1998

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Recommended Citation

Weiss, Brian R., "Effects of Temperature, Water Hardness, and Recirculation on Copper Corrosion" (1998). *Electronic Theses and Dissertations*. 3563.
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EFFECTS OF TEMPERATURE, WATER HARDNESS, AND RECIRCULATION ON COPPER CORROSION

by

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A thesis submitted in partial fulfillment

of the requirements for the

Master of Science

South Dakota State University

1998

EFFECTS OF TEMPERATURE, WATER HARDNESS, AND RECIRCULATION ON COPPER CORROSION

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable for meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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ACKNOWLEDGEMENTS

A tremendous thanks is expressed to Dr. Delvin DeBoer for his patience, encouragement, and guidance in this undertaking.

A special thanks is extended to my parents Roger and Marsha Weiss and my in-laws Ron and Tamera Tschetter for their encouragement and support.

Finally, a very special thanks to my wife Richel, for her love, patience, and encouragement throughout this project.

ABSTRACT

EFFECTS OF TEMPERATURE, WATER HARDNESS, AND RECIRCULATION ON COPPER CORROSION

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In previous work, the effects of water quality have been shown to influence the formation of scale from copper corrosion. A general understanding of the effects of water quality on copper corrosion have been difficult to obtain because of complex interactions of water quality variables on copper corrosion in different water supply systems. The objective of this study was to examine the effects of temperature and water hardness on copper corrosion occurring in a household water supply system. The effects of recirculation were also studied in concurrence with the above water quality parameters.

Electrochemical corrosion testing and corrosion by-product release testing were used to determine the effects of temperature, water hardness, and recirculation on corrosion rates and copper corrosion by-product release.

The results of this testing revealed that increasing temperature dramatically reduced copper corrosion by-product release. Temperature was shown to effect the solubility of the corrosion by-product released into solution. Water hardness had little or no effect on copper corrosion by-product release. The effects of recirculation used in this experimentation were found to be in direct relationship to the effects of temperature on corrosion by-product release.

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Chapter 1

Introduction

Copper piping has been used extensively over the years in household plumbing and in industrial applications. Even though copper piping tends to be a trouble free plumbing material, copper corrosion occasionally causes problems such as pitting failure, fixture staining or blue water. Water quality plays an important role in preventing or inducing copper corrosion by affecting the formation of a protective scale layer.

The Lead and Copper Rule (LCR), promulgated in 1991 by US Environmental Protection Agency (USEPA), required public water systems and household plumbing systems to minimize lead and copper corrosion. The maximum contaminant level (MCL) set by USEPA for copper is 1.3 mg/l Cu. High exposure to copper can cause adverse health effects in people with Wilson's disease and can also cause stomach and intestinal distress in the general population.

Copper corrosion often appears nearly at random in a distribution system. The problem can be especially evident in new housing developments where some homes may have severe localized corrosion problems, and others are unaffected, or in corrosion problems that seem isolated to specific floors of tall buildings. Three distinct types of pitting are commonly recognized, encompassing cold, hot, and soft waters (Edwards *et al.* 1994). Pitting corrosion has also been observed in copper plumbing in apartment buildings when hot water is recirculated to maintain temperatures throughout the building.

In previous work, the effects of water quality have been shown to influence the formation of scale from copper corrosion (Edwards *et al.*, 1994). A general understanding of the effects of water quality on copper corrosion have been difficult to obtain because of complex interactions of water quality variables on copper corrosion in different water distribution systems. Benjamin *et al.*, (1990) stated that many studies have been performed on the effects of water quality on copper corrosion; however, a unified theory has not been developed and applied to corrosion control.

Objective

The purpose of this research was to study the effects of temperature and water hardness on copper corrosion occurring in a household water supply system. The effects of recirculation were also studied in concurrence with the above water quality parameters. This study consists of a review of literature to determine the extent of previous work completed in this area and laboratory testing of the effects of temperature, water hardness, and recirculation on copper corrosion.

Scope

This study was designed to provide practical insight into the effects of temperature, water hardness, and recirculation on copper corrosion in household water supply systems. The following activities were completed to accomplish this study:

1. Perform a review of literature to determine the extent of previous work and provide a summary of results and conclusions made by others studying this area.
2. Perform laboratory testing using electrochemical corrosion testing methods and corrosion by-product release testing methods to determine the differences of corrosion

rates and soluble copper concentrations caused by the effects of temperature, water hardness, and recirculation.

3. Correlate results of laboratory testing with results and conclusions developed by others in previous work.

Chapter 2

Review of Literature

A literature review was conducted to introduce basic corrosion theory, present methods for measuring corrosion activity, characterize scale layer formation, and discuss effects of certain water quality parameters, velocity, and recirculation on copper corrosion. The effects of water hardness, and temperature on copper corrosion were of particular emphasis in this review.

2.1 Basic Corrosion Theory

Two types of problems occur from copper corrosion within a distribution system. Pipe failure is one problem that results in leakage caused by perforation of the pipe wall. The second problem is high corrosion by-product release, which creates unwanted changes in water quality caused by corrosion products leaching into the water. The objective of this section is to present the basic principles which cause these problems.

2.1.1 Thermodynamics

Metals are generally unstable within their environment. This is the reason corrosion exists in a pipe system. Given the opportunity, metals will attempt to lower their energy by spontaneously reacting to form solutions or compounds that have a greater thermodynamic stability (Bradford 1993).

The Gibbs free energy change, ΔG, is the driving force for the chemical reactions occurring in metallic corrosion. The quantity of ΔG, either negative or positive, relates directly to the spontaneity of the reaction. A negative free energy is associated with reactions that occur spontaneously. On the contrary, reactions with a positive free energy will only occur if energy is supplied to the system to drive the reaction. (Benefield *et al.* 1982)

The driving force of corrosion measurements is often defined as potential. The following equation defines the relationship between the potential (E) and free energy change (ΔG). The minus sign in the equation causes a positive cell potential when the corrosion reactions are spontaneous.

$$E_{cell} = \frac{-\Delta G_{reaction}}{nF} \qquad \text{Eqn. 2.1}$$

E_{cell} = potential of the corrosion cell (volts)

$\Delta G_{reaction}$ = Gibbs free energy change

n = number of moles of electrons transferred

F = Faraday's constant

2.1.2 Electrode Reactions

For aqueous corrosion to occur, an electrochemical corrosion cell must consist of an anode, cathode, electrolyte, and a conducting metal. Oxidation of the corroding metal occurs at the anode where electrons are released and carried to the cathode through the conducting metal. The electrons then migrate to the cathode where they are released to a appropriate electron acceptor in the electrolyte. Positive ions produced at the anode will tend to move to the cathode and the negative ions produced at the cathode tend to move to the anode. This is caused by concentration gradients and must occur to maintain a electrically neutral solution (Cruse *et al.* 1985).

2.1.3 Forms of Copper Corrosion

Uniform corrosion and localized corrosion are two common types of copper corrosion found in water piping systems.

Uniform corrosion

Uniform corrosion occurs when the entire surface of copper tubing is attacked at an equal rate. Any location on the surface of the copper tubing could be anodic at one moment and cathodic the next. Although the rate of corrosion is usually not rapid enough to cause perforation of the pipe wall and associated failure, this type of corrosion can produce copper concentrations that exceed drinking water standards. Excessive uniform corrosion rates can cause consumer complaints of "green" or "blue" water. Other problems that occur are staining of fixtures or clothing, metallic-tasting water, or even nausea if enough copper is consumed (Edwards *et al.* 1994). The surface of the copper tubing under the influence of uniform corrosion is characterized by a loosely adhering powdery scale and beneath it, or in areas where no scale is present, by a tarnished copper surface (Cruse *et al.* 1985).

Localized corrosion

When localized or pitting corrosion occurs, the surface under the most aggressive attack becomes recessed with respect to the rest of the pipe surface and forms visible pits. Pitting occurs when the anodic region remains in the same area and is relatively small compared to the cathodic region. Pitting corrosion causes high corrosion by-product release and, more commonly, perforation of the copper tubing. Perforation of the pipe wall may occur in just a few months, although it typically takes a few years (Edwards *et al.* 1994).

2.2 Corrosion Activity Measurements

By-product release, weight-loss, electrochemical analysis, and surface inspection are corrosion testing techniques that can be utilized to determine corrosion activity. Because unstable scale layer formation has a tendency to cause large standard deviations in corrosion measurement data, corrosion control treatments are tested in duplicates or triplicates and cross-referenced with another testing technique. Corrosion control tests can be done in a variety of different testing schemes; however, in all testing techniques, metal samples or pipe segments are exposed to a water quality of interest over a specific period of time using either a flow-through or static testing scheme.

Static testing involves water that is either “stagnant” or “recirculated” within the testing apparatus. Various types of systems can be utilized for stagnant testing. A metal sample can be immersed into the test water, or a pipe segment can be filled with the water being tested. The metal sample or pipe segment is exposed to the water of interest over a specific period of time and corrosion rates are determined using either weight loss or by-product release measurements. Static testing does not directly simulate distribution systems, although an advantage is that a small quantity of water is required for testing (LCR Guidance Manual 1992).

Flow-through testing simulates continuous flowing conditions through a testing apparatus where water flows through the coupon and is not reused. This type of testing best simulates the conditions in the distribution system. A disadvantage of this type of system is that an extremely large amount of water is consumed over the period of testing, which requires the testing to be implemented in a water treatment facility or distribution system. Weight-loss or by-product release is commonly used to measure corrosion rates in this type of testing (LCR Guidance Manual 1992).

2.2.1 Weight-Loss

Weight-loss measurements generally use rectangular coupons or pipe inserts to measure corrosion in a distribution system. Both the rectangular coupons and pipe inserts have been standardized by the American Society of Testing and Materials (ASTM). In weight-loss analysis, the copper coupon or pipe insert is initially cleaned and weighed. Initial cleaning removes organic matter, which may interfere with the corrosion process. Next, the coupon or pipe insert is exposed to the water of interest for a specific period of time. At the end of the exposure time, the coupon or pipe insert is removed, re-cleaned and weighed. The final cleaning removes the corrosion scale that formed during testing. The difference between the initial and final weights represents the total corrosion activity, which occurred during the exposure time period. Weight-loss measurement takes into account both by-product released and scale formation; therefore, it represents the total corrosion activity occurring during the exposure period (LCR Guidance Manual 1992).

2.2.2 By-product Release

By-product release measures the concentration of soluble copper released into solution during the corrosion of the copper surface of rectangular coupons pipe inserts, copper coils, copper wire, or piping systems. In the by-product release method, complete copper corrosion is not analyzed since only the copper released into solution is measured. This measurement does not account for corrosion products that make up the scale layer. Generally, the amount of copper released is measured as soluble copper in mg/L. The insoluble or particulate copper in solution represents the amount that cannot pass a specified filter size, commonly a 0.45-micron filter. This type of testing is commonly used to verify other corrosion testing techniques. A disadvantage of by-product release is that obtaining viable results takes a long time.

2.2.3 Electrochemical Analysis

Electrochemical analysis can be used to determine instantaneous corrosion rates and to artificially accelerate the aging process to obtain, in a few days, corrosion scales that are representative of scales found in a distribution system. In electrochemical testing, the difference in electrostatic potential between a test electrode and reference electrode under applied current densities can be related to the rate of corrosion reactions. Electrochemical corrosion rate analysis measures complete corrosion activity and may not accurately represent the amount of soluble copper that is being released into the distribution system. A very important advantage of electrochemical corrosion rate analysis and accelerated aging is the significantly reduced amount of time needed to obtain accurate, long-term corrosion activities. However, electrochemical techniques require a higher degree of skill than other corrosion testing such as by-product release or weight-loss methods. Complete descriptions of electrochemical principles and validation tests are presented in a previous thesis (Bollig, 1995).

2.2.4 Surface Inspection

Surface inspection techniques include visual, chemical analysis, scanning electron microscopy (SEM), and x-ray diffraction. In visual inspection of the corroded surface, different characteristics of corrosion should be noted, such as: pitting, uniform corrosion, scale characteristics (continuous, patchy, non-existent), and coloration (LCR Guidance Manual 1992).

If a scale layer exists, chemical analysis of the scale can indicate the elements that characterize the chemical matrix; however, this analysis is limited because it does not identify the specific chemical compounds composing the scale layer. SEM and x-ray diffraction can also be used to study scale characteristics such as scale structure, morphology, and mineralogy.

2.3 Scale

The formation of a scale layer on the metal surface can provide a protective barrier against an oxidizing environment. Generally, the principal protective agent against internal corrosion in pipes is the scale layer, and its effectiveness determines the useful life of the system (Benjamin *et al.* 1990).

The identity and type of scale that forms on the metal surface influences copper corrosion. Corrosion scales that are highly soluble, conductive, porous, and friable are considered problematic, whereas the opposite conditions are considered beneficial. Characteristics of a scale layer are affected by water composition, temperature, and flow conditions (Edwards *et al.* 1993). The major components of the scale layer are corrosion by-products such as the corroding metal combined with hydroxide ions or other dissolved ions (Benjamin *et al.* 1990). Table 2-1 lists some of the typical solids that might form in a water distribution system.

Edwards *et al.* (1996) have shown, through pipe-rig experiments and monitoring experience of large utilities, that soluble copper corrosion by-product release increases as a linear function of alkalinity. They found these trends were consistent with measurements of copper solubility in simple laboratory experiments. Therefore, it appears that solubility is a key factor in copper corrosion by-product release. Using the data from the previous experiments, various solids that might be controlling copper solubility were evaluated using a chemical equilibrium model (MINEQL$^+$). The four cupric solids examined in the model were tenorite, cupric hydroxide, malachite,

Table 2-1: Typical copper solids that might form in a water distribution system. (Edwards, Ferguson, and Reiber, 1994)

Name of Solid	Formation Reaction of Solid	Characteristics
Cupric Hydroxide	$2Cu^{2+} - 2H^+ + 2H_2O \rightarrow Cu(OH)_2$	Light blue or blue-green
Malachite	$2Cu^{2+} - 2H^+ + 2H_2O + CO_3^{2-} \rightarrow$ $CuCO_3 \bullet Cu(OH)_2$	Blue-green
Bronchantite	$4Cu^{2+} - 6H^+ + 6H_2O + SO_4^{2-} \rightarrow$ $Cu_4(OH)_6(SO_4)$	Light blue
Tenorite	$2Cu^{2+} - 2H^+ + H_2O \rightarrow Cu(O)$	Black
Cuprite	$2Cu^+ - 2H^+ + H_2O \rightarrow Cu_2O$	Yellow, red, brown

and bronchantite. Of these solids, only the solubility predictions based on cupric hydroxide, $Cu(OH)_2$, were quantitatively and qualitatively consistent with the available data. By comparison, predictions of tenorite and malachite solubility were low by about one order of magnitude over the tested pH and alkalinity ranges, whereas predictions based on bronchantite overpredicted copper solubility by a factor of three or four (Edwards *et al.* 1996).

Also, bronchantite is suspected to be a key component in a corrosion-promoting scale. Changes in water quality that favor precipitation of bronchantite tend to increase pitting frequency, whereas malachite was not predicted to cause pitting (Edwards *et al.* 1994).

2.4 Effects of Water Quality on Corrosion

Since the formation of a corrosion scale is controlled by the effects of water quality, it is important to identify water quality changes that will influence the formation of scale types that reduce copper corrosion in a given water. A general understanding of the effects of water quality on copper corrosion has been difficult to obtain because of complex interactions of water quality variables on copper corrosion in different water distribution systems. Many studies have been performed on the effects of water quality on copper corrosion; however, a unified theory has not been developed and applied to corrosion control (Benjamin *et al.* 1990). Because changes in scale type influenced by water quality are difficult to predict chemically and have not been systematically evaluated experimentally, previous experience is the only guide to decision-making (Edwards *et al.* 1993). In Table 2-2, various water qualities are compared with different

Table 2-2: Summary of copper corrosion problems. (Edwards *et al*. 1994)

Characteristics	Uniform Corrosion	Type I Pitting (Cold Water)	Type II Pitting (Hot Water)	Type III Pitting (Soft Water)
Pit Shape	No Pits	Deep and Narrow	Narrower than type I	Wide and Shallow
Problem	Blue or green water, high by-product release	Pipe failure	pipe failure	Blue water, voluminous by-product releases, pipe blockage
Scale morphology on attacked surface	Tarnished copper surface or loose powdery scale	Underlying Cu_2O with overlying malachite, calcite, or other basic copper salts, occasionally CuCl underlies Cu_2O	Underlying Cu_2O with overlying brochanite, some malachite	Underlying Cu_2O with overlying brochantite, some malachite
Water Quality	Soft waters of low pH (<7.2)	Hard, cold, well water between pH 7 and 7.8 high sulfate relative to chlorides and bicarbonate, high CO_2	Hot waters, pH below 7.2, high sulfate relative to bicarbonate, occasional Mn deposits	Soft waters, pH>8.0
Initiating factors	None noted	Stagnation early in pipe life, deposits within pipe including dirt or carbon films, high chlorine residuals, water softeners, alum coagulation	Higher temperatures, high chlorine residuals, alum coagulation, particles	Stagnation early in pipe life, pHs>8.0, alum coagulation, low chloride residuals
Ameliorating factors and treatments	Raise pH or increase bicarbonate	NOM, increase bicarbonate and pH	Lower temperatures, higher pHs, increase bicarbonate and pH	NOM, avoid stagnation early in pipe life, increase hardness and alkalinity, elevate Cl_2 residual to 0.5 mg/L

forms of copper corrosion. This table summarizes the results of past experimentation and observations; and therefore, should only be used as a rule of thumb (Edwards *et al.* 1994).

Most of the past experimentation on the effects of water quality on copper corrosion were conducted using short-term laboratory studies and the results were extrapolated to predict long-term effects on a distribution system. An interpretation of the results of this experimentation is summarized in the 1985 AWWARF Guide to Internal Corrosion in Distribution Systems (Cruse *et al.* 1985).

> *Generally, it may be stated that cations (calcium, magnesium, sodium, and potassium) exert no effect on the rate of corrosion. However, anions (chloride, sulphate, bicarbonate) do exert some influence on the rate of corrosion. Chloride in particular is a strong corrosion catalyst. Sulfate is less corrosive than chloride, while bicarbonate generally tends to reduce the corrosivity of chloride and sulfate by inhibiting action. It is difficult to quantify these observations, but as a first approximation it may be assumed that effects due to equal quantities of bicarbonate and sulfate tend to cancel each other out, and that chloride is at least two or three times as active as sulfate.*

More recent research has questioned these statements, mostly research performed by Edwards and his associates (Edwards *et al.* 1993). They examined the long-term effects of chloride, sulfate, bicarbonate, nitrate, and perchlorate anions using accelerated aging techniques to produce a scale layer that would be representative of long-term corrosion in a distribution system. The results of their testing (Figure 2-1) show the

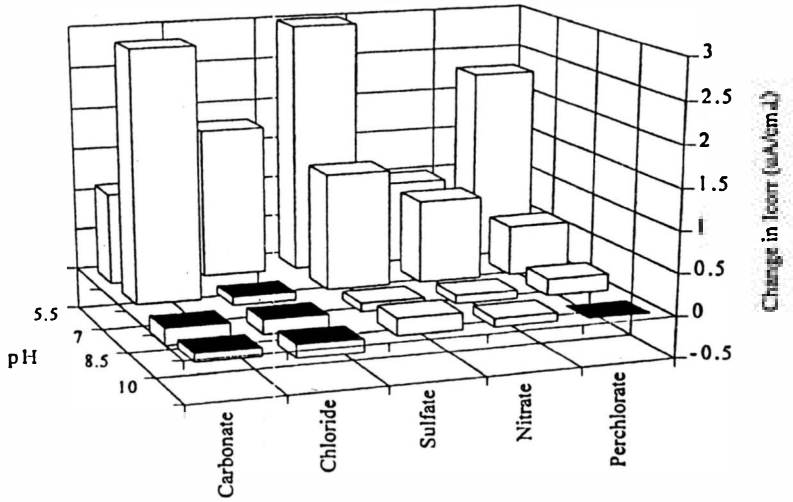


Figure 2-1: Change in corrosion rates for the given solution after aging. (Edwards *et al.* 1993)

effects of different anions at various pH values on copper corrosion rates. A positive net change in I_{corr} indicates corrosion rates increased with aging, whereas a negative change indicates that aging reduced corrosion rates. The following summary of the conclusions on the effects of the different anions on the net change in I_{corr} based on Figure 2-1 expressed by Edwards *et al.* (1993) is as follows:

- *Copper surfaces passivate in the presence of chloride at* $pH \geq 7.0$ *or carbonate at* $pH \geq 8.5$. *Copper activates (increased corrosion rates with aging) at pH values between 5.5 and 10 in the presence of nitrate, perchlorate, or sulfate.*
- *In the presence of bicarbonate, copper corrosion undergoes a critical transition somewhere between pH 7.0 and pH 8.5. Scale formed at pH 7.0 catalyzes oxygen reduction and increases the overall corrosion rate. In contrast, oxygen reduction rates are unchanged at pH 8.5, but the anodic reaction (copper dissolution) is inhibited, passivating the copper surface. An inner cubic scale layer present at pH 7.0 but absent at pH 8.5 might cause the transition, which is speculated to depend on bicarbonate concentration.*
- *Contrary to popular opinion, the aggressiveness of anions after aging (all 2-meq/L solutions) was* $HCO_3^- > SO_4^{2-} > NO_3^- > ClO_4^- > Cl^-$ *at pH 7.0, and* $SO_4^{2-} > ClO_4^- > NO_3^- > HCO_3^- > Cl^-$ *at pH 8.5. These observations are consistent with the findings of some prior experimental work related to long-term copper corrosion behavior (including by-product release) and will provide a foundation for further research aimed at rationally improving copper corrosion control.*

This research also stated that combinations of various anions might have very different effects than the effects of individual anions on copper corrosion. However, from the results of this study, the predicted worst-case water would contain high alkalinity, high sulfate, and low chloride at pH 7.0 (Edwards *et al.* 1993).

Several water quality variables have been shown to affect the formation of copper corrosion scale, which can be either protective or corrosion-promoting. Such variables include pH, alkalinity, hardness, chloride, sulfate, and temperature.

2.4.1 pH

pH is one of the most influential parameters in the controlling of copper corrosion. Although the hydrogen ion is not electrochemically active in the fundamental corrosion reactions, pH can influence copper corrosion in several ways. pH adjusts the distribution of chemical species in solution, thereby altering the equilibrium potential of all the redox reactions that are occurring. For example, by changing the activity of hydroxide ion and speciation of dissolved copper, a shift in pH changes the potentials of the major anodic and cathodic corrosion reactions. Also, pH is likely to affect the stability and protective qualities of the passivating scales that form on the copper surface. It is likely that significant decreases in pH can cause the protective scale to dissolve. Even though it is difficult to predict the effects of small changes in pH on protective scales, it is reasonable that pH affects the scale's properties in some way (Benjamin *et al.* 1990).

Past experience and experimentation has shown that as pH increases, copper corrosion rates decrease exponentially. Edwards *et al.* (1996) suggest the best way to reduce copper corrosion is by increasing pH, which most likely reduces the adverse effects of other water quality parameters such as alkalinity and sulfate.

2.4.2 Alkalinity

Although bicarbonate was historically assumed to be beneficial in preventing copper corrosion problems, recent work has conclusively demonstrated adverse effects from the bicarbonate under certain conditions (Edwards *et al.* 1996). Monitoring experiences of large utilities and laboratory experimentation has shown that the concentration of copper corrosion by-products in drinking water increases linearly with bicarbonate concentration at constant pH. Temperature and pH are key factors that affect the sensitivity of copper solubility to alkalinity (bicarbonate). Generally, increasing the pH at a given concentration of alkalinity decreases copper corrosion by-product release (Edwards *et al.* 1996).

2.4.3 Hardness

Hardness ions are not expected to influence copper corrosion because they do not directly participate in the mechanism of copper corrosion. However, hardness ions can affect copper corrosion (Edwards *et al.* 1994).

Beneficial effects of hardness are often associated with the formation of a protective scale layer of calcium carbonate. However, Ives and Rawson (1972) have also found benefits from calcium under conditions below calcium carbonate saturation (Edwards *et al.* 1994). Shalaby *et al.* (1989) proposed that the mechanism of pitting corrosion of copper in soft and hard waters is the same except for the nature of the precipitates formed on the top of the scale layer. “Edwards hypothesized that increased aggressiveness of softened water stems from insufficient hardness ions remaining to complex the more aggressive sulfate ion” (Bollig 1995).

Practical experience has shown that hardness ions have beneficial effects. Several researchers have observed that using ion exchange water softeners often increases cold water pitting.

- Cruse and Pomeroy (1974) observed from data reported from one community that eight of the first eleven copper pipe failures were from zeolite-softened water lines. A similar observation was reported by Woodside *et al.*, (1966).
- Observations were made of a hot water zeolite softened water, which induced a high concentration of sodium bicarbonate, was found to perforate a copper water line within ½ to 2½ years. Also, the same water unsoftened was not found to be corrosive because of a protective film of calcium carbonate containing some silicate deposited on the copper surface (Cohen and Lyman 1972).
- Cornwell *et al.* (1973) observed pitting corrosion in both soft and hard waters. The soft water showed to be more corrosive than the hard water. Noting that the hard water and soft water came from two different sites, other water quality factors could be of importance in the ability of one water to corrode more than the other.
- Wysock *et al.* (1991) studied the impacts of municipal ion exchange softening on lead, copper, and iron concentrations at the tap in Oakwood, Ohio. After four months of operation, the effects of partial softening did not impact lead, copper, and iron concentrations.

2.4.4 Temperature

In general opinion, corrosion rates increase with increased temperature. The rate of most chemical reactions is increased when the temperature is elevated, assuming the higher temperature does not alter the reactants or catalyst (Benefield *et al.* 1990). As a rule of thumb, each 10°C increase in temperature tends to double the chemical reaction rates.

