

**CORROSION AND DEPOSIT CONTROL IN ALKALINE COOLING WATER
USING MAGNETIC WATER TREATMENT AT AMOCO'S LARGEST REFINERY**

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ABSTRACT

Positive corrosion and deposit control in recirculating, alkaline cooling (tower) waters have been demonstrated at more than 30 cycles of concentration when the recirculating waters receive treatment in a magnetic field. Make-up and recirculating water characteristics, facility descriptions, and guidelines for proper design and use of magnetic devices are discussed.

INTRODUCTION

Reducing the volume of refinery effluents is a well-known concern to refiners because the NPDES Permit parameters are mass limited. Cycling up cooling towers offers a route to significant volume reductions, in addition to operating cost reductions, and limiting the amount of chromates in the refinery waste sludges.

At one time at Amoco's largest refinery cooling tower blowdown represented 60 per cent of refinery process water effluent because fears of scaling kept cycles of concentration low. This also caused increased operating costs due to costs of makeup water and those due to replacing the chemicals (biocides, corrosion inhibitors, dispersants, etc.) lost in the excess blowdown.

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In Amoco's next largest refinery, we currently recycle 30-38,000 m³/d (8-10,000,000 gpd) of treated refinery effluent to cooling towers and as fire water. While this has been an attractive method to reduce the volume of effluent discharged, the recycled effluent water has a higher hardness than normal makeup, and again scaling concerns keep the cycles of concentration in the system rather low which in turn keeps chemical treating costs up.

In a third, but fortunately much smaller Amoco refinery, ground water used for cooling tower makeup is hard, and only 1.75 cycles of concentration can be achieved before scaling is encountered. The refinery effluent is treated by the municipality. The costs of : makeup water, cooling tower chemical treatment, primary effluent treatment, and municipal charges for secondary treatment amounts to \$0.60/m³ (\$2.23/1,000 gala.). Using magnetic treatment of circulating cooling water to achieve increased cycles of concentration can result in dramatic savings as illustrated in Figure 1.

Scaling, of course, also contributes to serious energy losses and to operating problems. In Figure 2, for example, handbook' data for a fairly low pressure boiler show the costly effect of only 0.61 mm (0.024 inch) of CaSO₄ scale on boiler tubes; there is a 183⁰C (362⁰F) temperature drop across the scale. This results in higher tube skin temperatures which not only contribute to energy inefficiency, but may contribute to serious metallurgical problems with the tubes normally used for these boilers.

Other data shown in Figure 3 illustrate the significant decrease in heat transfer efficiency by various types of scale as a function of scale thickness. Obviously scaling presents severe economic penalties in process operations. Most refiners also can cite instances of severe process penalties and excessive maintenance costs in operations because of scaling.

Our interest in magnetic water treatment relates to environmental and operational needs; the successful application of this technology would address the environmental needs of reduction in water use and decreased quantities of chromate-bearing sludges and the operational need of large reductions in operational costs and potential process unit savings.

Water use reduction relates to the manner in which refinery NPDES Permit limits are stated; i.e., they are in mass units with the concentration levels used to calculate the mass units typical of BPCTCA. Thus if our discharge volume can be reduced by 25 per cent, we will make approximately the same reduction in kg/d of contaminants discharged. This is especially important to many refiners who never had any need to minimize water usage. The magnetic treatment of water supposedly offers the opportunity to increase tremendously the cycles of concentration in cooling towers without scaling concerns. This, of course, greatly reduces blowdown volumes which can have a major impact on reducing the NPDES calculations. Further, it gives hydraulic relief to the end-of-pipe treatment facilities. Savings accrue from less cooling tower makeup and less chemical usage to replace the chemicals and water lost via the blowdown.

In process operations, the scaling of heat exchangers or boilers cause severe economic penalties in process and O&M costs. Some of these penalties can be astronomical. Figure 3 illustrates the decrease in heat transfer coefficient as a function of the thickness and type of scale. Of course, scale on the water side of boiler tubes are a long recognized cause of tube failures. They are particularly serious in the furnace tubes of marine units because of the high heat absorption rates. Thus marine units appear to be an especial application target for magnetic descaling devices.

The international literature in the nonchemical treatment of water is, with a few exceptions, almost completely bifurcated.. The U.S. literature is almost completely negative on the subject, and the rest of the world is positive. Our earlier work at Standard optimizing the unit operations used for waste water purification had demonstrated clearly that the electrical properties of suspended solids were the means to control unit operations (1-4). Since we know that charged particles moving through a magnetic field, such as in mass spectrometry, are definitely affected by the magnetic field, we felt justified in further investigating the phenomena. Further, articles in the U.S. relied on ridicule, not data from technically defensible experimental protocols, to support their opinions.

Ridicule is used as the basis for many arguments against the possibility that magnetic fields can influence the course of chemical precipitation. This ridicule is based on the claim that there is no energy input by the magnetic field, and since there is no free lunch, the question is raised as to what work could be possibly be done. Eliassen et al. (5) argue "magnetic fields in the order of magnitude of 1,000,000 gauss are needed to dominate the motions of charged particles with atoms." Since this statement was expressed by MIT faculty, it intimidates the prospective investigator-unless, of course, he recognizes the statement is specious. Consideration of magnetohydrodynamics, electrical surface charge on particles, advances in magnetism, and questionable American interpretation of applicable technology led us to continue to accept the international literature as reasonable.

Magnetohydrodynamics (MHD)

The MHD technology is being widely studied as a topping cycle in power plants to increase the fraction of the energy recovered from fuels.

