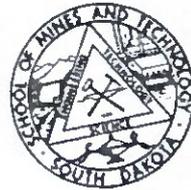


RESEARCH REPORTS

PERFORMANCE ANALYSIS OF PERMANENT MAGNET TYPE WATER TREATMENT DEVICES

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Rapid City, South Dakota
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RESEARCH AND EDUCATION IN WATER QUALITY



RESEARCH REPORTS MAGNETIC WATER TREATMENT DEVICES

EXECUTIVE SUMMARY

The Water Quality Association selected the South Dakota School of Mines and Technology to be the recipient of a study grant; the purpose of which was to evaluate the performance of permanent magnetic water conditioners in an environment representative of typical residential and light commercial application.

The objective of this research study is to quantitatively assess the effectiveness of permanent magnet type conditioners only. The first phase of the testing program was to develop a standardized series of tests that will be able to be duplicated at any time within acceptable experimental error and be acceptable to the academic community. These tests will demonstrate the accuracy or validity of the published performance claims regarding corrosion inhibition, scale formation, scale removal, and alteration of the physical and chemical properties of water. The second phase of the contract was the

actual testing of the devices under the testing protocol developed in Phase I. The devices were tested against their own performance claims and against the performance of conventional ion exchange treatment devices.

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.

—Dr. Dan D. Carda

Final Report
issued to
Water Quality Association

**MEASURABLE PARAMETERS IN WATER CONDITIONING
EQUIPMENT AS DETERMINED IN LABORATORY
SIMULATIONS, AT RAPID CITY, SOUTH DAKOTA**

Principal Investigators

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July 1981

South Dakota School of Mines and Technology

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1.0 INTRODUCTION

The ultimate objective of this study is to evaluate the performance of permanent magnetic water conditioners in an environment representative of typical residential and light commercial applications. In order to carry out such an evaluation, suitable experimental procedures must be developed that can yield definitive and repeatable results under the present conditions and can be extended to other potential environments, such as those related to industrial applications. The primary purpose of this study thus becomes one of exploring a variety of experimental procedures capable of determining the nature and extent of the effects of magnetic water treatment on the properties of water.

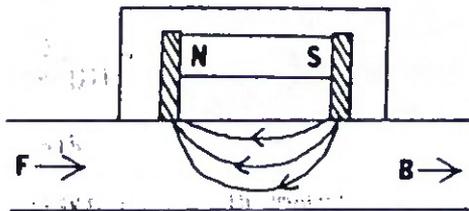
Passage of a water stream through a region of "high" magnetic field^(a) has often been reported to create substantial changes in the properties of the water. In particular it has been claimed that magnetic treatment strongly effects the scaling and corrosion properties of water without appreciably effecting its chemical composition. It has been implied that the physical properties of water are somehow altered without changing the molecular concentration of the inevitable host of dissolved substances in the water. Reports on the effects of magnetic water treatment date back to the nineteenth century, but it has only been in the last few decades that interest has really blossomed.

Recent interest in the subject was stimulated by Vermeirens⁽¹⁾ work in Belgium, followed by extensive reports of work done in Russia primarily by V. I. Klassen⁽²⁾. In the last two decades numerous experimental laboratory studies and operational tests have been carried out throughout the world. The numerous reports of reduced scaling and/or corrosion in operating environments such as steam boilers is what stimulated our current interest in the subject. Examination of the reports of laboratory investigations, although often contradictory even under controlled conditions, indicates a general lack of evidence that

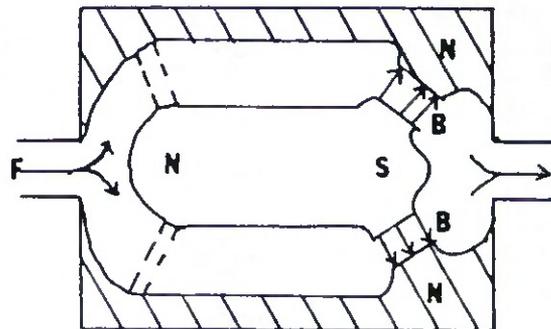
(a)Note: In what follows we will refer to magnetic field in units of Oersted or amperes/meter rather than magnetic flux density in units of Gauss or Tesla; since water is an impermeable medium the two quantities are simply proportional with proportionality constants of 1 in the first case and $4\pi(10^{-7})$ in the second.

magnetic treatment in any way affects the scaling/corrosion properties of water. Most studies of this kind, such as those carried out at MIT⁽³⁾, concentrated on chemical analysis of the water before and after treatment with completely negative results. Since much of the generally positive Russian literature reports on changes in physical properties (boiling/freezing point, surface tension, scaling rates, etc.) the study reported here also emphasizes the physical properties while still retaining chemical analysis as a corroborative tool. Since water with its inevitable array of solutes is an exceedingly complex medium--that is, difficult to analyze fully--this series of studies also includes a laboratory simulation of a typical domestic environment in which scaling plays an important role, i.e., a domestic water heater.

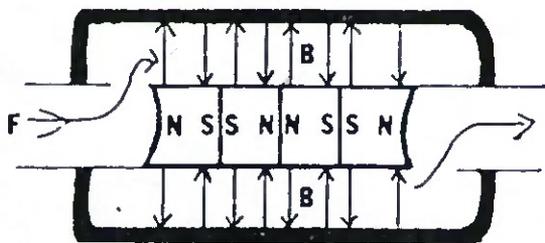
Currently available magnetic devices for water treatment (for corrosion and scale control) can be classified into four categories. Not included are the recently developed HFMG (high field magnetic gradient) devices designed primarily to remove particulate matter from a water flow stream. The four types are shown in Figure 1. Figure 1(a) shows the class I device. This device clamps onto the outside of a water pipe and produces a generally longitudinal magnetic field which concentrates and becomes transverse near the point of pole piece contact with the pipe as shown. Note that virtually no field penetrates the pipe wall in this case if the pipe is made of a ferromagnetic material such as iron. The class II device is shown in Figure 1(b). In this case the radial magnetic field is applied transverse to the flow as it passes through an annular ring between the magnet pole pieces. This device utilizes the largest gap field of any known to the present investigators. The class III device, shown in Figure 1(c), is based upon the Russian designs most often reported in the literature. Here again the field is radial with the water flow passing through an annular flow tube. In this case, however, the field polarity alternates periodically along the flow axis. This is accomplished by placing a series of alternately poled cylindrical permanent magnets along the axis of the unit. Also, in some cases a moderate swirl about the axis is induced by means of the inlet port geometry. Class IV is none of the above but more particularly a group of devices that generally have the magnetic field parallel to the flow, using a collinear solenoid, and some type of spiral



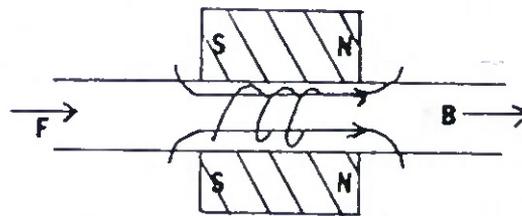
(a) CLASS I



(b) CLASS II



(c) CLASS III



(d) CLASS IV

FIGURE 1: CROSSSECTION VIEW OF TYPICAL MAGNETIC WATER CONDITIONERS. B-MAGNETIC FIELD LINES, F-WATER FLOW PATH

metallic element that rotates inside the pipe containing the field, shown as Figure 1(d). It is interesting to note that no known device applies a uniform magnetic field perpendicular to the flow axis.

1.1 Theoretical Considerations

Based upon the foregoing description of typical devices, we can briefly examine some of the principle physical phenomena associated with water flow in an intermediate strength magnetic field. Field strengths as measured in the liquid and reported in the literature range from 100 Gauss to 10,000 Gauss, depending upon the size and geometry of a particular device.

First and foremost among the pertinent electromagnetic phenomena is an effect related to the Hall Effect. This results from the ionic nature of water and the Lorentz force acting on ions moving with average velocity, v , (meters/second) perpendicular to a magnetic flux density, B , (tesla). The force, F , (Newtons) on an ion of charge, q , (coulomb) is given by

$$F = qvB$$

and acts in a direction mutually perpendicular to both the velocity and field directions. Negative charge moves one way and positive the other. Since the ions are mobile, an electric (ionic) current is induced in the flow that could be as great as 10.0 milliamperes in some cases. The current will be proportional to the product of F and the water electrical conductivity. If this current terminates on an electrically closed path such as a conducting boundary (the pipe wall) metal ions can be released to the flow stream, possibly disturbing the ionic equilibrium. For a field of 1.0 KG, conductivity of 0.1 S (1000 Ω -cm resistivity), and flow velocity 2.0 m/sec, the current density would be 2.0 micro-amperes/cm².

For class II and III devices the field is radial and the flow axial so the current simply circulates about the axis. This circulating current doesn't in any way change the ionic balance and in any case represents simply an average motion superimposed on the normal random motion of the ions. For class I and IV devices the field is predominantly parallel to the velocity so no significant force or current flow is induced at all.

The second effect relates to a force resulting from a gradient in the magnetic field. The force is proportional to the magnetic moment, m , (ampere-meters) possessed by an ion or molecule times the rate of change of the magnetic flux density with position in space. Paramagnetic particles that have a permanent moment move in the direction of increasing field strength and diamagnetic particles whose moment is induced by the field move away. The force is very small in fields of intermediate strength. For paramagnetic or ferromagnetic particles (such as iron, cobalt, or nickel compounds) with large moments, this force can be quite substantial. Most molecules and colloidal particles normally found in water, excepting iron compounds, have a microscopically small moment and are diamagnetic. The force is given by

$$F = \pm m \frac{dB}{dr}$$

The third effect arises in a similar fashion to the first. The charge within individual molecules is slightly displaced from equilibrium by the Lorentz force. Since water is predominantly a dielectric medium, a very small but calculable induced electric polarization results from flow through a magnetic field, equivalent to the application of an electric field $E = vB$ and again perpendicular to both v and B . The polarization produced, P , is approximately given by

$$P = (\epsilon_r - 1)vB\epsilon_0$$

where ϵ_r is the dielectric constant of water (~80) and $\epsilon_0 = 8.54 \times 10^{-9}$ (permittivity of free space). This effect can cause a slight excess electrical charge to build up on the walls of the containing vessel. Although the induced surface charge density is very small, it could slightly influence the adjacent Debye layer⁽⁴⁾ in the water.

