers are penetrated by surface wells, sharp increases in dissolved oxygen and pH result in rapid MnO₂ precipitation.

Figure 5 shows a number of regions in the United States where shallow groundwater manganese levels are significant. These regions include much of New England and the Connecticut River Valley, the Ohio River Valley, and the Delaware, Hudson and Chesapeake drainages. The Chattahoochee River of western Georgia, the Platte River in northeastern Colorado, and the Snake and Willamette River Regions of the Pacific Northwest also register significant manganese levels, as do the Ozark Mountains, the Sierra Nevadas, and regions of Wisconsin, Texas, and New Mexico. The manganese map in figure 5 is limited to selected aquifers that comprise a national water quality assessment program managed by the United States Geological Survey, and as such the map does not provide a comprehensive survey of elevated ground and surface water manganese levels. Even so, the electric utility locator map shows that many power stations are situated in regions where cooling water from surface or wellwater sites is known to contain significant levels of manganese.

Numerous cases of manganese deposition in cooling water systems are reported each year in the United States. Although the heat transfer impact of these deposits remains a dominant concern in cooling systems, the impact on pitting corrosion is significant and merits increased attention. Regions where stainless steel or copper alloy pitting has been linked to MnO₂ deposition include Northern Virginia¹³, the Ohio River Valley^{2,7}, central Maine¹⁴, eastern Nebraska¹⁵, South Carolina¹⁶, and the Gulf Coast region¹⁷.

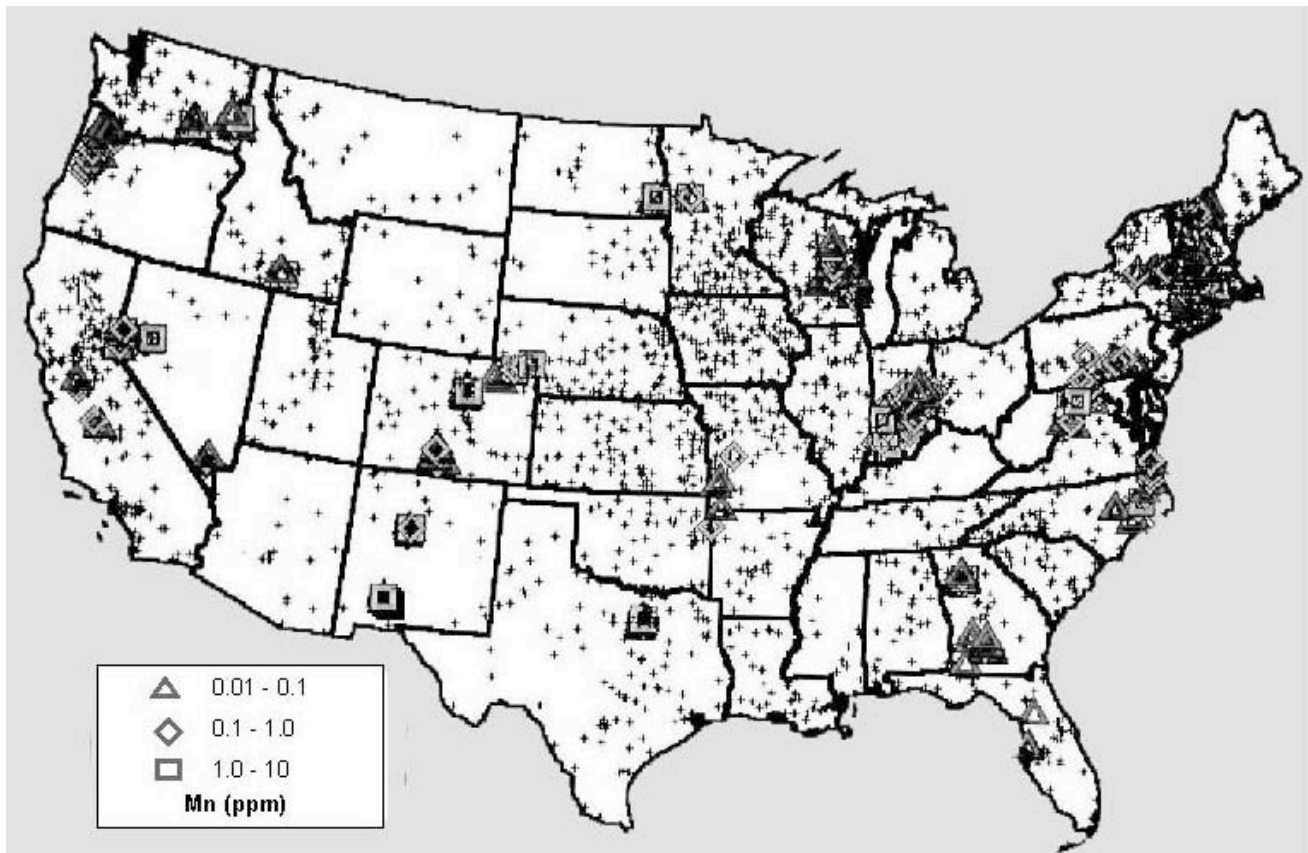


Figure 5. Comprehensive locator map for US Electric Power Stations (+). The manganese overlay map highlights regions with elevated manganese in shallow groundwater wells. The overlay is based on available data for selected aquifers and does not provide comprehensive geographic coverage. Sources: United States Department of Energy – Energy Information Administration, Form EIA-860A, Annual Electric Generator Report – Utility, 1999 and United States Department of Interior, US Geological Survey - National Water Quality Assessment Program

METHODS OF EVALUATION

The potential for manganese deposition and consequent heat transfer and corrosion problems in a cooling system can be evaluated through a combination of chemical, biological, and electrochemical measurements that detect the presence of manganese-depositing microorganisms and that identify changes in water chemistry and metal corrosion potential that signal fouling conditions. Monitoring programs that apply these techniques can be used to preempt or mitigate damaging deposition.