Faraday first observed magnetohydrodynamic (MHD) energy conversion when he demonstrated (1832) that if an ionized fluid is passed across the lines of force of a magnetic field, an electrical current is produced. Thus, with reference to Figure 4. when a conductive fluid flows through a pipe surrounded by an external magnet system and the magnetic field is perpendicular to the direction of fluid flow, a force is created that acts on the moving charged particles in the fluid to separate the negatively and positively charged materials. This force is called the "Lorentz force," and provides the electrical potential by which a current can be drawn off when a load is attached.

The charge separation achieved by the Lorentz force creates a potential difference that can produce an electrical current (Faraday) if there is an electrical load to absorb the power generated; i.e., the Faraday current produced by a MHD system is the result of the Lorentz force acting on the charged particles in the ionized fluid flow. The current generated is perpendicular both to the direction of fluid flow and the external magnetic field (Figure 4).

In 1879, E. H. Hall discovered that when a current-carrying conductor (ionized fluid) is placed in a magnetic field to produce the Faraday current, the Faraday current creates an electrical field around it that results in a "drift force" on the current which is called the "Hall effect." The Hall effect is proportional to the current density and the magnetic field strength and is at right angles to both the current and the magnetic field. With MHD, the electrical field is perpendicular to the current but parallel to the flow of the fluid. The induced electrical field counterbalances the current produced by the external magnetic field and deflects the Faraday current.

In addition to magnetic and electrical field effects in an MHD system, fluid and hydrodynamic effects must be considered. A magnetic Reynolds number has been developed which depends upon permeability, electrical conductivity, fluid velocity, and the length or size of the container. Magnetic Reynolds number in an MHD system is important so as to keep the fluid in the nonturbulent flow regime.

While the fundamental of MHD goes back 150 years to Faraday, there are two more recent developments that may provide the basis for reducing to useful applications these phenomena; they are in the areas of magnetism and zeta potential of solids.

Magnetism

MHD technology requires the use of magnetic fields. As reported by Chin (6), there have been giant strides in magnetic alloys achieved in the past decade. They are: 1) the rare earth-cobalt alloys, 2) chromium-cobalt-iron permanent magnets, and 3) the high induction, grain-oriented soft magnetic silicon steels. The rare earth-cobalt alloys have intrinsic coercivities more than 20 times and maximum energy products more than four times Alnico, 5, the most widely used permanent magnet alloy to date. Figure 5 shows the progress in quality of the rare earth alloys and permanent magnet materials over the years.

Zeta Potential of Solids

In our research we have determined that solids, in the presence of a solvent, have an intrinsic electrical surface charge that, in the case of colloids, is called zeta potential (ZP). Almost all matter dispersed in spent process water, such as oil particles, silt, biocolloids, inorganic matter, etc., has a negative ZP. All minerals, oil particles, bacteria, etc., that we have checked have an isoelectric point, i.e., a pH at which on the alkaline side the electric charge is negative and on the acidic side the charge is positive.

These coulombic repulsive forces are responsible for the solvent dispersion of solids. In every case in which we have studied unit. operations for solids removal, we have found optimization of the unit operation depended on controlling the ZP of the dispersed solids. Examples of this include: granular media filtration; dissolved air 'flotation; induced air flotation; sedimentation, etc.

LITERATURE

A computer literature search quickly generates well over 100 references on the subject of magnetic treatment of water. Most of the references are of international origin, and most of those are of Soviet origin_ although _Vermeiren (7) is identified as the discoverer of the fact that magnetic fields have an effect on water (8).

The following discussion of the literature is not meant to be, and by no means is, comprehensive. However, key articles are quoted directly to give the reader the tenor of the literature from various sources.

Soviet Literature

Basically, the Soviets claim that when a supersaturated aqueous solution of CaCO_3 is passed through a magnetic field (of proper design), the magnetic field apparently has structure-transforming forces causing a large number of microscopic nucleating sites to be created which cause the solid material to precipitate in the bulk of the solution. That is, the precipitate shows little tendency to adhere to surfaces of the pipe, etc., and is removable as sludge. Further, previously formed scale has been observed to separate under the influence of water treated in a magnetic field.

If these claims are found to be true, these findings would be of enormous importance in cooling towers, boilers, water treating (softening), compressor jackets, etc. For example, Tebenikhin et al. (9) comment:

"The essence of magnetic treatment of water is that the rate of scale formation is reduced under the action of a magnetic field through the formation of crystal nuclei within the water, and the scale formed has reduced mechanical strength."

Golubtsov et al. (10) comment

"Recently, a simple and economic method of magnetic treatment has become widespread in thermal power engineering.

"The principle of the magnetic treatment of water is that under the effect of magnetic lines of force, salts of hardness dissolved in water, can be precipitated in the form of tiny solid particles in the mass of water, later with heating forming loose, comparatively easily removed sludge. The source of the magnetic field is provided by electromagnets and permanent magnets

"The treatment of water with a magnetic field is now being used successfully for fresh water of the calcium-carbonate class with the observance of certain conditions.* Encouraging results have also been obtained recently for sea and highly mineralized water in general. The effect of the treatment of water with magnetic fields is determined basically by two factors:

thermodynamic nonequilibrium of the water system, i.e., its supersaturation with salts of hardness (CaCO_3 , CaSO_4) at the time of the effect of the magnetic field;

presence of iron oxides in the treated water.