Research performed Edwards *et al.* (1996) examined the effects of temperature on copper solubility where he hypothesized that increasing the temperature would reduce copper corrosion by-product release. From their research, qualitative and quantitative trends in soluble copper corrosion by-product release were shown to be consistent with solubility predictions based on $Cu(OH)_2$ equilibrium, modeled with a chemical equilibrium model (MINEQL$^+$). If enthalpy values for the $Cu(OH)_2$ solid in the MINEQL$^+$ equilibrium model are considered (Figure 2-2), copper-carbonate

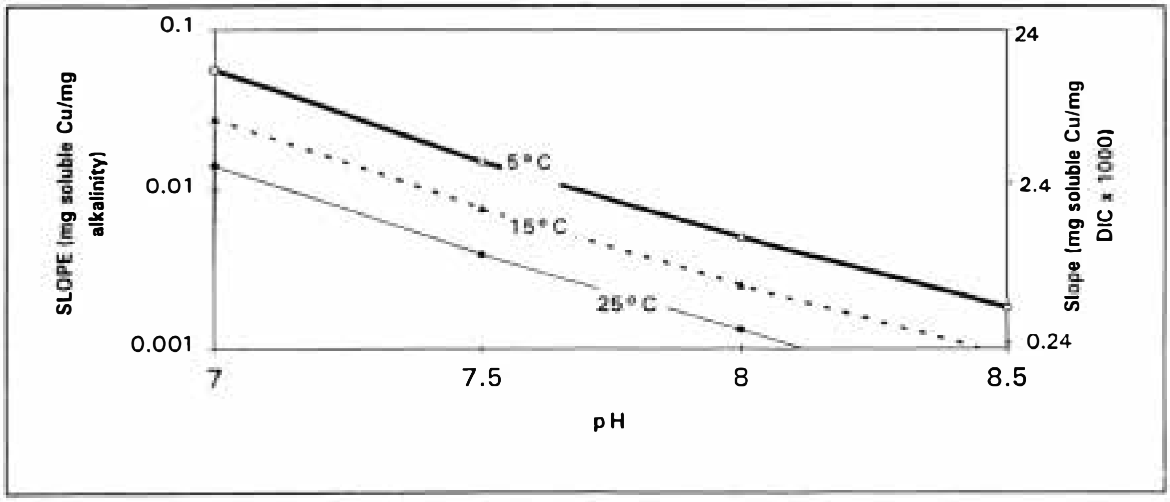


Figure 2-2: Sensitivity of copper solubility to alkalinity and temperature. (Edwards *et al.* 1996)

complexation is predicted to be a strong function of temperature, with each 10°C increase halving the slope. In other words, because $Cu(OH)_2$ dissolution is exothermic reaction, a given concentration of bicarbonate is predicted to complex about twice as much copper at 5°C as it would at 15°C.

2.4.5 Chloride

Chloride is commonly considered to be very aggressive in copper corrosion. In previous research, short-term studies have shown considerable increases in corrosion rate and pitting tendencies with increasing chloride concentrations (Edwards *et al.* 1994). However, in recent studies, chloride was shown to reduce corrosion in long-term copper corrosion experiments. As more scale was formed over exposure time, chloride tended to reduce corrosion rates (Edwards *et al.* 1994).

In another study by Edwards *et al.* (1996), the addition of chloride to solutions, with a given amount of alkalinity, decreased corrosion rates considerably. Therefore, the presence of chloride can counter adverse effects of bicarbonate. Also, a comparison of scales formed in the presence and absence of chloride validated the dominant effect of chloride on scale appearance. Chloride supported the formation of a reddish scale that was nearly identical to that observed at pH 7.0 in the presence of chloride only.

2.4.6 Sulfate

Sulfate ion is thought to be relatively inert toward copper, as explained by its absence from current pitting theory and experimental studies (Edwards *et al.* 1994). However, in recent studies the sulfate ion was found to increase corrosion rates in long-term copper corrosion tests. With increased scale buildup over exposure time, sulfate tends to be more aggressive in copper corrosion because the presence of sulfate tends to promote copper corrosion (Edwards *et al.* 1994).

2.5 Effects of Velocity and Recirculation on Corrosion

The water velocity in copper tubing can have two adverse effects on copper corrosion. One effect is the ability of high velocities to physically erode protective scales. Another is the effect velocity has on oxygen flux to the cathode (Cruse *et al.* 1985). High flow velocities are usually associated with erosion corrosion in copper pipes in which the protective scale layer or pipe material is removed mechanically (Singley *et al.* 1985).

Corrosion rates would tend to increase during flow conditions (as opposed to stagnant conditions) due to improved mass transport (Edwards *et al.* 1996).

2.6 Summary of the Effects of Temperature, Water Hardness, and Recirculation on Copper Corrosion

In general opinion, increasing the temperature results in increased reaction rates (Cruse *et al.* 1985). However, if a current hypothesis which states that copper corrosion is based on the function of solubility is true, then increasing the temperature would reduce the amount of corrosion by-product released into solution (Edwards *et al.* 1996).

Basic theory shows that since hardness ions do not participate directly in the mechanism of copper corrosion, they would not be expected to influence it strongly (Edwards *et al.* 1994). Nevertheless, hardness can affect copper corrosion as shown in previous experimentation and experience.

The effects of recirculation on corrosion can be related to the water velocity or mass transport of corrosion by-products. High velocities can cause the erosion of protective scales (Cruse *et al*. 1995). Corrosion rates would tend to increase during flowing water conditions versus stagnation due to improved mass transport (Edwards *et al*. 1996).

Chapter 3

Methods and Materials

This chapter describes the apparatus, materials, and methods used for both the electrochemical and by-product release testing conducted in this study. These two types of corrosion tests were implemented in this study to generate data on the effects of temperature, water hardness, and recirculation on copper corrosion.

Electrochemical testing was used to determine instantaneous corrosion rates and to artificially accelerate the aging process to obtain, in a few days, corrosion scales that are representative of scales found in a distribution system. A computer-controlled potentiostat in combination with corrosion cells allowed accelerated aging of copper samples and corrosion analysis to determine corrosion rates. In this study, target water was continuously refreshed as it was circulated through the corrosion cell. Electrochemical corrosion rate analysis was used in this study because of the short amount of time needed to obtain accurate, long-term corrosion rates.

By-product release testing using copper pipe loops was used to determine the amount of soluble copper released into the target water over an extended period of time. The target water was pumped either continuously or intermittently through individual copper pipe loops. The target water was replaced after three days of exposure time. The results of these tests were compared with corrosion rates from the electrochemical testing.

In order to determine the effects of temperature and water hardness on copper corrosion, tap water from a distribution system was treated with a household water heater and/or a household ion exchange water softener to provide the desired water quality.

3.1 Electrochemical Testing

Electrochemical testing techniques were used to determine instantaneous corrosion rates and to artificially accelerate the aging process to generate corrosion scales which are representative of scales found in a distribution system. The following is a discussion of the equipment and techniques used in this experimentation.

3.1.1 Apparatus

The apparatus used in this investigation (Figure 3-1) includes an electrochemical system with potentiostat, eight corrosion analysis cells (Reiber cells), and target solution reservoirs.

The electrochemical equipment used in controlling the corrosion cells consisted of a computer controlled potentiostat, ECM8 Multiplexer, and software. This equipment was obtained from Gamry Instruments, Langhorne, PA. The potentiostat precisely controlled the voltage of the corrosion cells. The potentiostat, coupled with the ECM8 Multiplexer, allowed automatic and sequential corrosion analysis of eight independent corrosion cells, or concurrent operation of the eight cells in a potentiostatic mode. Software designed by Gamry provided the capability to conduct standard electrochemical tests automatically and also to evaluate data collected from testing.

Figure 3-1: Electrochemical corrosion testing apparatus.

A corrosion (Reiber) cell and its components are shown in Figure 3-2. The components of a Reiber cell consist of a test electrode, reference electrode, and counter electrode. The Reiber cell simulates pipe flow conditions, found in household plumbing systems, permits the use of actual plumbing materials for the test electrode, is easily constructed, does not rely on expensive instrumentation, and prevents distortions in current flow during

Figure 3-2: Reiber corrosion test cell.

polarization extremes because the counter electrode penetrates the axial center of the copper cell along its entire length (Benjamin *et al.* 1990). The test electrode or working electrode consisted of a copper sample which was subjected to electrochemical analysis. The counter electrode was used to apply a voltage to the interior surface of the copper sample. A platinum wire was used as the counter electrode because of its inert behavior in a corrosive environment. In electrochemical experiments, the counter electrode is held at a desired voltage with respect to the reference voltage versus the test electrode voltage. The reference electrode in this investigation was a stable Ag/AgCl electrode encased in a narrow, flexible, polyethylene stem with a ceramic frit junction at the end which allows a high leak rate to ensure a stable reference voltage.

The target solution reservoir was a four-liter polypropylene container. The containers for the individual Reiber cells were placed in a rectangular, galvanized sheet metal water bath. The water bath was used to maintain a constant relative temperature in each target solution reservoir. During experimentation, the water temperature was held constant at ± 1 °C relative to all the cells. Also, pumps were used to maintain flow rates of 0.5 ± 0.05 gpm through each of the cells. A more detailed description of the apparatus used in this investigation is given in a previous thesis (Bollig 1995).

3.1.2 Materials

Target Solution

The water used in the investigation was obtained from the Brookings water distribution system through a tap in the Northern Great Plains Water Resources Research

Lab located in Grove Hall on the campus of South Dakota State University. A Van Guard Energy Efficient Water Heater (Model No. 6E720) with a capacity of 30 gallons was used to heat the target water to the desired temperature. A MacClean Water Softener (Model 3P973/NELSM1001) was used to soften water to the desired water hardness. Figure 3-3 shows the water softener and water heater used in this experimentation.

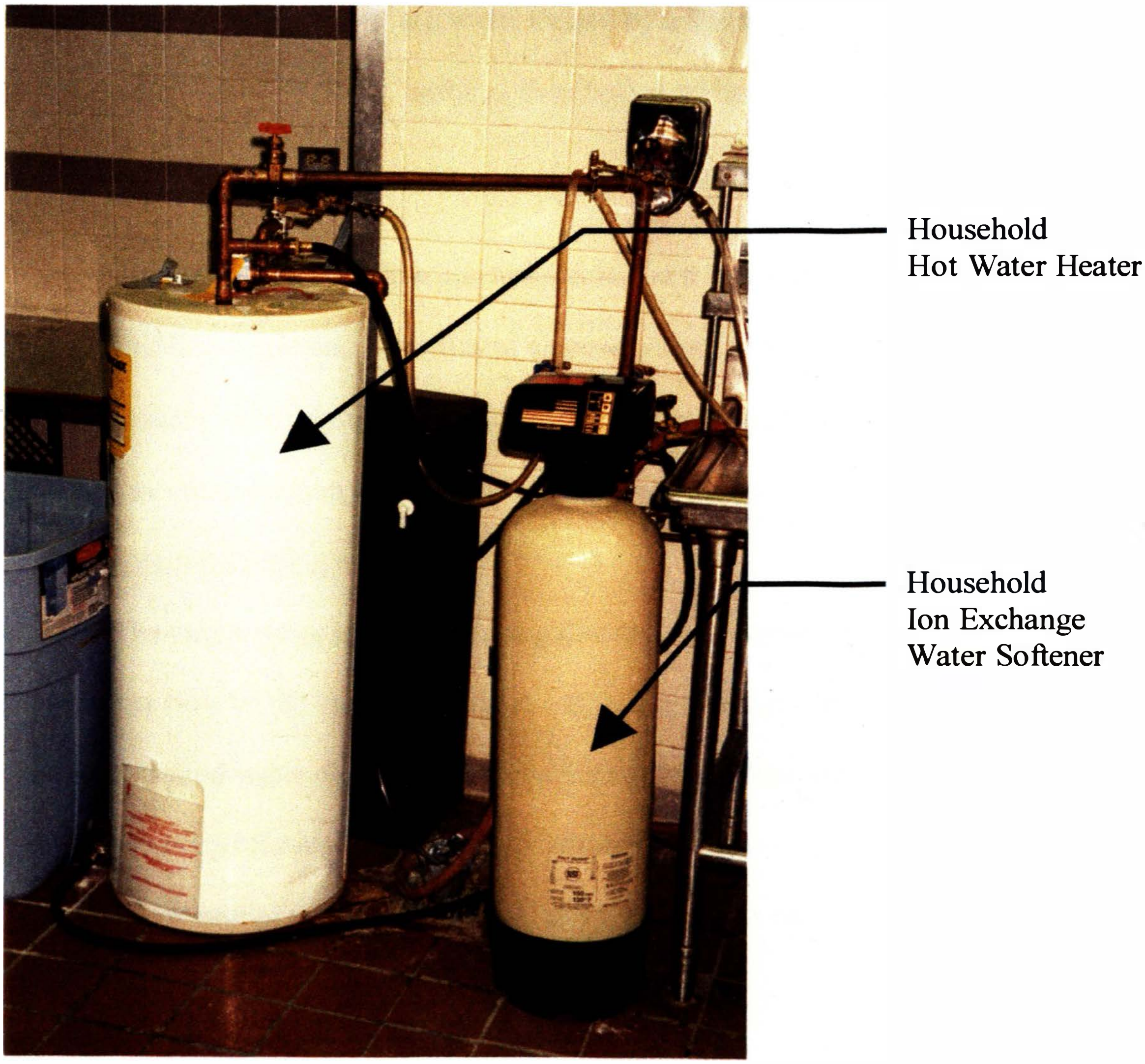


Figure 3-3: Hot water heater and ion exchange water softener used in experimentation.

The types of water tested in this investigation are as follows:

- Cold hard water - tap water with no treatment.
- Cold soft water - tap water treated by a household ion exchange water softener.
- Hot hard water - tap water heated by a household water heater.
- Hot soft water - tap water treated by a household ion exchange water softener then heated by household water heater.

3.1.3 Methods

This section will outline electrochemical and water quality testing procedures used in this investigation. Specifics of electrochemical testing and the apparatus have been reported previously (Bollig 1995). Electrochemical analysis and accelerated aging testing was conducted on the four different types of water quality listed above.

Target Solution Preparation

The target water reservoirs (one gallon polypropylene bottles) were refreshed by a continuous flow of the target solution at a flowrate of 0.2 ± 0.05 gpm to each reservoir from the desired water supply. The target solution was then pumped from the target solution reservoir through the corrosion cell and recirculated back to the reservoir at a constant flow rate of 0.5 ± 0.05 gpm. A schematic of this setup is shown in Figure 3-4.

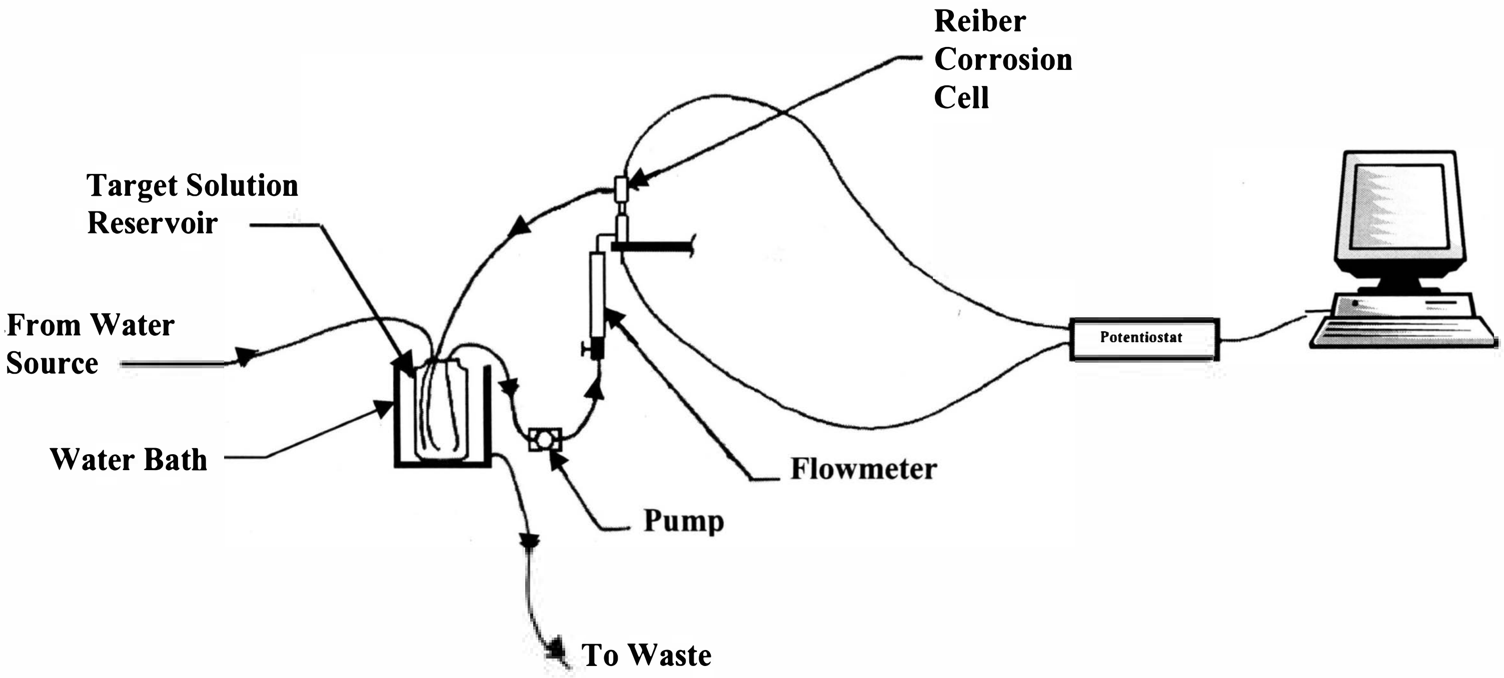


Figure 3-4. Schematic of electrochemical corrosion testing setup.

Copper Coupon Preparation

Copper samples used in the electrochemical experiments were 5/8" diameter copper couplings with an internal surface area of 3.1 in^2 (20 cm^2) and actual inner diameter of 3/4". The couplings were obtained from a local plumbing supply company. The copper coupons were washed in 0.1 N NaOH for two minutes to remove organic deposits. The copper coupons were then rinsed four times with Nano-Pure water. More rigorous cleaning methods were not used because they tend to increase surface area of the coupons and increase the potential for pitting to occur (Edwards *et al.* 1993).

Electrochemical "Accelerated Aging" Testing

The electrochemical "accelerated aging" was performed using the potentiostatic technique within the Gamry software system. The "accelerated aging" or potentiostatic tests were designed to form characteristic corrosion scales on the copper surface that are similar to those found in a specific water quality and also to determine the protective nature of the scale layer. The surfaces of the copper coupons were first subjected to the target solution of interest and allowed to corrode naturally for one hour, at which time initial corrosion rates were determined electrochemically. Then, scale was formed by anodic polarization (E = +120 mV versus reference electrode) for 72 hours, forcing the copper to corrode at an accelerated rate. After the 72 hour period, the applied potential was removed. Water samples were collected for measurement of the corrosion by-products. Then, the coupons were exposed to the target solutions for 24 hours before corrosion rates were determined electrochemically for the aged copper surfaces. After corrosion rates were determined, the copper coupons were then dried under a weak jet of pure nitrogen to prevent exposure of coupons to oxygenated, ambient air. The copper coupons were then stored in a desiccator before visual analysis (Edwards *et al.* 1993).

During the "accelerated aging" testing, anodic current versus time plots were generated (Figure 3-5). Although these plots do not provide quantitative or qualitative information concerning the corrosion rate of the unperturbed copper sample, the plots are useful in determining whether pitting corrosion or passivation of the surface occurs

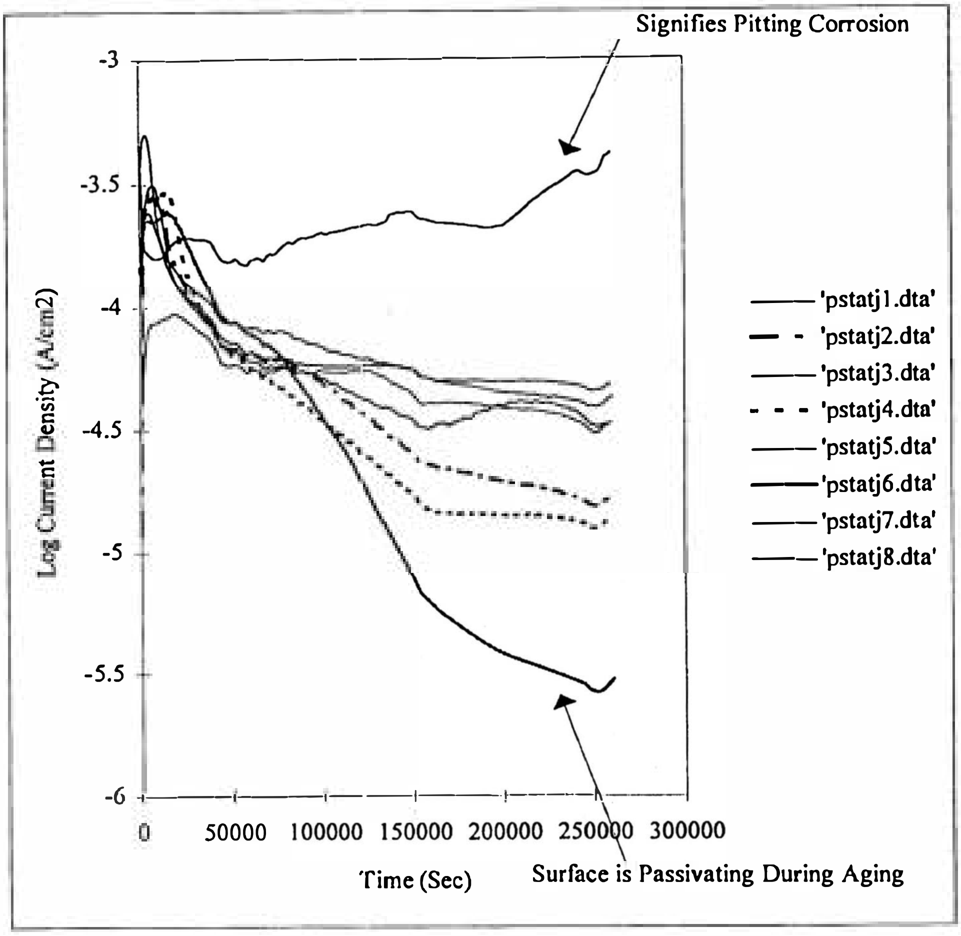


Figure 3-5: Cumulative anodic current versus time plot. (Bollig 1995)

during aging. An increase in anodic current versus time indicated pitting corrosion, while a decrease indicated passivation of the surface.

Electrochemical Corrosion Rate Measurement

Electrochemical corrosion rates were measured to determine the protective nature of the scale layer formed on the copper surface by a specific water quality during the accelerated aging process. Electrochemical corrosion rate measurements were conducted utilizing the potentiodynamic technique in the Gamry Electroanalysis System. First, the system measured E_{oc}, which is the rest potential of the copper coupon in the absence of electrical connections. Then the copper surface was subjected to a potentiodynamic scan with a perturbation of 150 mV (E_{oc} - 75 mV to E_{oc} + 75 mV) with a scan rate of 0.2 mV/sec and a recording rate of 1 data point per second. After the current versus potential data was collected, it was analyzed using Gamry corrosion analysis software, which calculated the corrosion rate (i_{corr}) and the Tafel slopes β_a and β_c in accordance with electrochemical theory (Edwards *et al.* 1993). While most of the potentiodynamic results exhibited Tafel behavior (Figure 3-6) and were fit accurately using the corrosion analysis software, the data was occasionally non-ideal (Figure 3-7). Irregularities that occur in the anodic region of the scan are usually due to passivation of the surface during measurement. In such cases, i_{corr} was determined as the current density at which the cathodic Tafel slope intersects the rest potential (E_{oc}).

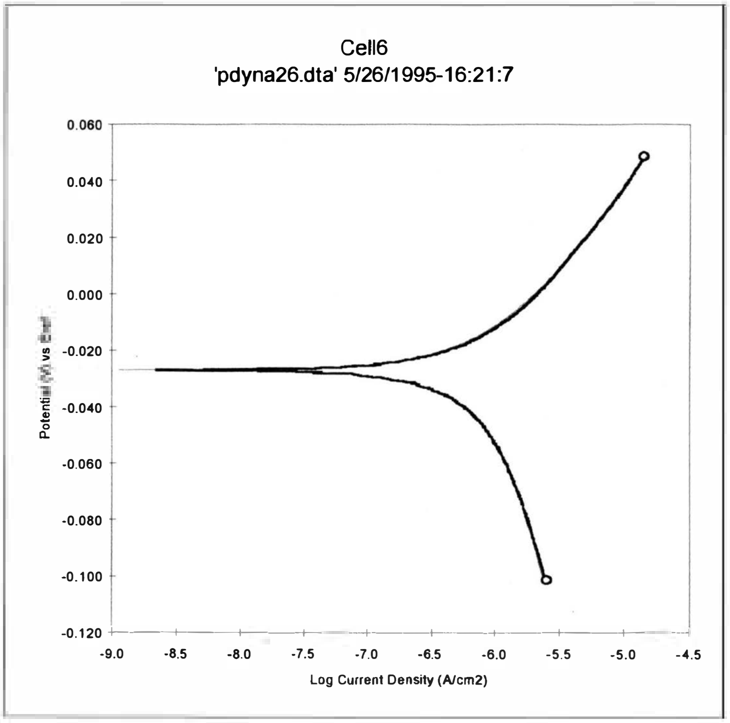


Figure 3-6: Excellent Tafel analysis fit of a potentiodynamic scan.