Chemical Analysis

Bulkwater manganese concentration is an important determinant of the manganese fouling potential of a cooling system. Based on the work of Sly¹⁸ and others^{19,20}, we propose three fouling thresholds:

- 1 Waters containing less than 10 ppb Mn(II) exhibit low manganese fouling potential
- 2 Between 10 and 50 ppb Mn(II), water may produce fouling if manganese-oxidizing microorganisms are present or if excessive levels of oxidizing biocides are applied
- 3 Greater than 50 ppb Mn(II) the risk of deposition due to biological or chemical oxidation is high.

Despite these guidelines, it is important to realize that low levels of manganese do not rule out fouling. As noted above, high biological throughput in waters containing less than 20 ppb dissolved manganese can generate extensive MnO_2 deposition. Moreover, low bulkwater manganese levels may reflect high removal rates. If the removal is taking place within the cooling water system, rapid MnO_2 deposition may result. In addition, manganese is introduced into natural waters through a variety of weathering and biologically mediated processes that can cause extensive shifts in manganese concentrations (Figure 6), resulting in seasonal variations in the risk of fouling. For these reasons, it is important to track variations in bulkwater manganese levels and to establish a treatment strategy that anticipates seasonal and possible sourcewater-based shifts in manganese concentration.

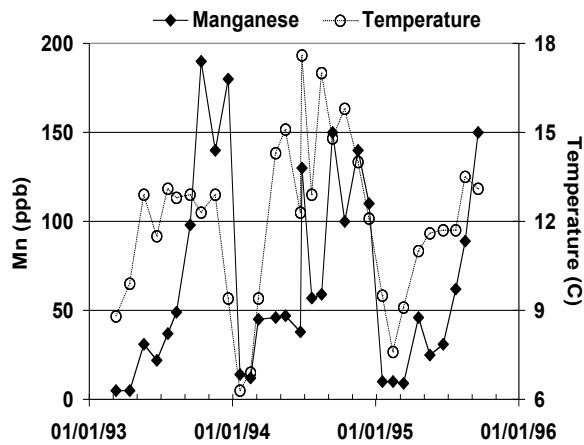


Figure 6a. Seasonal bulkwater manganese and temperature variations for the Chattahoochee River near Norcross, Georgia. Manganese and temperature covariation indicates strong seasonal mobilization of manganese. Four steam electric power stations with a combined generating capacity of greater than 4,000 megawatts use this river for cooling water purposes. Nine hydroelectric facilities also utilize the river as prime mover.

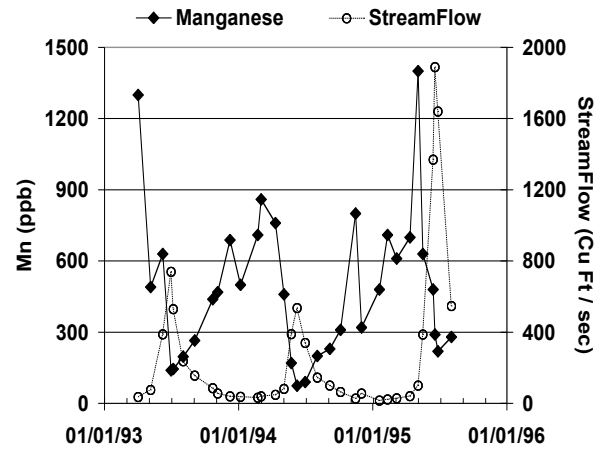


Figure 6b. Seasonal bulkwater manganese and streamflow variations for Clear Creek, Colorado, located on the eastern slope of the Rocky Mountains. The site illustrates the effect of seasonal snow melt on naturally high manganese concentrations.

Source: United States Department of Interior, US Geological Survey - National Water Quality Assessment Program

Manganese Analysis and Trending. In systems where makeup water manganese exceeds approximately 20 ppb either continuously or seasonally, bulkwater manganese in the makeup and cycled cooling water should be monitored on a daily basis and the manganese cycles of concentration calculated. A preferred method of data analysis trends the ratio of manganese cycles to conductivity cycles; with a target ratio of unity. This approach eliminates concentration effects due to changes in makeup water or due to off-line and startup conditions. Decreases in the cycles ratio indicate a loss of bulkwater manganese, and probable MnO_2 formation. Corrective action should be taken if the cycles ratio shows a decreasing trend that exceeds a few days duration. Manganese levels in water that has passed a 0.45 μm filter may also be compared to unfiltered water to identify possible trends in the manganese oxidizing potential of the water. A decreasing ratio of filtered to unfiltered manganese signals increased oxidation effects; however if the corresponding unfiltered manganese remains constant, it can be assumed that the MnO_2 is still effectively dispersed and that the rate of deposition has not increased.

Figure 7 shows a record of manganese to conductivity cycles ratio for Sikeston Power Station, Sikeston, MO over a roughly five year period, illustrating dramatic shifts in manganese stability. This facility experienced manganese-related fouling and corrosion problems and is the subject of the case history presented later in this article.

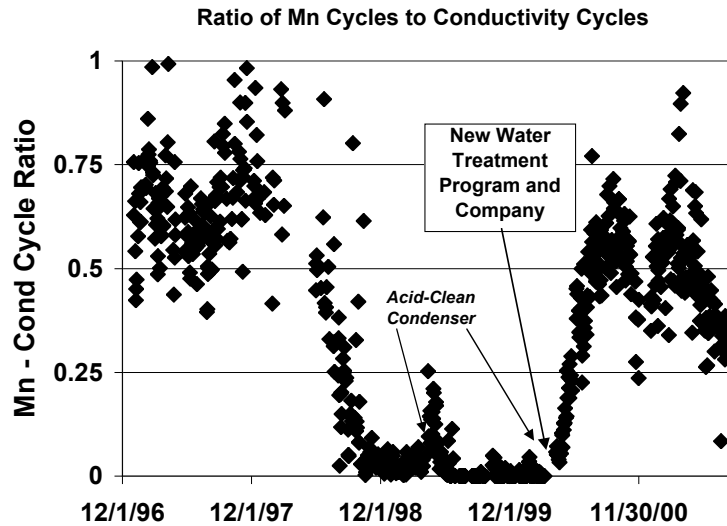


Figure 7. Ratio of manganese to conductivity cycles of concentration for cooling water at Sikeston Power Station. Manganese-rich deposits were removed from condenser tubes by acid-cleaning in March 1999 and 2000. After the second cleanup, a new treatment program was initiated to control deposition.