"In a supersaturated solution, a magnetic field causes the precipitation of the excess amount of salts of hardness until supersaturation is eliminated and equilibrium is established under given conditions. When heated, crystal nuclei formed due to the magnetic field pass through all phases of a disperse state and are precipitated in the form of solid particles, smaller and more numerous than without treatment; they are in the water in a suspended state and play the role of centers of crystallization. Thus, instead of scale, sludge is formed in the water tank.

Effective treatment of water with magnetic fields is possible only when the water entering the magnetic device is supersaturated in relation to calcium carbonate and sulfate. The state of supersaturation in relation to calcium carbonate is determined by lack of aggressive carbon dioxide in the water, i.e., by observance of the condition $\text{CO}_2 \text{ stabl} > \text{CO}_2 \text{ free}$."

Professor Skorobogatov (11) comments:

"At present, to reduce deposits of scale in various steam-forming, heat exchange and condensing devices, along with chemical methods, physical methods of treating water are also used. Among the latter are magnetic, ultrasonic, and electric methods. The first two have been the most widespread.

"It is well known* that magnetic treatment of water is carried out in special magnetic sleeves (first method). In other devices, flowing water is treated by alternating magnetic fields, changing in time (second method)."

The paper by Martynova and Gusev (12) provides a rich source for quotations:

"The theoretic possibility of the effect of a magnetic field on reduction of the intensity of scale formation on the walls of the heat exchanger is basically determined by two factors connected with properties of the

*Emphasis added.

treatment solution. The first factor is thermodynamic imbalance of the solution, i.e., its supersaturation with salts of hardness at the moment of the magnetic effect. In this case, rapid crystallization of the excess amount of salt occurs in the tank; the process continues until equilibrium is established under given conditions. Tiny crystals formed as a result of the magnetic treatment of the water before its entry into the heat exchanger (for example, calcium carbonate and sulfate) play the role of 'seeds,' i.e., centers of crystallization. With a sufficient number of these centers of crystallization, further crystallization of salts (for example, with evaporation of water in a steam generator) occurs to a greater degree on them, and not on the heating surface, i.e., the intensity of scale formation is reduced.

"The second factor is the presence in treated water of oxides of iron (or their hydrate forms), always present in any circulating water, including distilled. Admixtures of iron are primarily products of corrosion of the equipment; a number of these products, such as Fe_3O_4 , $\delta-FeOOH$, $\gamma-Fe_2O_3$, have ferromagnetic properties. These partially hydrated oxides are basically colloids, as their solubility is very low and, as a result, is below concentrations of iron typical of the majority of water in thermal power facilities (10^{-6} - 10^{-4} mol/kg); and ion forms cannot be stable, as they are subject to deep hydrolysis as the result of extremely low constants of dissociation of corresponding hydrate forms, especially at high temperatures. With increase in the concentration of iron, crystal nuclei (centers of crystallization) enlarge after magnetic treatment of the water. The mechanism of effect of iron oxides in softening water (supersaturation of the salt solution) is still not clear; it is either a shifting of ferromagnetic particles in the magnetic field or their coagulation. Some other process is also possible."

"Conversion of readily soluble bicarbonate to hard-to-dissolve calcium carbonate ($Ca(HCO_3)_2 \leftrightarrow CaCO_3 + CO_2 + H_2O$) is characterized by a certain ratio between balanced concentrations of dissolved carbon dioxide and all other components of the system:

$$C_{CO_2}^{bal} = K_1 \pi P_{CaCO_3} \cdot C_{Ca^{2+}} + f_{Ca^{2+}} \div C_{HCO_3^-}^2 f_{HCO_3^-}^2$$

ap

where K_1 - constant of the dissociation of carbon dioxide;

πP_{CaCO_3} - product of solubility of calcium carbonate;

$C_{Ca^{2+}}$, $C_{HCO_3^-}$ respectively, coefficients of concentration, mol/kg

$f_{Ca^{2+}}$, $f_{HCO_3^-}$ respectively, coefficients of activity.

Under the condition $C_{CO_2}^{free} < C_{CO_2}^{bal}$, sea water is

supersaturated with $CaCO_3$, which can precipitate; the process of crystallization in this case can be intensified by a magnetic

field. With the condition $C_{CO_2}^{free} < C_{CO_2}^{bal}$, water is not

saturated, formation of solid phase of calcium carbonate is impossible, and therefore, a magnetic field can have no effect on reducing the intensity of carbonate scale formation. With concentration of carbon dioxide at 0.44 mg/kg (water in equilibrium with the

atmosphere; $P_{CO_2} = 3 \cdot 10^{-4}$ kgf/cm² at 20°C) water of the Caspian Sea can be unstable, i.e., supersaturated in relation to CaCO₃. However, at a temperature of 100°C, both waters are unstable. Thus, solutions of calcium bicarbonate (including sea water) can easily be converted from an unsaturated to a supersaturated state with relatively small changes in a number of parameters, for example, temperature or partial pressure of carbon dioxide above solution."

"Magnetization is most effective for water supersaturated both with calcium carbonates and with calcium sulfate."

Conclusions:

1. magnetic treatment must not be considered separately from parameters of the heat exchanger (evaporator), the intensity of heat flux, quality of water, etc.
2. The antiscaling effect of magnetized water, besides being the effect of a magnetic field (parameters of magnetic instrument) is also a function of operational parameters of the heat exchanger (evaporator). Each regime requires a certain intensity of the magnetic field ensuring optimum antiscaling effect of magnetization.
3. Optimal conditions of the magnetization of sea water in each specific case should be a simulation of industrial conditions and test magnetization with change and selection of its individual parameters as occurs, for example, in selecting the optimal regime for coagulation of surface fresh water.