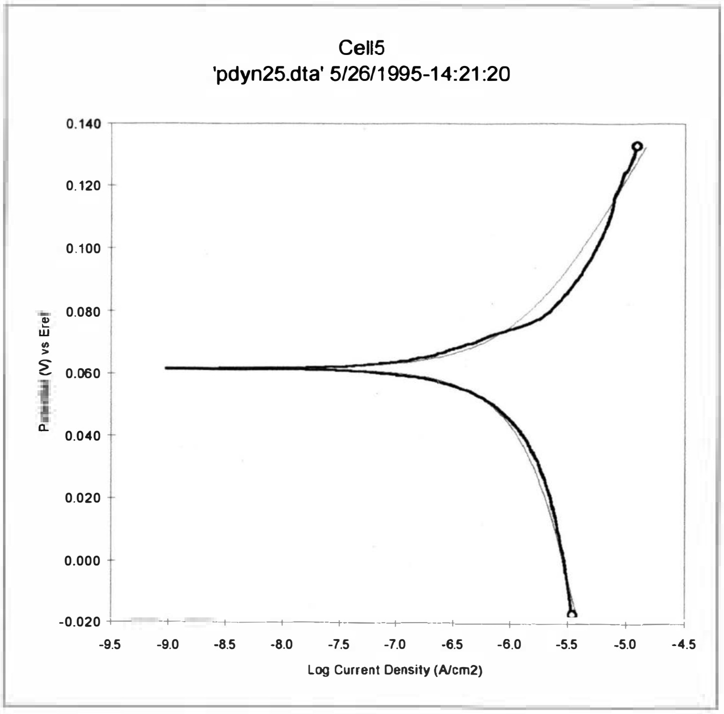


Figure 3-7: Improper Tafel analysis fit of a potentiodynamic scan.

Water Quality Analysis

Water quality testing procedures were selected to obtain the concentrations of certain water quality parameters associated with the formation of the corrosion scale layer. The methods and instruments used for all water quality analysis are tabulated in Table 3-1. Samples were collected daily from the target reservoirs to assure

Table 3-1: Description of method and instrumentation used for laboratory analysis

Parameter	Standard Methods	Instrument
Temperature	SM #2550 B, Laboratory and Field Methods	Orion 230 portable pH/temperature meter
pH	SM #4500-H^+ B, Electrode Method	Orion 230 portable pH/temperature meter
Alkalinity	SM #2320 B, Titration Method	Not Applicable
Calcium	SM #3500-Ca D, Direct-Air Acetylene Flame Method	Perkin Elmer Atomic Absorption Spectometer Model 3100
Magnesium	SM #3500-Mg D, Direct-Air Acetylene Flame Method	Perkin Elmer Atomic Absorption Spectometer Model 3100
Copper	SM #3111 B, Direct-Air Acetylene Flame Method	Perkin Elmer Atomic Absorption Spectometer Model 3100
Sodium	SM #3500-Na D, Direct-Air Acetylene Flame Method	Perkin Elmer Atomic Absorption Spectometer Model 3100
Sulfate	SM #4500-SO_4^{-2} E	Shimadzu UV160U Spectophotometer
Chloride	SM #4500-Cl^- E Automated Ferrocynanide Method	Technicon Alpkem
Orthophosphate	SM #4500-P E. Absorbic Acid Method	HACH DR2000 Spectophotometer

Methods are from Standard Methods 17th Edition that water quality parameters were not varying over the testing period. The samples were analyzed for pH, alkalinity, calcium, magnesium, sodium, sulfate, chloride, orthophosphate, and temperature. The pH, alkalinity, temperature, and orthophosphate of each sample were analyzed upon collection. 125 ml samples were collected for calcium, magnesium, and sodium measurements and preserved with 4% nitric acid to pH < 2 and stored at approximately 4°C for later analysis. 250 ml samples were collected for sulfate and chloride and stored at approximately 4°C for later analysis. Samples for soluble and total copper were not collected because the solutions in the target reservoirs were continuously refreshed with new target solution, thus the copper released into solution was flushed out of the system continuously.

3.2 By-product Release Testing

By-product release testing measures the concentration of soluble copper released into solution during the corrosion of the copper surface. In the by-product release method, complete copper corrosion is not analyzed since only the copper released into solution is measured. The following discussion describes the apparatus and methods used in this testing.

3.2.1 Apparatus

Figure 3-8 contains pictures of the apparatus used for this portion of the study. The apparatus included loop systems constructed of ½” copper tubing, peristaltic pumps, water bath, and two-liter target solution containers.

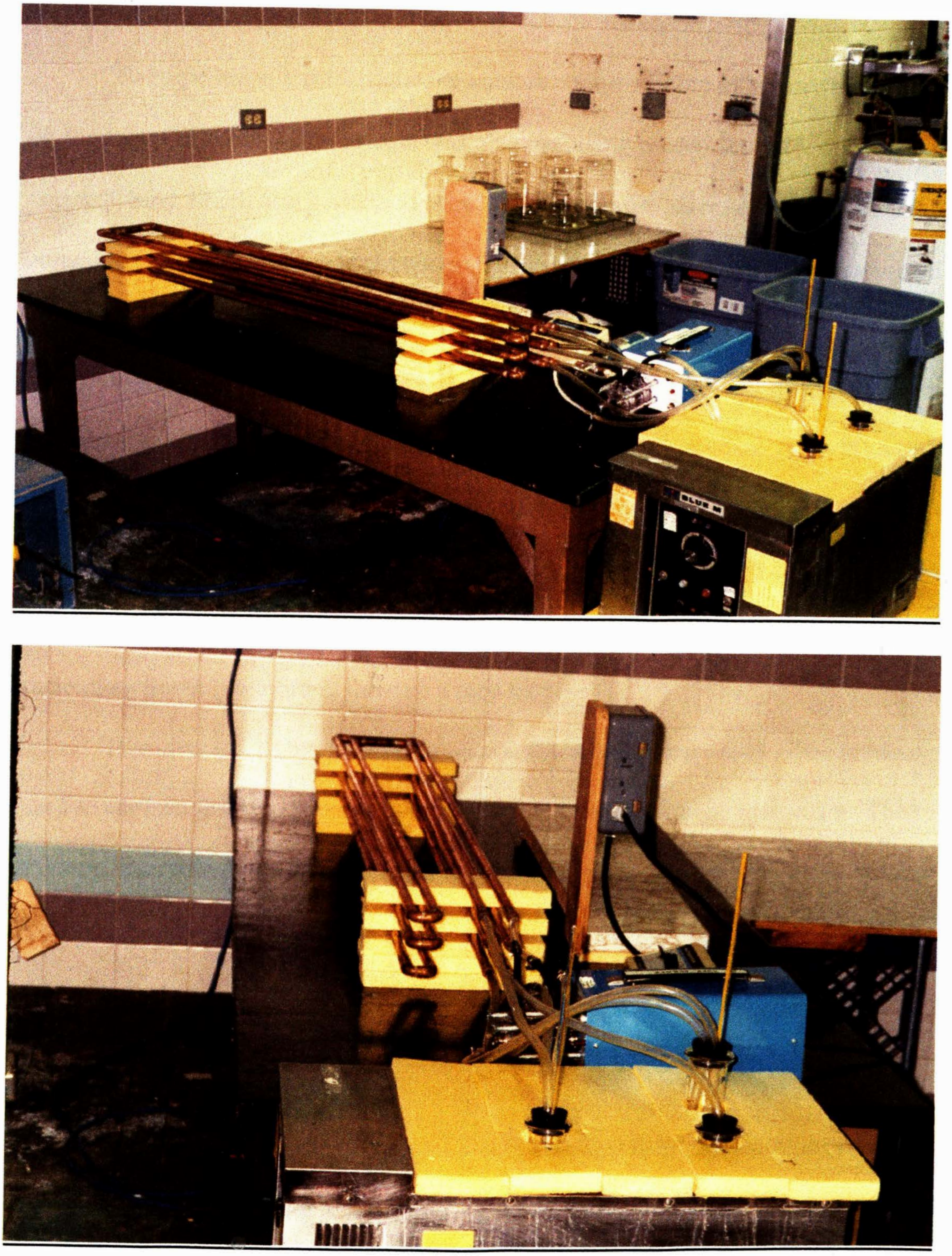


Figure 3-8: Corrosion by-product release testing apparatus.

Design and Construction

The pipe loops were designed to contain a total volume of approximately one liter of the target solution. This volume was obtained using twenty feet of ½-inch Type M copper tubing which was purchased from a local hardware store. A diagram of an assembled pipe loop system is shown in Figure 3-9. The pipe loops were assembled with six 90° elbows, two ½-¼" reducers, and lead-free solder.

Peristaltic pumps were used to pump target solution through the pipe loops at a flow rate of 0.2 gpm. A Cole Parmer Masterflex Pump (Model No. 7620-25) with two pump heads using Masterflex Tubing No. 6404-17 was used to continuously recirculate the target solution through two individual pipe loops. A Cole Parmer Micropump (Model No. 7144-04) with an Intermatic Timer (Model No. ET173C) was used to intermittently recirculate the target solution through a pipe loop.

Two-liter glass bottles were used as target solution reservoirs. Plastic tubing was used to connect the pipe loops with the pumps and target solution reservoirs. The target solution reservoirs were placed in a temperature controlled water bath which was used to maintain a specified temperature ± 1°C.

3.2.2 Materials

Target Solution

The water used in the investigation was obtained from the Brookings water distribution system through a tap in the Northern Great Plains Water Resources Research Lab located in Grove Hall on the campus of South Dakota State University. The types of

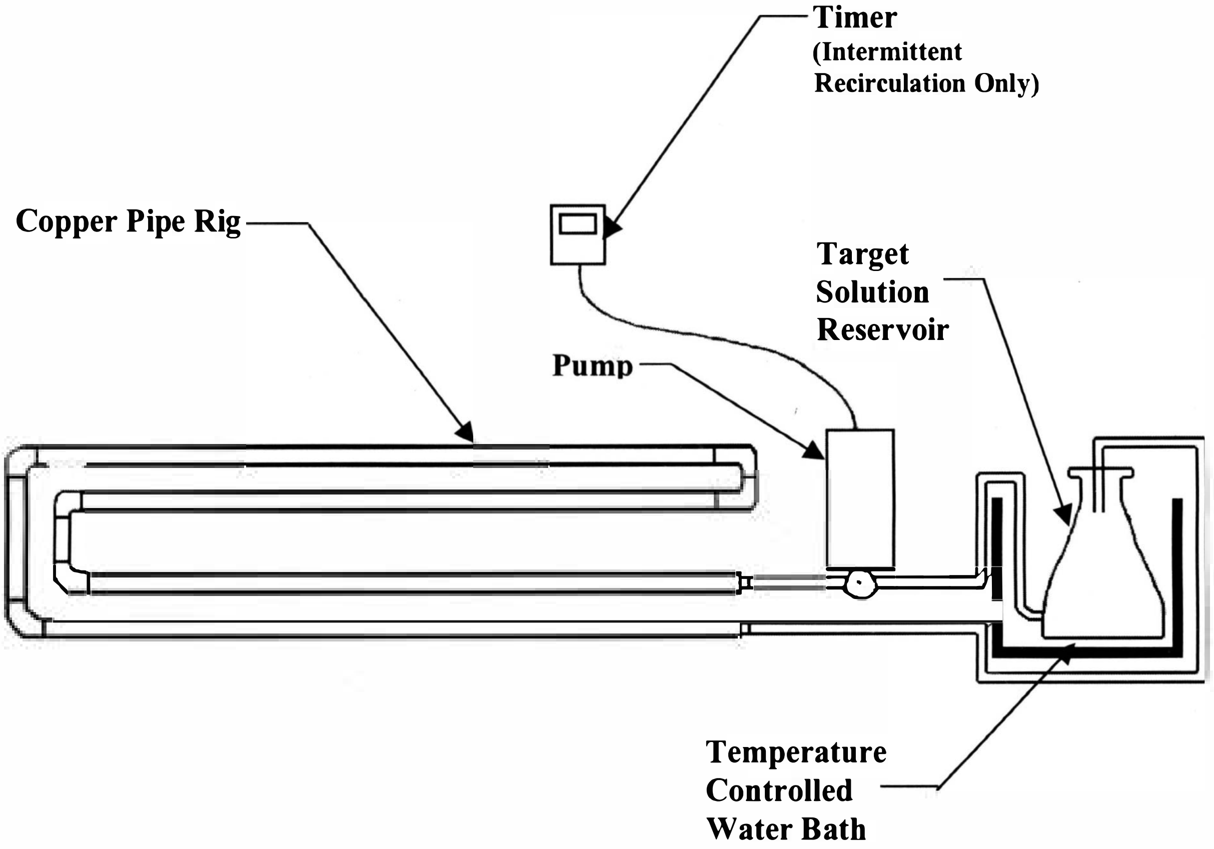


Figure 3-9: Schematic of corrosion by-product release testing apparatus.

water tested in this investigation are the same as those discussed in the previous section for electrochemical studies (Section 3.1.2).

3.2.3 Methods

Experiments

Two separate experiments were performed with each experiment having a different water temperature. Three pipe loops were used in each experiment. Two of the pipe loops were continuously recirculated while the other was recirculated four times per day (intermittently recirculated) at 8 a.m., 12 p.m., 5 p.m., and 9 p.m. An electronic timer was used to turn the pumps on and off at the appropriate times. The intermittently recirculated pipe loop was recirculated for ten minutes, which was long enough to heat the water in the pipe loop to the water temperature in the continuously recirculated pipe loops. Each pipe loop system, including the reservoir, contained three liters of target solution. The target solution in each of the pipe loops was changed every third day. First, all of target solution was removed from the pipe loop and reservoir for sampling, then the pipe loops were filled with new target solution and recirculation was reinitiated. The pipe loops were exposed to these conditions for two months. Six different copper loop systems were setup to perform by-product release testing on the following situations:

Loop 1: Hot hard water - continuously recirculated
Loop 2: Hot soft water - continuously recirculated
Loop 3: Hot hard water - intermittently recirculated
Loop 4: Cold hard water - continuously recirculated

Loop 5: Cold soft water - continuously recirculated

Loop 6: Cold hard water - intermittently recirculated

Water Quality Analysis

Water quality testing procedures were selected to obtain the concentrations of certain water quality parameters associated with the formation of the corrosion scale layer. The methods and instruments used for all water quality testing analysis are tabulated in Table 3-1. Samples were collected from a new target solution which was replacing the old target solution in each of the pipe loop systems. Samples were also taken from the old target solutions collected from each pipe loop system. New target solutions were tested for pH, alkalinity, calcium, magnesium, sodium, chloride, sulfate, orthophosphate, and temperature. Old target solutions were tested for the same parameters and also for dissolved copper and total copper. The pH, alkalinity, temperature, and orthophosphate were analyzed upon collection of samples from the new target solution and old target solution. 125 ml samples were collected from the new target solution and old target solution for calcium, magnesium, and sodium and preserved with 4% nitric acid to pH < 2 and stored at approximately 4°C for later analysis. 250 ml samples were collected from the new target solution and the old target solution for sulfate and chloride and stored at approximately 4°C for later analysis. 125 ml samples were collected from the old target solutions and new target solutions for soluble copper which were filtered and then preserved with 4% nitric acid to pH < 2 and stored at approximately 4°C for later analysis. 125 ml samples were collected from the old target solutions and new target solutions for total copper which were unfiltered and preserved with 4% nitric acid to pH < 2 and stored at approximately 4°C for later analysis.

Chapter 4

Results and Discussion

This chapter contains a review and discussion of the experimental results of by-product release and electrochemical testing techniques to determine the effect of temperature, water hardness, and recirculation on copper corrosion by-product release and corrosion rates. The chapter contains three sections:

- the effects of temperature and water hardness on copper corrosion with accelerated aging using electrochemical corrosion testing techniques,
- the effects of temperature, water hardness, and recirculation on copper corrosion using corrosion by-product release testing techniques, and
- summary and discussion of the experimental results obtained from both the electrochemical corrosion testing and corrosion by-product release testing.

4.1 Electrochemical Corrosion Testing

These experiments were completed to determine the effects of temperature and water hardness on corrosion rates for copper corrosion. Electrochemical procedures utilized in these experiments are identical to those discussed in Chapter 3: Methods and Materials. This segment will proceed with a summary of background water quality data which was taken during the experimentation. The next section will discuss the effects of temperature on corrosion rates. The effects of water hardness on corrosion rates will be discussed in the following section. The last section will provide a summary of the results of these experiments.

The sections examining the effects of temperature and water hardness on copper corrosion through electrochemical testing will provide a review of corrosion rates and results of anodic current plots. The corrosion rates will provide a quantitative and qualitative basis for determining the tendency of the copper surface to corrrode. Analysis of the anodic current versus time plots are useful in determining whether pitting corrosion or passivation of the surface occurs during aging.

Temperature and Water Hardness

Two temperatures were tested in these experiments. Water that was held at a constant temperature of 55°C was classified as hot water, whereas water that was held at a constant temperature of 13°C was referred to as cold water.

Water hardness is described by either being hard water or soft water. Hard water was characterized by having an average calcium hardness of 81 mg/l Ca, magnesium hardness of 42 mg/l Mg, and sodium content of 14 mg/l Na. Soft water was characterized by having an average calcium hardness of 1.0 mg/l Ca, magnesium hardness of 0.1 mg/l Mg, and a sodium content of 162 mg/l Na.

Four different combinations of the above water temperatures and water hardness were used in this experimentation. These waters will be classified as either hot hard water, hot soft water, cold hard water, and cold soft water.

4.1.1 Summary of Background Water Quality Data

The key water quality parameters tested in this experimentation were temperature, calcium, magnesium, and sodium. Other parameters tested were pH, alkalinity, chloride, sulfate, and orthophosphate. These parameters were shown to remain constant, therefore assumed to not affect the corrosion differences. The average water quality characteristics of the Brookings tap water after modifications to obtain the different water qualities specified in this testing are described in Table 4-1. A more in-depth summary of results of water quality tests performed during this experimentation are provided in Appendix A.

Table 4-1: Water quality characteristics of Brookings tapwater after modifications for electrochemical testing.[1]

		Description of Water			
Water Quality Characteristics		**Hot Hard**	**Hot Soft**	**Cold Hard**	**Cold Soft**
Temperature	(°C)	55	56	12	13
Ca^{++}	(mg/L)	75	1	87	1
Mg^{++}	(mg/L)	44	0.1	39	0.1
Na^{+}	(mg/L)	19	167	9	157
pH	-------	8.16	8.27	8.12	8.25
Alkalinity	(mg/L CaCO$_3$)	162	165	164	164
Cl^{-}	(mg/L)	11	12	11	11
SO$_4^{=}$	(mg/L)	218	196	241	202
o-PO$_4^{-3}$	(mg/L-P)	0.08	0.05	0.03	0.03

[1] Average water quality characteristics of samples taken during the testing period.

A. pH

The average pH for both hot hard and cold hard water were approximately the same having a pH of 8.16 and 8.12, respectively. In the hot soft and cold soft water, the pH was also closely related with a pH of 8.27 and 8.25, respectively. The results show that there was a difference in pH of approximately 0.1 units between hard waters and soft waters. This difference is deemed insignificant so further evaluation is not provided.

B. Alkalinity

The alkalinity for all four types of water were all closely related. Average results of alkalinity ranged from 162 to 164 mg/l $CaCO_3$. Average alkalinity for all four types of water tested was 163 mg/l $CaCO_3$.

C. Chloride

Chloride content was generally the same for all four different types of water tested. The chloride content for all types of water was approximately 11 mg/l Cl.

D. Sulfate

The average sulfate content for hot hard, hot soft, cold hard, and cold soft were 218, 196, 241, and 202 mg/l SO_4, respectively. The variability of the sulfate results was likely due to a lack of precision of the available testing method. Sulfate was tested to give a general description of its content in these waters. The average sulfate for all types of water was 214 mg/l SO_4.

E. Orthophosphate

All four types of water contained a small amount of orthophosphate. Average orthophosphate levels for hot hard, hot soft, cold hard, and cold soft were 0.08, 0.05, 0.03, and 0.03 mg/l P, respectively. The orthophosphate was generally a little higher in the higher temperature waters because the polyphosphate in the water generally breaks down to orthophosphate as the temperature is increased.

4.1.2 Effects of Temperature on Copper Corrosion

The following discussion will pertain to the analysis of corrosion rates and comparisons of anodic current versus time plots. Two temperatures were tested. Hot water was defined by a constant temperature of 55°C whereas cold water was held at a constant temperature of 13°C.

A. Analysis of Corrosion Rates

Four copper samples for each type of water were subjected to electrochemical analysis. Average results from the testing are shown in Table 4-2. Plots of the potentiodymanic curves from which corrosion rates were determined are found in Appendix A. Statistical analysis was completed using a completely random design with comparison of results using Duncans New Multiple Range Test. Detailed statistical analysis and corrosion rate data are located in Appendix A.

Table 4-2: Comparisons of data from electrochemical testing to show the effects of temperature on corrosion rates.

Water Description	Average Corrosion Rates (μA/cm^2)	Mean Difference (μA/cm^2)	Statistical Significance
Hot Hard Water	1.38	0.22	99
Cold Hard Water	1.15		
Hot Soft Water	0.41	0.20	99
Cold Soft Water	0.21		

1. Hot Hard Water versus Cold Hard Water

Average corrosion rates for hot hard and cold hard water were 1.38 and 1.15 μA/cm^2, respectively. Increasing the temperature by 42°C produced a difference in corrosion rates of 0.22 μA/cm^2. The difference in corrosion rates was statistically significant at the 99% confidence level.

2. Hot Soft Water versus Cold Soft Water

Hot soft and cold soft waters had average corrosion rates of 0.41 and 0.21 μA/cm^2, respectively. The mean difference between the two waters is 0.20 μA/cm^2. This difference was achieved with a statistical confidence level of 99%.

3. Summary

Increasing temperature had a small, but significant effect on corrosion rates for aged copper surfaces (Figure 4-1). For both hard and soft water, raising the temperature by 42°C increased the corrosion rate by 0.22 and 0.20 µA/cm^2, respectively. The changes in corrosion rates are statistically significant at the 99% confidence level. These results are consistent with the theory that chemical reaction rates increase when the temperature is increased (Benefield *et al.*, 1982).

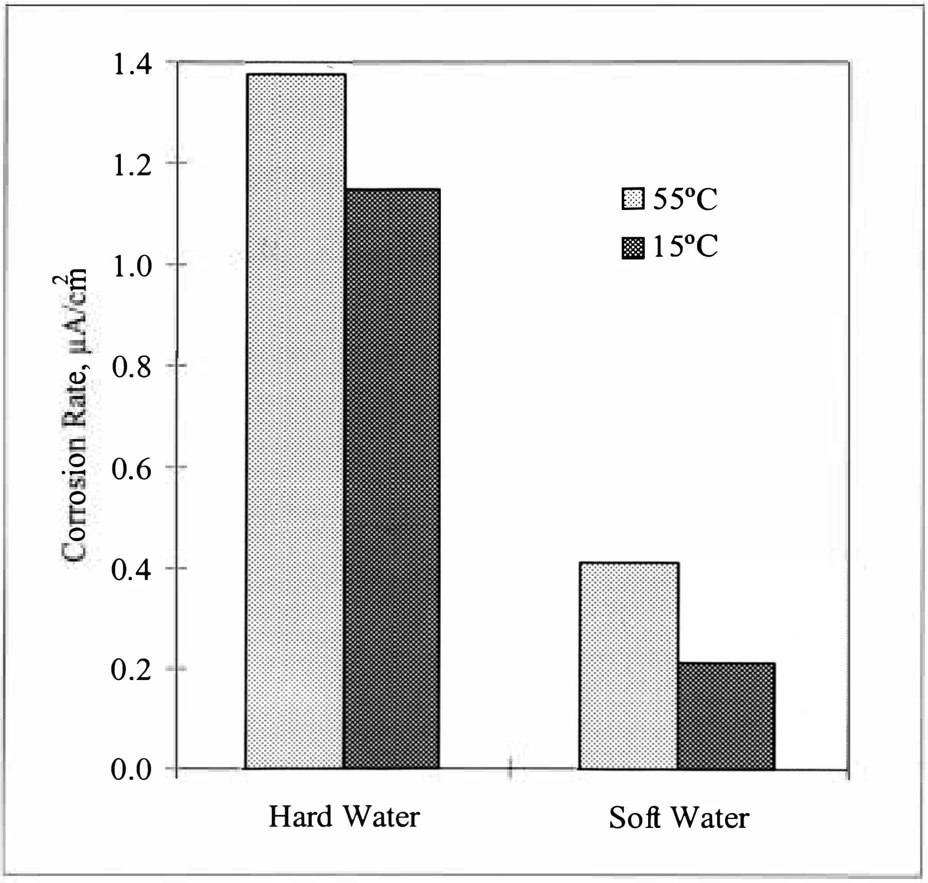


Figure 4-1: Temperature effects on corrosion rates.

B. Anodic Current versus Time Plots

During the "accelerated aging" testing, anodic current versus time plots were generated. These plots are useful in determining whether pitting corrosion or passivation of the surface occurs during aging.