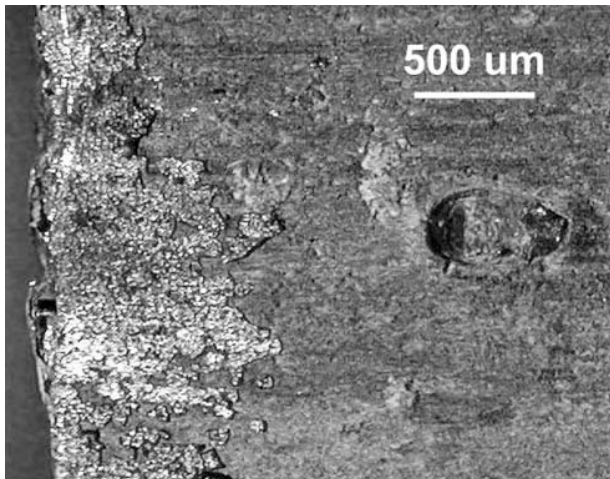


Figure 8a. Section of 90:10 copper-nickel condenser tube from Sikeston Power Station showing smooth manganese-rich deposit (26% MnO_2). Spalling at left near the specimen edge shows the contiguous, cohesive nature of the deposit. Pitting corrosion tubercle appears as the ellipse to the right.

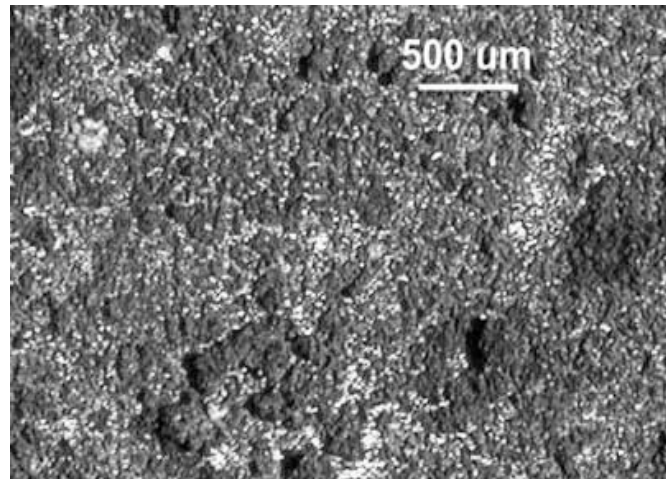


Figure 8b. Granular manganese-rich deposit (50% MnO_2) on four inch diameter stainless steel pipe. The pipe was removed from the service water system at a northeastern US nuclear power station. Extensive through-wall pitting at this station mandated costly walkdowns of the service water system and replacement of leaking tube sections. (See reference 13 for detailed case history)

Deposit Analysis. Accumulation of orange-brown to black deposits within a cooling water system can indicate MnO₂ deposition. The wet deposits may have a slick or greasy feel and may develop near points of oxidizing biocide feed. Dried deposits can be smooth (Figure 8a) or granular (Figure 8b) when viewed with a hand lens (ca. 10 - 30x) with smooth or glassy deposits more frequently encountered under high flow and temperature conditions along condenser tube walls and other heat exchanger surfaces. Pump suction screens or other low flow or splash areas can be useful areas to check for deposition.

Routine testing conducted by larger water treatment companies will detect and quantify the presence of manganese in cooling system deposits. Energy dispersive x-ray analysis is used for this purpose. For field analysis, colorimetric spot tests⁹ can be used to confirm the presence of MnO₂. These tests employ an oxidizable dye that changes from colorless to deep violet on contact with MnO₂. Complementary testing for total inorganic material (ash content) provides a measure of the organic content in the deposit. In the absence of known hydrocarbon fouling, organic content offers evidence of a microbial component in the deposits.

Biological Analysis

Microbial oxidation processes are the probable cause for deposition when MnO₂ is formed in waters having low manganese content (less than 20 ppb) or in higher manganese waters that are not treated with oxidizing biocides. If chlorination or other oxidizing treatments are used, both chemical and biological deposition may occur and the true mechanism of deposition becomes complex. The biological seeding and autocatalytic characteristics described in the foregoing "Chemical Oxidation" section, illustrate this complexity. The potential for microorganisms to initiate and gain protection from MnO₂ deposition makes it important to detect and control these organisms before deposition begins.

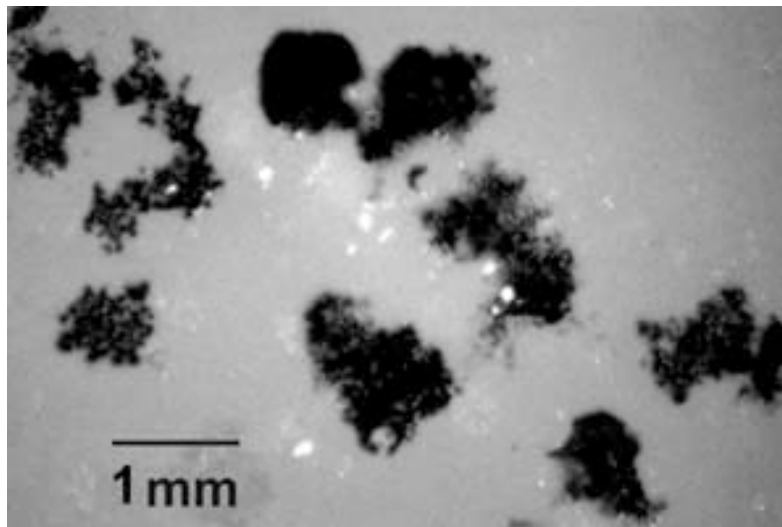


Figure 9. Manganese-depositing bacterial colonies grown on yeast-extract agar supplemented with manganese (II). Inoculum was obtained from wet deposits at the site referenced in figure 8b.