Kishnevskii et al. (13) summarize their pilot plant results with the following conclusions:

1. It has been shown that the role of a magnetic field is analogous to the action of inoculator seeds, but with the difference that the 'timers' are introduced artificially, and in magnetic treatment, are formed from saturated solutions of scale-formers as a result of their adsorption on ferromagnetic oxides of iron that have coagulated in the magnetic field.
2. The feasibility, advisability, and optimal conditions for the use of magnetic water treatment can be determined on the basis of a calculation of the degree of supersaturation and through the use of the Purbet diagram with respect to water of the given salt composition; analytically measurable indices are the salt concentration and the values of pH and eh.

Much work has been done by the Russians on boilers. For example, in their article Lapotyshkina et al. (14) covered many areas of water treatment and boiler operation:

"Schemes for the treatment of makeup water, including magnetic treatment,* depend on the source of the initial water. If tap water is used, the scheme includes only antiscaling magnetic treatment.* if initial water comes from an open reservoir, the scheme for treating makeup water must include coagulation and clarification with subsequent magnetic treatment and thermal deaeration. Coagulation and clarification can be combined in KO-2 pressure contact clarifiers proposed by the Academy of Municipal Economy, which provides single-pass water purification with water moving at a rate of 5-10 m/hr. This is the scheme of water purification (with productivity up to 500 m/hr) used in the direct discharge district heating plant at the Saratov State Regional Power Plant (GRES).

"The use of magnetic treatment to prevent scale is based on the experimental fact that the main mass of calcium carbonate (80-85 per cent) is precipitated when magnetized water is heated to 102-104°C, being contained in the water in the form of finely dispersed particles measuring less than 1μμ. These particles of colloid dispersity are suspended in water and are a stable system."

"From Table 1 (omitted) it can be seen that increase in the intensity of the magnetic field in the effective area of the unit helps raise the proportion of colloid dispersity. This should have a favorable effect on the condition of the heating surface, as the rate of precipitation of these particles is an order lower than that of particles measuring more than 1μμ.

"The main problems which were solved in the exploitation of water treatment schemes, including magnetic treatment, were determining the working conditions for individual equipment units in water containing finely dispersed suspended matter."

"From the data, it follows that the optimal regime of magnetic treatment corresponds to 1500 oersted in the effective area. In this case, about 80 per cent of calcium carbonate is in heated deaerated water in the form of particles measuring less than 0.5μμ, the precipitation of which from a moving flow is practically negligible. Observation of the condition of district heating plant equipment at the GRES with the use of makeup water treated according to the above-described method revealed features of the operation of individual heat exchangers and equipment."

"Reduction of the size of calcium carbonate crystals two times or more as the result of the magnetization of water verifies the efficiency of magnetic devices."

"In conclusion, it must be noted that the water treatment scheme, including magnetic anti-scaling treatment of water, is more economical

*Emphasis added.

than other currently used schemes of chemical (ionite) water treatment. Realization at the Saratov State Regional Power Plant (GRES) of a simplified water treatment scheme, instead of the one previously designed (clarification-Na cation exchange), saved 344 thousand rubles in capital expenditures and reduced the cost of treated water from 6.81 to 3.01 kopecks/T. The use of magnetic treatment in the Astrakhan Municipal Power Plant in a unit with productivity of 250 T/hr., instead of the design scheme with N-cation exchange. 'starvation' filters, saved over 130 thousand rubles in capital expenditures and reduced operational expenses to practically zero. The use in treating makeup water of the heating plant of schemes, including magnetic treatment instead of Na-cation exchange, can also be recommended by reason of its complete lack of waste water, polluting reservoirs, and helping raise the total salinity of surface waters.

"Results of the operation of industrial units for treating supplementary water for district heating plants with direct water discharge verify the applicability of simplified water treatment schemes, including anti-scaling magnetic treatment,* both in a variant with preliminary coagulation and clarification in contact units, and without prepurification in the case of using tap water.

"Industrial realization of simplified water treatment schemes including magnetic anti-scaling treatment, will significantly reduce capital expenditures and operational expenses for treating supplementary water for district heating plants."

The work of Drozdov and Kherson (15) emphasize that sludge from magnetic water treatment is not indiscriminately charged to boilers:

"To increase the effectiveness of deposit control, magnetic treatment must be combined with removal of sludge from the boiler water and removal of the sludge from the steam boiler.

The determination of the main features of sludge formation in the magnetic method of water treatment has made it possible to outline and implement measures that ensure the successful application of the method of magnetic water treatment for hot-water water-tube boilers with a small ratio of boiler water volume to heating surface. For this purpose, it was proposed to use a preboiler sludge remover which would be included in the boiler feed system after the electromagnet apparatus and which would be included in the boiler feed system after the electromagnet apparatus and which would be positioned in the region of feedwater supply. Improvement of the magnetic method of water treatment was carried out in production for three years (1968-1971) . In this period, four designs of preboiler sludge removers that work together with electromagnetic units were tested. The industrial tests of these first designs made

*Emphasis added.

it possible to formulate the basic requirements for sludge removers of this kind. They consist in the following ---"

Sperankiiy et al. (16), in their area of responsibility, found it necessary to develop a boiler water treatment scheme. They emphasized that they followed the State Mining Engineering Administration rules for magnetic treatment, and that under their rules, sludge handling was important.