It should be noted that these phenomena terminate immediately upon leaving the region of magnetic field. They cannot persist.

On the microscopic level another set of physical phenomena can be identified. First, in the presence of a magnetic field, water (and many other) molecules tend to align with and precess around an axis defined by the magnetic field. This is a result of the net nuclear magnetic moment possessed by most molecules and in no way affects the physico-chemical activity of the particle. Second, most ions in water are hydrolyzed or coordinated with water molecules forming a cluster.

If this cluster moves through a region of magnetic field, a slight distortion in the geometry of the coordinated ion could take place, again due to the Lorentz force. The available magnetic energy associated with these and other molecular level effects (such as Zeeman splitting) is at least two orders of magnitude smaller than the ambient thermal energy (kT) and thus negligible compared with the thermal effects.

Numerous attempts have been made to explain possible effects of magnetic fields on the (scale forming) crystal growth process. Homogeneous nucleation of a crystal begins with formation of a critical embryo (or subnucleus) which reaches a critical dimension through random agglomeration processes in the bulk liquid. Once a critical nucleus is formed and the water is supersaturated with respect to the crystal forming species (CaCO_3 , for example) the microscopic crystal could continue to grow in vitro until supersaturation ceases to exist. In water the degree of supersaturation for a given crystal forming solute concentration generally depends upon pH, temperature, and the presence of other dissolved molecules. The growth rate of the microcrystal in general will depend upon the level of supersaturation and the embryo density. Heterogeneous nucleation takes place on a surface or in the presence of a foreign particle or solid body that energetically favors accumulation of the crystal growing molecular species (usually via adsorption or chemisorption) on its surface. The crystal then adheres to the nucleating material as it grows.

The only way a magnetic field could affect either of these processes is by altering the energies associated with the crystalline inter-molecular forces (both bulk and surface energies). With diamagnetic substances (including all usual scale forming materials) this is completely unreasonable. However, it has been demonstrated by Duffy⁽⁵⁾ that for ferromagnetic substances, such as ferric hydroxide sols and metallic iron in water, interfacial energy states are measurably influenced by the presence of strong magnetic fields. How this could possibly affect a crystal growth process is certainly not apparent.

One thing is clear in all this: magnetic field phenomena, such as whatever they may be, cannot involve the water molecules alone.

1.2 Experiments

The experiments carried out in this study are intended to assess the value and validity of the experimental procedures used as much as to determine the efficacy of two types of magnetic water conditioners. In order to carry out both objectives, all experiments are carried out simultaneously on four independent water flow streams derived from a common source. The primary source is the Rapid City, South Dakota, city water main supplying the research laboratory in the Mineral Industries Building on the South Dakota School of Mines and Technology campus. The four flow streams used in this study are raw water, water processed by a conventional residential ion exchange water softener, and two streams processed by magnetic treatment devices. The two magnetics are a class I device and a class III device both of which have been described previously.

All experiments are classified into four categories: corrosion, scaling, electrochemistry, and physical property measurements. In addition the usual wet chemical analysis of the supply water has been obtained. Experiments are further designated by the time duration involved as long-term and short-term, or point measurements. A list of the included experiments performed is shown below. Each will be discussed in turn.

Corrosion and Scaling Experiments

Long-Term Experiments

Coupon Corrosion

Water Heater Tests

Test Parameters

Anode Dissolution

Element and Thermistor Scale Formation

Short-Term Experiments

Limestone Dissolution

Polarograph

Scaling Rate Sensor

Reflux Boiler Scale Formation

SEM/X-Ray Scale Analysis

X-Ray Diffraction

Physical Property Measurements

Boiling Point Depression

Surface Tension

Electrical Conductivity

Electrochemical Measurements

pH

Calcium Specific Ion Measurements

Dissolved Oxygen

Dissolved CO₂

2.0 LABORATORY APPARATUS

The apparatus necessary to perform the experiments reported here was constructed in such a way to reduce to a minimum any possible interference with the physico-chemical properties of the supply water. Since four separate but simultaneous measurements were to be obtained in most cases, the separate flow streams had to be provided in as nearly an identical configuration as possible.

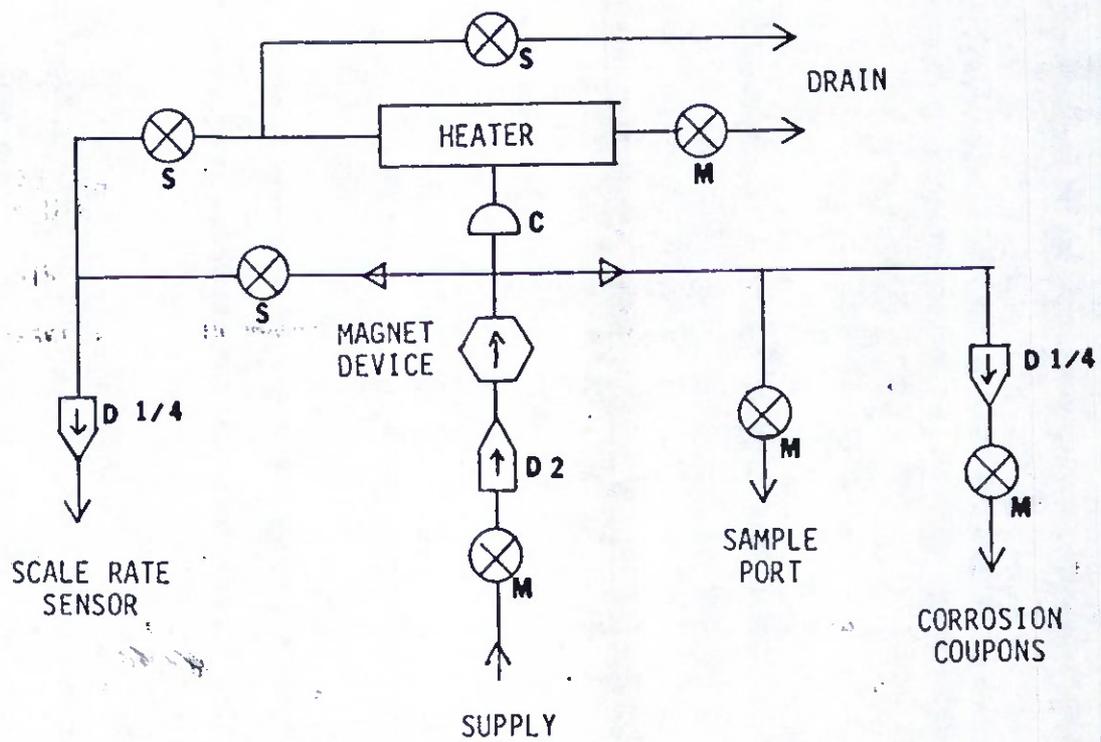
Water is supplied to the laboratory from the city water main via the campus distribution system and the existing copper piping and valves in the Mineral Industries Building. A four port, valved (copper) manifold was established to supply the individually valved flow test streams. Figures 2.1a and 2.1b show schematically the water flow geometries used in all of the experiments reported here. The symbols shown are as follows: (M) manual CPVC shutoff valve, (S) brass solenoid valve, (D) Dole flow regulator, and (C) checkvalve.

All flow piping and fittings were CPVC plastic to avoid insofar as possible galvanic effects and inadvertent metal dissolution. The solenoid valves, Dole flow controls, and a few associated fittings were plumbing brass. Hot water heater nipples were brass (cold) and plated steel (hot).

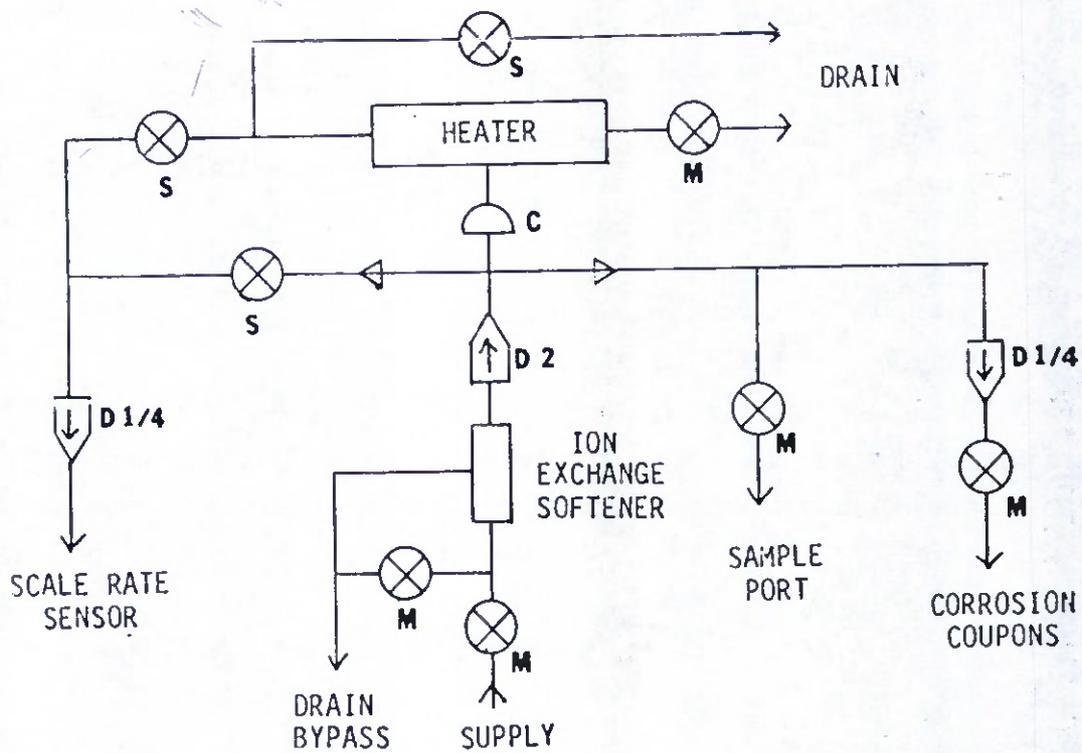
The raw water stream configuration is exactly the same as that for the magnetic conditioners (see Figure 2.1a) except that a piece of plastic pipe of similar length replaces the conditioner. The magnetic devices were installed in strict accordance with instructions supplied with the units.