A simple method to detect manganese-oxidizing bacteria consists of culturing the organisms on solid growth medium supplemented with low levels of divalent manganese. Formation of brown colonies denotes manganese oxidation which is confirmed using colorimetric MnO₂ spot tests. Frequently, colonies can be recognized after room temperature incubation for 24-48 hours, however incubation for 7

days is recommended to confirm a negative result. Standard dilution plate counts are suitable for enumeration, and colony isolates can be subcultured for microscopy and/or growth-kill studies. As an illustration of this method, culture plates of buffered yeast extract-agar supplemented with 0.5 ppm manganese (II) were used to confirm manganese-oxidizing microorganisms in wet samples of the deposits shown in figure 8b. Colonies grown in this manner are shown in figure 9.

Selected Manganese-oxidizing Species. Although MnO_2 deposition is widespread among aquatic and soil microorganisms, several commonly encountered bacterial groups deserve special consideration due to the rapid and abundant deposition associated with their growth. These are the genera *Leptothrix* and *Siderocapsa* and the *Pedomicrobium-Hyphomicrobium* group.

Leptothrix spp. are gram-negative, aerobic, rod-shaped bacteria morphologically similar to *Sphaerotilus* spp. They are common in unpolluted, slowly flowing waters and are characterized by a sheathed growth habit in which a few to several hundred individual cells align chain-like within a continuous tubular sheath to form a filament. Individual filaments may span distances of millimeters and may entwine to form filamentous mats. These bacteria readily colonize submerged surfaces and accumulate dense encrustations of MnO_2 on the external sheath. Figure 10 illustrates the filamentous characteristic of the *Sphaerotilus-Leptothrix* group and also shows colonies of *Siderocapsa* bacteria.

Members of the genus *Siderocapsa* are aerobic, unicellular, non-thread forming, coccoid or ovoid bacteria characterized by the ability to deposit MnO_2 in extracellular mucoid material. Frequently, growth is in the form of cell clusters with two to several dozen individual cells embedded within a common manganese-rich capsule²¹. *Siderocapsa* spp. are found in ponds, lakes, streams, and drainage areas as well as in deep wells and soils. They rapidly colonize submerged surfaces to form orange-brown to dark-brown manganese-rich masses that may appear as a contiguous film or coating visible by eye. Figure 10 shows colonies with characteristics of the species *Siderocapsa Truebii* in which cell clusters and surrounding manganese-rich capsular material are evident.

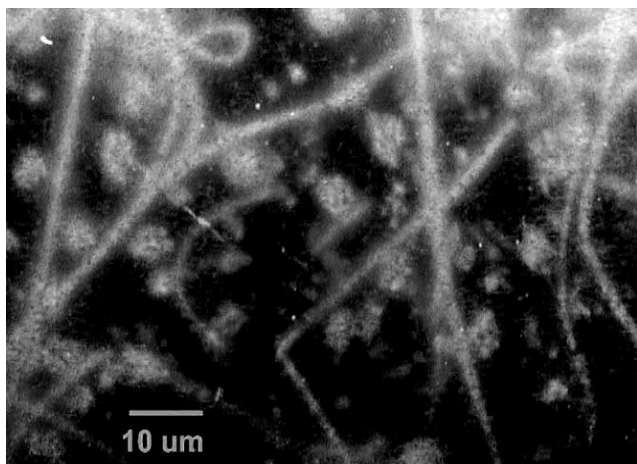


Figure 10a. Epifluorescence micrograph of acridine-orange stained biofilm formed on stainless steel in fresh river water. Clusters of bacterial cells centrally located within annular manganese-rich deposits as well as filamentous bacteria of the *Sphaerotilus-Leptothrix* group are evident.

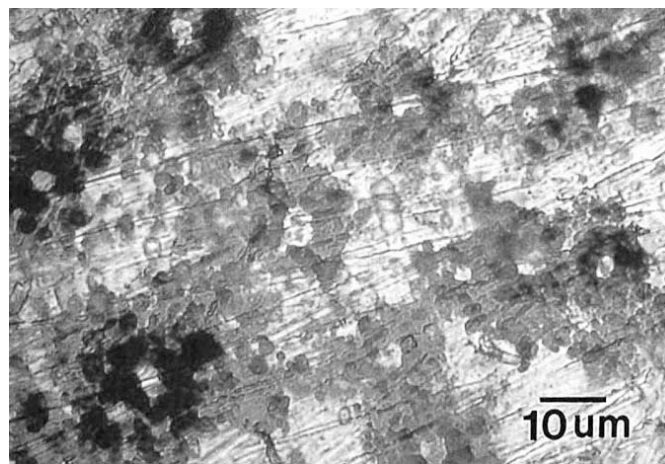


Figure 10b. Reflected light micrograph of stainless steel exposed to fresh river water. Deposits are highly enriched in MnO_2 which began to form within 24 hours of immersion. Annular deposit morphology is characteristic of *Siderocapsa* spp. bacteria (see reference 10 for detailed exposure conditions).

Hyphomicrobium and *Pedomicrobium* belong to a group of microorganisms classified as budding or appendaged bacteria. These aerobic bacteria are ovoid to rod-shaped and are characterized by appendages or hyphae that extend from the cell wall and that produce buds at the hyphal tips. The appendages are always thinner than the mature cell, and may be several times the cell length. A single cell may have multiple hyphae extending from the cell in a lateral or polar orientation. These bacteria have been associated with outbreaks of “black-water” in freshwater pipelines of Australia²² and the accumulation of MnO₂ within sessile assemblages of these bacteria has been reported elsewhere¹. The familiar iron-depositing genus *Gallionella* is a member of the appendaged bacteria group.

Electrochemical Analysis

As described, a key characteristic of galvanic MnO₂ deposition on stainless steel and other passive metals is the positive shift in corrosion potential (E_{corr}) known as Ennoblement. This positive shift, combined with increased cathodic current from the MnO₂ deposit, aggravates the risk of pitting. The same positive shift can serve as a practical diagnostic for MnO₂ buildup on system surfaces.