1. Hot Hard Water versus Cold Hard Water

A plot of anodic current versus time is shown in Figure 4-2 for cold hard versus hot hard water. Four samples of each type of water are shown in this plot. The samples for the cold hard water had a consistent anodic current over time. There was a small amount of variation between the four samples of cold hard water. However, the anodic current for the HH water samples decreased over time, indicating that a protective scale was forming on the copper surface. Even though there was some variation between

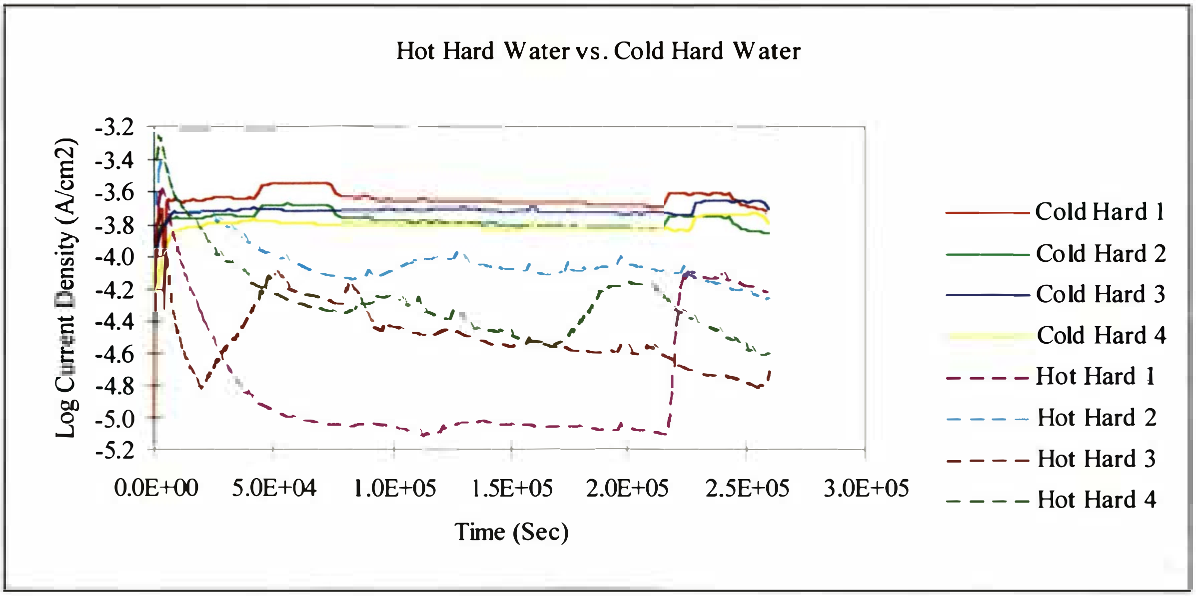


Figure 4-2: Anodic current versus time curve for cold hard versus hot hard water.

samples, the samples followed the same trend. A comparison of the samples of hot hard with cold hard water shows that the anodic current of the cold hard water to be higher than hot hard water. The hot hard water samples were shown to possibly form a passivating surface on the copper samples. The cold hard water samples showed no change in anodic current, and thus possibly had no effect on forming a passivating surface.

2. Hot Soft Water versus Cold Soft Water

Figure 4-3 shows a plot anodic current versus time for samples of hot soft and cold soft water. Each of the four samples of cold soft water were found to have a consistent anodic current over time, with very little variation between these four samples. The anodic current in each of the four samples for hot soft water decreased over time.

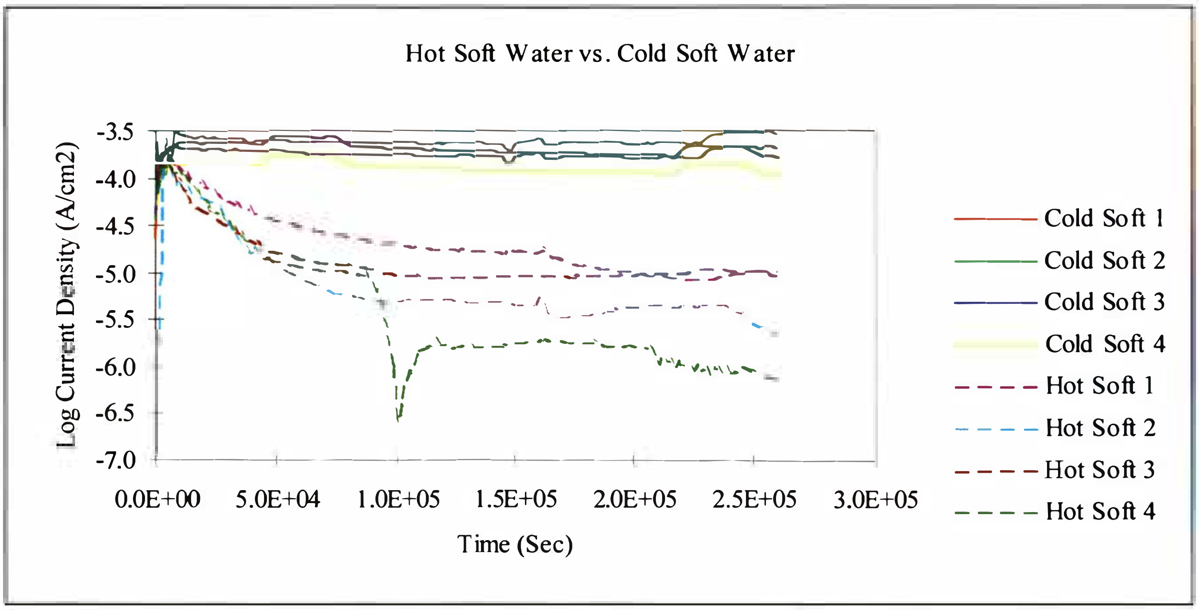


Figure 4-3: Anodic current versus time curve for cold soft versus hot soft water.

These samples were shown to follow the same trend, which varied slightly between samples. A comparison of the anodic current curves for hot soft and cold soft water showed that temperature had the same effects as those found in the anodic curves for samples of cold hard versus hot hard water, where hot soft water samples were shown to possibly form a passivating surface and cold soft water did not show any evidence of forming a passivating surface under the continuous flow conditions of these experiments.

3. Summary

A comparison of the anodic current curves for cold hard, hot hard, cold soft, and hot soft shows that temperature definitely has an effect on the corrosion of the copper surfaces. An increase in temperature resulted in a passivation of the copper surface. Thus, the increase in temperature is suggested to promote a protective scale on the copper surface. The lower temperature was shown to have no effect on the anodic current, thus possibly producing a corrosion inducing scale or no protective scale on the copper surface.

C. Copper Surface Inspection

The following are descriptions of observations of the copper surfaces for cold water, cold soft, hot hard, and hot soft waters:

Water Type	Visual Observations
Cold hard water	Uniform light yellow-brownish color
Cold soft water	Uniform light yellow-brownish film overlying a dark brown-reddish surface

Hot hard water	Uniform light blue-greenish film over a tarnished brown surface
Hot soft water	Uniform yellow-blue precipitate overlying a dark brown-reddish surface

The most observable difference between the cold and hot waters was that the surfaces exposed to the hot water contained a blue precipitate that was not found on the surfaces exposed to cold water.

4.1.3 Effects of Water Hardness on Copper Corrosion

The following is a discussion of the analysis of corrosion rates and comparisons of anodic current versus time plots. Two different levels of hardness were tested using electrochemical testing techniques. Hard water was characterized by having an average calcium hardness of 81 mg/l Ca, magnesium hardness of 42 mg/l Mg, and a sodium content of 14 mg/l Na. Soft water was characterized by having an average calcium hardness of 1.0 mg/l Ca, magnesium hardness of 0.1 mg/l Mg, and a sodium content of 162 mg/l Na.

A. Analysis of Corrosion Rates

Electrochemical analysis was conducted on four samples of each type of water. Averaged results from the testing are shown in Table 4-3. Plots of the potentiodynamic curves from which corrosion rates were determined are found in Appendix A. Statistical analysis was completed using a completely random design with comparison of results using Duncans New Multiple Range Test. Details of the statistical analysis and corrosion rate data are located in Appendix A.

Table 4-3: Comparisons of data from electrochemical testing to show the effects of water hardness on corrosion rates.

Water Description	Average Corrosion Rates ($\mu A/cm^2$)	Mean Difference ($\mu A/cm^2$)	Statistical Significance
Hot Hard Water	1.38	0.97	99
Hot Soft Water	0.41		
Cold Hard Water	1.15	0.94	99
Cold Soft Water	0.21		

1. Hot Hard Water versus Hot Soft Water

Average corrosion rates for hot hard and hot soft water were 1.38 and 0.41 $\mu A/cm^2$, respectively. Softening of the water was shown to reduce the average corrosion rates by 0.97 $\mu A/cm^2$. This difference was achieved with a statistical confidence level of 99%.

2. Cold Hard Water versus Cold Soft Water

Cold hard and cold soft water had average corrosion rates of 1.15 and 0.21 $\mu A/cm^2$, respectively. The mean difference in corrosion rates for these waters was 0.94 $\mu A/cm^2$. The difference in corrosion rates was statistically significant at the 99% confidence level.

3. Summary

Water hardness had a very significant effect on corrosion rates as shown in Figure 4-4. In both hot and cold waters, the corrosion rates of the soft water were lower than the hard water by 0.97 and 0.94 μA/cm^2 (80% and 83%), respectively. Therefore, these results show that softening had a positive effect on reducing the rate of corrosion occurring on the copper surface. Since the percent difference between these values is only 3%, it could be concluded that the effects of water hardness are independent of the effects of temperature on corrosion rates. The reason for this conclusion is that if the

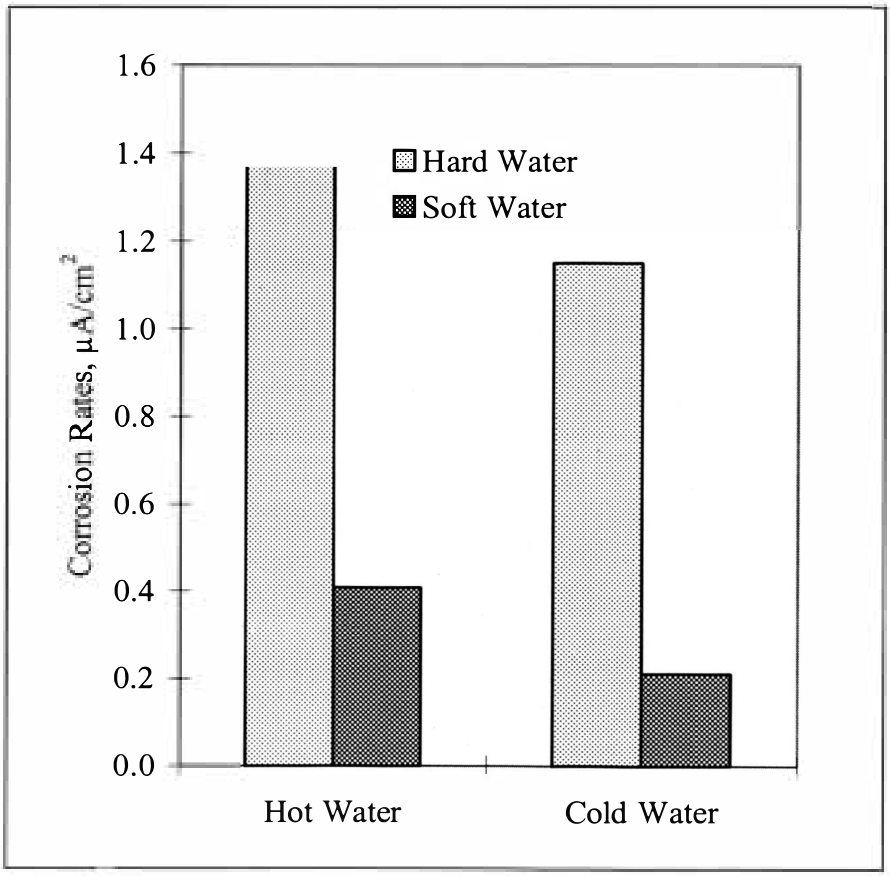


Figure 4-4: Water hardness effects on corrosion rates.

effects of water hardness on corrosion rates were dependent on temperature, the difference between the average differences of the corrosion rates between hot and cold water would be larger. If there is an effect on corrosion rates affected by water hardness that is dependent on temperature it is by a small margin.

B. Anodic Current versus Time Plots

During the "accelerated aging" testing, anodic current versus time plots were generated. These plots are useful in determining whether pitting corrosion or passivation of the surface occurs during aging.

1. Hot Hard Water versus Hot Soft Water

A plot of anodic current versus time of hot hard and hot soft is shown in Figure 4-5. Four samples of each type of water are shown in this graph. All the samples of both

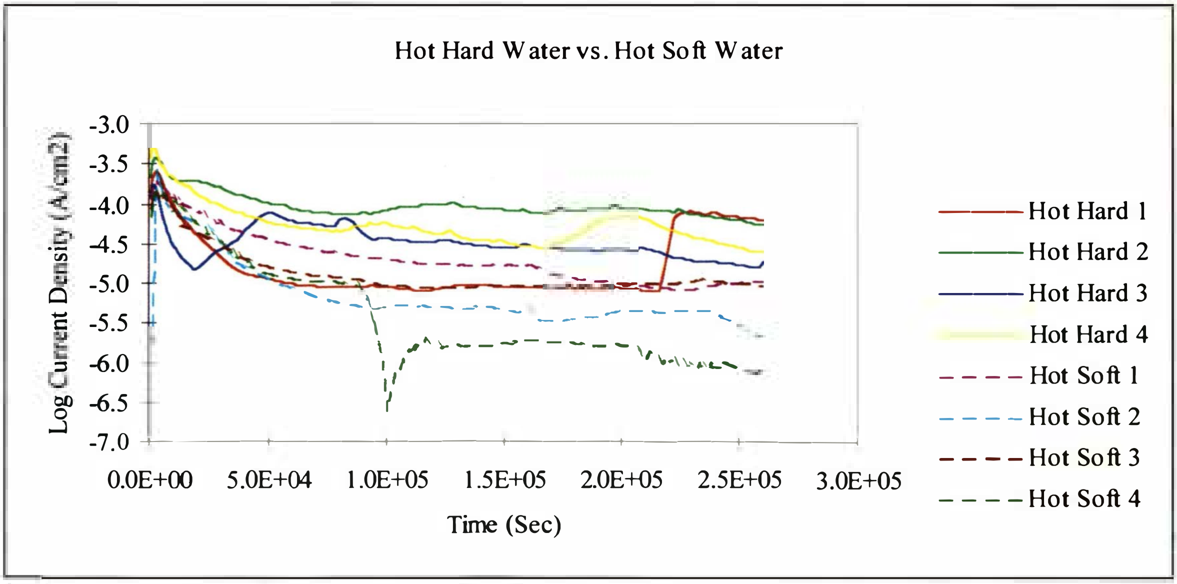


Figure 4-5: **Anodic current versus time curve for hot hard and hot soft water.**

hot hard and hot soft show a decreasing trend in the anodic current over time. It is believed this trend is affected by temperature. There appears to be no distinct difference in trends between hard and soft water in the anodic current versus time curves.

2. Cold Hard Water versus Cold Soft Water

Figure 4-6 shows anodic current versus time curves for samples of cold hard and cold soft waters. Four samples of each type of water are illustrated in this plot. There appears to be no distinct differences between samples of cold hard versus cold soft waters. Thus, water hardness seems to have no effect on the formation of a corrosion by-product scale as indicated by the potentiostatic test results.

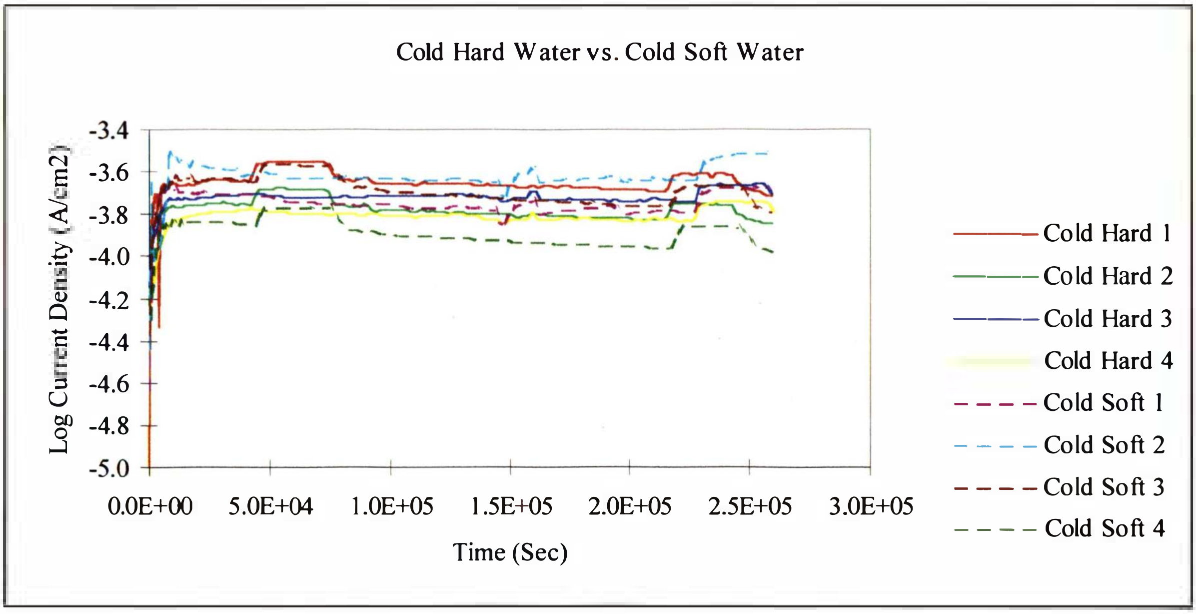


Figure 4-6: Anodic current versus time curve for cold hard versus cold soft water.

3. Summary

A comparison of the anodic current curves for hot hard versus hot soft and cold hard versus cold soft shows that water hardness does not have a profound effect on corrosion of the copper surfaces during the short-term potentiostatic tests. The curves for both comparisons generally followed the same pattern. There was more variability in the hot water curves than in the cold water curves as shown in a comparison of Figures 4-5 and 4-6. This could be caused by the increased ability of the copper surface to form a protective scale in the higher temperature water, as discussed in Section 4.1.2 Effects of Temperature on Copper Corrosion.

C. Copper Surface Inspection

The following are descriptions of observations of the copper surfaces for cold hard, cold soft, hot hard, and hot soft waters:

Water Type	**Visual Observations**
Cold hard water	Uniform light yellow-brownish color
Hot hard water	Uniform light blue-greenish film over a tarnished brown surface
Cold soft water	Uniform light yellow-brownish film overlying a dark brown-reddish surface
Hot soft water	Uniform yellow-blue precipitate overlying a dark brown-reddish surface

The most observable difference between the hard and soft waters was that the surfaces exposed to the soft water had a brown-reddish surface not found on the surfaces exposed to the hard water.

4.2 By-product Release Testing

These experiments were done to determine the effects of temperature, water hardness, and recirculation on corrosion by-product release. Procedures utilized for the corrosion by-product release experiments are identical to those discussed in Chapter 3: Methods of Materials. This section will proceed with a summary of background water quality data which was taken during the experiments. The next part will discuss the effects of temperature on copper corrosion by-product release. The effects of water hardness on copper corrosion by-product release will be discussed in the following section. Also, a section will discuss the effects of recirculation on copper corrosion by-product release. The last section will provide a summary of the results of this experimentation.

The sections examining the effects of temperature, water hardness, and recirculation on copper corrosion through corrosion by-product release testing will provide a review of copper corrosion by-product released over the testing period and visual inspection of copper surface for each of the different waters tested.

Temperature, Water Hardness, and Recirculation

Two temperatures were tested in these experiments. Water that was held at a constant temperature of 55°C was classified as hot water, where as water that was held at a constant temperature of 15°C was referred to as cold water.

Water hardness is described by either being hard water or soft water. Hard water was characterized by having an average calcium hardness of 83 mg/l Ca, magnesium hardness of 44 mg/l Mg, and sodium content of 19 mg/l Na. Soft water was characterized by having an average calcium hardness of 0.6 mg/l Ca, magnesium hardness of 0.4 mg/l Mg, and a sodium content of 182 mg/l Na.

Four different combinations of the above water temperatures and water hardness were used in this experimentation. These waters will be classified as either hot hard water, hot soft water, cold hard water, and cold soft water.

In these experiments, water was either continuously or intermittently recirculated through the pipe loops. The intermittently recirculated pipe loops were recirculated four times per day at 8 a.m., 12 p.m., 5 p.m., and 9 p.m.. The intermittently recirculated pipe loop was recirculated for ten minutes which was long enough to heat the water in the pipe loop to the same water temperature as in the continuously recirculated pipe loops.

4.2.1 Soluble versus Total Copper Released

Samples taken from each of the copper pipe loops were analyzed for soluble and total copper released. Average results of the testing are presented in Table 4-4. Soluble and total copper released are plotted against time and are illustrated in Figures 4-7 through 4-13 for each of the copper pipe loops. A more extensive summary of data is found in Appendix B.

When taken as a whole, the water samples generally contained from 70-93% soluble copper (which passed a 0.2 μm pore-sized filter). Soluble copper for hot hard water samples was about 84-87% of the total copper. Although the soluble copper for hot soft water was about 70% of the total copper, the soluble copper in the three cold water experiments ranged from 91-92%. These results show that temperature plays an important role in the solubility of copper. Those waters with lower percentages of soluble copper are believed to more likely produce a scale layer on the surface of the copper pipe. This has been shown in observations of the copper surfaces discussion in later sections. If not for scale formation, the differences in percentages of soluble versus total copper could be much higher. The lower percentage of soluble copper in the hot soft water could possibly be caused by interference of the effects of softening on the ability to form a greater amount of scale.

Table 4-4: Comparison of soluble and total copper released.

Water Description	Type of Recirculation	Loop	Average Soluble Cu Conc. (mg/L)	Average Total Cu Conc. (mg/L)	Mean Difference (mg/L)	Percent Passing 0.2 µm filter
Hot Hard	continuous	1	0.37	0.43	0.06	87.0
Hot Soft	continuous	2	0.46	0.65	0.19	70.2
Hot Hard	intermittent	3	0.57	0.67	0.11	84.4
Cold Hard	continuous	4	1.05	1.13	0.08	92.8
Cold Soft	continuous	5	1.17	1.26	0.09	92.8
Cold Hard	intermittent	6	0.98	1.07	0.09	91.3

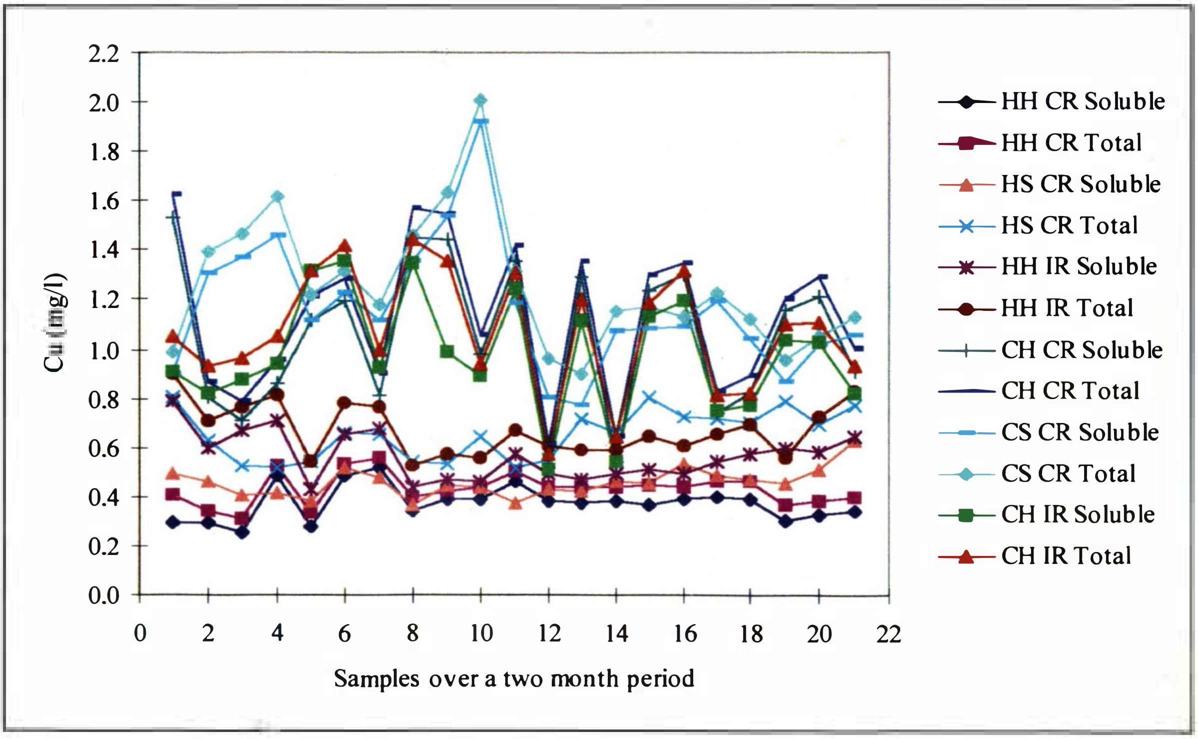


Figure 4-7: Soluble and total copper released for all copper pipe loops.