The class III water conditioner is sized for a 2.0 GPM flow rate. The device was installed on a plywood panel in the vertical position remote from any high current carrying conductors. The unit is attached directly to a Dole 2.0 GPM flow control which in turn is fixed to the manifold shutoff valve.

The class I device was installed on a 3.5-foot length of 3/4 inch copper tubing attached directly to a 2.0 GPM Dole flow regulator using the supplied clamping straps as recommended by the manufacturer. The copper pipe was separately connected electrically, via grounding strap, to the common building ground as per instructions supplied with the unit. Although they were physically separated by a substantial



(a) MAGNETIC CONDITIONERS



(b) ION EXCHANGE WATER SOFTENER

FIGURE 2.1

distance, the magnetic fields of the two magnetic devices were intentionally oriented perpendicular to one another to obviate any coupling between them.

The ion exchange softener was leased from a local source and maintained by them. Due to the recycling requirements of the softener a separate drain bypass loop was established for the unit as shown in Figure 2.1b.

The solenoid valves were standard brass 110 VAC dishwasher valves. The manual valves are all PVC plastic. Control for the solenoids was derived from a switch panel that includes a sequential 24-hour timer. This device activates the four water heater drain solenoids sequentially for 10-minute intervals four times each 24-hour period.

Dole flow controls are installed at several points in the system. Both 2 gal/min and .25 gal/min units are used. All of them were tested prior to and after installation and found to be accurate to within 10 percent or better.

Total water flow through the water heaters was obtained by totalizing the "on" time of the heater solenoid and applying the 1.75 gal/min flow factor (.25 gal/min flows continuously in the corrosion experiment). Check valves are installed at the water heater inlets to prevent reverse flow of hot water.

All temperatures (inlet water and tap) were monitored by a 10-channel digital thermistor probe unit. The probes could be scanned automatically or manually switched. All thermistors were calibrated prior to use.

Figure 2.2 shows an overall view of the laboratory facility.

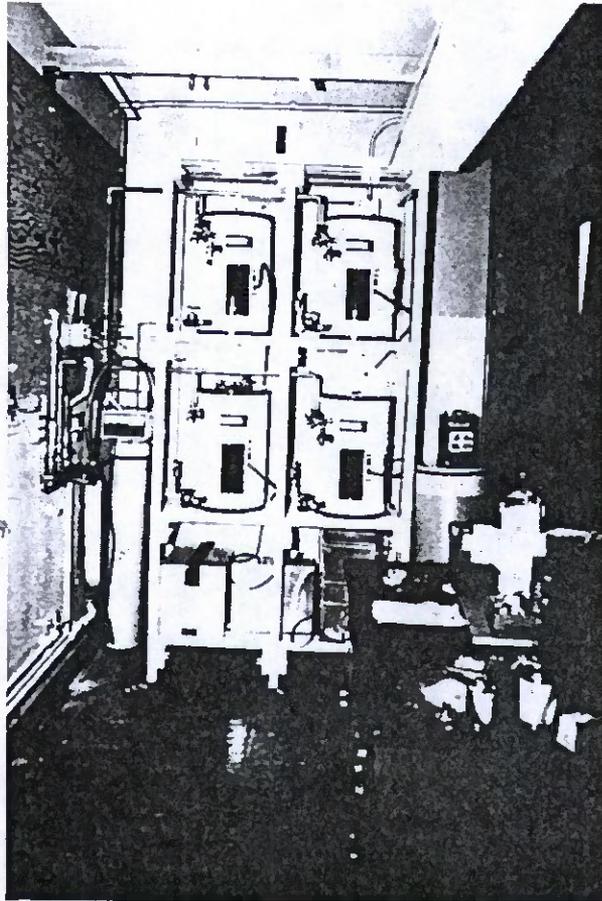


Figure 2.2

PHOTO OF EQUIPMENT ASSEMBLAGE

3.0 WATER HEATER EXPERIMENTS

3.1 Experimental Parameters

Four 10-gallon capacity electric water heaters were installed, one in each of the four test streams. Individual tanks in the separate water flow streams will be identified as follows:

Tank No. 1 - Water Softener

Tank No. 2 - Class III Magnetic Conditioner

Tank No. 3 - Raw Water

Tank No. 4 - Class I Conditioner

The single heater elements are rated at 1700 watts electrical. Each heater contains a magnesium sacrificial anode and a calibrated thermistor temperature sensor, both installed in ports at the top of the glass-lined tank. The anodes are original equipment with the heaters. The thermistor sensors are sealed in the end of an 8-inch length of copper tubing. The tube was inserted through a hole drilled in the center of an accessory port located at the center of the top of the water heater tank. A leak tight seal was provided by compression of a rubber hose washer between the tank outer wall and a flange on the end of the copper tube using a drilled pipe nipple supplied with the tank. Tank temperatures were monitored using the multiprobe temperature sensing unit.

Water temperature control was obtained with the normal thermostat supplied with the heaters. Preliminary adjustment of the set points was carried out so that the turn-off temperature of each heater was $62 \pm 1.5^{\circ}\text{C}$ (144°F).

The water supply to each individual tank was cycled on for a $10 \pm .2$ minute period four times per day (or rather each 24-hour period). The tank flows were cycled sequentially so that no two were on at the same time. The on times correspond closely to 6:00 a.m., 12:00 a.m., 6:00 p.m., and 12:00 p.m. Automatic control of this cycling was obtained from an adjustable control unit which actuated dishwasher solenoid valves in each of the tank hot water outlet lines. The hot water was normally dumped into a common waste drain.

Tank water inlet total volume and flow rate were not measured directly but were obtained by totalizing the solenoid valve on time for each tank. Since each supply stream contains a 2 gal/min Dole flow control and the corrosion experiments use .25 gal/min Dole controls, the

total flow rate to each tank during its cycle on time is 1.75 gal/min or 17.5 gallons during each flow cycle. These valves were experimentally verified to within ± 5 percent. Approximately two tank volumes are thus cycled through each tank during each on period.

Total electrical energy input to each water heater was obtained by KWH meters obtained from and calibrated by Black Hills Power and Light Company, Rapid City, South Dakota. Measured energy input includes both energy required to heat cold inlet water and to make up for tank heat loss between cycles. A measure of the latter quantity was obtained prior to start of the experiments.

Testing and setting of water heater and flow controls was carried out from 30 May through 6 June 1980.

The water heater experiment under fully controlled operating conditions was initiated on 6 June 1980 at 10:00 MDT.

On 9 June a failure of Heater No. 4 occurred, blowing the thermistor sensor out of the port on top of the tank. The assembly was redesigned, all sensors removed and recalibrated, and all heaters examined. A thin layer of scale was removed from all thermistor copper tube housings. The system was again activated on 6 July 1980.

Operation of the water heater system continued without problems until 27 August 1980, when the tests were terminated due to a small leak in Heater No. 2 thermistor housing. Brief periods of extra hot water flow occurred during testing of the scale rate sensor. From 27 August to 10 September the tanks and tank components were carefully examined.

3.2 Energy Measurements

In the initial testing stage of the water heater experiment, approximate thermal losses for each tank were obtained with the tanks full and no water flow. Over a 50.3-hour and a 72-hour period, energy inputs to the tanks were respectively

Heater No. 1 - 3.6 KWH \pm .25	4.8 \pm .25 KWH
Heater No. 2 - 3.7 KWH \pm .25	5.2 \pm .25 KWH
Heater No. 3 - 3.9 KWH \pm .25	5.3 \pm .25 KWH
Heater No. 4 - 3.9 KWH \pm .25	5.1 \pm .25 KWH

Since the measurements are nearly equal, within experimental accuracy, we can presume heat losses remain approximately equal for all tanks for the remainder of the test period. After the initial test Tank No. 1 temperature was raised 3^oF to correct the slight error in turn-on point.

Figure 3.1 shows energy input to the water heaters versus time for the remainder of the test period. It can be seen that the deviation from the mean energy use (KWH) among the four flow streams amounts to less than 2.5 percent of the mean value. In addition, the cumulative energy consumption is linear with time with the same slope (within experimental error) for each flow stream. The 10 KWH initial offset of the stream No. 4 reading and its slightly higher slope is attributed to initial meter reading error and unavoidable minor errors in setting the shut-off temperature of the heater, respectively. The energy consumption rate is calculated from the slope of the curves as $9.2 \pm .05$ KWH/DAY. From the tank heat loss measurements, approximately 1.75 KWH/DAY is attributed to measured tank heat losses and the remainder, 7.45 KWH/DAY, to heating cold water.

Assuming the inlet water temperature is the measured value of ($20 \pm 2^{\circ}\text{C}$) and the heater shut-off temperature is 62°C , the energy required to heat approximately 40 gallons of water per day is obtained from

$$E = V \cdot \rho \cdot \Delta T \cdot C_p / 3413 \text{ KWH/DAY.}$$

With $V = 40 \text{ gal}$, $\Delta T = 75.5^{\circ}\text{F}$, $\rho = 8.33 \text{ lb/gal}$, $C_p = 1 \text{ BTU/lb/}^{\circ}\text{F}$, we get 7.4 KWH/DAY. The agreement between measured and calculated heat losses is excellent.

Clearly there is no measurable difference in energy consumption for the four different flow streams as one would expect. One could argue that measurements over a longer term would show the effects of scaling on heat transfer processes in the tanks more strikingly. However, as will be shown in the next section, substantial and stable scale buildup is observed on the heater and other metallic elements in the tank (except in the case of stream No. 1), so that no change in operational performance should be observed until the scale fragments at the bottom of the tank engulf the heater element.