To test for galvanically coupled MnO₂ deposition in cooling water systems, stainless steel coupons are placed within the system and monitored for positive shifts in E_{corr} . Monitoring can be accomplished manually by withdrawing the coupon and measuring the potential against a standard reference electrode (eg. silver chloride or copper sulfate), or the coupon and reference electrode may be semi-permanently installed in a coupon rack, using commercial insertion probes, to allow continuous monitoring. For typical cooling water conductivities, the reference electrode can be located several meters distant from the test coupon, allowing it to be placed in the tower sump or other convenient location. A pseudo-reference electrode consisting of a second stainless steel coupon located at a site not prone to fouling may be substituted for the reference electrode. E_{corr} for the test coupon is monitored electronically with a standard high-impedance voltmeter or as a sensor input to the power station instrumentation. Monitoring alarms may be set to alert the operator of MnO₂ fouling when sustained E_{corr} values exceeding +200 mV_{sce} are detected or when the potential difference between the pair of metal coupons exceeds 150 mV. By trending E_{corr} , it is possible not only to detect but to correlate MnO₂ deposition to other chemical or operational parameters such as halogenation schedules or shifts in makeup water source. MnO₂ buildup on the test coupon can be confirmed using the colorimetric MnO₂ spot tests.

The foregoing electrochemical method will detect MnO₂ deposits that are galvanically coupled to the metal surface. Poorly adherent deposits that form in the bulkwater or settle in the sump or other slow flow areas will generally not be detected in this way, however these latter deposits pose little threat to the heat transfer or corrosion performance of the metals.

METHODS OF MANGANESE CONTROL

Chemical Control

Upstream Removal. Manganese(II) is commonly removed from process water supplies by upstream oxidation and filtration. These pre-oxidation steps use permanganate, chlorine dioxide, peroxide, ozone or other chemicals to oxidize manganese(II) to insoluble MnO₂ followed by settling or filtration of the solid material. Permanganate greensand filters are widely used for this purpose. Pre-oxidation is highly effective in removing iron and manganese, as well as lowering organic carbon levels and reducing halogen demand in the process water, however high capital and operating costs coupled with the risk of aggressive oxidant carry-over make these approaches impractical for many applications. Spray ponds and aeration chambers commonly used to remove iron are not effective in removing manganese due to the much slower kinetics of manganese air oxidation.

Chemical Stabilization. High levels of bulkwater manganese are maintained without deposition by using chemicals to interfere with the formation and growth of MnO₂ particles. Polyphosphate has long been used for this purpose in drinking water systems, where the formation of a manganese polyphosphate complex inhibits deposition²³. Threshold inhibitors such as carboxylic and phosphonic acid derivatives are used to maintain particulate MnO₂ in a colloidal, more easily dispersed state by coupling to and preventing growth at active sites on the particle surface. Polymeric dispersants including polyacrylates and multifunctional copolymers are used to disperse this colloidal material and prevent aggregation and settling. Halogenation and high pH degrade the effectiveness of these treatments by increasing the rate of manganese oxidation. High levels of hardness, silt, or iron also diminish performance by competing for both the threshold inhibitor and the dispersant. Nevertheless, under appropriate conditions, combined inhibitor-dispersant chemistry provides nearly quantitative MnO₂ inhibition.

Figure 4, (see Chemical Oxidation section) shows the results of a controlled laboratory evaluation of manganese-halogen stabilization using 5 ppm hydroxyethylidene, 1,1 diphosphonic acid (HEDP) as a threshold inhibitor and 12 ppm of sulfonate-carboxylate-nonionic functional terpolymer as dispersant. The experiment was conducted in 500 ml volumes of stirred cooling water containing 600 ppm Ca, 750 ppm total hardness, 55 ppm m-alkalinity (all as CaCO₃), 1150 ppm total dissolved solids, and 2.9 ppm initial dissolved manganese. Solution temperature was 40° C and pH 8.1. At time zero, concentrated chlorine-bromine solution was added to give 1.5 ppm free halogen residual. The high initial halogen spike was sufficient to seed all solutions with MnO₂ as reflected in the diminished level of dissolved manganese at 14 hours. This step ensured that subsequent manganese-halogen reaction took place in the presence of particulate MnO₂. Dissolved manganese was then monitored as halogen was periodically dosed to give 0.2 ppm free residual. Invariant dissolved manganese at 19-23 hours corresponds to a period of zero free residual halogen (data not shown), confirming that manganese loss was due to reaction with the added halogen. The chemical treatment provided quantitative manganese stabilization against oxidation by 0.2 ppm halogen indicating treatment efficacy against the low oxidizing residuals often maintained between shock halogen treatments in cooling water systems. In addition, halogen demand exerted by manganese oxidation was diminished. To provide superior protection against manganese oxidation during shock halogen treatment, stabilizer dosing should be synchronized to occur shortly before the halogen addition.

Biological Control

Although inhibitor-dispersant chemistry performs well in controlling chemical MnO₂ deposition, the effectiveness of these treatments against biological MnO₂ formation is not well established. Enzyme catalyzed oxidation may negate the surface effects of threshold inhibitors, and the mucoid conditions within biofilms are likely to limit dispersion of newly formed MnO₂ material. Studies to evaluate the performance of conventional inhibitor-dispersant chemistry and to identify specific inhibitors for control of biological MnO₂ production are being pursued.

Biofilm Prevention. As recapped below, manganese-oxidizing microorganisms exert a variety of adverse effects on chemical and biological fouling control. For the reasons listed, biofilm prevention is a more effective approach to controlling microbial MnO₂ deposition than are attempts to remove or control established biofilms.

- Manganese-oxidizing bacteria have the ability to concentrate even trace levels of manganese to produce visible MnO₂ deposits on submerged surfaces within a few days of exposure

- Once seeded by microbial processes, MnO₂ deposits accelerate further manganese-halogen reaction and may cause chemical deposition in systems that would be otherwise unaffected
- Manganese oxidation within biofilms consumes halogen and diminishes the effectiveness of the oxidizing microbicide treatment.