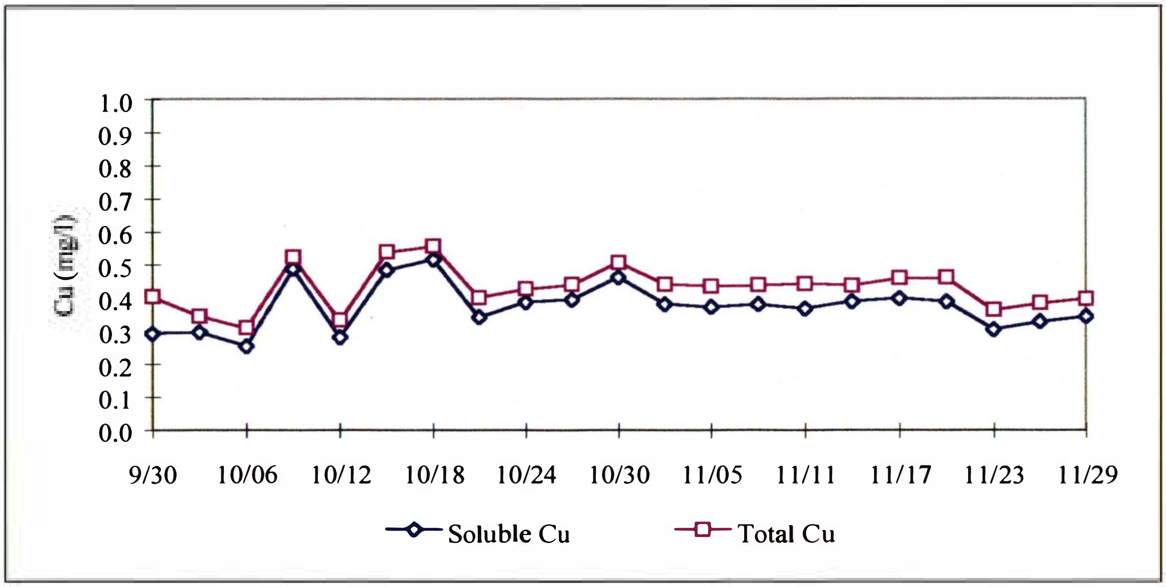


Figure 4-8: **Soluble versus total copper released.**
(hot hard water - continuously recirculated)

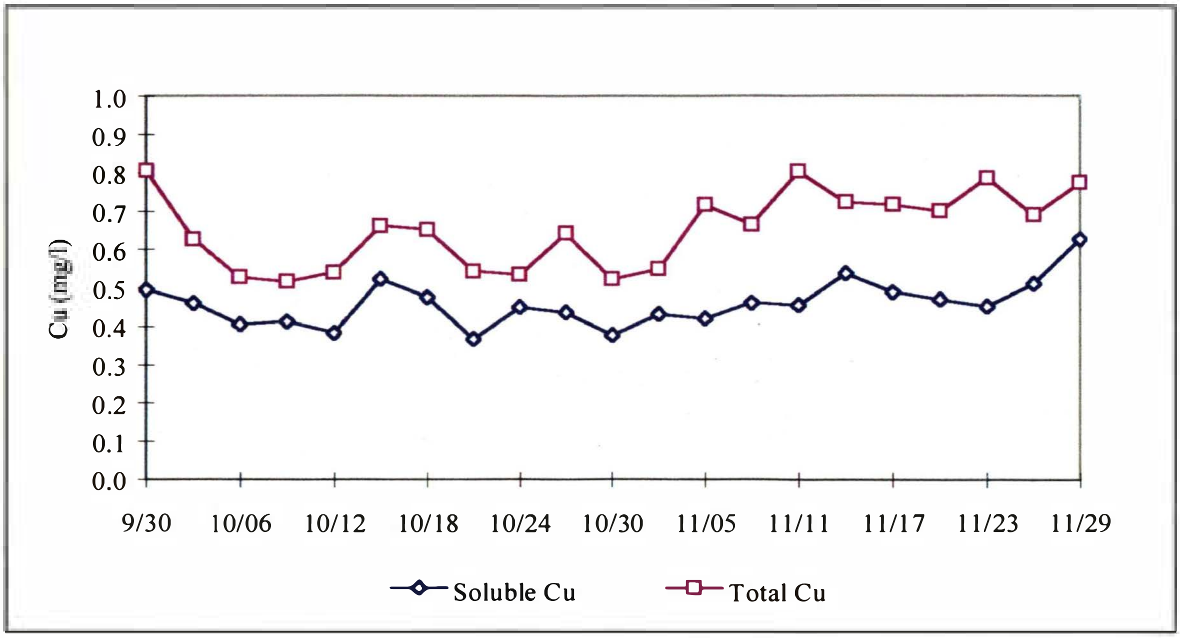


Figure 4-9: **Soluble versus total copper released.**
(hot soft water - continuously recirculated)

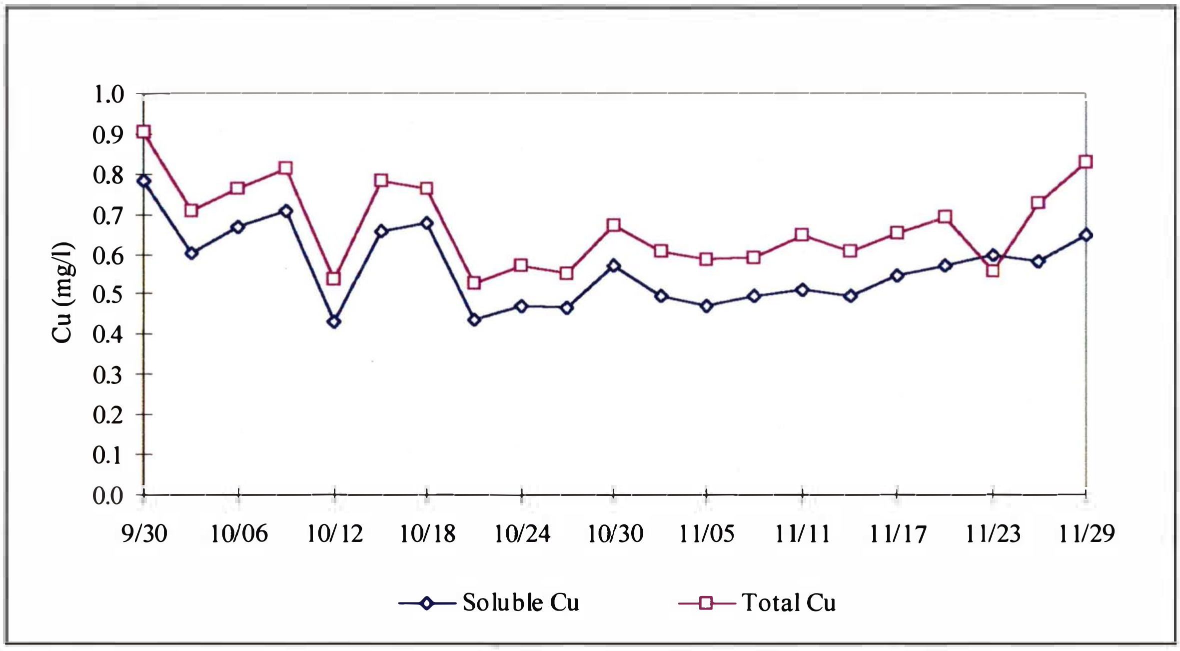


Figure 4-10: Soluble versus total copper released.
(hot hard water - intermittently recirculated)

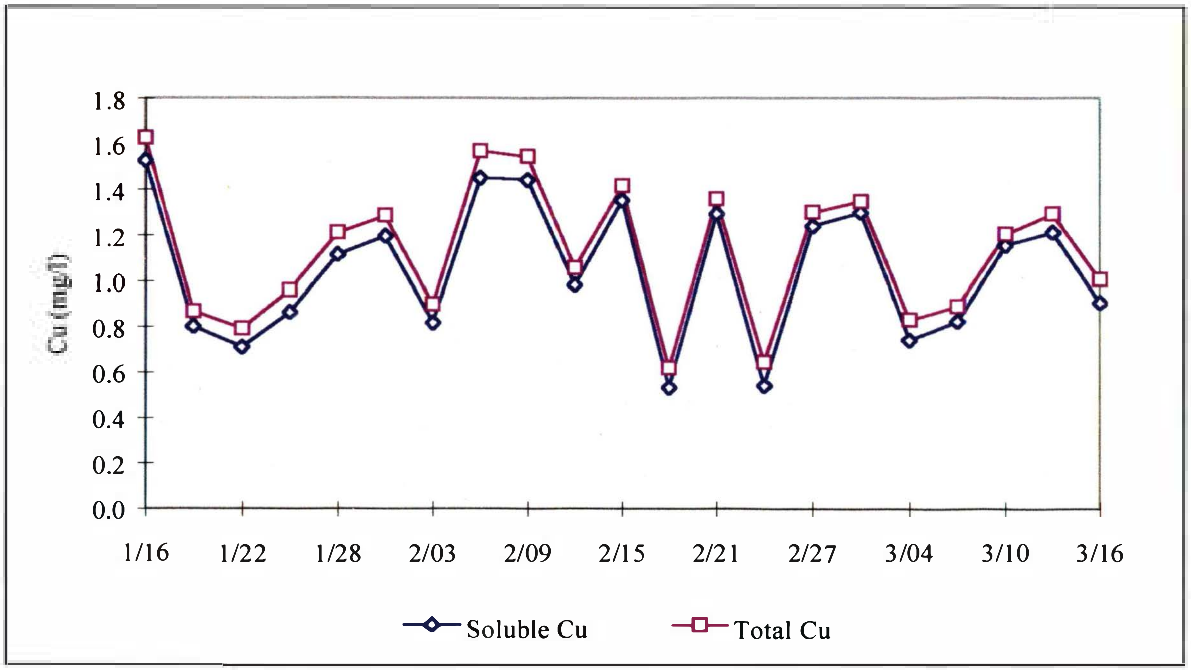


Figure 4-11: Soluble versus total copper released.
(cold hard water - continuously recirculated)

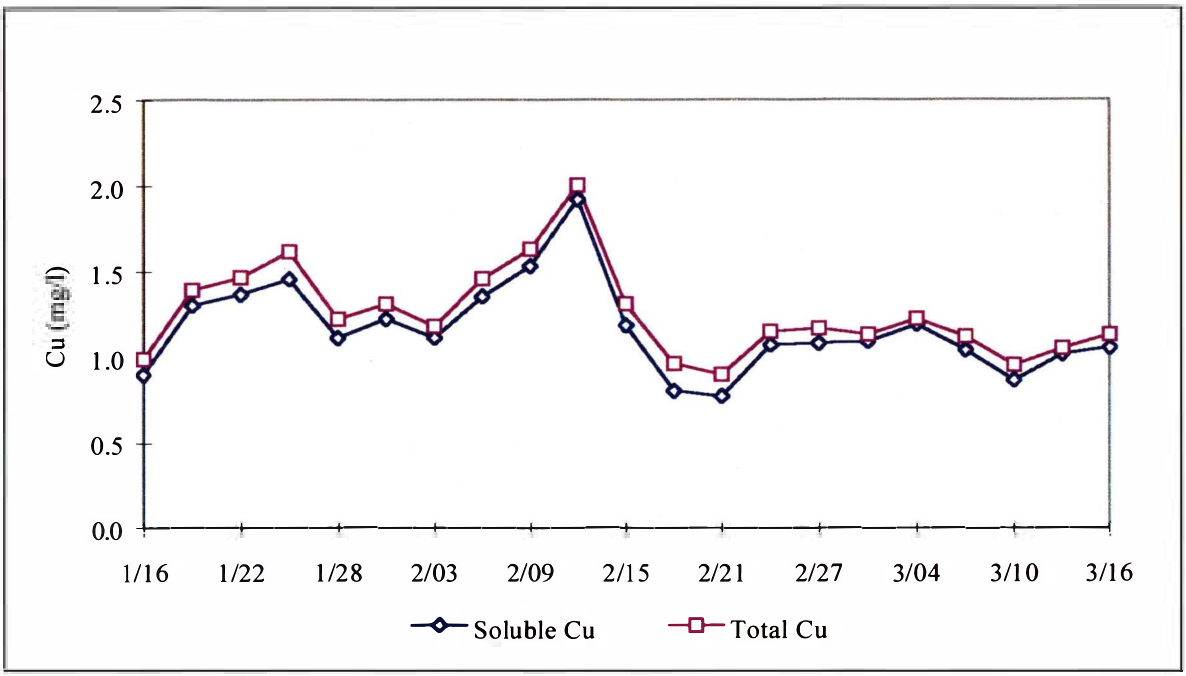


Figure 4-12: Soluble versus total copper released.
(cold soft water - continuously recirculated)

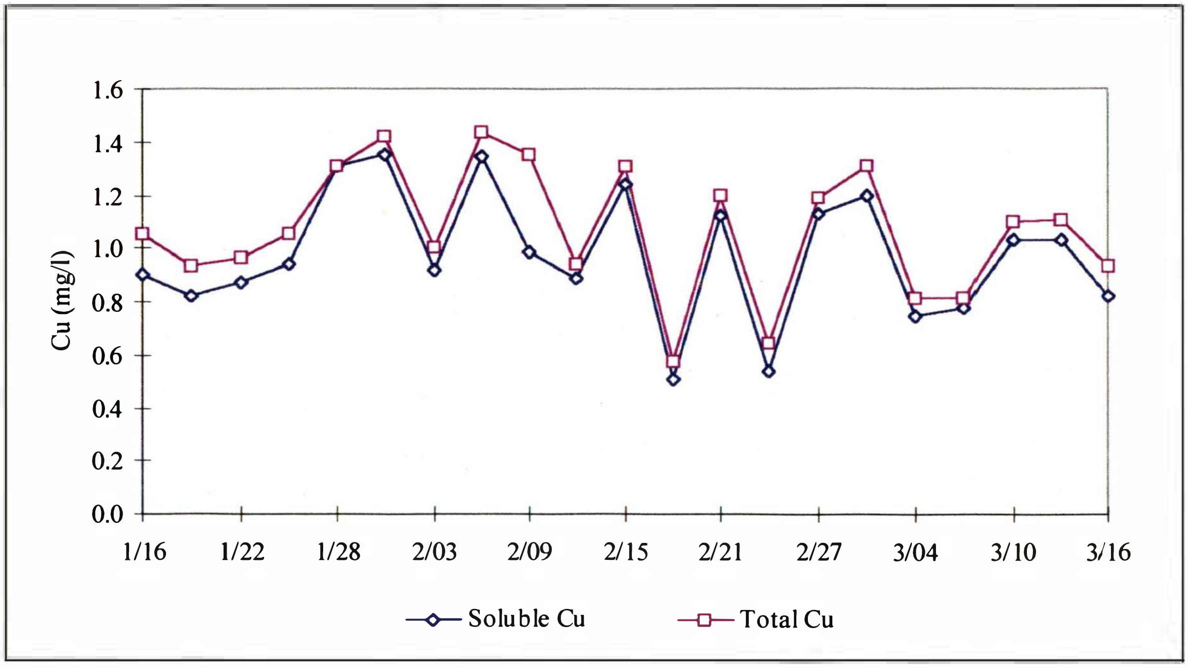


Figure 4-13: Soluble versus total copper released.
(cold hard water - intermittently recirculated)

4.2.2 Summary of Background Water Quality Data

The following is a discussion of the water quality parameters tested during the by-product release testing. The key water quality parameters tested in this experimentation were temperature, calcium, magnesium, and sodium. pH, alkalinity, chloride, sulfate, and orthophosphate were also tested; however, these parameters were shown to remain constant and therefore assumed to not affect the corrosion differences as time passed in the experiments. The average water quality characteristics of the Brookings tap water after modifications to obtain the different water qualities specified in this testing are described in Table 4-5. A more in-depth summary of results of water quality tests performed during this experimentation are provided in Appendix B.

Table 4-5: Water quality characteristics of Brookings tap water after modifications for by-product release testing.

		Description of Water					
Water Quality Characteristics*		**Hot Hard**	**Hot Soft**	**Hot Hard**	**Cold Hard**	**Cold Soft**	**Cold Hard**
Type of Recirculation**		CR	CR	IR	CR	CR	IR
Pipe Loop		1	2	3	4	5	6
Temperature	(ºC)	55	55	55	15	15	15
Ca^{++}	(mg/L)	83	0.6	83	81	0.3	81
Mg^{++}	(mg/L)	44	0.4	44	38	0.1	38
Na^{+}	(mg/L)	19	182	19	18	171	18
PH	-------	7.96	8.26	7.96	8.14	8.24	8.14
Alkalinity	(mg/L $CaCO_3$)	171	174	171	177	185	177
Cl^{-}	(mg/L)	12	12	12	12	12	12
SO$_4^{=}$	(mg/L)	225	215	225	225	187	225
o-PO$_4^{-3}$	(mg/L-P)	0.15	0.06	0.15	0.04	0.04	0.04

* Average water quality characteristics of samples taken during the testing period.

** CR = Continuous Recirculation and IR = Intermittent Recirculation

A. pH

The average pH’s for both hot hard and cold hard water were approximately 7.96 and 8.14, respectively. The pH of hot soft and cold soft water were 8.26 and 8.24, respectively. The results show that there was a difference in pH of approximately 0.2 units between hot hard and cold hard waters and approximately 0.1-0.3 units between hard and soft waters. This difference is not significant enough to warrant further evaluation.

B. Alkalinity

The alkalinity for hot hard, hot soft, and cold hard types of water were consistently in the range of 171 to 177 mg/l $CaCO_3$. Average alkalinity for cold soft water tested was 185 mg/l $CaCO_3$.

C. Chloride

Chloride content was generally the same for all four different types of water tested. The chloride contents for all types of water was approximately 12 mg/l Cl.

D. Sulfate

The average sulfate content for hot hard, hot soft, cold hard, and cold soft were 225, 215, 225, and 187 mg/l SO_4, respectively. The variability of the sulfate results was likely due to lack of precision of the available testing method. Sulfate was tested to give a general description of its content in these waters. The average sulfate for all types of water was 213 mg/l SO_4.

E. Orthophosphate

All four types of water contained a small amount of orthophosphate. Average orthophosphate levels for hot hard, hot soft, cold hard, and cold soft were 0.15, 0.06, 0.04, and 0.04 mg/l P, respectively. The orthophosphate was generally a little higher in the higher temperature waters because of the polyphosphate in water which generally breaks down to orthophosphate in higher temperature waters.

4.2.3 Effects of Temperature on Copper Corrosion

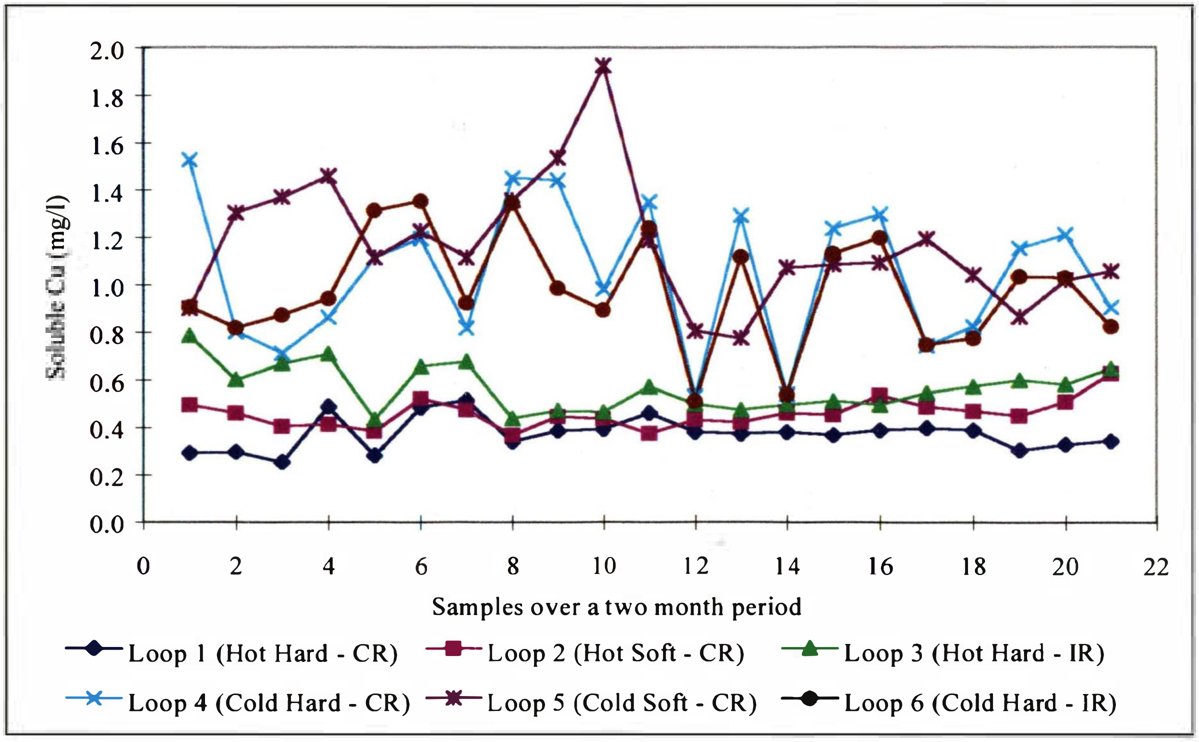
The following discussion will pertain to the analysis of by-product release data and evaluation of inspections of the copper surfaces. Two temperatures were tested. Hot water was defined by a constant temperature of 55°C whereas cold water was held at a constant temperature of 15°C.

A. Analysis of By-product Release Data

Samples were obtained every three days for a period of two months with a total of 21 samples for each type of water. Results are based on the amount of soluble copper released into solution. Average results from testing are shown in Table 4-6. Results of by-product release tests for all the loops are illustrated in a plot of soluble copper released over the period of sampling in Figure 4-14. A more detailed summation of results and data on statistical analysis are found in Appendix B.

Table 4-6: Comparisons of data from by-product release testing to show the effects of temperature on by-product release.

Water Description	Type of Recirculation	Loop	Average Soluble Cu Concentration (mg/L)	Mean Difference (mg/L)	Statistical Significance
Hot Hard Water	continuous	1	0.37	0.67	99
Cold Hard Water	continuous	4	1.05		
Hot Soft Water	continuous	2	0.46	0.71	99
Cold Soft Water	continuous	5	1.17		
Hot Hard Water	intermittent	3	0.57	0.41	99
Cold Hard Water	intermittent	6	0.98		



CR-Continuously Recirculated IR-Intermittently recirculated

Figure 4-14: Results of soluble copper released from loops over two month testing period.

1. Hot Hard Water versus Cold Hard Water (Continuously Recirculated)

Results from the testing of these two waters are plotted in Figure 4-15. The chart displays that there is a distinct difference between these two waters. Average soluble copper concentrations for hot hard and cold hard waters were 0.37 and 1.05 mg/l Cu, respectively. Therefore, increasing the temperature by 42°C produced a decrease in corrosion by-product release of 0.67 mg/l Cu. As shown in Table 4-6, this difference in corrosion by- product released was statistically significant at the 99% confidence level.

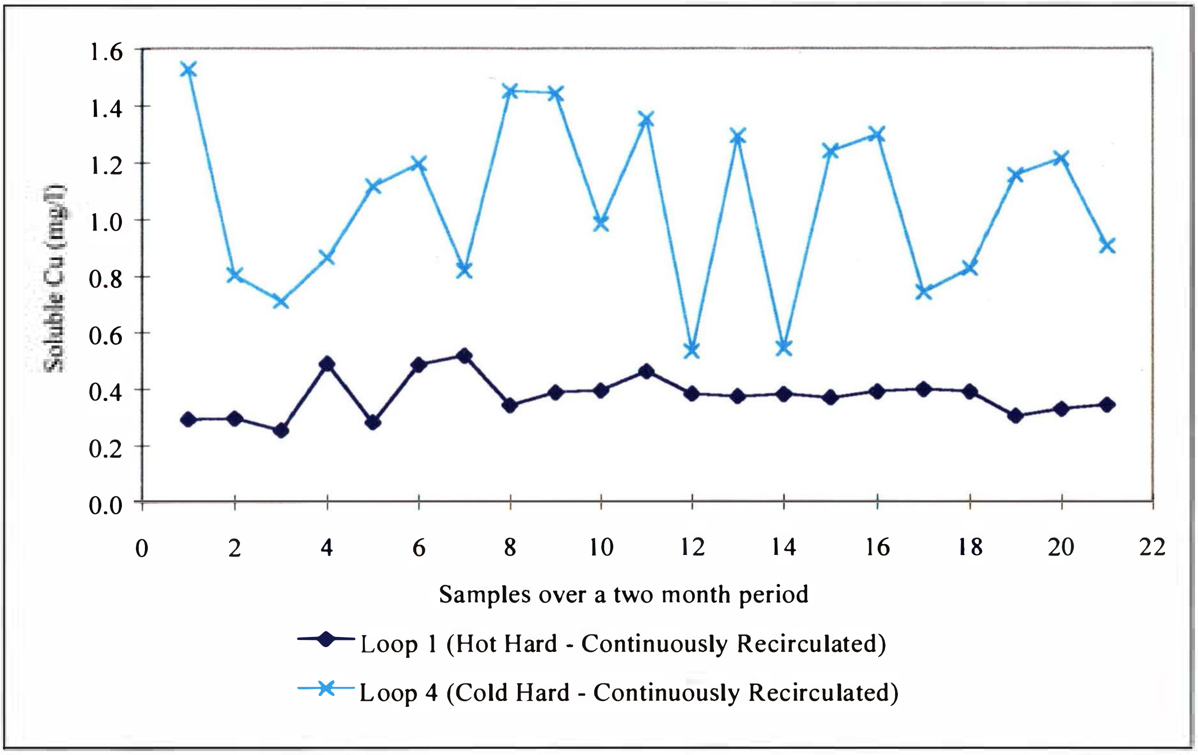


Figure 4-15: Results of soluble copper released for hot hard water versus cold hard water both continuously recirculated.

A comparison of curves for each water in Figure 4-15, shows that there was less corrosion in the hot hard water versus the cold hard water. The decreased corrosion in the hot water could be caused by either the formation of a protective scale or because copper is less soluble at the higher temperature or a combination of both.