"It was necessary to develop a water treatment scheme, simple in design, cheap to manufacture, reliable in operation, and not requiring special personnel for servicing. These demands are met by a scheme using devices with ferrite-barium permanent magnets, or devices designed by the Ivanov Energy Institute. The use of this plan for treating artesian water does not violate the rules of Gosgortekhnadzor (State Mining Engineering Administration), as the following conditions are met: 1) content of free CO₂ in initial water by analysis is less than equilibrium; 2) specific water volume of the boiler (45 l/m²) is less than maximum permissible (50 l/m²) with an existing screen surface of 5 m²; 3) hardness of initial water of artesian wells (up to 4.8 mg-equiv/l) does not exceed maximum permissible level (5 mg-equiv/l).

"In developing a plan for the magnetic treatment of water to feed PKN-1s and PKN-2s boilers equipped with clarification and sodium-cation exchange filters, it was feasible to use these filters to clarify feed water, passing through magnetic treatment, without regeneration of sodium-cation exchange filters. The plan in which magnetic devices are used together with anthracite and sulfur-carbon filters without regeneration of the latter gives a significantly better anti-scaling effect than the plan without filters.

"Magnetic treatment of feed water can be considered as a variety of in-boiler water treatment. A condition of the use of the latter is prompt and appropriate removal of sludge, which is carried from the boiler (periodically or continuously). Periodic removal of sludge is most effective if it is carried out from a part of the boiler where it can be continuously stored. In the absence of this part of the boiler, scavenging is carried out from a sludge filter-separator included in the scavenging line. As [the sludge forming in magnetic treatment of the water is finely dispersed and does not settle in moving liquid](#), belting fabric is recommended as a filtering element, attached between flanges of the sludge separator."

"Power engineering at the Priluki administration of drilling operations is still limited to established in their facilities of magnetic devices only, using neither sludge separators nor filters. As examination of a number of facilities with open boilers and inspection of internal heating surfaces have shown, scale is practically absent, but a large amount of finely dispersed sludge was found in lower collectors and boiler drums. Therefore, we must not be limited to establishment of only devices for the magnetic treatment of water. The organization of continuous

withdrawal of sludge from the boiler will create conditions when magnetic treatment can be a reliable method of water treatment."

Tel'nov et al. (17) were concerned with scaling in engines:

"The problem of preventing scale in the cooling systems of automotive and tractor engines has long interested operators and scientists. For fixed thermal engineering units, there are a number of methods, chiefly reagent methods. However, the use of many of them requires the construction of costly devices and teams of specialists, and turns out to be unprofitable. Nonreagent methods (magnetic, ultrasonic) of which the method of water treatment using a magnetic field, is the most economical, therefore, have found application in recent years."

"The correct use of a magnetic field to treat water is of definite technical and economic interest. Water treatment using a magnetic field is used in unscreened low-pressure boilers, in heat recovery systems, and lately has been used for the cooling water of compressors and internal combustion engines."

"The essence of the magnetic treatment of water is that when water is intersected by a magnetic field of force, hardening salts may be released in the form of mobile sludge instead of hard scale.

"The role of the magnetic field reduces to the formation of crystal nuclei from supersaturated solutions of salts. Furthermore, previously formed scale separates under the influence of water treated with a magnetic field.

The practical feasibility of using a magnetic field to reduce the amount of scale in the cooling systems of internal combustion engines and steam generators (heat-exchange units) is determined above all by the thermodynamic nonequilibrium behavior of the solution, i.e., by its supersaturation with respect to the hardening salts CaCO_3 and CaSO_4 as water passes through the magnetic field. At this time, the excess quantity of hardening salts separates from the water, with the formation of crystal nuclei until equilibrium is established. When such water is heated in a heat exchanger or an engine cooling system, the particles formed will grow and serve as centers of crystallization for the solid phase that separates. If their number is sufficient, the total surface area of the particles will be greater than the active heating or cooling surface. As a result, the scale formers will precipitate throughout the entire volume of water forming sludge.

"If after treatment with a magnetic field supersaturated water is not heated, then the reaction of very small particles or their dissolution is possible. If this occurs, the number of crystal nuclei gradually decreases, and after a comparatively short time the water undergoes a decrease in the antiscaling properties that it has acquired ('magnetic memory')."

"Thus, effective treatment of water with a magnetic field is possible only when the water entering the magnet apparatus is saturated with calcium carbonate and sulfate."

The Soviets are firm believers in the use of magnets on ships. Kozlov (18) comments:

"On SRTM-800 ships a KVA 0.5/5-D fire-tube boiler with a heating surface of 7.3 m², steam capacity of 500 kg/hr and operating pressure of 5 kgf/cm² is used as an auxiliary. The manufacturing plant recommends for these boilers a combination regime, reagent (phosphate-nitrate) with the addition of nonreagent (magnetic).

"For this purpose in the feed pipe is installed a device providing eight-fold intersection of the water with a permanent magnetic field.

"In the course of operation, boilers on SRTM "Solnechnyy," "Kotoboy," and Radist" were fed with water with general hardness from 1.3 to 1.7 mg equiv/l and chloride content up to 140 mg/l (this is three times higher than the limits established by the manufacturing plant). A phosphate-alkali regime was maintained by introducing 200-300 g per month of antideposit A or trisodium phosphate along with the additional treatment of the water with a magnetic field.