In addition⁴:

- Mineral deposits introduce a diffusion barrier that limits microbicide penetration and creates underdeposit conditions suitable for anaerobic bacterial growth.
- MnO₂ has the oxidizing potential to degrade abundant but refractory organics such as humic and fulvic acids into small organic acids and alcohols that increase the BOD of the system. These constituents are available to sulfate-reducing bacteria (SRB) and other bacteria with a limited ability to utilize more complex organics.
- Cathodic MnO₂ deposits located near reducing, underdeposit sites generated by SRB growth form a particularly corrosive combination.

Oxidizing Microbicides. Oxidizing microbicides are the most common agents used for microbial control in cooling water systems. Where high levels of manganese are present however, care must be taken to avoid excessive oxidizer levels that may cause chemical deposition. Halogenation at a sustained 0.2 ppm residual provides effective microbial control in unpolluted waters¹⁸ and is compatible with manganese levels below approximately 20 ppb manganese. For higher manganese levels, chemical stabilization is recommended to prevent manganese oxidation. Bromination will impart greater microbial control and less manganese oxidation than chlorination at equivalent doses for systems operating above pH 7.0. Stabilized chlorine compounds such as chloroisocyanurates also react more slowly with manganese and are useful in high manganese systems²⁴. For systems with high organic or microbial content, shock halogen treatment may be the preferred method of antimicrobial application. If applied synchronously with chemical stabilizers, shock halogen treatment rapidly suppresses microbial growth with little manganese oxidation between-doses.

Non-oxidizing Microbicides. Small process or comfort cooling systems may employ non-oxidizing microbicides for biological control. Larger power utility applications may also need to supplement halogen programs with non-oxidizing treatments to control microbial outbreaks during periods of peak growth or during system upsets. Quaternary and polyquaternary amines, organobromine, and organosulfur compounds, or combinations of these compounds provide broad-spectrum control of biofilm microorganisms - including manganese-oxidizing bacteria - that can be tailored to meet the needs of specific applications.

Remediation

Biofouling Removal. Mineralized mucoid deposits produced by manganese-oxidizing bacteria, as well as the sheathed growth habit of *Leptothrix* spp. present additional barriers to microbicide efficacy. To control established biofilms containing these organisms, it is advantageous to apply surface-active agents and penetrants to wet the deposits and improve dispersion. In addition to dislodging existing deposits, these compounds enhance microbicide penetration to reduce microbial growth and the risk of further deposition. Improved penetration of oxygenated bulkwater into the deposits also limits the growth of SRB's and other corrosive anaerobes that develop in underdeposit conditions. Alkyl amides and sulfonic acid derivatives are examples of biodispersants that are used for this purpose.

Chemical MnO₂ deposits. Loosely adherent flocs of MnO₂ that form in cooling system bulkwater due to chlorination will frequently settle in the tower sump, where they are removed during routine

cleanup. Deposits that settle in dead-legs or areas of low flow will generally be too poorly adherent to present a galvanic corrosion problem, but may create deleterious underdeposit conditions. These conditions can be mitigated with dispersants used for the control of silt and other suspended solids. Adherent deposits formed due to biofouling or by chemical production of sticky manganic hydrogels pose the threat of galvanic corrosion and will typically require acid or reducing chemical treatment to remove. Citric acid/tannin or bisulfite treatments are applied for these types of cleanups in cooling systems.

CASE STUDY: MANGANESE-RELATED CORROSION AT AN ELECTRIC POWER UTILITY

Fouling and corrosion problems related to variable amounts of manganese in the cooling water at a municipal electric utility illustrate the importance of manganese control.

System Description

Sikeston Power Station is a small municipal utility located in southeastern Missouri serving the electrical power needs for a community of roughly 20,000 people. The plant generates power through a single 235 megawatt, coal fired, steam turbine-generator rated at 1,750,000 lb/hr (795,500 kg/hr) of main steam. The primary surface condenser is a shell-and-tube design consisting of 15,852, 40 ft (12.2 m)-long, 1-in (2.54 cm) OD, 20 gauge, 90:10 CuNi tubes, cooled by heat exchange with a 2.5 million gallon (9.5 Mliters) recirculating cooling water system. Mild steel piping is used for water transmission within the cooling water system. The cooling water is supplied from local wells and maintained at 3.5 cycles-of-concentration by recirculation through an evaporative, forced draft cooling tower. Under average electrical load conditions, the cooling system operates at 135,000 gpm (511,000 lpm) recirculation, 2,500 gpm (9,462 lpm) evaporation, and 1140 gpm (4,315 lpm) blowdown resulting in a flow rate of 8 ft/sec (2.4 m/sec) and a temperature rise of 20° F across the condenser tubes. Appreciable levels of dissolved iron and manganese in the well water mandate addition of chemical dispersants to control deposition in the system. Chemical retention half-life in the system is 25.4 hours.

Water Chemistry

Representative makeup and circulation water chemistry from Sikeston Power Station is shown in Table 1. The samples were collected in September, 1999 near the end of a year-long period of poor manganese stability reflected in the low manganese concentration in the recirculation water. The water chemistry indicates approximately 3.5 cycles of concentration and shows a Langelier Saturation Index of 1.5 indicating slight scale forming potential. Alkaline pH, moderate hardness, and low chloride are indicative of a non-corrosive water.

Problem Description

The Sikeston system began commercial operation in September 1981 and operated for several years without significant iron or manganese-related problems. During this time however, iron levels in the makeup water increased from 1.5 ppm to 3.5 ppm and in early 1987 serious fouling in the condenser tubes caused the overall heat transfer coefficient to decrease to less than 55% of theoretical²⁵. The problematic deposit - a soft, reddish-brown material containing high levels of iron and lesser amounts of silica - was easily removed by scraping, and the condenser tubes were restored to satisfactory heat transfer performance by cleaning with water driven scrapers. This mechanical treatment removed about 450 lb. (204 kg) of deposit from the half-section of the condenser that was initially cleaned. No evidence of copper or nickel was detected in the deposit to suggest degradation of the tube wall material.

Table 1. Representative chemical composition of makeup and recirculation water at Sikeston Power Station. September 1999, combined wells E and F.