2. Hot Soft Water versus Cold Soft Water (Continuously Recirculated)

Figure 4-16 displays the results from the testing of these two waters. The chart shows that there is a distinct difference in the corrosion by-product released into solution for these two types of water. Hot soft and cold soft water had average soluble copper concentrations of 0.46 and 1.17 mg/l Cu. Therefore, increasing the temperature by 42°C produced a decrease in corrosion by-product released of 0.71 mg/l Cu. This difference was achieved with a statistical confidence level of 99%. As was seen in the hot

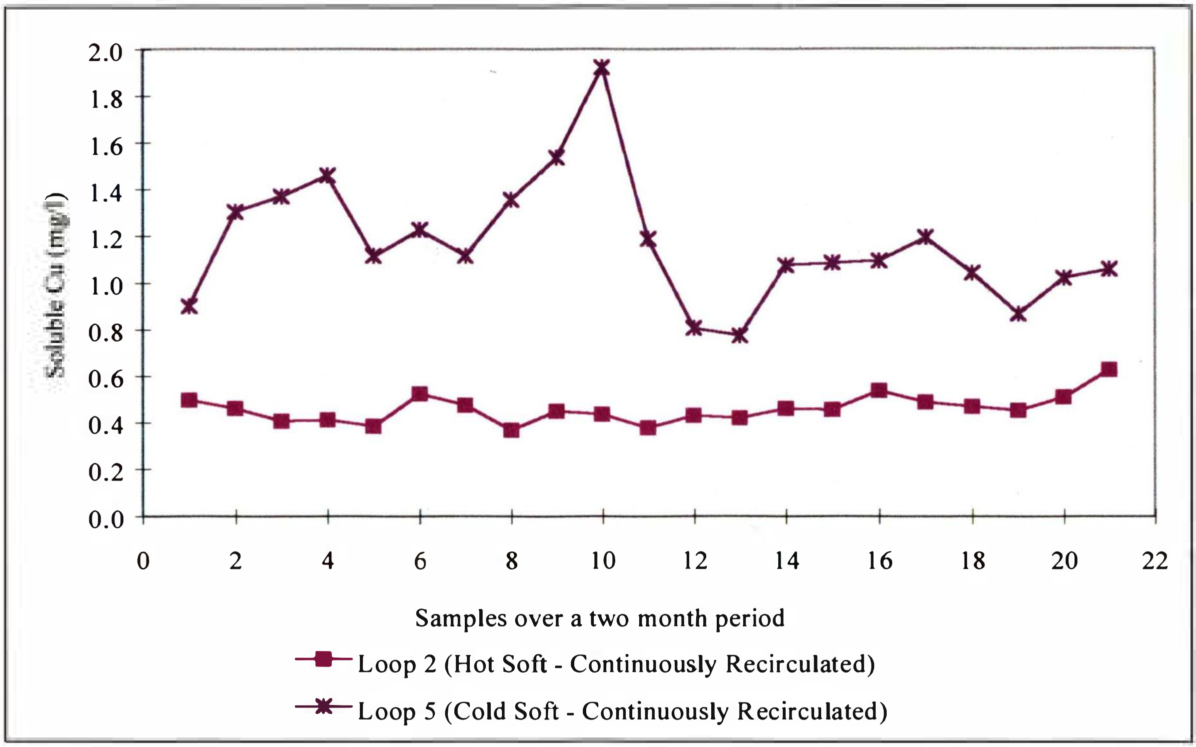


Figure 4-16: Results of soluble copper released for hot soft water versus cold soft water both continuously recirculated.

42°C produced a decrease in corrosion by-product released of 0.71 mg/l Cu. This difference was achieved with a statistical confidence level of 99%. As was seen in the hot hard and cold hard waters, the curves in Figure 4-16 show that less corrosion by-product was released by hot soft water than by cold soft water. The decreased corrosion in the hot water could be caused by either the formation of a protective scale or because copper is less soluble at the higher temperature or a combination of both.

3. Hard Water versus Cold Hard Water (Intermittently Recirculated)

A graph of the results from by-product release testing for these two waters is shown in Figure 4-17. Even though both waters are intermittently recirculated, there is a distinct difference in the two waters, as was seen in the continuously recirculated waters of hot hard versus cold hard and hot soft versus cold soft. Average copper concentrations of corrosion by-product released for hot hard and cold hard water were 0.57 and 0.98 mg/l Cu. The mean difference between these waters was 0.41 mg/l Cu. The difference in corrosion by-product released was statistically significant to the 99% confidence level. The curves in Figure 4-17 display increased variability in cold water copper concentrations when compared with those of the hot water. The decreased corrosion in the hot water could be caused by either the formation of a protective scale or because copper is less soluble at the higher temperature or a combination of both.

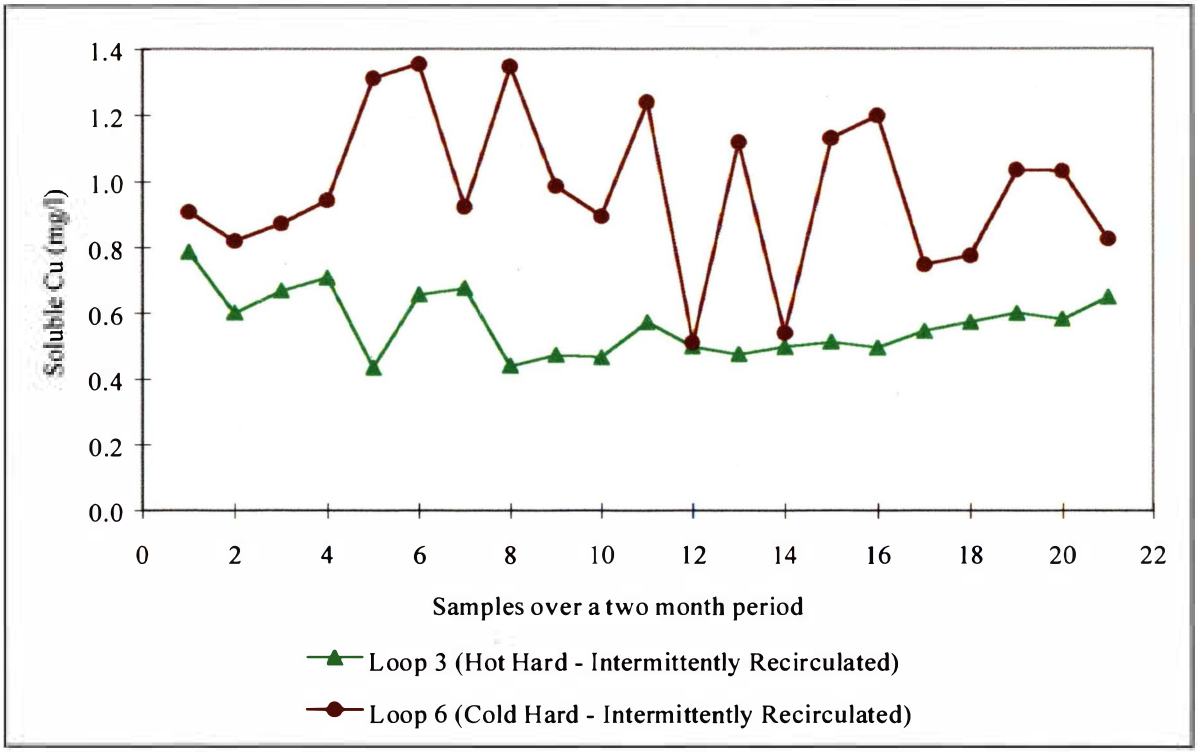


Figure 4-17: Results of soluble copper released for hot hard water versus cold hard water both intermittently recirculated.

4. Summary

Temperature had a significant effect on corrosion by-product released as shown in Figure 4-18. Increasing the temperature had a statistically significant effect on the copper corrosion by-product released in the soft and hard waters continuously recirculated and also in the hard waters intermittently recirculated. During the experiments where hard and soft water were continuously recirculated, raising the temperature by 40°C reduced the amount of copper released into solution by 0.67 and 0.71 mg/L (64 and 61%), respectively. These results correlate with predictions of a model developed by Edwards *et al.* (1996) which predict that copper corrosion by-product release is dependent on

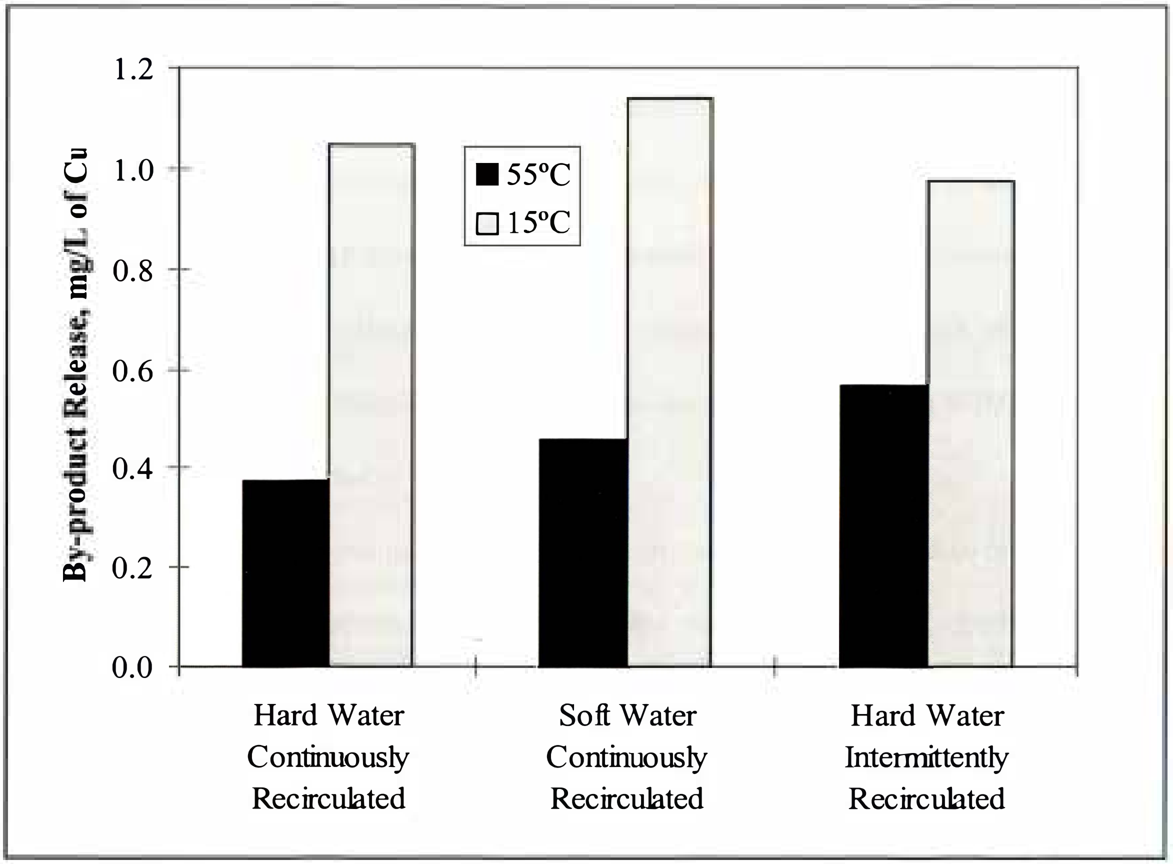


Figure 4-18: Water temperature effects on copper corrosion by-product released.

temperature. Increasing the water temperature would reduce the amount of copper corrosion by-product released into solution.

Also raising the temperature by 40°C reduced the amount of copper released by 0.41 mg/L (42%) in the experiment in which hard water was recirculated intermittently. In comparing the change in by-product release caused by the temperature change on intermittently versus continuously recirculated hard water, it can be hypothesized that the amount of by-product released caused by the type of recirculation is dependent on temperature. This will be discussed in more detail in Section 4.2.4 Effects of Recirculation on Copper Corrosion.

B. Visual Scale Observations

Visual observations were made of the copper surface after the pipe loop rigs were dismantled and portions of the rig cut into samples. These samples were then cut into halves and the texture and color of the scale formed on the surface of the copper sample was observed. Descriptions of the visual observations are listed for each of the water types in Table 4-7. Illustrations of type of water are shown in Figures 4-19 through 4-24.

Summary and Conclusions

The hot waters were generally observed to have a black-brownish to a brownish-red colored scale on the surface of the copper pipe sections. However, the hot hard intermittently recirculated pipe rig exhibited light brownish color to no scale formation on the copper surface. The reason for this is discussed in the following Section 4.2.4 Effects of Recirculation on Copper Corrosion.

The surface of the copper samples that were exposed to cold water ranged from a light brownish color to a shiny copper color (no scale formed). A few brownish speckles were observed on these surfaces.

From these observations, it appeared that hot water caused scale formation, whereas the copper samples exposed to cold water showed little to no scale formation.

Table 4-7. Visual Scale Observations

Water Type	Type of Recirculation	Figure	Visual Observations
Hot Hard	Continuous	4-19	A black-brownish to brownish-red scale was observed on the surface of the copper pipe sections. The scale varied from a smooth black-brownish color to a brownish-red speckled color. Speckled colors ranged from black, brown or reddish in color.
Cold Hard	Continuous	4-20	The surface of the samples varied from having no scale formation to a light brownish scale. Overall there was very little scale formation observed on the surfaces.
Hot Soft	Continuous	4-21	The color of the observed scale on the copper tubing ranged from dark brown to reddish brown. The scale coated the entire surface with speckles of brownish color over the surface.
Cold Soft	Continuous	4-22	The surface of the copper tubing had only a small amount of scale formation. The colors of the surface ranged from a light copper color to a light brownish color. Dark-brownish speckles were observed a portion of the samples. Overall scale formation was very limited to none on the surface of the copper pipe.
Hot Hard	Intermittently	4-23	The surface of the copper pipe samples ranged from no scale formation to a light brownish colored scale on the surface of the samples. There were dark brown spots on portions of the copper surface.
Cold Hard	Intermittently	4-24	The surface of the samples can be defined as having very little to no observable scale formation. The color of the surface ranged from a shiny copper color to a light brownish color. Very few light brown speckles were observed on the copper surface. Overall very little scale formation was observed on the surface of the copper pipe.

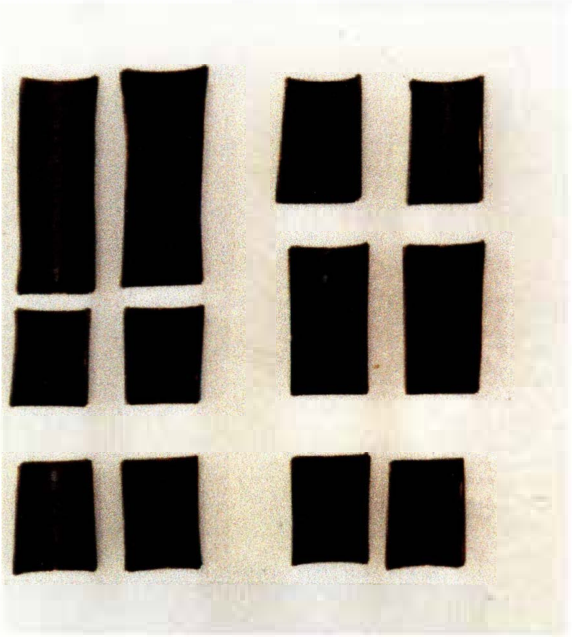


Figure 4-19: Loop 1 - hot hard water continuous recirculation.

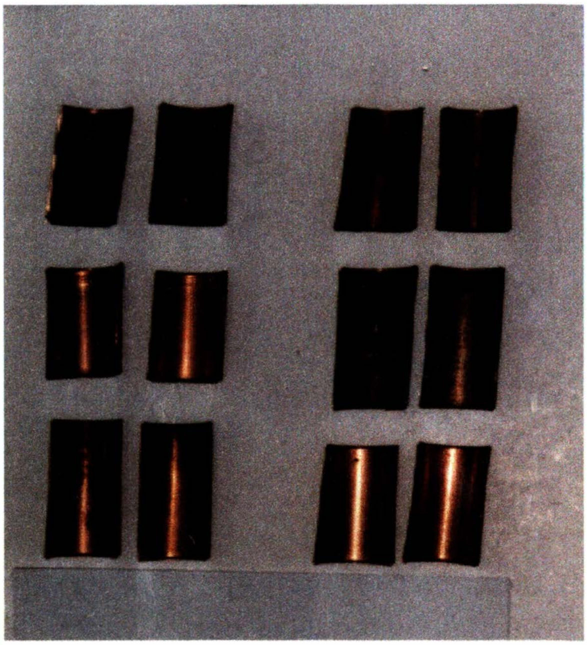


Figure 4-20: Loop 4 - cold hard water continuous recirculation.

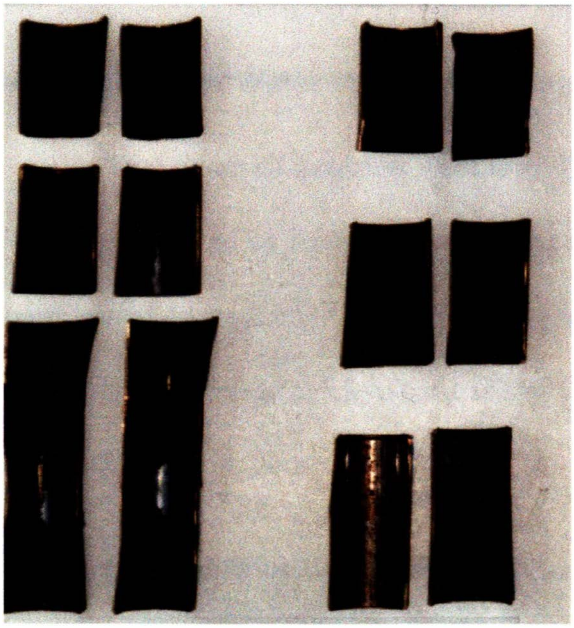


Figure 4-21: Loop 2 - hot soft water continuous recirculation.

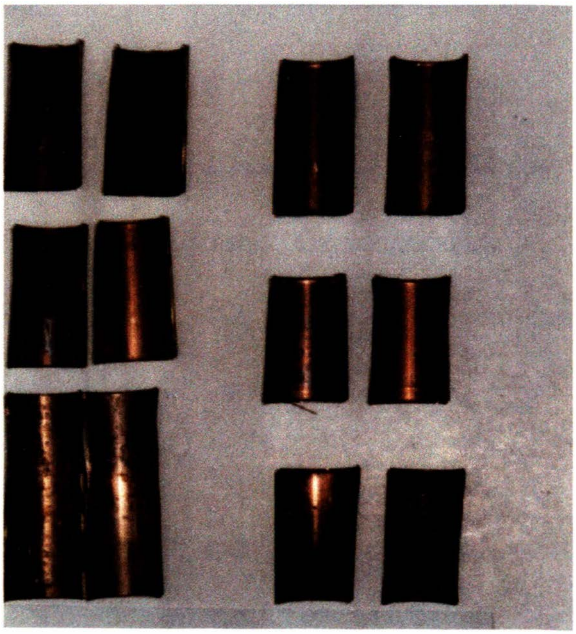


Figure 4-22: Loop 5 - cold soft water continuous recirculation.

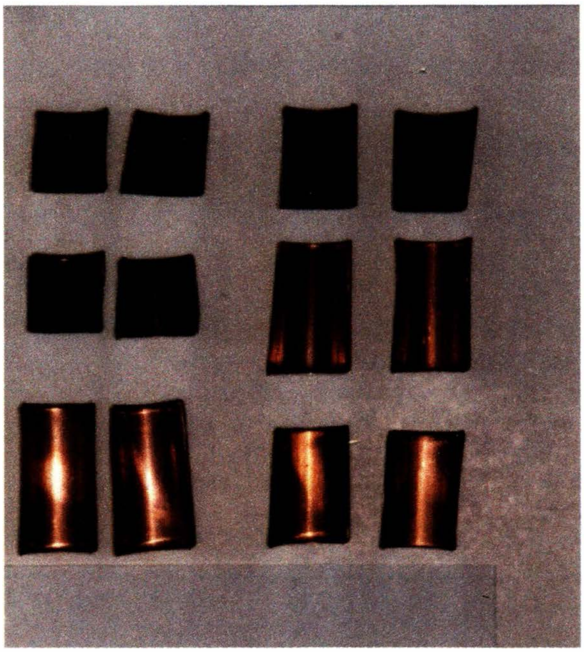


Figure 4-23: Loop 3 - hot hard water intermittent recirculation.

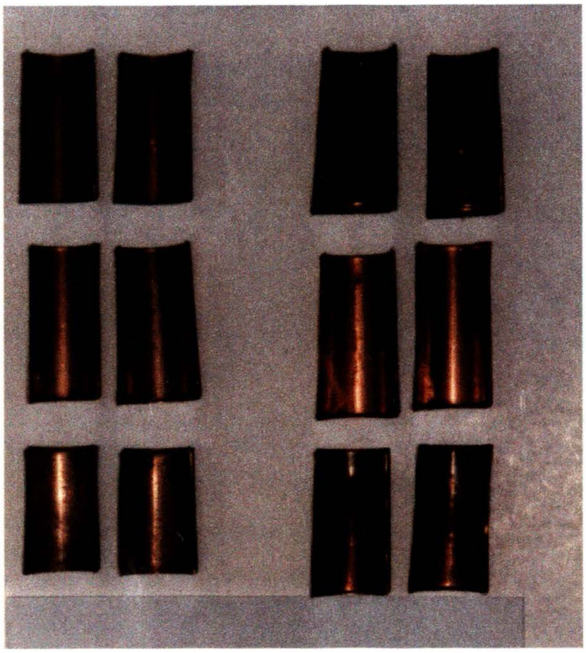


Figure 4-24: Loop 6 - cold hard water intermittent recirculation.

4.2.4 Effects of Water Hardness on Copper Corrosion

Two levels of hardness were tested in the recirculation experiments. Hard water was characterized by having an average calcium hardness of 83 mg/l Ca, magnesium hardness of 44 mg/l Mg, and sodium content of 19 mg/l Na. Soft water was characterized by having an average calcium hardness of 0.6 mg/l Ca, magnesium harness of 0.4 mg/l Mg, and a sodium content of 182 mg/l Na.

A. Analysis of By-product Release Data

- Samples were obtained every three days for each type of water for a period of two months. Table 4-8 shows the results from this testing for each type of water. Results of the by-product release tests for all loops that show the effect of water hardness are illustrated in a plot of soluble Cu released over the period of sampling in Figure 4-25. Detailed tabulation of results and statistical analysis are found in Appendix B. Analysis of Variance was used to complete a comparison of results.

Table 4-8: Comparisons of data from by-product release testing to show the effects of water hardness on by-product release.

Water Description	Type of Recirculation	Loop	Average Soluble Cu Concentration (mg/L)	Mean Difference (mg/L)	Statistical Significance
Hot Hard Water	continuous	1	0.37	0.08	99
Hot Soft Water	continuous	2	0.46		
Cold Hard Water	continuous	4	1.05	0.12	80
Cold Soft Water	continuous	5	1.17		

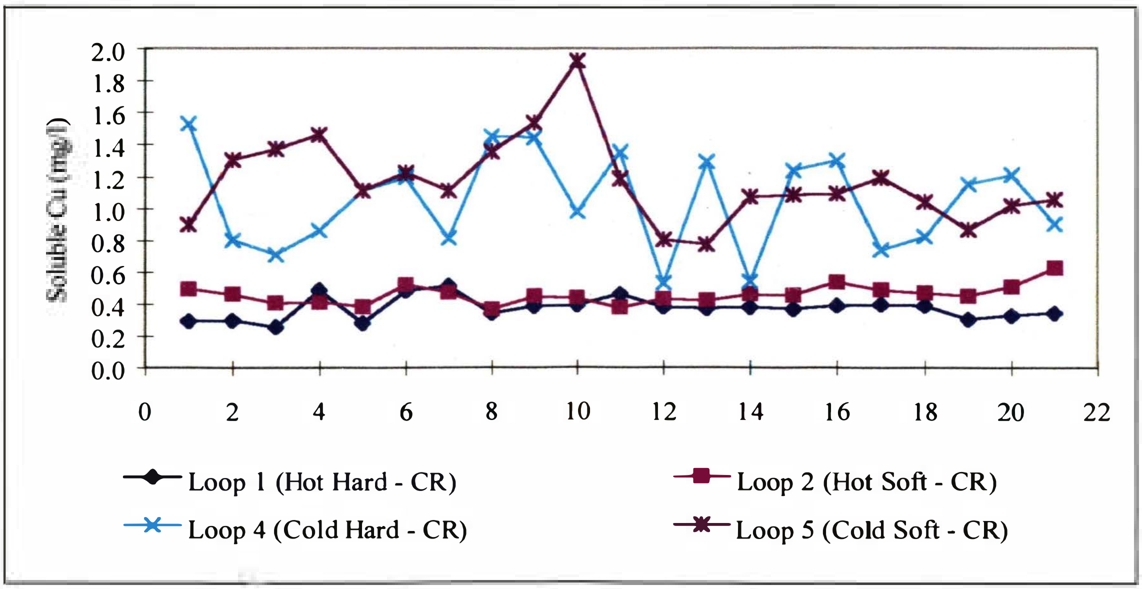


Figure 4-25: Results of soluble copper released for loops over the two month sampling period.

1. Hot Hard Water versus Hot Soft Water

Figure 4-25 shows a plot of the results of testing for these two waters. The chart shows that results of the corrosion by-product released for these two waters are similar with the soft water having slightly higher results than the hard water. Hot hard and hot soft waters have average copper concentrations of 0.37 and 0.46 mg/l Cu, respectively. The mean difference between corrosion by-product released for these two waters was 0.08 mg/l Cu. Although there was not a very large difference between these waters, the difference between the concentrations was highly significant to the 99% confidence level. Therefore as compared to the hard water, the soft water slightly increased the amount of corrosion by-product released into the solution.

2. Cold Hard Water versus Cold Soft Water

A plot of results from the corrosion by-product release testing for these two waters is shown in Figure 4-25. Visually, it is difficult to see any pattern of difference between these waters. Average concentrations of corrosion by-product released into solution for cold hard and cold soft waters were 1.05 and 1.17 mg/l Cu. The mean difference between these results was 0.12 mg/l Cu. Although the difference is somewhat higher than the mean difference previously for hot hard and hot soft, the difference in corrosion by-product released was only statistically significant to the 80% confidence level. Though the results were not significantly certain, they showed that the soft water slightly increased the amount of soluble copper corrosion by-product released into solution when compared to the hard water.

3. Summary

Figure 4-26 shows the results of corrosion by-product testing for the effects of water hardness on copper corrosion in both hot and cold continuously recirculated waters. In the experiments where hot water was recirculated continuously, hard water released less copper corrosion by-product into solution than the soft water by 0.08 mg/l Cu. Experiments where cold water was recirculated continuously, hard water released less copper corrosion by-product into solution than the soft water by 0.12 mg/l Cu.