"Here the alkali number of boiler water was 28-50 mg/l, chloride content 500-700 mg/l. The time of operation of the boilers between boiler cleanings varied from 1800 to 2400 hours (instead of 1200 hours, established by the manufacturing plant). Inspections showed the, good conditions of heating surfaces, almost complete absence of hard scale and corrosion damage.

"The results led to the conclusion that it was feasible to convert the auxiliary boilers of SRT, SRTR, and SRTM ships to the non-reagent (magnetic) treatment of feed water with introduction once a month of 0.1-2 kg of trisodium phosphate to maintain the alkali number of boiler water at 20-40 mg/l, increasing the period between boiler cleanings from 1200 to 2400 hours.

"Periodicity of ship analyses of boiler water for alkalinity and chloride content was reduced to once every 10 days.*

Kozlov goes on to give case histories for the following ships that installed magnetic devices: Ural, Ukraina, Anakriya, Lavkaz, and the Sovetskiy Sakhalin. Considerable detail is given concerning the equipment, performance water properties, and he makes recommendations for equipment and operations, differentiating between fishing, transport, and depot ships. He concludes:

"Magnetic treatment with observance of the rules of technical operation of boilers prevents greasing of heating surfaces. With prolonged proper operation of the magnetic device and the boiler, oil zones almost

completely disappear, as verified by the quite complete elimination of oil from the water. Observations of the operation of piston mechanisms established that gland packings and cylindro-piston groups of engines operate better and with less wear under conditions of the magnetic treatment of water.

"It is necessary to reduce to a minimum, and with normal quality of feed water after installation of devices for the magnetic treatment of water and with complete removal of old hard scale to exclude entirely, the introduction of anti-scaling compounds. In this case, it is advisable to remove salt from feed water before the boiler by preliminary heating, significantly reducing sludge deposits and making it possible to reduce the number and duration of scavengings. Magnetic treatment of water also contributes to increasing the economy of ship power plants as a result of reducing the consumption of chemical reagents for treatment and analysis of boiler water, increasing the period between boiler cleanings and shortening their duration and labor consumption. As the periods between boiler cleanings are increased from 1000-1500 to 2000-3000 hours, the navigation time of each ship, because of the lower number of boiler cleanings, will increase an average of 7-15 days.

"Change in the character of scale formation decreases labor consumption and reduces the length of boiler cleanings 1.5-2 times, and also lowers the probability of mechanical damage in cleaning heating surfaces."

"In our opinion, reagent-less, (magnetic) treatment of water can guarantee, under conditions of the boilers being fed with 70-90 per cent condensate and 10-30 per cent coastal (fresh) water, a scaleless regime for any modern designs of ship steam boilers."

Clearly the Soviets' use of magnetic water treatment is very extensive, and they are firmly convinced of the role and value of magnetic water treatment.

Other Investigators

Norway

Hoff (19) had serious scaling problems in a "lime transporting pipeline" at the Baerum Waterworks in Baerum, Norway. It was a plastic pipeline, 38 mm (1.5 inches) diameter and about 45 meters (50 yards) long. Sludge and hard scale often clogged the pipeline every week or 10 days and was very difficult to clear. Hoff installed a magnetic unit in the pipeline and claims the scaling stopped. Hoff comments:

"The lime-transporting pipeline was now cleaned and put back into service. After another three months' period with the same lime dosage as before, the dosage was stopped. This time we let fresh water run through the pipes for about half an hour before the inspection. Now there was hardly any scale in the pipeline and mixing chamber and very little of the powder-like sediment which we had noticed the previous time. The reason for this is probably that the pipeline was 'washed out' before we

opened it. This, we believe, is important if it is necessary to stop dosage for some reason or other. Thus, it is possible to avoid all problems with lime in the pipelines.

"From certain quarters, it has been stated that magnetical treatment of water is sheer nonsense. It is pointed out that there is no theory which can explain what is said to happen, for instance, in ships' boilers. Regardless of theoretical background, the permanent-magnet unit has abolished a laborious practical problem for us."

"The literature leaves no doubt that magnetic treatment of water has an effect on its nature. The effect varies with concentration of dissolved salts in the water and with the magnetic field strength. The structural changes which take place give rise to crystallization cores. This means an instable state. The water structure is stabilized again when new ions are hydrated.

"How this happens, if it for instance occurs directly as an equilibrium shift from the solid phase, depends on which reaction gives the largest energy gain.

"This increasing ability to keep lime in suspension which we observed when water was treated magnetically, can be due to such crystallization cores. These will, on account of their molecular disperse size, be dominated by their surface active qualities and sediment slowly.

"This will lead to a reduced rate of sedimentation for the whole suspension and change the consistence of the precipitate."

Ellingsen and Kristiansen (20) report the results of studies carried out to investigate the rate of precipitation of calcium carbonate from supersaturated natural water after passing through a magnetic field. Their work indicated the rate of precipitation to increase with increasing magnetic field strength. Ellingsen noted that **there are** some installed units which do not work properly. Consequently, a program with **grants from the Norwegian Government**,* has been initiated to find out why it is so.

India

Joshi and Kamat (21)** were intrigued by the Russian work and investigated the effect of a magnetic field on the physical properties of water. They set up laboratory apparatus in which they compared pH, surface tension, and dielectric constant effects on water exposed to a magnetic field to water not exposed to a field. **The authors claimed that pH and surface tension were changed by passing through the magnetic field**, the delta increasing with increasing field strength over the range of 1900 to 5700 gauss. The dielectric constant change was identical with changing field strength. The change observed in pH was also a function of the initial pH of the water,

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*Emphasis added.