Constituent (expressed as)	Makeup Water (ppm)	Recirculation Water (ppm)
pH	7.1	8.2
m-alkalinity	160	195
Calcium (as CaCO ₃)	184	670
Tot. Hardness (as CaCO ₃)	239	863
Chlorides (as Cl)	3.4	30.7
Sulfate (as SO ₄)	49.5	567
Phosphates (as PO ₄)	0.8	3.7
Silica (as SiO ₂)	24.8	77.7
Iron (total)	3.0	8.5
Manganese (total)	0.9	LT 0.1
Copper (total)	LT 0.1	LT 0.1
Zinc (total)	LT 0.1	0.2
Sodium	4.1	14.9
Total Dissolved Solids	347	1110
Total Suspended Solids	14	52
Conductivity	450	1440

Subsequent scrutiny of iron in the system showed dissolved levels up to 4 ppm in the makeup water and several times this amount in the cycled recirculating water. Manganese was not routinely monitored at this time, however analyses conducted during a changeover of water treatment companies showed dissolved manganese levels of 1.4 ppm in the makeup water.

In the spring of 1989, the condenser again suffered a severe loss in heat transfer performance (43% of theoretical heat transfer coefficient) this time associated with a hard, black, tightly adherent deposit that was uniformly distributed over the inner tube walls (Figure 8a). This material could not be removed by scraping and required chemical cleaning with a citric acid/tannin treatment to dissolve the mineral and restore heat transfer performance. The deposit consisted largely of MnO₂ at roughly 8 g of MnO₂ per square foot of dry deposit with lesser amounts of iron, silicon, and calcium, and significant amounts of copper (Table 2).

Severe localized corrosion was visible on condenser tube samples removed during the cleanup. Attack was in the form of corrosion nodules (Figure 11) underlain by pits which in some cases penetrated more than 20% of the tube wall thickness. The nodules were up to 1 mm² base area x 0.5 mm high and were generally randomly distributed over the inside of the tubes, although longitudinal alignment along the length of the tube was not uncommon. The surface density of nodules was several thousand per square foot. Most nodules effervesced vigorously on contact with 10% hydrochloric acid indicating the presence of carbonates, and when dissolved with acid revealed a shiny brass colored area of attack under the entire nodule. When the nodules were mechanically dislodged, a glassy, dark deposit was generally visible at the tube surface which could be easily scraped away to reveal the bright base metal.

Table 2. Chemical Composition of Black Deposit on Tube Specimen shown in Figure 8a and 11.

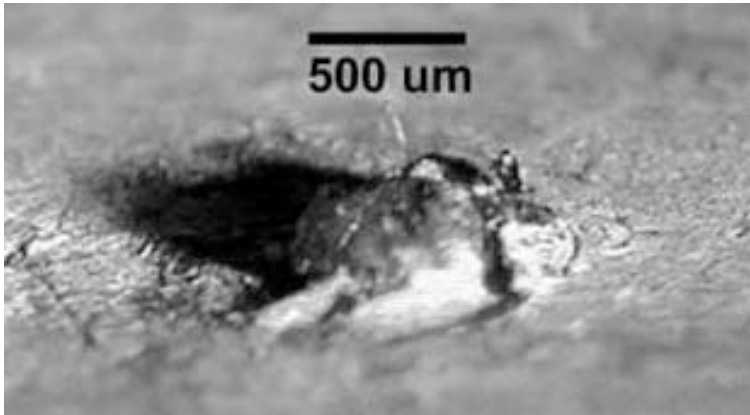


Figure 11. Corrosion tubercle on 90:10 CuNi condenser tube. Manganese-rich scale is visible as the fractured and uplifted material at the lower-right edge of the tubercle.

Constituent (as)	DryWeight %
Manganese (MnO ₂)	26.1
Iron (Fe ₂ O ₃)	12.4
Silicon (SiO ₂)	9.8
Calcium (CaO)	8.7
Copper (CuO)	3.6
Phosphorous (P ₂ O ₅)	3.4
Magnesium (MgO)	1.2
Barium (BaO)	1.2
Zinc (ZnO)	0.9
Aluminum (Al ₂ O ₃)	< 1
Sulfur (as SO ₃)	<1
Oil and Grease	<1
Loss on Ignition	27.5

In 1994, eddy current testing of condenser tube integrity showed pitting in approximately 25% of the condenser tubes with depths ranging from 20% of wall thickness to full through-wall penetration. Pitting was much more abundant in the outlet than the inlet tube bundle suggesting that elevated temperature contributed to the attack. In the spring of 1996, continued fouling again necessitated acid-cleaning of the condenser tubing and at this time, 23 tubes were capped and removed from service due to leakage caused by through-wall pitting.

In the summer of 1998 following a several month outage, the concentration of manganese in the recirculation water dropped sharply, from well-stabilized to undetectable levels (Figure 7). Increased manganese in the makeup water following startup may have contributed to the manganese instability, possibly aggravated by microbial growth during the prolonged layup and the consequent need for increased oxidizing microbicide treatment. Once deposition occurred, the autocatalytic mechanism of oxidation promoted further deposition making control difficult to regain. The deposition problems forced condenser cleaning in March 1999, at which time iron and manganese-rich deposits were again identified and 57 tubes were capped due to leakage caused by pitting corrosion. Following the cleanup, manganese stability improved briefly but rapidly deteriorated. In March 2000, acid-cleanup was repeated and the chemical treatment program and services of another water treatment company were initiated to help control the ongoing corrosion and fouling problems.

System Analysis

Evaluation of the Sikeston Cooling Water System in the winter of 2000, showed a number of areas of concern. Corrosion rates for mild steel averaged 6 mpy and mineral deposits were causing heat transfer losses and pitting in the plant's surface condenser. Control of microbiological growth also appeared to be problem, with no free halogen residuals during chlorination and visible algal slime masses on the tower structure and fill.