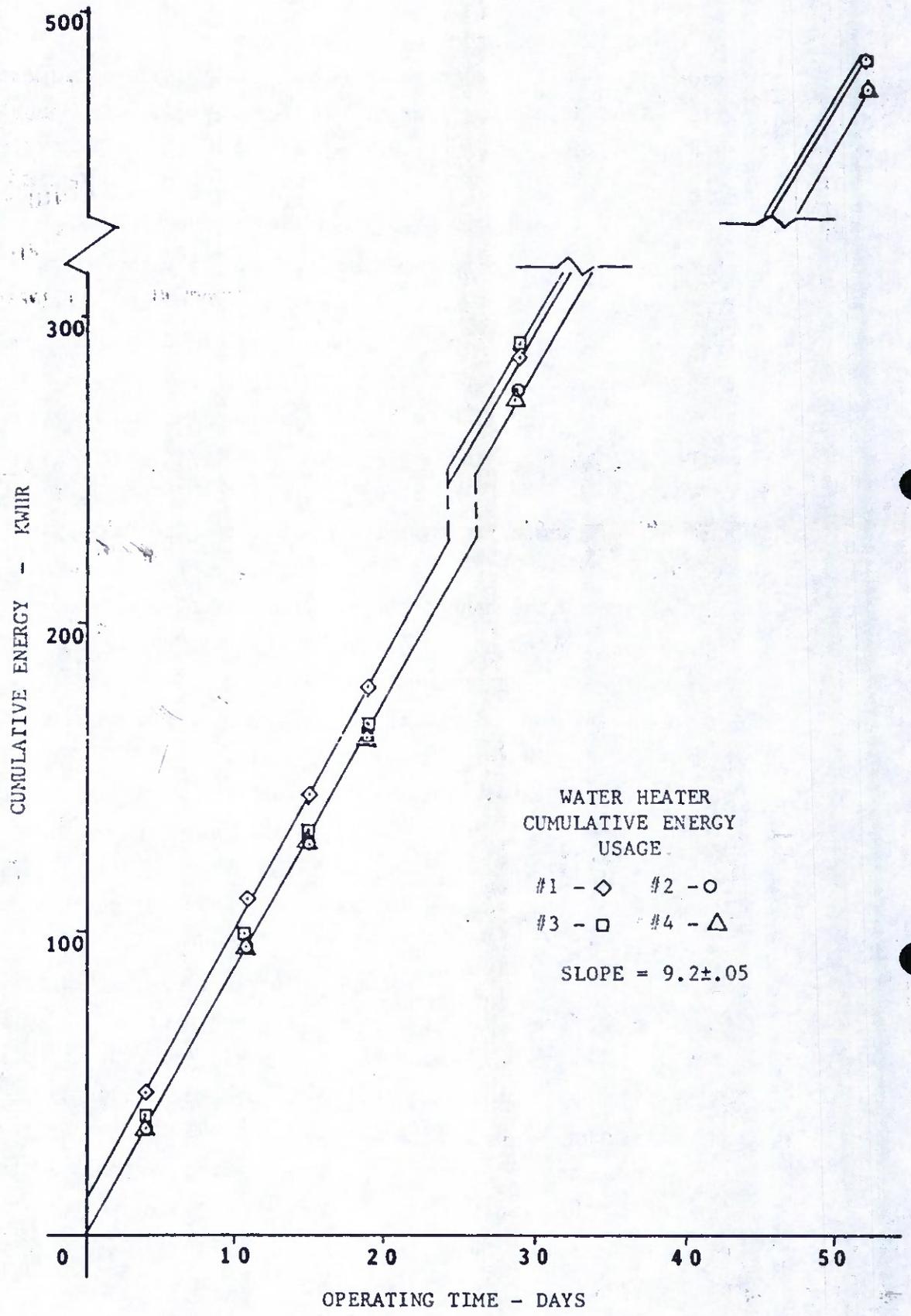


FIGURE 3.1

3.3 Anode Dissolution

At the end of the continuous test period for the water heaters the magnesium sacrificial anodes were removed for examination and weighing. Each virgin rod had been weighed prior to filling the tanks with water on 3-12-80. The rods from heaters No. 2, No. 3, and No. 4 appeared outwardly identical in all respects. Substantial etch pits had formed uniformly distributed over the entire rod surface except for an increase in pit density and depth at the water line near the top of the tank (a small void volume always forms at the top of a vertical tank due to slow release of entrained air in the water). Photos of all four anodes immediately after removal from the tanks are shown in Figure 3.2. The etch pits were partially filled with very strongly adherent scale and a similar layer of scale appeared in large patches over much of the unetched surface of the rods. A curious small cone-shaped button of scale material about 4 millimeters thick and 6 millimeters in diameter formed at the exact center of the flat end of each rod, apparently adhering to the face of the steel core of the anode rod.

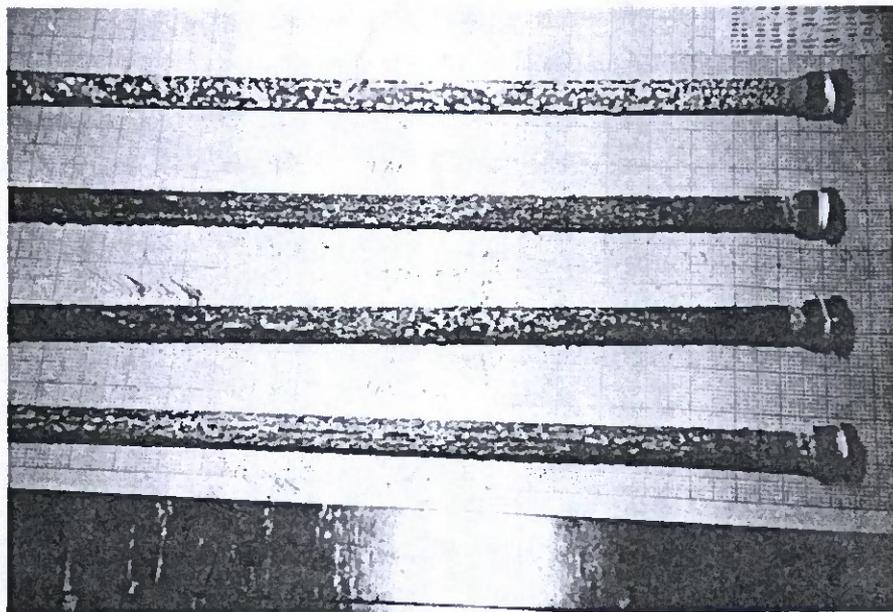
The anodes were prepared for weighing by laboriously removing all accessible scale from the rod surface by scraping with a wire brush. The weight loss was then obtained as shown in Table 3.1.

TABLE 3.1
ANODE WEIGHT LOSS

TANK	INITIAL WEIGHT	FINAL WEIGHT	WEIGHT LOSS
Heater No. 1	333.5 grams	316.6 grams	16.9 grams
Heater No. 2	326.4	321.4	5.0
Heater No. 3	333.0	326.8	6.2
Heater No. 4	327.6	322.0	5.6

Scrape samples of scale removed from all the anode rods were preserved for later analysis (except for tank No. 1).

The rod from heater No. 1 was distinctly different from the other three. First, there was no evidence of scale on its surface. Second, the degree of etch pitting was much greater than for any of the others. At some points on the surface substantial material removal had taken place to a depth of 4 to 6 millimeters, especially at the water line. This result is of course to be expected, since the ion exchange process removes substantially all the magnesium ion from solution, thereby



Heater No. 1

Heater No. 2

Heater No. 3

Heater No. 4

Figure 3.2

PHOTO OF SACRIFICIAL ANODES

shifting the ionic equilibrium far towards subsaturation. Dissolution reactions would be expected at a metallic magnesium surface.

Analysis of the anode weight loss from Table 3.1 for heater No. 2 through 4 shows that one could expect a value of approximately .09 g/day \pm 10 percent due to corrosion processes in a normal tank of this type. The difference between water streams using raw water and magnetic conditioners are negligible and well within experimental error limits determined by how well the scale could be removed from the etch pits (estimated at \pm 15 percent).

3.4 Scale Measurements

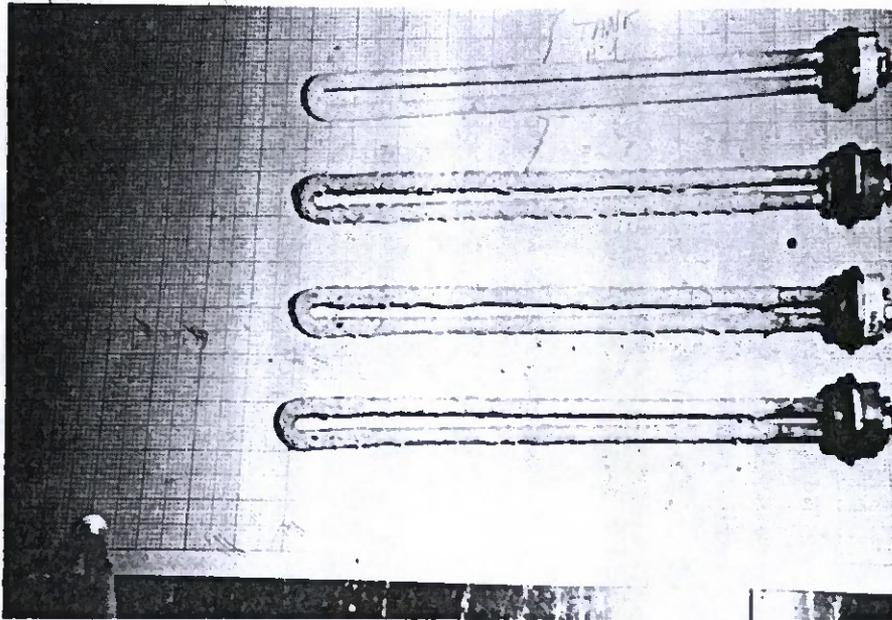
The heater elements (1700 W) were carefully removed from the tanks at the end of the test period. In heaters No. 2, No. 3, and No. 4 each was coated with a heavy layer of scale. Expansion and contraction of the element during a heating cycle causes the scale to flake off in the form of thin cylindrical shell pieces. Only the layer immediately adjacent to the metal element surface and at the sharply curved end of the element is at all adherent.