**Dr. Joshi is the Director of the Institute of Science, Bombay, India.

"The study found that there is no change in the physical and/or chemical properties of water treated with permanent magnetic devices. The boiling point was not lowered; the surface tension measurements indicated no measurable difference between raw water and magnetically treated water; there was no evidence of a reduction of scale-forming tendencies in water using magnetic devices; and the electrical conductivity of the water was unchanged. The calcium ion concentration of the water was unchanged by magnetic treatment, indicating that magnetic treatment could not be causing the precipitation of calcium carbonate."

Clearly, there is a negative attitude concerning magnetic treatment of water expressed in the limited amount of American literature.

Literature Evaluation

There is little doubt that 98+ per cent of the technical literature on magnetic water treatment is of Soviet 'origin. The Soviets hold symposia dedicated to the subject, and many workers in many divergent institutes investigate the subject and report it in the literature. Some institutes set up guidelines for the use of the technology; other institutes design the units. Clearly the Soviets have a positive attitude concerning the fact that magnetic fields affect chemical reactions. They report positive results, and many "theoretical" papers appear hypothesizing the cause for the observed phenomena.

The American scene on the subject might first seem nonexistent, but there have been at least 30 manufacturers of magnetic-type devices. A cursory review of the devices show that most do not follow the Soviet design guidelines; therefore, many negative experiences would be expected. Further, these devices were marketed as a nontechnical item, and the suppliers promised "magic" results and most of their applications did not follow Soviet guidelines.

When 25 year old work of Eliassen et al. and the current work of Gruber and Carda is reviewed in light of the Russian work, this limited American work to evaluate the technology could be criticized for not using proper test protocols. They were, of course, using protocols recommended by vendors who were trying to market an item without understanding the applicable technology.

Thus, in light of the extensive positive results reported in international sources, a review of the U.S. literature leads one to the rationalization that the negative attitude expressed reflects experience with (1) an improper application or experimental protocol, and/or (2) a poorly or improperly designed magnetic unit. Accepting this rationalization suggests that if these points are addressed properly, positive results might be obtained.

EXPERIMENTAL

Our goal was to select a magnetic unit with a strong, focused magnetic field and pass the water containing the coulombically charged particles through the magnetic field at a velocity that generates MHD energy.

Magnetic Unit Selection

Gruber and Carda (25) conveniently catalogued magnetic devices in four classes as illustrated in Figures 6 to 9. There are units available representative of all these classes.

Class I units seem totally inappropriate. The magnetic field is not perpendicular to the flow of ionized fluid, and the magnetic field would never impact fluid in an iron pipe. It was believed that units of this type are responsible for much of the negative results reported for magnetic devices.

Class II is the device for which Ellingsen and Kristiansen (17) report both positive and negative results. Mixed results derive from the fact that the flow is perpendicular to the magnetic field but in highly conductive fluids the design may not yield the full potential of the magnetic field.

Class III resembles one Soviet design. This design may result in life expectancy and field strength dampening problems with the magnetics, and it is not optimum for assuring that the fluid flow will be perpendicular to the magnetic lines of force.

Class IV is a design incompatible with assuring that the ionized fluid passes through a magnetic field perpendicular to the lines of force.

After analysis of designs from all classes, a unit in Class II was selected for test.

The specific device selected for testing mounted magnets in arrays as shown in Figure 10. The magnetic arrays are mounted in a spool piece with opposite poles across from each other to strongly focus the magnetic field across a slot as shown in Figure 11. The addition of flow diverters to the stacked arrays as shown in Figure 12 aid in providing a venturi effect with minimal pressure drop due to entrance losses. The venturi effect across the magnetic field is illustrated in Figure 13. The stacked array of magnets that fit into the spool piece are as in Figure 14, where the flow diverters are not shown for simplicity. This test device met our goals of: strong magnets, highly focused magnetic field perpendicular to the fluid flow, a venturi effect as used in conventional MHD units (Figure 4), and a reasonable pressure drop of about 4 psi at the velocity through the venturi required to generate MHD energy.

Test Program

Experimental-Phase 1

The first test program (Phase 1), designed to obtain data on the antiscaling effectiveness of magnetic water treatment, involved a cooling tower on a 200 T/D air conditioning system at a refinery maintenance shop. Figure 15 is a schematic typifying the system and shows the location of the magnetic device. The cooling tower recirculation rate was 600 gpm, and the basin volume is 1,200 gallons. The cooling tower is shown in Figure 16, and the installed magnetic unit spool piece is shown in Figure 17. This exchanger had a history of serious scaling problems.

Totalizing water meters were added to the makeup and blowdown water lines. Temperatures were monitored and routine analyses made for calcium, magnesium, bicarbonate, chloride, sulfate, alkalinity, total hardness, pH, conductivity, total dissolved solids, silica, turbidity, and total suspended solids. The strategy was to operate the tower for a month at normal cycles, but with no pH control, then shut off the blowdown and let the salts concentrate.

Experimental Test Conditions

The effect of this test protocol on the cycles of concentration calculated from calcium, magnesium, chloride, and conductivity is shown in Figure 18. The chloride is an unsatisfactory indicator of cycles because HTH was used as a biocide. Calcium, of course, was precipitating somewhere in the system. The magnesium and conductivity data indicate the cycles of concentration achieved were in excess of 35. The pH of the recirculating water was in the range of 8.1 to 8.7 during normal operations and typically 8.6 during the period the cooling tower blowdown was shut off. The test protocol achieved our desired operating conditions of very high cycles of concentrations and a quite alkaline pH.