Analysis of the water chemistry indicated that zinc levels used for mild steel corrosion control were between 0.2 and 0.5 ppm total; however Zn residuals in filtered water were less than 0.02 ppm, insufficient to maintain proper corrosion rates. Additionally, during an off-line inspection, zinc-based deposits were found widespread across the surface condenser tubesheet, confirming that dispersant levels in the system were inadequate to provide good dispersion of insoluble metals. Fouling of the condenser tubes with a soft deposit, later identified as primarily iron and silica with lesser amounts of calcium and manganese also pointed to inadequate dispersion. Manganese was undetectable in the circulating water despite almost 1 ppm entering with the makeup water. Whereas some oxidized manganese had settled to the bottom of the tower basin, manganese deposits were also identified in the area of the surface condenser.

Condenser deposits showed significant organic content, suggesting that biofouling due to low halogen residual and possibly low bromine/chlorine dosage ratios, may have contributed to the deposit problem. Once formed, the mucoid biofilm matrix would accumulate silt and mineral material to form an insulating deposit, resulting in a large drop of efficiency across the condenser.

Figure 7 shows the history of manganese to conductivity cycles ratio over an extended period spanning conversion to a new water treatment program in April 2000. During the five year period, makeup water manganese levels ranged between 0.5 and 2.5 ppm but remained stable at 0.8 +/- 0.2 ppm during the period July 1999 to July 2001. As illustrated, the cycles ratio seldom exceeded 0.75, indicating some manganese deposition had occurred throughout the period; however the sharp decrease in July 1999 generated renewed concern that was resolved only after implementation of a new chemical treatment program.

Revised Water Treatment Program

To address the issues affecting cooling water performance at Sikeston, an alternative chemical treatment program was developed and tested. The program of single component, concentrated products comprises:

- Organic phosphate threshold inhibitor to stabilize iron and manganese against oxidation, as well as providing steel corrosion inhibition
- A high performance polymer for dispersion of colloidal material including iron and manganese
- Phosphoric acid for steel corrosion inhibition
- Sodium bromide for 100% conversion of chlorine gas to hypobromous acid during chlorination

Treatment with 100% hypobromous acid was viewed as essential to improve microbial control under the alkaline system conditions while exerting less oxidizing effect on system manganese. Polymer and organic phosphate additions were timed to provide maximum manganese stabilization during periodic halogen treatment.

The program, implemented in April 2000, has resulted in corrosion rates for mild steel less than 2 mpy, dramatic improvements in manganese control (Figure 7), good control of microbiological growth through proper sodium bromide application, and excellent deposit control as reflected in stable values of surface condenser cleanliness that the plant monitors continuously.

PITTING CORROSION MECHANISM

The nature of the pitting corrosion that developed at Sikeston Power Station does not fit into classic definitions (eg. Type I, II, or III) of copper pitting²⁶. There are similarities however, between the Sikeston case and the pitting characteristics observed in corrosion of freshwater copper tubing.

Freshwater copper pitting develops in well waters of high dissolved solids with pH in the range 7 to 8.2 and is accompanied by carbonate rich tubercles underlain by a cuprous oxide layer²⁷. Carbonate in the tubercle is indicative of alkalyzing cathode reactions - usually ascribed to oxygen reduction - that take place in the immediate vicinity of the localized anode. The tubercles are often aligned longitudinally along the tube length and removal of the tubercles reveals a bright metallic site on the tube wall. This type of pitting is unpredictable and the exact mechanism is uncertain. Chemical, physical, and metallurgical conditions that lead to severe pitting in the plumbing system of one building often produce no attack in an adjoining structure.

A general characteristic of pitting corrosion is the requirement of a large ratio of cathode-to-anode area. The large cathode area is essential to sustain locally high anodic current density and form the acidic, counter-anion rich conditions that establish the pitting site. In the absence of a suitable cathode, the anodic reaction is depolarized and pit nucleation terminates. As described in preceding sections, MnO₂ is an efficient cathode that diminishes anodic depolarization during nucleation and initial pit growth. Cathodic reduction of MnO₂ is also an alkalyzing reaction that generates hydroxide close to the pitting site and would lead to carbonate rich-nodules such as those observed at Sikeston. In addition, the observation that severe corrosion was associated with the manganese-rich but not with the iron-rich condenser fouling at Sikeston suggests that underdeposit conditions alone were not sufficient to generate pitting. The corrosion characteristics and the water chemistry found in the Sikeston system, show patterns consistent with a poorly understood phenomenon of freshwater copper pitting, however the fact that MnO₂ was present at Sikeston and that this material exerts a corrosive galvanic effect on the metal hints that manganese accretion played a role in the corrosion process.

Manganese has previously been implicated in copper corrosion^{2,8,28} and is cited in several references to "hot water" pitting^{29,30}. According to these reports, hot water pitting of copper occurs in soft waters and is associated with black, manganese rich scale. Cold water pitting – not generally associated with manganese - takes place in hard or moderately hard waters with formation of carbonate-rich nodules. The Sikeston case shows aspects of both pitting types; high hardness, high alkalinity, and carbonate-rich nodules characteristic of cold water pitting and pervasive manganese deposits at elevated temperature consistent with the hot water type. Again, the case does not fit neatly into classic definitions and illustrates that manganese can impact corrosion under a variety of conditions. In view of this corrosive potential, the fact that many facilities do not routinely analyze for manganese even when copper pitting has been a problem^{31,32} suggests a need for greater awareness of the importance of manganese control in preventing cooling system corrosion.

CONCLUSIONS

Manganese in utility cooling water circuits poses the threat of refractory scale deposition and pitting corrosion in copper and stainless steel tubing. This risk cannot be easily predicted from general water chemistry, water temperature, and classic corrosion definitions. Where makeup water sources are known to carry appreciable levels of manganese, or if fouling is suspected due to microbial oxidation of trace levels of manganese, it is essential to monitor and trend this constituent on a regular basis to enable prompt response to indications of deposition. Microbial manganese oxidation can seed chemical deposition and reduce microbicide efficiency, making it important to maintain a biological control program that prevents biofilm formation. Bromine and stabilized chlorine treatments can accomplish this with less risk of chemical manganese oxidation than conventional chlorine. Chemical technology utilizing threshold-inhibitors and dispersants provides effective manganese stabilization against chemical oxidation by halogens and is an important measure in preventing cooling system corrosion.

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