The elements in the as-removed condition are shown in Figure 3.3. As can be seen, there is no perceptible difference between the three elements mentioned above (raw water and the two magnetically conditioned streams). Heater No. 4 scale was slightly less adherent. This may be a result of having the rod removed first and, therefore, it was slightly drier. As the scale dries, adhesion is significantly reduced. The heater No. 1 element was in a nearly new condition. No evidence of scaling was observed. A very thin powdery coating was all that appeared anywhere on the element.

Samples of scale (and powdery coating) were removed and saved for further analysis. The elements were cleaned using a combination of scraping with a wire brush and acid wash and weighed before and after cleaning. The metal surface scale was difficult to remove in the three similar tanks. Since the outer scale layer flakes off readily, the weight of scale removed from the elements is probably of little significance, but the following values were obtained:

No. 1 - .5 grams

No. 2 - 6.3 grams



Heater No. 1

Heater No. 2

Heater No. 3

Heater No. 4

Figure 3.3

PHOTO OF HEATING ELEMENTS IN AS REMOVED CONDITION

No. 3 - 4.5 grams

No. 4 - 3.4 grams

It must be noted that after scale removal, no apparent evidence of corrosion of the metal element surfaces existed for any of the four elements.

The interior of the tanks was observed through the element ports. In the three similar heaters--No. 2, 3, and 4--there was a substantial deposit of scale flakes laying on the curved bottom of the tanks to a depth of at least three-quarters of an inch. Unfortunately, this loose deposit could not be effectively removed without destroying the tanks, so no weight comparisons were made. Clearly, however, there were no observable differences among the heaters 2, 3, and 4.

The copper temperature sensor probes were removed from the top of tanks as shown in Figure 3.4. A very heavy layer of adherent scale was apparent at the water line in all cases except tank No. 1, where no coating of any kind was observed. The sensor probes were weighed before and after acid removal of the attached scale. Since a leak had developed around probe No. 2, an additional amount of scale had developed around the point where the sensor joined the nipple and on the outside of the nipple, all very adherent. The weights of the scale removed were (total weight about 150 grams):

Heater No. 1 - 0.0 gram

Heater No. 2 - $0.7 \pm .1$ gram

Heater No. 3 - $0.4 \pm .1$ gram

Heater No. 4 - $0.2 \pm .1$ gram

Again within experimental error there are no differences between the three similar flow streams from heaters 2, 3, and 4.

3.5 Scaling Rate Sensor

An attempt was made to construct a real time scaling rate sensor to evaluate both dissolution and surface precipitation rates for calcium carbonate. The device that was designed and constructed is shown as Figure 3.6.

The operational concept is as follows. A transparent (glass) tube is prepared with a thin layer of carbonate scale on the inside surface formed by either evaporation of raw water or by heating the liquid

No. 3 - 4.5 grams

No. 4 - 3.4 grams

It must be noted that after scale removal, no apparent evidence of corrosion of the metal element surfaces existed for any of the four elements.

The interior of the tanks was observed through the element ports. In the three similar heaters--No. 2, 3, and 4--there was a substantial deposit of scale flakes laying on the curved bottom of the tanks to a depth of at least three-quarters of an inch. Unfortunately, this loose deposit could not be effectively removed without destroying the tanks, so no weight comparisons were made. Clearly, however, there were no observable differences among the heaters 2, 3, and 4.

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Heater No. 1 - 0.0 gram

Heater No. 2 - 0.7 ± .1 gram

Heater No. 3 - 0.4 ± .1 gram

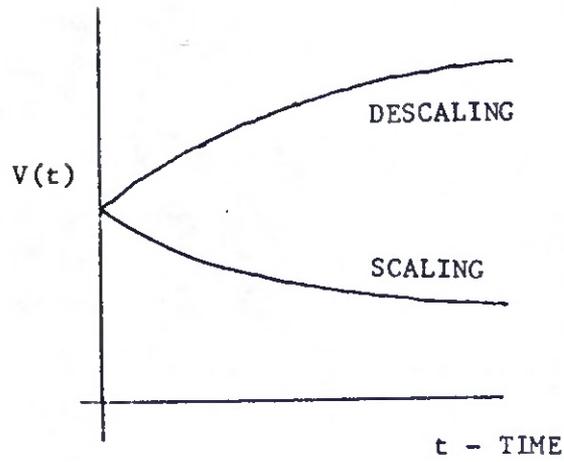
Heater No. 4 - 0.2 ± .1 gram

Again within experimental error there are no differences between the three similar flow streams from heaters 2, 3, and 4.

3.5 Scaling Rate Sensor

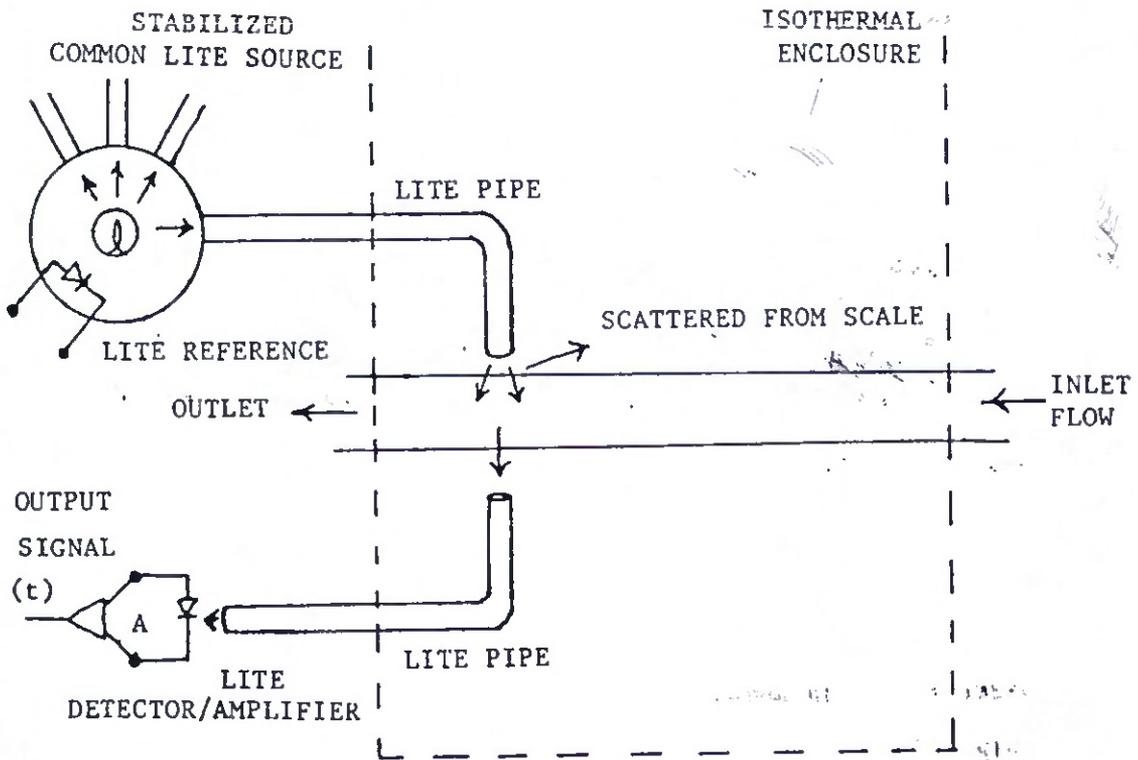
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(a)

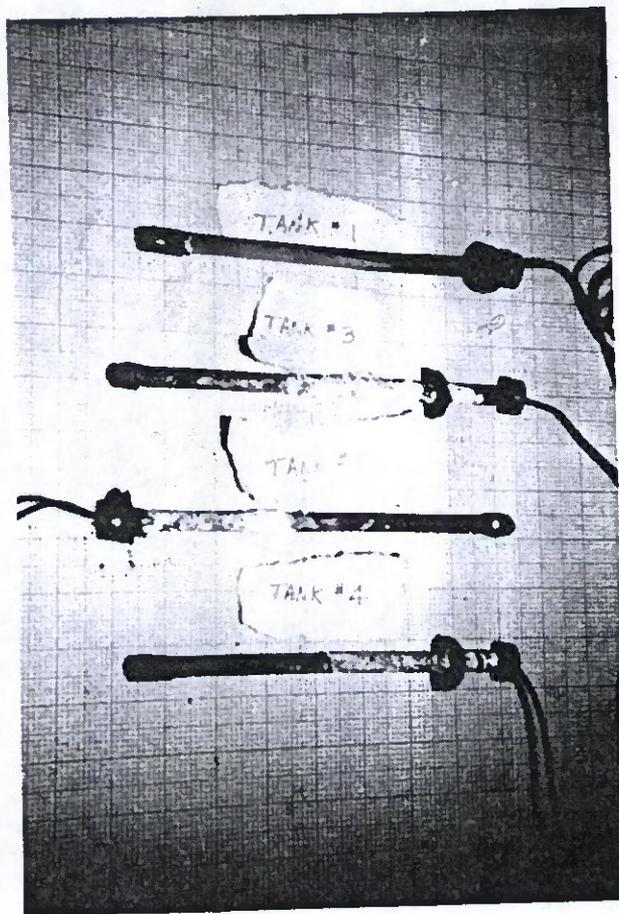
3 OTHER IDENTICAL UNITS



(b)

FIGURE 3.6

SCALING RATE SENSOR



Heater No. 1

Heater No. 3

Heater No. 2

Heater No. 4

Figure 3.4

PHOTO OF TEMPERATURE SENSING PROBES

filled tube until precipitation occurs. Considerable experimentation was carried out to find the appropriate technique for film formation with excellent results being obtained. "Films" of thickness up to several tens of micrometers could be obtained in as little as one hour.

Transmission of a narrow beam of light across the tube is strongly attenuated by scattering due to roughness of the surface film. The scattering is closely proportional to the density of precipitated CaCO_3 on the tube inside wall. Measurement of the transmitted light intensity becomes a sensitive measure of the scale layer total mass (thickness) with slight variations caused by crystallite size. The latter effect is reduced to negligible importance by using visible white light as the source. An isothermal environment is provided so that the scaling can be accelerated or inhibited by heating the entire assembly. Light is coupled to and from the tube assembly via fiberoptic light pipes. Linear photovoltaic sensors are used to detect transmitted light intensity. Four separate flow streams could be monitored simultaneously.