The solubility curve for CaCO_3 in Figure 19 shows that we always had scaling conditions for CaCO_3 ; the CaSO_4 data in Figure 20 show that once the blowdown was shut off the recirculating water rapidly became scaling with respect to CaSO_4 . (The samples were sequentially numbered and plotted.) Both the Langelier Index and Ryznar Index calculations also predict scaling.

The actual concentrations of five parameters are shown in Figure 21. Clearly, high cycles of concentrations were achieved. The makeup water quality is compared to the recirculating water in Figure 22. These data indicated that makeup water was of reasonably uniform quality over this rather short time frame.

Results

At the end of the test period, the exchanger was opened and inspected for scaling. No scaling was found.

One surprise was the observation that the recirculating water was always clean; that is, the turbidity and suspended solids were very low. With only two minutes theoretical retention time in the basin, we expected the precipitated solids to be recirculated with the water. Instead, they collected in the basin. The solids are "sticky" but nonscaling. The "sticky" character is illustrated in Figure 22 which shows the precipitated solids collecting on corrosion coupons suspended in the cooling tower basin. When wet these solids easily wipe off. Therefore, it is important to maintain sufficient water velocity to prevent collection of these solids at undesirable locations. Also, once dry they are difficult to remove. It is, therefore, desirable to keep the solids wet until removed from the system.

The phase 1 installation has been on-stream for a little over two years at this writing. On two occasions, the water velocity through the magnetic field decreased significantly because of strainer blockage. On both occasions of significantly reduced flow, scaling was initiated. Once the flow problems were remedied, no scaling was observed.

The corrosion control program for phase 1 consisted of using chromate Nalco balls. Chromate levels in the recirculating cooling water varied from 40 to 100 mg/L. With the brackish water conditions at very high cycles of concentration and the equilibrium pH of 8.6, corrosion levels of 0.41 to 0.57 mils./yr. were measured by average penetration of mild steel.

Experimental--Phase 2

After the initial data were available from phase 1 showing that magnetic treatment was effective for scale control, a second magnetic unit of slightly modified design was installed on another, larger air conditioning system at the refinery warehouse. The cooling tower recirculation rate was 1,150 gpm.

Experimental Test Conditions

Once the magnetic unit was installed, the control of pH was discontinued, the blowdown shut off, and the minerals allowed to concentrate. Because the drift and fugitive losses were very low, very high cycles of concentration approximately 40 to 50, were observed. The system was allowed to run essentially unattended.

Results

After operating for four months in the scaling mode, the exchanger was opened and inspected for scaling. The tubes were all clean and bright with no evidence of scaling anywhere. This system operated for a total of ten months with no maintenance nor heat loss observed.

The corrosion control program for phase 2 was similar to phase 1.

Experimental--Phase 3

The positive results achieved with phases 1 and 2 encouraged further exploratory work with magnetic water treatment. The single problem with the data from phases 1 and 2 was the fact that the temperature drop across the exchanger was only 4 to 6°C (7-11°F). The next step in the program was to test a situation where the temperature drop was much greater, that is, greater than about 10°C (>20°F). ap

Unfortunately, a small installation comprising a modest risk was not available. Fortunately, an operating superintendent of a large reformer had such a severe, longstanding problem with scaling that he determined it was worth the comparatively large risk to determine if magnetic water treatment would solve his heat transfer problems. Accordingly, two very large (36 inch) magnetic units identical to the unit used in phase 1 were added to the cooling tower circuit. One of the units is shown in its shipping crate in Figure 23. Craftsmen installing the units are shown in Figure 24, and the installed system is shown in Figure 25. The cooling water recirculates at about 95m³/min. (25,000 gpm). The system started up July 1, 1983.

Results

As of this writing, the phase 3 system has been operating 11 weeks. Most of the operation has been in the scaling mode according to the Langelier and Ryznar Indices. The cycles of concentration achieved ranged up to 15 and have been limited because of fugitive losses.

No loss in heat transfer has occurred in the critical exchangers being monitored. Typically the unit experiences severe heat transfer problems only a few weeks after startup when operating the cooling tower at three to five cycles and with pH control. After 11 weeks, enough operating time has accumulated to convince operating personnel that, without a doubt, scale control is being achieved.

The corrosion control program uses chromate. Initial data are limited but at levels of 7 to 12 mg/l chromate, instantaneous (corrator) rates of 2.7 mils./yr. for mild steel and 0.75 mils./yr. for admiralty were measured.

Conclusions and Guidelines

1. Carefully selected magnetic water treating devices, designed and installed to operate to yield MHD energy, were highly successful controlling scaling when operating in an industrial environment under conditions of CaCO_3 and CaSO_4 scaling.
2. All three installations reported used Brazos River water.
3. No pH control is necessary and the pH of recirculating cooling water equilibrated at 8.6 to 8.8 in the reported installations.
4. A magnetic device having two focused magnetic fields of about 1,700 gauss with the water flowing through the magnetic field at a rate of at least 6 m/s (20 fps) resulted in adequate treatment for scale control.
5. MHD energy may play a role in determining the effectiveness of the magnetic water treatment unit as evidenced by the experience that low flow rates through the magnetic fields resulted in scaling whereas at 6 m/s no scaling was observed.
6. Corrosion problems have not been encountered.

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