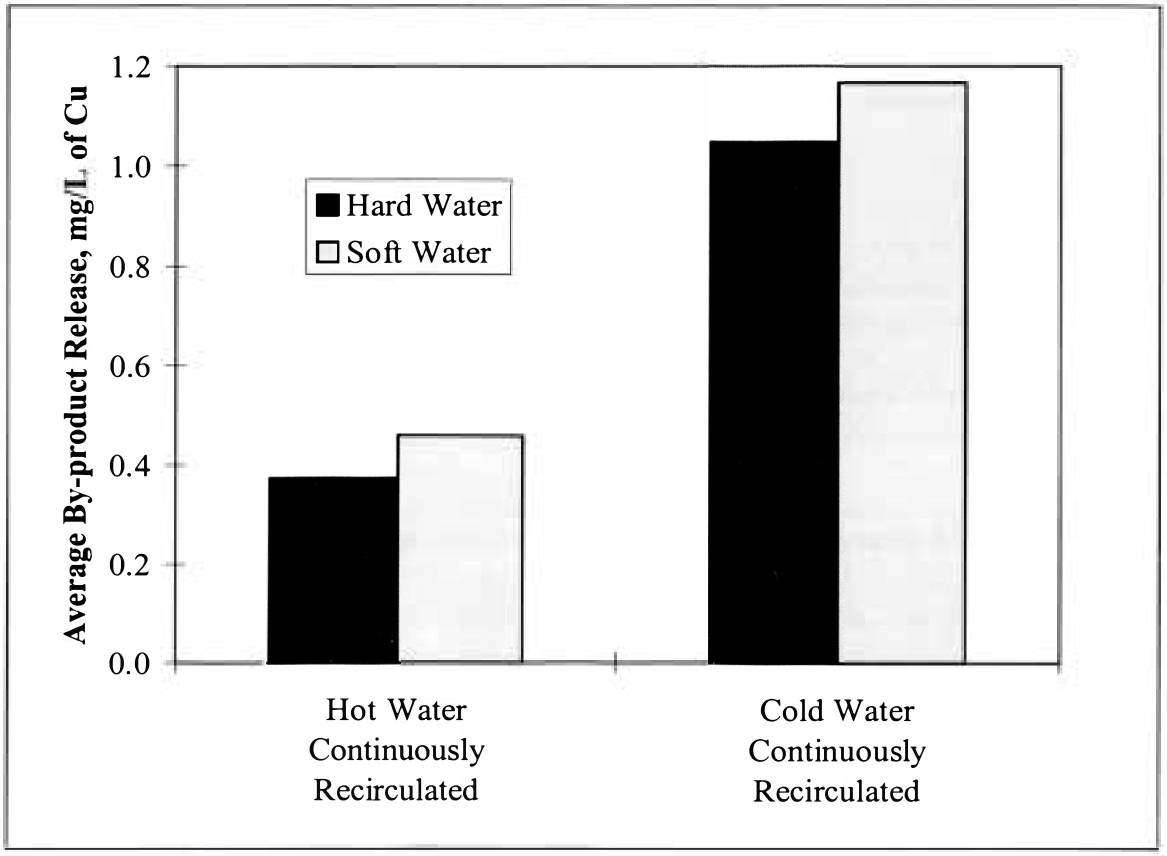


Figure 4-26: Water hardness effects on copper corrosion by-product release.

Comparison of the hard versus soft water in each of the hot and cold continuously recirculated experiments have a confidence level of the 99th and 80th percentile, respectively. Although there is a difference in confidence levels, the overall trend shows that softening slightly increased the amount of copper corrosion by-product released into solution. In review of literature, researchers have observed that softening increases the corrosion of copper pipe.

B. Visual Scale Observations

Visual observations were made of the copper surface after the pipe loop rigs were dismantled and portions of the rig cut into samples. Descriptions of the visual observations are listed for each of the water types in Table 4-9. Illustrations of type of water are shown in Figures 4-27 through 4-30.

Summary and Conclusions

Comparison of the copper surfaces for hot hard versus hot soft waters showed no distinguishable differences. The scale on these surfaces were black-brownish to brownish-red in color.

In comparing cold hard versus cold soft, there were generally no distinguishable differences between the copper surfaces exposed to these waters. The surfaces were shown to have a light brown scale to no scale formation.

The visual scale observations between hard and soft waters were unable to show any differences in the copper surfaces between these waters.

Table 4-9: Visual scale observations.

Water Type	Type of Recirculation	Figure	Visual Observations
Hot Hard	Continuous	4-29	A black-brownish to brownish-red scale was observed on the surface of the copper pipe sections. The scale varied from a smooth black-brownish color to a brownish-red speckled color. Speckled colors ranged from black, brown or reddish in color.
Hot Soft	Continuous	4-30	The color of the observed scale on the copper tubing ranged from dark brown to reddish brown. The scale coated the entire surface with speckles of brownish color over the surface.
Cold Hard	Continuous	4-31	The surface of the samples varied from having no scale formation to a light brownish scale. Overall, very little scale formation was observed on the surfaces.
Cold Soft	Continuous	4-32	The surface of the copper tubing had only a small amount of scale formation. The colors of the surface ranged from a light copper color to a light brownish color. Dark-brownish speckles were observed a portion of the samples. Overall, scale formation was very limited to none on the copper pipe surface.

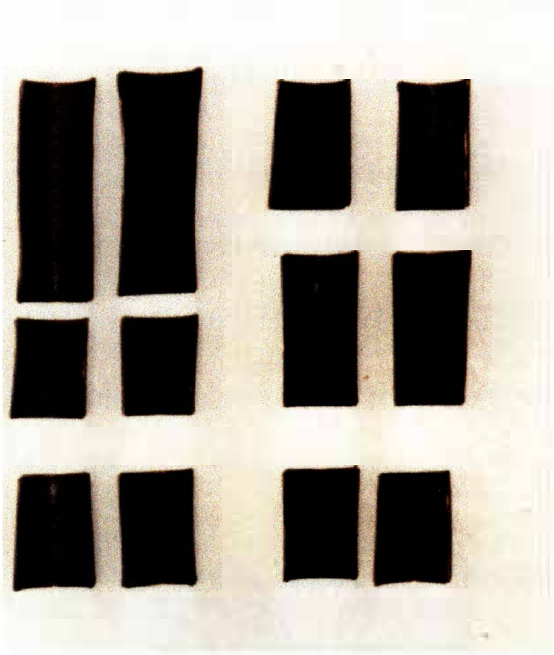


Figure 4-27: Loop 1 - hot hard water continuous recirculation.

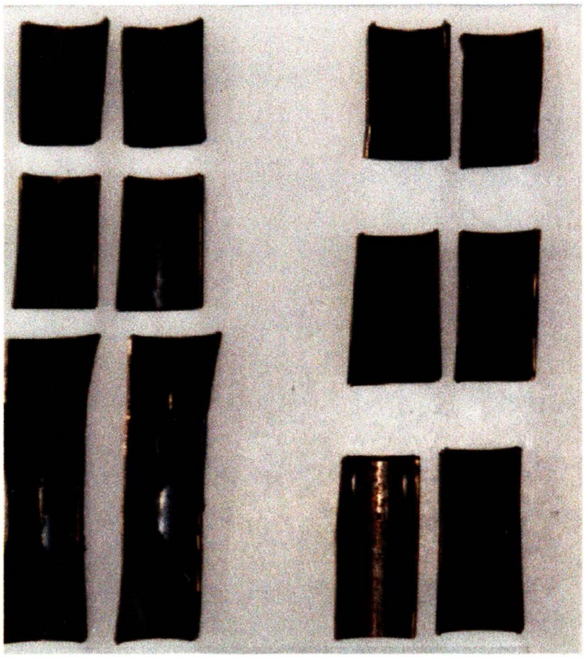


Figure 4-28: Loop 2 - hot soft water continuous recirculation.

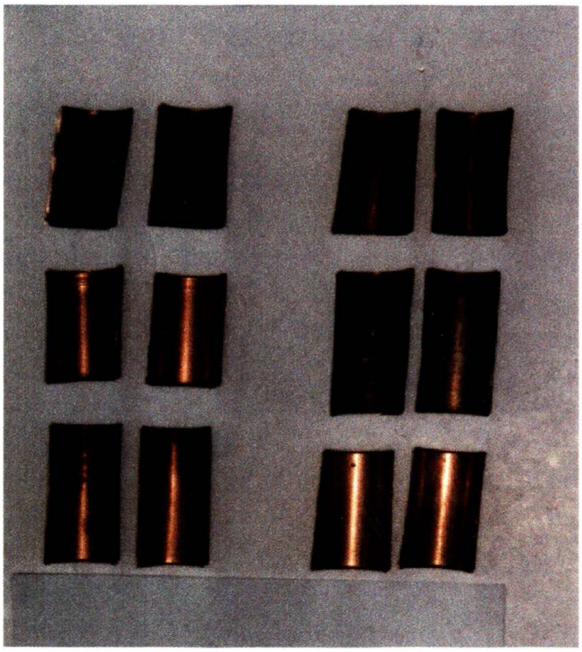


Figure 4-29: Loop 4 - cold hard water continuous recirculation.

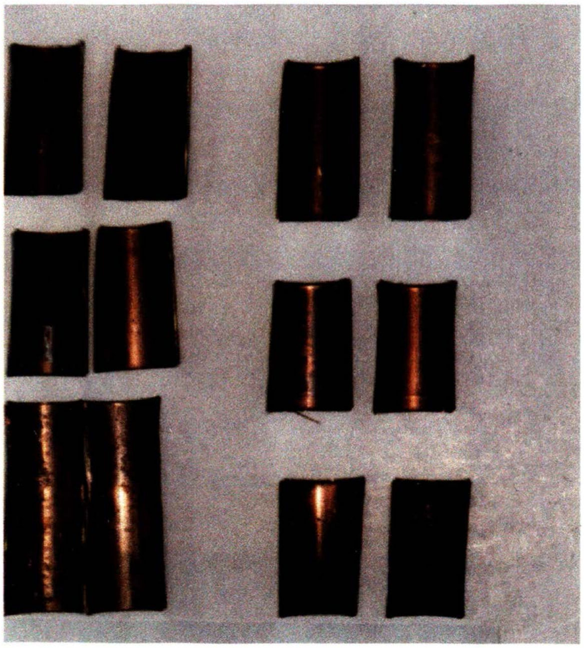


Figure 4-30: Loop 5 - cold soft water continuous recirculation.

4.2.5 Effects of Recirculation on Copper Corrosion

The following discussion will pertain to the analysis of corrosion by-product release data and evaluation of inspections of the copper surfaces. Test waters were either continuously recirculated or recirculated intermittently four times per day. The intermittently recirculated pipe loops were recirculated long enough to heat the water in the pipe loops to the temperature in the continuously recirculated pipe loops.

A. Analysis of By-product Release Data

Average results of the amount of soluble copper corrosion by-product released into solution are shown in Table 4-10. Samples were obtained every three days for each type of water for a period of two months. Results of the corrosion by-product release tests for all loops that show effects of recirculation are illustrated in a plot of soluble copper released over the period of sampling in Figure 4-31. More detailed summation of results and statistical analysis are found in Appendix B. Statistical analysis was completed using Analysis of Variance for comparison of results. The following is a comparison of results for these combinations:

- hot hard water (continuously versus intermittently recirculated)
- cold hard water (continuously versus intermittently recirculated)

Table 4-10: Comparisons of data from by-product release testing to show the effects of recirculation on by-product release.

Water Description	Type of Recirculation	Loop	Average Soluble Cu Concentration (mg/L)	Mean Difference (mg/L)	Statistical Significance
Hot Hard Water	continuous	1	0.37	0.19	99
Hot Hard Water	intermittent	3	0.57		
Cold Hard Water	continuous	4	1.05	0.07	Not Confident
Cold Hard Water	intermittent	6	0.98		

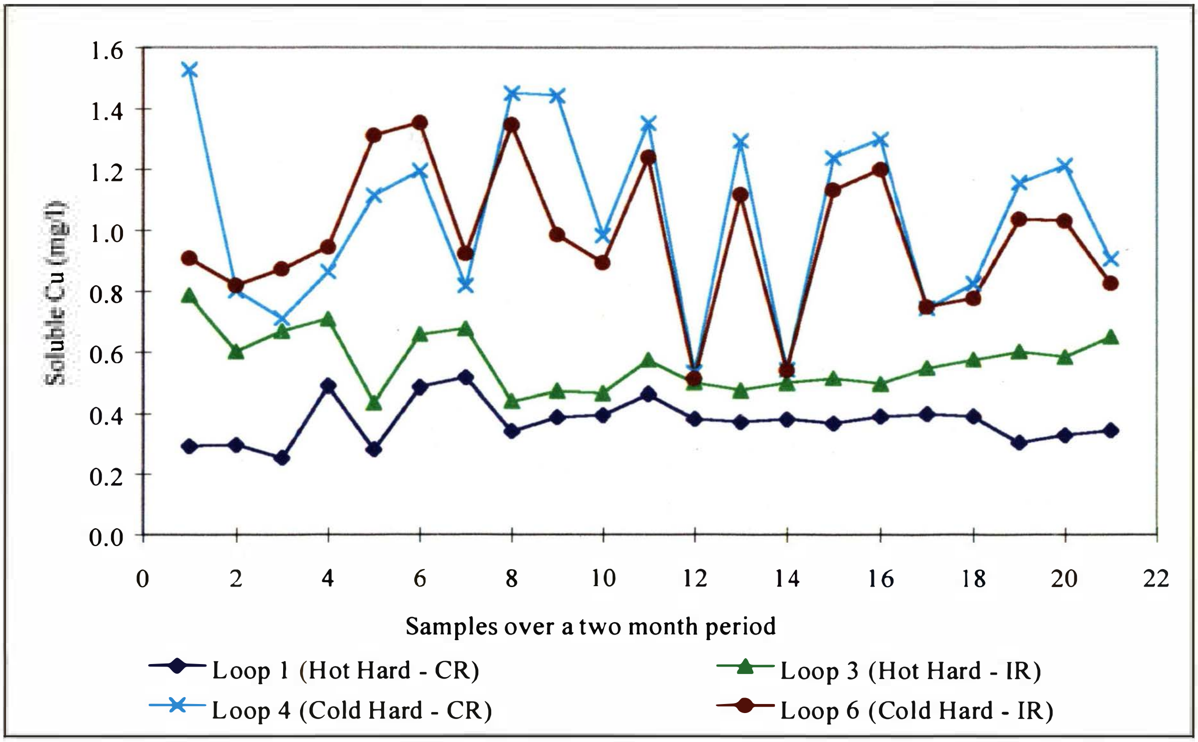


Figure 4-31: Results of soluble copper released for loops over the two month testing period.

1. Hot Hard Water - Continuous versus Intermittent Recirculation

Results from the testing of these two waters are plotted in Figure 4-31. The chart shows that there is a distinct difference in the two waters. Also, the two waters seem to follow the same trends closely. Average soluble copper concentration for corrosion by-product released into solution for hot hard - continuously recirculated and hot hard - intermittently recirculated were 0.37 and 0.57 mg/l Cu. The mean difference between these two values was 0.19 mg/l Cu. This difference in corrosion by-product released was statistically significant to the 99% confidence level.

2. Cold Hard Water - Continuous versus Intermittent Recirculation

Figure 4-31 displays the results for the corrosion by-product release data for these two waters. The chart shows only small differences between the two waters. Cold hard - continuously recirculated and cold hard - intermittently recirculated waters have an average copper concentration of corrosion by-product released into solution of 1.05 and 1.00 mg/l Cu. The mean difference between the by-product released was 0.07 mg/l Cu. Statistical analysis showed that there was no significant difference between these results of the two waters.

3. Summary

A comparison of continuous versus intermittent recirculation of both hot and cold hard water is shown in Figure 4-32. Recirculation had a significant effect on copper corrosion by-product release in the hot hard water experiment, whereas there was no significance in the cold hard water experiment.

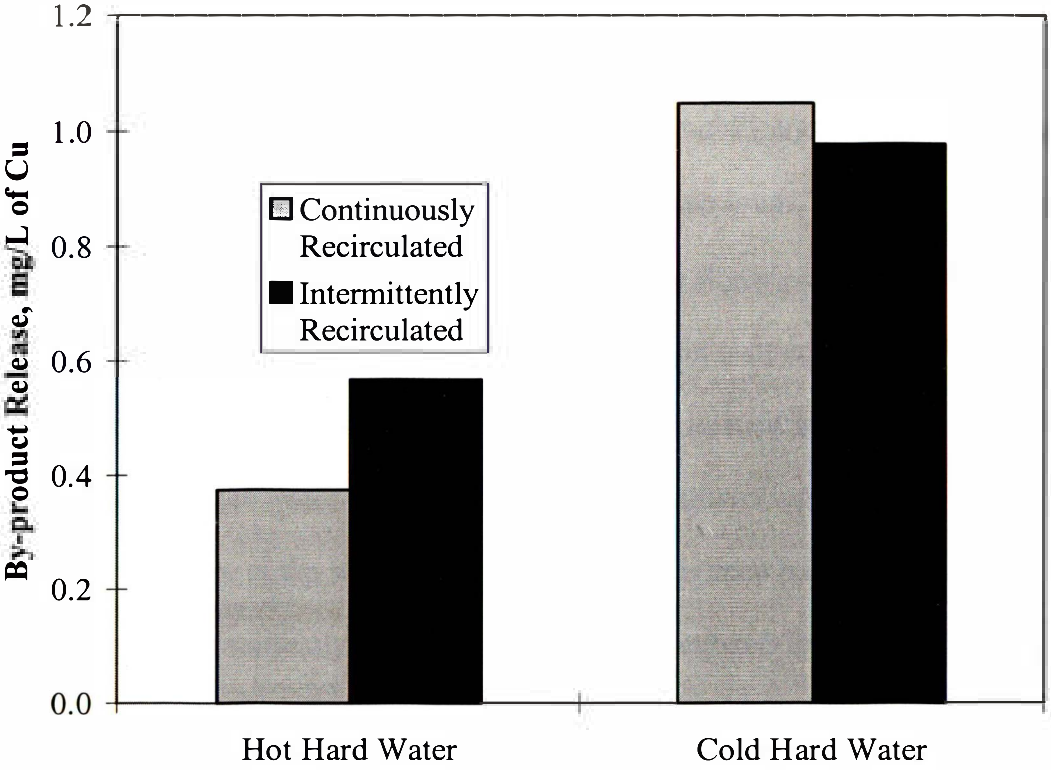


Figure 4-32: Recirculation effects on copper corrosion by-product release.

In the hot hard water setup, the loop that was continuously recirculated released 0.19 mg/L (52%) less copper corrosion by-product into solution than the loop that was intermittently recirculated. The increased copper corrosion by-product release in the intermittently recirculated loop is thought to be caused by temperature. In the intermittently recirculated loop, the water in the loop was raised to the temperature of the water in the continuously recirculated loop by recirculating water for ten minutes through a temperature controlled water bath. After the ten minutes the water in the loop was allowed to cool to room temperature. Because the loop was allowed to cool, the lower temperature increased the amount of copper corrosion by-product released to the solution.

Thus, the changes in temperature caused more by-product to be released in the intermittently recirculated loop than the continuously recirculated loop.

In the cold hard water setup, there was no statistically significant difference between intermittently and continuously recirculated pipe loops. However, the intermittently recirculated loop was observed to release slightly less copper by-product than the continuously recirculated loop. This decrease in copper corrosion by-product release could be caused by a temperature change in the intermittently recirculated loop. The temperature of the water in the continuously recirculated loop was constantly kept at the same temperature of tap water which is a little cooler than room temperature. After the water in the intermittently recirculated loop was circulated for ten minutes, it was allowed to warm up to room temperature. Since raising the temperature reduces copper by-product release, this could explain the slight decrease in by-product release in the intermittently recirculated loop over the continuously recirculated loop.

B. Visual Scale Observations

Visual observations were made of the copper surface after the pipe loop rigs were dismantled and portions of the rig cut into samples. Descriptions of the visual observations are listed for each of the water types in Table 4-13. Illustrations of type of water are shown in Figures 4-33 through 4-36.

Table 4-11: Visual Scale Observations.

Water Type	**Type of Recirculation**	**Figure**	**Visual Observations**
Hot Hard	Continuous	4-33	A black-brownish to brownish-red scale was observed on the surface of the copper pipe sections. The scale varied from a smooth black-brownish color to a brownish-red speckled color. Speckled colors ranged from black, brown or reddish in color.
Hot Hard	Intermittently	4-34	The surface of the copper pipe samples ranged from no scale formation to a light brownish colored scale on the surface of the samples. There were dark brown spots on portions of the copper surface.
Cold Hard	Continuous	4-35	The surface of the samples varied from having no scale formation to a light brownish scale. Overall there was very little scale formation observed on the surfaces.
Cold Hard	Intermittently	4-36	The surface of the samples can be defined as having very little to no observable scale formation. The color of the surface ranged from a shiny copper color to a light brownish color. Very few light brown speckles were observed on the copper surface. Overall very little scale formation was observed on the surface of the copper pipe.

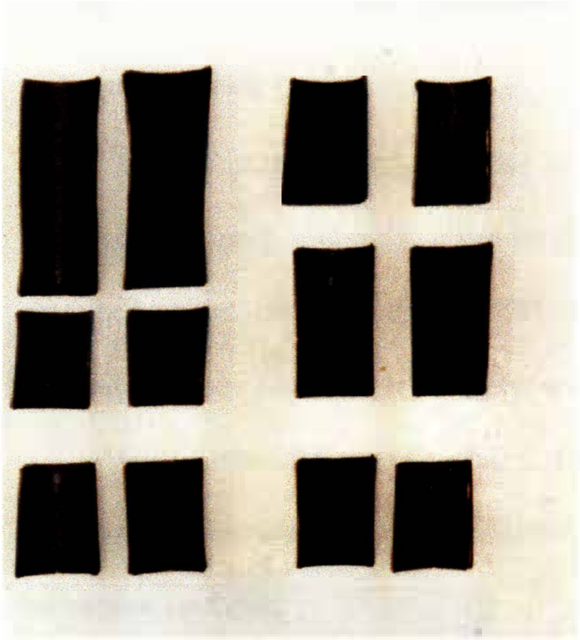


Figure 4-33: Loop 1 - hot hard water continuous recirculation.

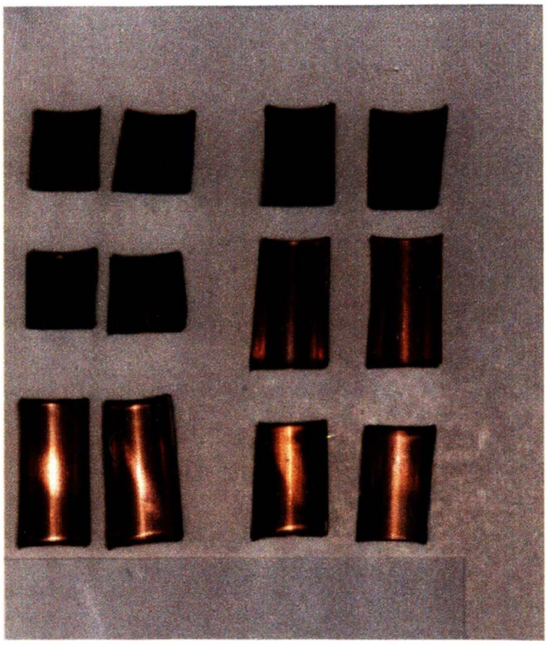


Figure 4-34: Loop 3 - hot hard water intermittent recirculation.

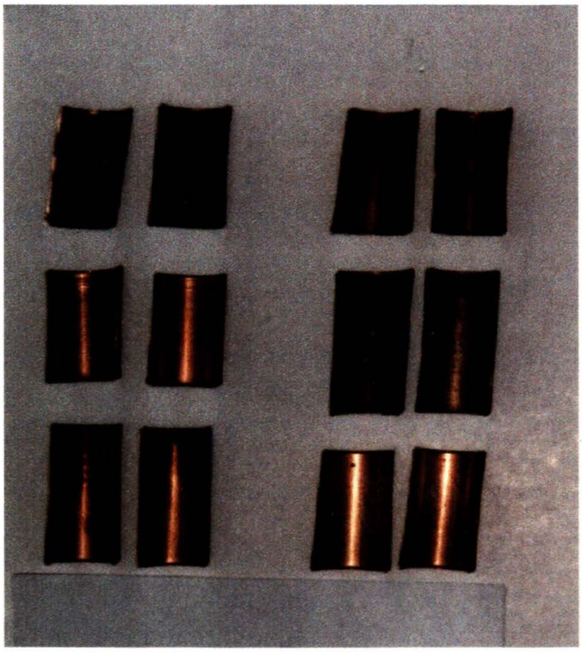


Figure 4-35: Loop 4- cold hard water continuous recirculation.

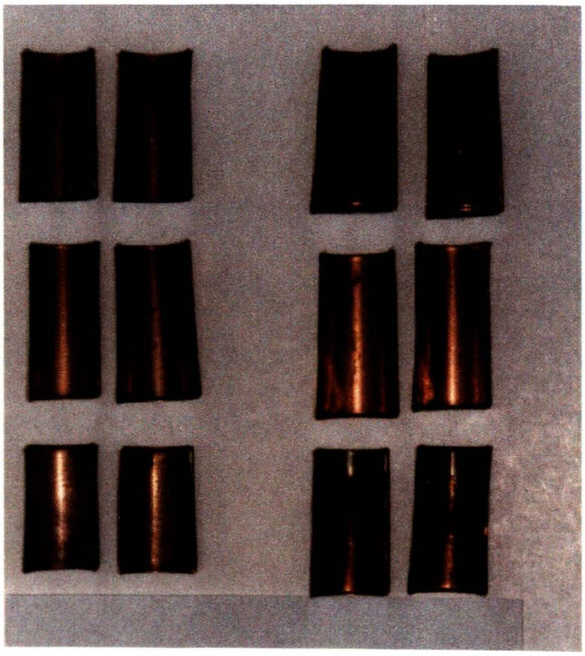


Figure 4-36: Loop 6 - cold hard water intermittent recirculation.