The device was initially constructed in a somewhat crude fashion due to time and money limitations. The initial tests were attempted with uncoated tubes to see if nucleation could be obtained on bare (pyrex) glass. The results were quite encouraging, but several problems developed necessitating redesign of the apparatus. The principal problems encountered revolved around providing a very stable white light source using an incandescent bulb with feedback intensity control. Drift in the source biases the output. Second, the detectors must be located outside the enclosure so that temperature variations do not affect the sensitivity. Thirdly, the adhesion of the scale formed is not strong, so that low flow rates of the test water stream through the scale tubes must be maintained. Finally, temperature control of the water streams as applied was difficult to obtain since heat transfer through glass is not very efficient.

Despite the problems and necessity of redesigning the system very favorable results were obtained. The source water for the apparatus could be obtained either directly from the treatment devices or from the associated water heaters. Both were used. When liquid flow through the test tubes is initiated, an invisible-to-the-eye but distinctly

measurable exponential decay in transmission occurs over the first 15 to 20 minutes of flow time, after which it stabilizes at a constant value. With 15-millimeter diameter tubes and a .25 gpm flow rate, the flow velocity is very high tending to dislodge the fine scale crystals from the surface resulting in a steady state between precipitation and removal. It was later found that scale buildup requires less than .05 gpm flow rates. The three scaling test streams--heaters 2, 3, and 4--all showed similar results. The net change in optical transmission measured was about 2 percent.

This experiment could be optimized by placing the test cells and light pipes in a microwave oven to provide controlled even heating of the flow streams and at the same time an isothermal environment. Excellent results should be obtainable in this way.

4.0 PHYSICAL PROPERTY MEASUREMENTS

4.1 Boiling Point Depression

A Cottrell reflux boiling point temperature apparatus with Beckman thermometer was used to obtain data on variations of boiling point of the four test water streams. The increase in boiling point temperature of water due to an increase in the concentration of ionic and other dissolved substances is given by $\Delta T_V = .513^\circ\text{C}/\text{gm-molecular weight of solute}$. Since boiling point temperatures can be measured to within an accuracy of $\pm .01^\circ\text{C}$ the technique can be sensitive to slight changes in ionic concentration. For instance any small changes in Ca^{++} ion concentration due to magnetic water treatment, resulting in precipitation of CaCO_3 however finely divided, will be manifested in a slight increase in boiling point temperature. Claims implying substantial reduction in boiling point have been made by the distributors for the Class I device.

It was found in the course of these measurements that as expected the elevated temperature greatly accelerated CaCO_3 precipitation after an extended boiling period (about one-half hour). This effect was used to prepare scale samples as explained elsewhere. By the same token effects of magnetic treatment should be enhanced and accelerated in the reflux boiler if such effects exist and do involve precipitation of microcrystals in vitro.

Measurements using 100 milliliter samples of the four water streams were made at various times and with varying delays after treatment. Typical results are shown in Table 4.1 for three such measurements. Only the significant figures to the right of the decimal point in the temperature measurement are shown.

TABLE 4.1

	Boiling Point Temperatures - $^\circ\text{C}$		
Softener	Class III	Raw Water	Class I
.510	.510	.520	.515
.479	.485	.462	.475
.520	.530	.530	not repeated

Since approximately 30 minutes is utilized to carry out a given test, changes in barometric pressure--even though corrected for--can affect the results if they take place rapidly enough.

Statistically the boiling points for the four streams are indistinguishable on an average basis. If one were to assume that the TDS of the water is approximately 2000 ppm, one would not expect the total solute molarity ($\sum M_i$) to exceed .01 M. From this one can deduce no more variation in the boiling point temperature than $\Delta T_b = \pm .005^\circ\text{C}$; a value below our experimental accuracy and certainly not detectable by casual observation. For water samples with much higher TDS one might expect a greater measurable variation.

4.2 Surface Tension

Unlike the colligative properties, the surface tension of water is sensitive to both solute concentration (ionic or otherwise) and the nature of the chemical species in solution (or micelle suspension in the case of soaps). In general, the presence of ionic species in solution causes a linear increase in surface tension proportional to ionic concentration ($\sum M_i$) as in the colligative properties. Surfactant materials, of course, cause a dramatic lowering of surface tension.

Repeated measurements of surface tension of the four separate experimental flow streams were obtained using a Cenco DuNuoy interfacial tensiometer with 100 milliliter samples obtained either from the sample ports or after passage through the coupon corrosion cells. No differences between the two sampling points were noted.

Results of surface tension measurements indicate no measurable differences between the raw water and magnetically treated flow streams. The ion-exchange treated water has a slightly reduced surface tension on a statistical basis, probably due to significantly different ionic species present (Na). The difference is only 2 percent, however, and at the margin of measurement accuracy. Typical values are shown in Table 4.2 below.

TABLE 4.2

Surface Tension - dyne/cm @ 27.0°C

No. 1 Softener	No. 2 Class III	No. 3 Raw Water	No. 4 Class I
73.1	74.3	74.2	74.5

4.3 Water Conductivity

Electrical conductivity of a water sample depends upon the sum overall of ionic species present, the product of molarity, ionic charge, and ion mobility--the latter being dependent upon ionic strength as well as ambient environmental parameters (e.g., temperature). The measured conductivity thus is sensitive to ionic concentrations of all species present as well as concentration of (colloidal) particles present in suspension. Removal of ionic calcium by precipitation of colloidal size or larger CaCO_3 crystals would be expected to combine to measurably reduce electrical conductivity of a solution.

Conductivity of the four separate flow streams was measured with a Beckman Conductivity Meter with samples taken from the sampling ports. KCl calibration samples were used as conductivity standards for the measurements. Typical results are shown in Table 4.3 below.

TABLE 4.3

Water Conductivity - $\mu\text{v}/\text{cm}$			
Softener	Class III	Raw Water	Class I
$5.75(10^2)$	$5.35(10^2)$	$5.35(10^2)$	$5.25(10^2)$

Accuracy of the measurements is about $\pm 0.05(10^2)$ from which it is concluded that there is no measurable difference between the raw water and magnetically treated flow streams. The ion exchange treated flow stream, of course, contains a high concentration of higher mobility sodium ion; therefore, as would be expected, the conductivity of this sample stream is about 10 percent higher than the others.

5.0 WATER CHEMISTRY

The water supplied to the Rapid City water mains is derived from several sources: springs, collection galleries, and wells. Table 5.1 gives the values obtained by the South Dakota Public Health Service. Some of these values, notably the pH and alkalinity, vary and this is due to the fact that these parameters were not obtained on site but rather in the laboratory.

Several of these parameters were checked periodically in the laboratory and did not give any real difference in values beyond that of experimental deviation. This indicates that by the time the water is delivered to the water mains it is quite well mixed.

Even though Table 5.1 does indicate variations based on the tests run in the laboratory, it appears that the water is of a static composition which should yield suitable long-term data.

The following four parameters were carried out in the wet chemical lab: chloride, iron, conductivity, and dissolved oxygen. All of these tests were performed on effluent taken from the sample ports ahead of the corrosion test cell, after all the conditioning had been performed on the water. These were selected as the most likely to vary if the properties of the water were being altered. The tables of experimental values are all listed sequentially in the appendix.

The chloride test was performed by silver nitrate titration and was used to verify the amount of chloride in all four test streams. The results of the chloride test indicated that there was not an excess or unusually large amount of chloride coming from the ion exchange resin test stream relative to the other test streams. This then indicates that the regeneration system was working properly and that no chlorides were being added to the test stream.

Iron content of the water was checked several times and it was noted that occasionally a small amount of iron would be detected initially when the water was first withdrawn. This was apparently due to the fact that the test port was located in such a manner that the valve formed a collection pocket and ferric and ferrous hydroxides could form in the stagnant portion of the test stream which in turn resulted in high iron values when the valve was initially opened. The iron tests were performed using a colorimetric procedure utilizing the ferrozine

TABLE 5.1*

Source	Alk	pH	Total Hardness (as CaCO ₃)	Calcium	Magnesium	Bicarbonate	Sulfate	Sodium	Potassium	Total Solids
1 Well, 1460'	166	7.7	214	59	16	203	59	7	2.5	285
3 Well, 957'	186	7.9	222	5.2	22	227	47	5	2.3	271
4 Well, 1075'	176	7.7	254	72	18	215	78	5	2.3	327
Walpole 550'	180	7.9	200	50	18	220	20	4	1.8	238
Jackson Spring	168	7.7	192	48	18	205	31	7	2.5	236
Gallery Meadow	200	7.7	276	75	21	244	71	7	3.1	344
Gallery Girl Scout	204	7.6	312	91	21	249	110	7	3.0	411

* South Dakota Health Service Report

All values reported in mg/L

test reagent. When the sample ports were permitted to flow for approximately one minute which was equivalent to approximately one gallon of liquid, the iron content of all four test streams was essentially equal indicating that there was not a large amount of iron being contributed by any of the test devices. The fact that iron was found initially when the sample port was opened is a phenomena which is noted throughout campus. Whenever a valve is oriented in such a position that it forms a trap, a small amount of iron will collect at this point and on opening there will be a rusty yellow to brown coloration until this is purged from the system. This is no doubt due in part to the fact that much of the piping on campus is of the unlined cast iron variety and therefore iron can be entrained in the water system from these iron components.

The conductivity of water from the four test streams was examined and in this test the conductivity did show an increase in the ion exchange test stream. This was higher due in part to the fact that there was a higher concentration of sodium ions present as would be expected from this type of treatment system. The conductivity measurements were performed with a Beckman field tester system using the standard platinized electrodes.

The dissolved oxygen content of the water from the four test streams was performed via the Winkler method. The values of the dissolved oxygen were all essentially the same indicating there was not a significant amount of oxygen being added to the ion exchange system due to the regeneration tank or the in-line magnetic conditioner.

The sodium content of the four test streams was checked using the atomic absorption spectrometer. In this case the level of sodium was determined to be considerably higher in the ion exchange resin test procedure which was to be expected.

TABLE 5.2

	Dissolved Oxygen	Sodium	Iron	Chloride
	ppm	ppm	ppm	ppm
Softener	7.0	92.0	.01	4.0
Class III	7.1	4.0	.01	4.0
Raw Water	6.9	4.0	.01	4.0
Class I	7.2	4.0	.01	4.0

5.1 Corrosion

The weight loss corrosion test performed on the four test streams involved the installation of three test alloys into each stream. These test alloys were circular disks approximately 2 inches in diameter by 1/8 inch in thickness. These disks were isolated electrically on a plastic support rod. The weight of the metal alloy coupons was taken initially, then the samples were placed into the flowing stream and permitted to corrode. At the end of approximately 90-day periods, the alloys were removed, photographed, descaled, and reweighed. The weight loss in all cases appeared to be greatest for the iron alloy and approximately equal for the copper and the admiralty brass alloy. This test was performed twice so that there were two sets of values available for the weight loss experienced in the four flowing streams.

Figure 5.1 shows the materials tested for corrosion which are included below--both before the scale has been removed and afterwards. The dark areas on the iron coupons are due to the mill scale which was not removed prior to testing, in order to simulate as near as possible what might be experienced in most iron appliances and piping.

5.2 Scale Evaluation

The first scales evaluated were those that were formed by boiling a glass slide in water from the test stream. These glass slides were then examined on both the optical microscope and the scanning electron microscope to determine the general morphology of the scale. Afterwards, some portions were scraped off and X-ray diffraction examinations were performed. The X-ray diffraction indicated that the material deposited on the glass slides was calcium carbonate and in general it was calcite with some mixed aragonite. If any vaterite was present, its concentration was of such a small amount that it was not detected on X-ray diffraction and not detected on the microscopy examination. The scales that were formed in the laboratory in general were all alike with the exception of the ion exchange test stream where no calcite or aragonite was found as the calcium was quite effectively removed by the ion exchange resin. Further examination of the scales that were formed on the walls of the hot water heaters and also the heating elements from the hot water heaters and the sacrificial anodes were examined

again by X-ray diffraction and the two forms of microscopy with similar results being yielded.

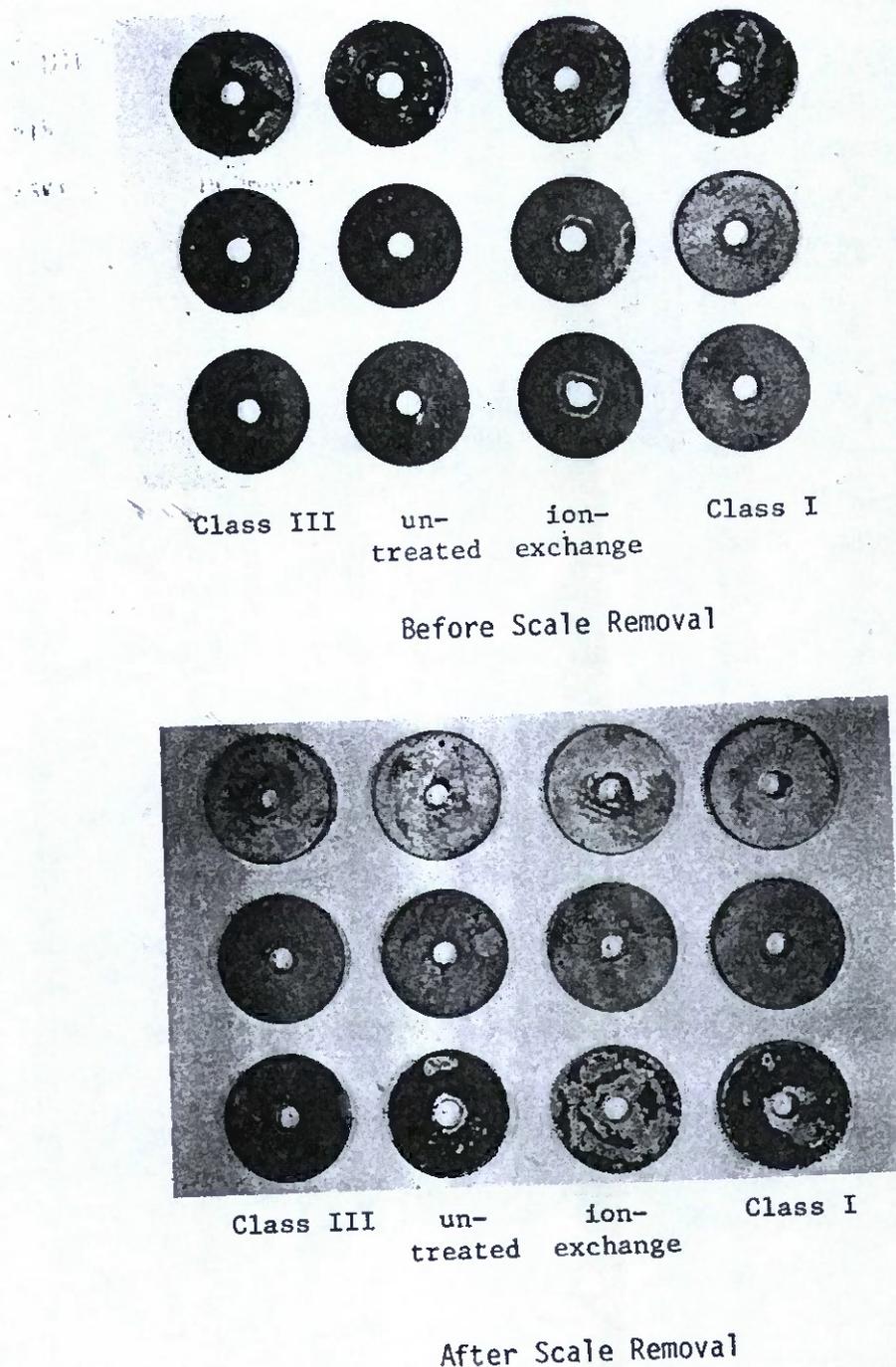


Figure 5.1. Corrosion test coupons.

6.0 ELECTROCHEMICAL MEASUREMENTS

Measurements of four quantities important to the bicarbonate chemical equilibrium state as outlined in the appendix 9.0 were obtained using electronic probes. These are pH, calcium ion concentration, dissolved oxygen, and dissolved carbon dioxide. Measurements were made at various times to observe long-term changes in the chemical equilibrium of all four water test streams.

pH was obtained with a Beckman Digital pH Meter. No differences between the four flow streams were ever apparent within normal measurement accuracy. The mean value for the tap water was 7.4 with a deviation less than ± 1 .

A calcium specific ion electrode was used to obtain total Ca^{++} concentration using an Orion probe with digital readout instrument and a double junction reference electrode. No measurable differences were observed between the tap water and two magnetically treated flow streams. The calcium ion concentration remained remarkably constant with time during our active testing period. The value for the concentration was 127 ± 10 ppm as CaCO_3 or 51 ± 4 ppm as Ca^{++} . According to the figure presented in the appendix, this value corresponds very closely to or slightly less than the saturation value at the measured pH and temperature level. Due to mixing of stream and deep well waters in the city mains, this value is to be expected. Measurement deviation between the three streams was never more than ± 2 ppm as CaCO_3 . A 100 ppm Ca standard was used for calibration. Clearly if any precipitation of CaCO_3 occurs due to magnetic treatment, the Ca^{++} ion concentration relative to raw water must change. No change was observed.

The measured Ca^+ ion concentration for the ion-exchange test stream never exceeded 1.5 ppm as would be expected for ion exchange treated water.

Dissolved CO_2 was obtained using a Lazar CO_2 electrode and the Orion Digital Specific Ion Meter. Some question about what is actually being measured arose in the course of the investigation. It is not clear whether the instrument measures total alkalinity, CO_3^{--} concentration, excess neutral CO_2 in solution if supersaturated, or some combination thereof. Further investigation of the electrode calibration

factors needs to be carried out in order to present reliable data,
so none is reported here.

7.0 SUMMARY

In general the tests performed on all four flowing streams indicated that the water was not changed beyond acceptable experimental limits. The only observable chemical change was in the ion exchange stream. This change is, obviously, a result of the substitution of calcium and magnesium ions in the water with sodium ions as a result of the softening process. The generally reported claims of the magnetic water conditioning manufacturers that there is a change in the physical properties, i.e., lowering of boiling point, surface tension reduction, and the treated water is non-scaling, were not substantiated by the research project.

The only thing that was evident was that the ion exchange resin type of water softener did indeed yield lower amounts of scale. There were differences in the corrosion effects in the four streams between ferrous and nonferrous alloys. The differences in nonferrous alloys were insignificant.

The results of this laboratory study indicate that there was no significant change in the water quality of the Rapid City water when permanent magnetic conditioning devices were used.

8.0 CONCLUSIONS AND RECOMMENDATIONS

With the conclusion of this set of tests, it is now evident that it is possible to perform a series of tests which can evaluate claims for scaling, changes in water chemistry, and also boiling point deviations. The changes of scaling can be evaluated by the form of scale produced and the SEM very clearly will indicate changes in morphology which in turn should indicate changes in rigidity of the scale firmness, attaching methods, and so on. The X-ray diffraction will very clearly indicate what mineral species has been formed. These scaling tests were performed on a once-through system typical of a domestic installation and are not perhaps representative of multi-pass "treating" that might be experienced in a boiler-type environment.

The entire apparatus that has been used for testing corrosion and scaling could be fitted conveniently into a small trailer and moved from site to site for further testing of claims on other water types.

No tests for rates of corrosion were performed using the polarographic device due to material and component supply problems. Any future experimental testing should include such testing procedures. This is one test procedure which will produce very rapid collection of data. This in turn will permit evaluation of corrosion and/or scaling claims as some recent literature indicates that the polarograph can be used to evaluate rates at which scale is formed by using a special electrode configuration in highly scaling waters.

Further testing on rates of scale formation on different substrates should also be performed preferably on the common materials used in water heaters, piping, valves, and materials of this nature. Suggested materials are polyvinyl chloride substrate (either the PVC or CPVC type), teflon, brass, copper, carbon steel, and stainless steel. These materials may have somewhat different rates of scale formation and different sites at which scale can start, and so it appears at this time that these are some investigations that should be performed in the laboratory on a future project.

Since there were no real differences in chloride content of the four test streams, this is one test that may be perhaps dropped as there is little data being gained by its performance. The dissolved oxygen

also did not show any real changes so this test would also be one that could perhaps be dropped.

The sodium content is a test that would have value at other test sites because it could be a function of how much sodium is already present in the water and thereby have some value in evaluating ion exchange type conditioners. Conductivity is a relatively simple test and it does serve as a backup for the sodium and total ionic strength of the water and so it would be worthwhile being retained. Iron tests should be retained as it also will vary from site to site and there could be more reactive waters which could attack perhaps some inner components of the magnetic-type conditioners.

Boiling point elevation did not yield any real changes and would very likely continue in the same vein and this is a test that could also be dropped. Surface tension might be a function of some of the ions and some of the more highly mineralized waters so it is a test that is perhaps worth retaining in future investigations. The weight loss testing is very valuable and in addition to the polarization it should also be retained. The evaluation of the scale should also be retained as different waters will have different chemical makeups and correspondingly will perhaps show different formation of minerals and so it should be retained and perhaps expanded slightly.

At the present time these are the only major revisions or additions that should be considered in the testing program. These tests, if performed at other sites with different water mineralization, should confirm the percent test results.

9.0 APPENDIX

The Chemistry

The chemistry of aqueous solutions--even those resulting from natural potable water sources, treated or untreated--is greatly complicated by the host of ionic (and often organic) species present in solution. Although in most cases constituents are present in concentrations ranging from tens to--at most--a thousand ppm, some ions (or sols) present in sub-ppm concentrations can have a profound effect on the chemistry of the water as a whole. In addition, soluble atmospheric gases such as CO_2 and O_2 have an enormous effect upon the corrosive and scaling properties of water. Because corrosion processes strongly influence the ionic balance of the aqueous medium in a very complex manner, any attempt at analysis of this process is probably doomed to failure. This is especially true when several dissimilar metals are present. In these experiments therefore we will, as far as possible, use the non-metallic materials in construction of our experimental systems. Even (organic) plastics influence some corrosion processes to a certain degree. As a result, approximately four to six weeks are required to chemically stabilize any water containment (flowing or stagnant) system. After this period one could expect to achieve repeatable results as long as the supply water chemistry is not altered appreciably.

The scaling problem involving deposition (and dissolution) of calcium carbonate from solution is more amenable to analysis. Even though this process is complicated by the presence of other metal ions, primarily magnesium, iron, etc., and anions of sulphate, chloride, sulphide, etc., the primary scale-forming species is calcium carbonate (CaCO_3). The so-called bicarbonate equilibrium (or CaCO_3 solubility) is very sensitive to solution pH, temperature, and dissolved carbon dioxide produced in the medium or provided by the atmosphere in contact with the liquid. Since at least some of the physico-chemical processes involved are dynamically slow (even on a geologic time scale, it turns out) one can assume a true chemical equilibrium is seldom if ever achieved between the aqueous medium and its surroundings. The real questions that remain revolve around the mechanisms of precipitation and growth of CaCO_3 crystals from solution. The sensitivity of the process to

foreign nucleants, micelle dynamics, and possibly external electromagnetic fields (particularly magnetic) remains as, at best, a qualitatively understood process. As previously discussed the constituent atoms, molecules, and ions are all diamagnetic so there should be no effects on the process from application of even a strong magnetic field. However, if paramagnetic ions (or sols) in solution play a role in nucleation by somehow complexing the reactants, there may be an influence produced by application of a magnetic field. It is interesting to note that dissolved oxygen is also weakly paramagnetic and must be considered as a possible interactant.

$$[H^+] [OH^-] = K_w \quad (4)$$

$$\frac{[H^+] [CO_3^{2-}]}{[HCO_3^-]} = K_2 \quad (5)$$

$$[Ca^{++}] [CO_3^{2-}] = K_c \quad (6)$$

Following Kristiansen's (and others) approach, we can derive an expression for the dissolved Ca^{++} ion concentration as a function of $[H^+]$, or $pH = -\log[H^+]$ based upon solution charge neutrality expressed as

$$2[Ca^{++}] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \quad (7)$$

from which, after algebraic manipulation,

$$[Ca^{++}] = \frac{(K_w - [H^+]^2) + ((K_w - [H^+]^2)^2 + 8K_c/K_2 [H^+]^2 (2K_2 + [H^+]))^{1/2}}{4[H^+]} \quad (8)$$

From this we can plot saturation equilibrium concentrations of $CaCO_3$ (in equilibrium with solid $CaCO_3$) as a function of pH and temperature since all the activity products are temperature dependent. Four problems arise with this calculation. First the ionic strength of the solution influences the activities of the ion species. The activities are related to the actual molar concentrations (M) by the activity coefficient γ_m such that

$$[M] = \gamma_m(M) \quad (9)$$

The activity coefficient in turn is a function of the ionic strength I defined as

$$I = 1/2 \sum_i Z_i^2 (M_i) \quad (10)$$

where Z_i is the ionic charge and the sum over all ionic species is taken. The activity coefficients are best related to the ionic strength by Davies' formula, valid for solutions with $I < 0.1$ M, a value exceeding that encountered in most water systems of concern here. This is

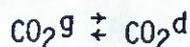
$$-\log \gamma_m = 0.51 Z_i^2 (I)^{1/2} / (1+I)^{1/2} - 0.2 I \quad (11)$$

The corrected values for the activity products are given by

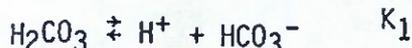
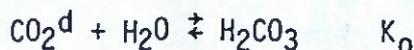
$$K_w' = K_w 10^x, K_2' = K_2 10^{2x}, K_c' = K_c 10^{4x} \quad (12)$$

with $x = 1.02(I)^{1/2} / (1+I)^{1/2} - 0.2I$ and the activities $[M]$ in the charge balance equation replaced by actual concentrations (M). Plots of Equations 8 to 12 have been obtained by Kristiansen, based upon K values given in Table 1 and shown as Figure 3. For a given pH and temperature the saturation concentration of CaCO_3 can be read. These curves are based upon K_c for calcite in the solid form which is $4.57(10^{-9})$ as given by Buswell and Larson. K_c for aragonite is $6.0(10^{-9})$ which, if used, will increase the solubility of Ca^{++} and shift the curves upward particularly in acidic solutions. Additional ions in solution will raise I again causing the solubility to increase.

The second effect relates to the presence of dissolved CO_2 which follows the following reactions,



where g refers to gaseous and d to dissolved state



The last reaction represents the first ionization of carbonic acid. The concentration of H_2CO_3 will thus, in equilibrium, be proportional to the partial pressure of CO_2 in the surrounding atmosphere. The concentration of $[\text{H}^+]$ and $[\text{HCO}_3^-]$ are thus related to $[\text{H}_2\text{CO}_3]$ by

$$[\text{H}^+] [\text{HCO}_3^-] = K_1 [\text{H}_2\text{CO}_3] \quad (13)$$

With $p_{\text{CO}_2} = 1$ atmosphere and $T = 25^\circ\text{C}$, $K_0 \approx 10^{-1.47}$ and $K_1 = 10^{-6.4}$ (from Krauskopf), and the solubility of gaseous CO_2 is .76 l/l or .031 M. From Equation 13 we can derive a relation between pH ($[\text{H}^+]$) and $[\text{Ca}^{++}]$ which fixes both quantities given only the ionic strength and the equilibrium condition as

$$\frac{K_s [\text{H}^+]^2}{K_2 [\text{Ca}^{++}]} = K_1 [\text{H}_2\text{CO}_3] \quad (14)$$

In Equation 14 correcting for activity gives $K_1' = K_1 e^{\chi}$. K_c should be corrected for fugacity if necessary in a similar fashion. As conditions (pH and temperature) change, CO_2 will either be evolved or absorbed from the surroundings.

If an excess of dissolved CO_2 is present as is usually the case when water is in contact with the atmosphere, the activity of $[CO_2]^d$ can be taken as unity.

The third effect centers around the fact that the calcium and carbonate doubly charged ions have a slight tendency to form neutral ion complexes and this, in effect, results in a small concentration of dissolved molecular $CaCO_3$ according to



With $K_n = 10^{+3.2}$ at $25^\circ C$ we can obtain the concentration as

$$[CaCO_3]^d = K_s K_n = 10^{-5.15} \quad (16)$$

or about 0.7 ppm under normal conditions.

The final problem arises from common ion effects, as well as non-ionic species in solution. The principal common ions in the present situation are Mg^{++} and Fe^{++} and SO_4^{--} , the latter occurring in very low concentration in most of our natural waters. The potpourri of foreign ions in natural waters tends primarily to effect the ionic strength, the result being that ionic strength can be approximately proportional to the TDS (total dissolved solids) present in aqueous solution.

As a sample calculation it is interesting to compute values for all concentrations for the laboratory water used in these experiments. The conditions are: pH = 7.4 and T $25^\circ C$. From Equation 8

$$[Ca^{++}] \cong (K_c / 2K_2 [H^+])^{1/2}$$

From Equation 14 the carbonic acid concentration is

$$[H_2CO_3] = 2.6(10^{-4})M$$

and the dissolved CO_2 is

$$[CO_2]^d = 8.3(10^{-3})M$$

much smaller than the atmospheric partial pressure. The laboratory measured value of $[Ca^{++}] = 49 \pm 2$ ppm so the natural laboratory water is undersaturated.

From the above analysis one can deduce that appropriate measurements to determine the chemical state of a $CaCO_3$ solution should involve

determination of temperature, pH, $[Ca^{++}]$, and the concentration of dissolved CO_2 and O_2 --all of which can be electronically measured in real time. Any change in the physico-chemical state resulting from application of magnetic fields to the solution should be manifested in changes in one or more of the above parameters. No change necessarily implies no effect and this without perturbing the chemical state.

The measurement of dissolved O_2 is necessary to observe any effects due to the ferric ion which may be present. This can influence the bicarbonate equilibrium through an interfering reaction between dissolved O_2 , $[HCO_3^-]$, and $[Fe^{++}]$ and potentially provide a mechanism for magnetic interaction with the scaling process.



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