1. Summary and Conclusions

Comparison of samples exposed to hot hard - continuously recirculated and hot hard - intermittently recirculated waters showed that the continuously recirculated water produced a black-brownish to brownish-red scale on the copper surface, whereas the intermittently recirculated produced no scale formation to a light brownish colored scale.

Visual observations of surfaces of cold hard - continuously recirculated versus cold hard - intermittently recirculated showed that both had little or no scale formation on the copper surfaces.

As a result of these observations, it can be shown that cold water has little effect on formation of a scale layer when either recirculated continuously or intermittently. However, in the results of hot water either recirculated continuously or intermittently, the continuously recirculated water was able to produce a scale layer, whereas the intermittently recirculated water was unable to form little or no scale layer. A reason for this observation is that after recirculating the water to the temperature of the water in the continuously recirculated loop, the water was left to cool down to equilibrium with room temperature or about the same as the temperature of the cold water. This resulted in the same observations shown in the cold water loops.

Chapter 5

Conclusions and Recommendations

This chapter will present a summary of results and conclusions from both electrochemical and corrosion by-product release testing and provide recommendations for future studies.

5.1 Effects of Temperature on Copper Corrosion

5.1.1 Electrochemical Corrosion Testing:

1) Increasing temperature had a small, but significant effect by increasing corrosion rates for aged copper surfaces. For hard and soft waters, raising the temperature by 42°C increased the corrosion rate by 0.16 and 0.22 $\mu A/cm^2$, respectively.
2) Analysis of anodic current curves indicated an increase in temperature resulted in a passivation of the copper surface. Thus, the increase in temperature promotes a protective scale on the copper surface. The lower temperature appeared to have no effect on the anodic current, thus producing a corrosion inducing scale or no productive scale on the copper surface.

5.1.2 By-product Release Testing:

1) Increasing the temperature significantly reduced the copper corrosion by-product released in both the continuously recirculated soft and hard waters and also in the intermittently recirculated hard water. During the experiments where hard and soft water were continuously recirculated, raising the temperature by 40°C reduced the amount of copper released into the solution by 0.67 and 0.71 mg/L,

respectively. Also raising the temperature by 40°C reduced the amount of copper released by 0.41 mg/L in the experiment in which hard water was recirculated intermittently.

2) Upon visual inspection, the copper pipe exposed to hot waters exhibited a black-brownish to a brownish-red colored scale on the surface of the copper pipe sections, whereas the copper surfaces exposed to cold water had a light brownish color to no scale formation (shiny copper surface). From these observations, hot water is prone to scale layer formation, while the copper samples exposed to cold water showed little or no scale formation.

5.1.3 Conclusions

A comparison of results of corrosion rates versus corrosion by-product released showed that these results conflict with each other. The corrosion rates increased with temperature, whereas the by-product release decreased with increased temperature. If the experiments are representative of the real conditions, the results should agree with each other.

This conflict might be resolved by understanding that the corrosion rates were obtained using a flow-through system rather than a system where water was recirculated through the coupon. In the flow through system, the scales built up during the anodic polarization are apparently not as representative as those built up during experiments where the target water is recirculated through the corrosion cell. It is hypothesized that if the electrochemical testing was conducted for a longer term the results would be more representative of those results from the by-product release testing.

Corrosion by-product release data correlate with anodic current data from electrochemical testing. These data indicate that an increase in temperature reduces the amount of copper corrosion either by the reduction in solubility of the copper or the formation of a protective scale layer or both. Visual inspection of the copper surfaces from the by-product release testing showed formation of a scale layer on the copper surfaces exposed to the higher temperature.

These results also concur with predictions made by Edwards *et al.* (1996) who concluded that if copper corrosion is based on solubility then increased temperature would reduce corrosion by-product released.

5.2 Effects of Water Hardness on Copper Corrosion

5.2.1 Electrochemical Corrosion Testing:

1) Water hardness had a very significant effect on electrochemically measured corrosion rates. In the hot and cold waters, the corrosion rates of the soft water were lower than the hard water by 0.97 and 0.94 $\mu A/cm^2$, respectively.
2) A comparison of the anodic current curves for hot hard with hot soft and cold hard with cold soft shows that there were no profound differences between hard and soft waters.

5.2.2 By-product Release Testing:

Softened water exhibited a small increase in copper corrosion by-product release. In experiments where hot and cold water were recirculated continuously, hard water released less copper corrosion by-product into solution than that of soft water (0.08 and 0.20 mg/L Cu, respectively).

5.2.3 Conclusions

A comparison of results of corrosion rates versus corrosion by-product released showed that these results conflict with each other. This conflict has been addressed previously in the section above.

The minimal effect of hardness on the corrosion by-product release corroborates the results from anodic current curves where no profound differences were exhibited between the hard and soft waters. Also, visual observations of the copper surfaces in the by-product release testing showed no distinguishable differences between the hard and soft waters.

These results agree with previous work where hardness ions do not directly influence copper corrosion, but have been shown to have some beneficial effects in reducing corrosion (Edwards *et al.* 1994).

5.3 Effects of Recirculation on Copper Corrosion

5.3.1 By-product Release Testing:

1) Intermittent recirculation had a significant effect on copper corrosion by-product release in the hot hard water, whereas there was no significance in the cold hard water. In the hot hard water setup, the continuously recirculated loop released 0.19 mg/l less copper corrosion by-product than the loop that was intermittently recirculated. This is believed to be caused by the temperature change as the water

in the intermittently recirculated loop was allowed to cool during the times when water was not recirculated. Therefore, as previously discussed, the cooler water tends to promote the release of corrosion by-product.

2) Visual comparison of samples exposed to hot hard - continuously recirculated and hot hard - intermittently recirculated waters showed that the continuously recirculated water produced a black-brownish to brownish-red scale on the copper surface, whereas the intermittently recirculated produced no scale formation to a light brownish colored scale. Visual observations of surfaces of cold hard - continuously recirculated versus cold hard - intermittently recirculated showed that both had little or no scale formation on the copper surfaces. As a result of these observations, it can be shown that cold water has little effect on formation of a scale layer when either recirculated continuously or intermittently.

5.3.2 Conclusions

The results obtained from these recirculation tests show that temperature has a direct effect on the amount of corrosion by-product released for either intermittent or continuous recirculation. Corrosion increases as systems are allowed to cool.

5.4 Recommendations

The following recommendations are made for future corrosion studies:

1) In the electrochemical testing, more research needs to be performed to correlate corrosion rates from flow-through testing with those from static testing. Flow-through testing could be performed for a longer period of time to simulate scale

formation that has been simulated through static testing and that are representative of scales found within a water supply system.

2) Further testing could be performed at different temperature intervals to determine a correlation of temperature with the amount of corrosion by-product released.

3) More investigations could be completed to evaluate the relationship of temperature and solubility with their effects in the formation of corrosion scale layers.

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APPENDICES

APPENDIX A

Table A-1: Water Quality Observations of Cold Hard Water During Electrochemical Testing.

Date	Temperature (°C)	pH	Alkalinity (mg/L as $CaCO_3$)	Ca^{++} (mg/L)	Mg^{++} (mg/L)	Na^{+} (mg/L)	Cl^{-} (mg/L)	$SO_4^{=}$ (mg/L)	PO_4^{-3} (mg/L-P)
4/07/95	11	8.16	168	88.1	39.9	9.4	10.88	224	0.03
4/08/95	11	8.10	168	77.0	39.0	8.6	11.38	252.4	0.03
4/09/95	11	8.10	166	101.9	39.6	8.9	11.13	244.8	0.03
4/10/95	11	8.10	167	93.4	39.7	9.7	12.12	246.2	0.03
4/11/95	11	8.15	165	77.8	39.6	8.7	11.15	242.4	0.03
Average	11.0	8.12	167	87.6	39.6	9.1	11.33	242.0	0.03
4/18/95	13	8.14	160	96.6	38.0	8.5	11.25	235.4	0.03
4/19/95	13	8.13	162	79.4	40.0	8.7	11.27	247.6	0.03
4/20/95	13	8.11	161	75.3	38.4	8.5	11.44	233.8	0.03
4/21/95	13	8.10	160	79.0	38.4	8.7	12.33	232.4	0.03
4/22/95	12	8.10	159	97.5	39.1	9.0	11.20	252.4	0.03
Average	13	8.12	160	85.6	38.8	8.7	11.50	240.3	0.03
Overall Average	12	8.12	164	86.6	39.2	8.9	11.42	241.1	0.03

Table A-2: Water Quality Observations of Cold Soft Water During Electrochemical Testing.

Date	Temperature (°C)	pH	Alkalinity (mg/L as $CaCO_3$)	Ca^{++} (mg/L)	Mg^{++} (mg/L)	Na^{+} (mg/L)	Cl^{-} (mg/L)	$SO_4^{=}$ (mg/L)	PO_4^{-3} (mg/L-P)
4/07/95	11	8.36	167	1.07	0.08	165.0	10.90	217.2	0.03
4/08/95	11	8.21	168	1.00	0.07	157.5	11.21	222.4	0.03
4/09/95	11	8.23	170	1.05	0.07	154.1	11.12	242.6	0.03
4/10/95	12	8.23	167	0.93	0.08	162.6	11.09	209.0	0.03
4/11/95	11	8.24	164	0.91	0.09	157.6	11.79	213.0	0.03
Average	11	8.25	167	0.99	0.08	159.4	11.22	220.8	0.03
4/18/95	14	8.24	162	1.01	0.05	152.7	11.27	176.6	0.03
4/19/95	14	8.28	164	1.28	0.05	156.4	11.29	207.2	0.03
4/20/95	14	8.22	161	0.87	0.04	154.8	11.25	179.6	0.03
4/21/95	14	8.27	162	1.02	0.05	154.4	12.33	169.0	0.03
4/22/95	13	8.18	157	1.15	0.18	154.8	11.66	178.6	0.03
Average	14	8.24	161	1.07	0.07	154.6	11.56	182.2	0.03
Overall Average	13	8.25	164	1.03	0.08	157.0	11.39	201.5	0.03

APPENDIX A, Continued

Table A-3: Water Quality Observations of Hot Hard Water During Electrochemical Testing.

Date	Temperature (ºC)	pH	Alkalinity (mg/L as $CaCO_3$)	Ca^{++} (mg/L)	Mg^{++} (mg/L)	Na^{+} (mg/L)	Cl^{-} (mg/L)	$SO_4^{=}$ (mg/L)	PO_4^{-3} (mg/L-P)
5/16/95	55	8.36	166	82.0	43.9	18.9	11.1	208.6	0.09
5/17/96	54	8.18	160	74.8	45.4	20.0	10.9	219.6	0.11
5/18/95	55	8.13	158	82.3	46.5	21.2	10.6	236.9	0.12
5/19/95	56	8.18	158	73.8	43.2	19.4	10.8	224.0	0.09
5/20/95	56	8.14	163	61.1	38.4	13.4	11.6	160.8	0.07
Average	55.2	8.20	161	74.8	43.5	18.6	11.0	210.0	0.10
5/22/95	56	8.08	166	66.2	40.0	16.1	11.5	187.6	0.05
5/23/95	56	8.17	165	77.0	47.2	21.8	10.4	236.9	0.07
5/24/95	56	8.14	158	75.4	44.1	20.9	10.4	225.4	0.08
5/25/95	54	8.14	161	81.6	46.2	20.1	10.7	225.4	0.05
5/26/95	56	8.06	160	77.6	46.1	22.5	11.3	251.3	0.06
Average	56	8.12	162	75.6	44.7	20.3	10.9	225.3	0.06
Overall Average	55	8.16	162	75.2	44.1	19.4	10.92	217.7	0.08

APPENDIX A, Continued

Table A-4: Water Quality Observations of Hot Soft Water During Electrochemical Testing.

Date	Temperature (°C)	pH	Alkalinity (mg/L as $CaCO_3$)	Ca^{++} (mg/L)	Mg^{++} (mg/L)	Na^{+} (mg/L)	Cl^{-} (mg/L)	$SO_4^{=}$ (mg/L)	PO_4^{-3} (mg/L-P)
4/07/95	57	8.40	167	1.45	0.11	178.0	11.07	223.8	0.05
4/08/95	57	8.29	169	1.04	0.07	158.8	11.40	182.8	0.05
4/09/95	57	8.17	167	1.18	0.19	156.6	11.41	179.6	0.06
4/10/95	57	8.29	164	0.99	0.10	178.7	10.92	238.2	0.05
4/11/95	57	8.27	166	0.94	0.08	161.9	11.34	183.4	0.04
Average	57	8.28	167	1.12	0.11	166.8	11.23	201.6	0.05
4/18/95	55	8.30	165	1.01	0.05	156.4	11.63	166.4	0.05
4/19/95	54	8.25	161	1.40	0.07	183.3	13.45	237.8	0.06
4/20/95	54	8.21	162	0.90	0.04	158.1	11.54	181.6	0.04
4/21/95	53	8.30	164	1.02	0.07	177.5	11.23	209.6	0.09
4/20/95	55	8.25	161	1.12	0.18	156.6	12.20	158.8	0.05
Average	54	8.26	163	1.09	0.08	166.4	12.01	190.8	0.06
Overall Average	56	8.27	165	1.11	0.10	166.6	11.62	196.2	0.05

APPENDIX A, Continued

Table A-5: Aged Corrosion Rate Selection Process for Test Data 4-07-95.

		Corrosion Rates (mA/cm^2)				
Reiber Cell #	Treatment	Tafel Analysis			Arbitrary Intersection	
		LOG	LIN	AVG	Cathodic	Anodic
1	Cold Soft	0.109'	0.225'	0.161'	0.175	0.204'
2	Cold Soft	0.188	0.255	0.223	0.206	0.078
3	Cold Hard	1.734'	1.770'	1.747'	1.308	1.094
4	Cold Hard	2.422'	2.598'	2.451'	1.144	1.100
5	Hot Soft	0.393	0.422	0.411	0.410	0.273
6	Hot Soft	0.400	0.394	0.406	0.402	0.238

No (') or (*) signified that emperical data was fit very well
(') - emperical data was not fit exactly but close enough
(*) - emperical data fit poorly, data was not accepted

Accepted corrosion rates are outlined in dark border

Reiber Cell #	Corrosion Rate Selection
1	The anodic extrapolated corrosion rate better represents Tafel analysis.
2	LOG Tafel analysis worked.
3	The anodic extrapolated corrosion rate better represents Tafel analysis.
4	The anodic extrapolated corrosion rate better represents Tafel analysis.
5	LOG Tafel analysis worked.
6	LOG Tafel analysis worked.

APPENDIX A, Continued

Table A-6: Aged Corrosion Rate Selection Process for Test Data 4-18-95.

		Corrosion Rates (mA/cm^2)				
Reiber Cell #	Treatment	Tafel Analysis			Arbitrary Intersection	
		LOG	LIN	AVG	Cathodic	Anodic
1	Cold Hard	1.207	1.563'	1.230	1.178	0.830
2	Cold Hard	1.552'	3.016'	1.961'	1.204	2.732'
3	Cold Soft	0.237	0.269	0.272	0.222	0.245
4	Cold Soft	0.214	0.215	0.223	0.173	0.195
5	Hot Soft	0.312'	0.612'	0.475'	0.447	0.411
6	Hot Soft	0.324'	0.479'	0.390'	0.644	0.432

No (') or (*) signified that emperical data was fit very well
(') - emperical data was not fit exactly but close enough
(*) - emperical data fit poorly, data was not accepted

Accepted corrosion rates are outlined in dark border

Reiber Cell #	Corrosion Rate Selection
1	LOG Tafel analysis worked.
2	Only the cathodic extrapolated corrosion rate could be obtained.
3	LOG Tafel analysis worked.
4	LOG Tafel analysis worked.
5	The anodic extrapolated corrosion rate better represents Tafel analysis.
6	The anodic extrapolated corrosion rate better represents Tafel analysis.

APPENDIX A, Continued

Table A-7: Aged Corrosion Rate Selection Process for Test Data 5-16-95.

Reiber Cell #	Treatment	Corrosion Rates (mA/cm^2)				
		Tafel Analysis			Arbitrary Intersection	
		LOG	LIN	AVG	Cathodic	Anodic
5	Hot Hard	1.473	2.327'	1.770	0.172'	0.137'
6	Hot Hard	1.494	2.860'	2.429'	1.234	1.077

No (') or (*) signified that emperical data was fit very well
(') - emperical data was not fit exactly but close enough
(*) - emperical data fit poorly, data was not accepted

Accepted corrosion rates are outlined in dark border

Reiber Cell #	Corrosion Rate Selection
5	LOG Tafel analysis worked.
6	LOG Tafel analysis worked.

APPENDIX A, Continued

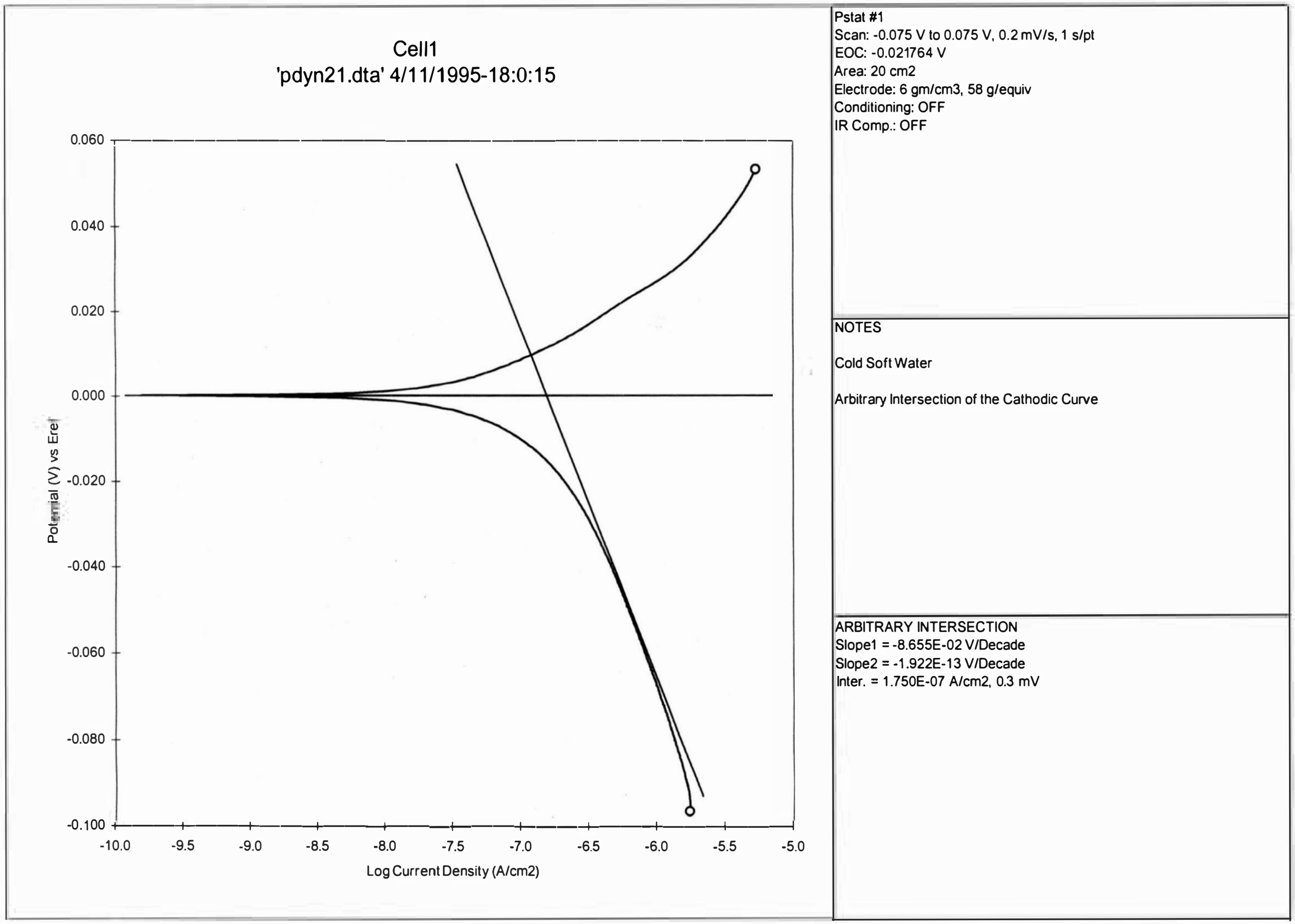
Table A-8: Aged Corrosion Rate Selection Process for Test Data 5-22-95.

Reiber Cell #	Treatment	Corrosion Rates (mA/cm^2)				
		Tafel Analysis			Arbitrary Intersection	
		LOG	LIN	AVG	Cathodic	Anodic
5	Hot Hard	1.364	4.743*	4.246*	1.347	1.111
6	Hot Hard	1.168	1.215	1.227	0.756	0.865

No (') or (*) signified that emperical data was fit very well
(') - emperical data was not fit exactly but close enough
(*) - emperical data fit poorly, data was not accepted

Accepted corrosion rates are outlined in dark border

Reiber Cell #	Corrosion Rate Selection
5	LOG Tafel analysis worked.
6	LOG Tafel analysis worked.



Pstat #1
Scan: -0.075 V to 0.075 V, 0.2 mV/s, 1 s/pt
EOC: -0.021764 V
Area: 20 cm2
Electrode: 6 gm/cm3, 58 g/equiv
Conditioning: OFF
IR Comp.: OFF

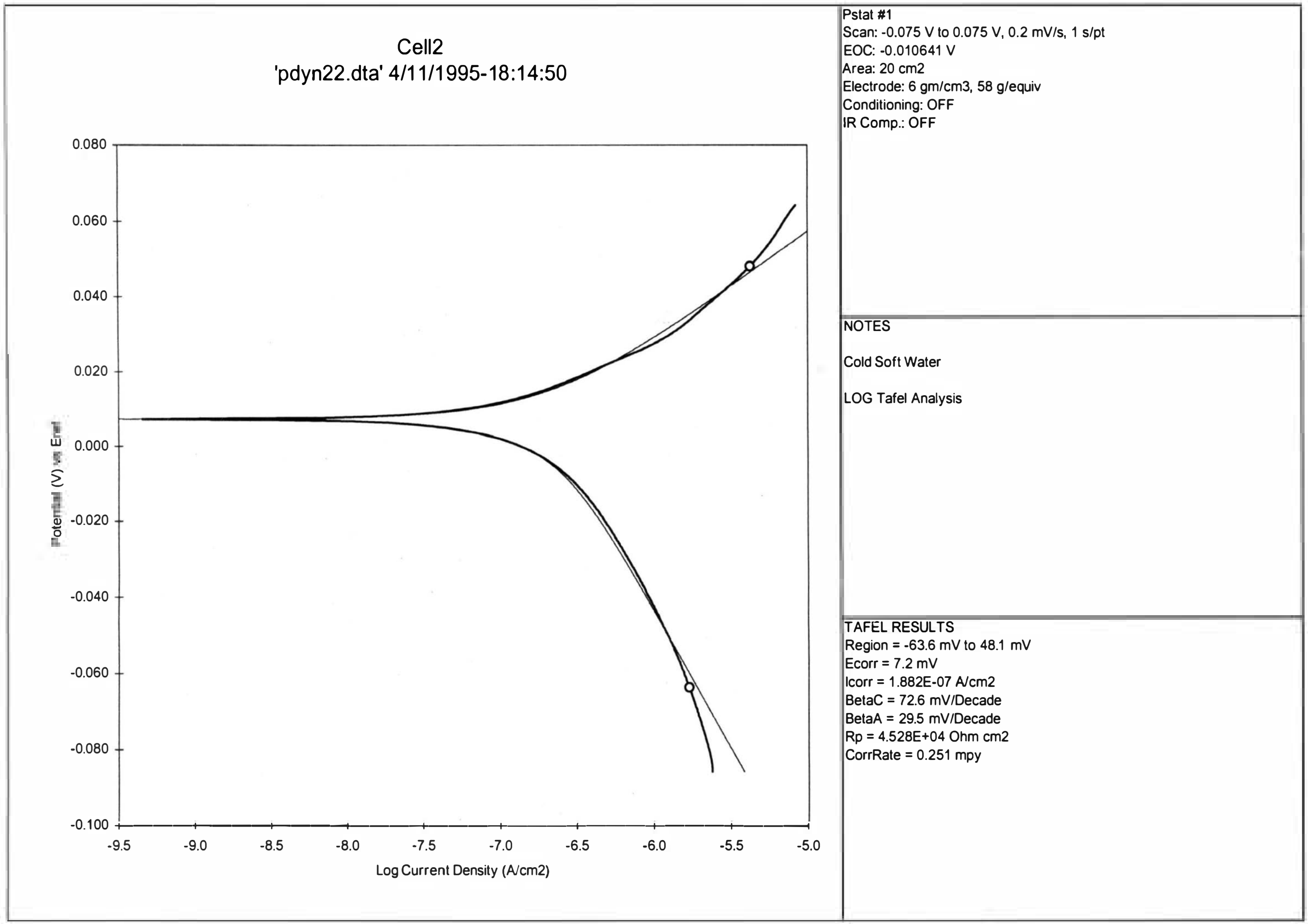
NOTES

Cold Soft Water

Arbitrary Intersection of the Cathodic Curve

ARBITRARY INTERSECTION
Slope1 = -8.655E-02 V/Decade
Slope2 = -1.922E-13 V/Decade
Inter. = 1.750E-07 A/cm2, 0.3 mV

Figure A-1: Plot of Final Potentiodynamic Scan.



Pstat #1
Scan: -0.075 V to 0.075 V, 0.2 mV/s, 1 s/pt
EOC: -0.010641 V
Area: 20 cm2
Electrode: 6 gm/cm3, 58 g/equiv
Conditioning: OFF
IR Comp.: OFF

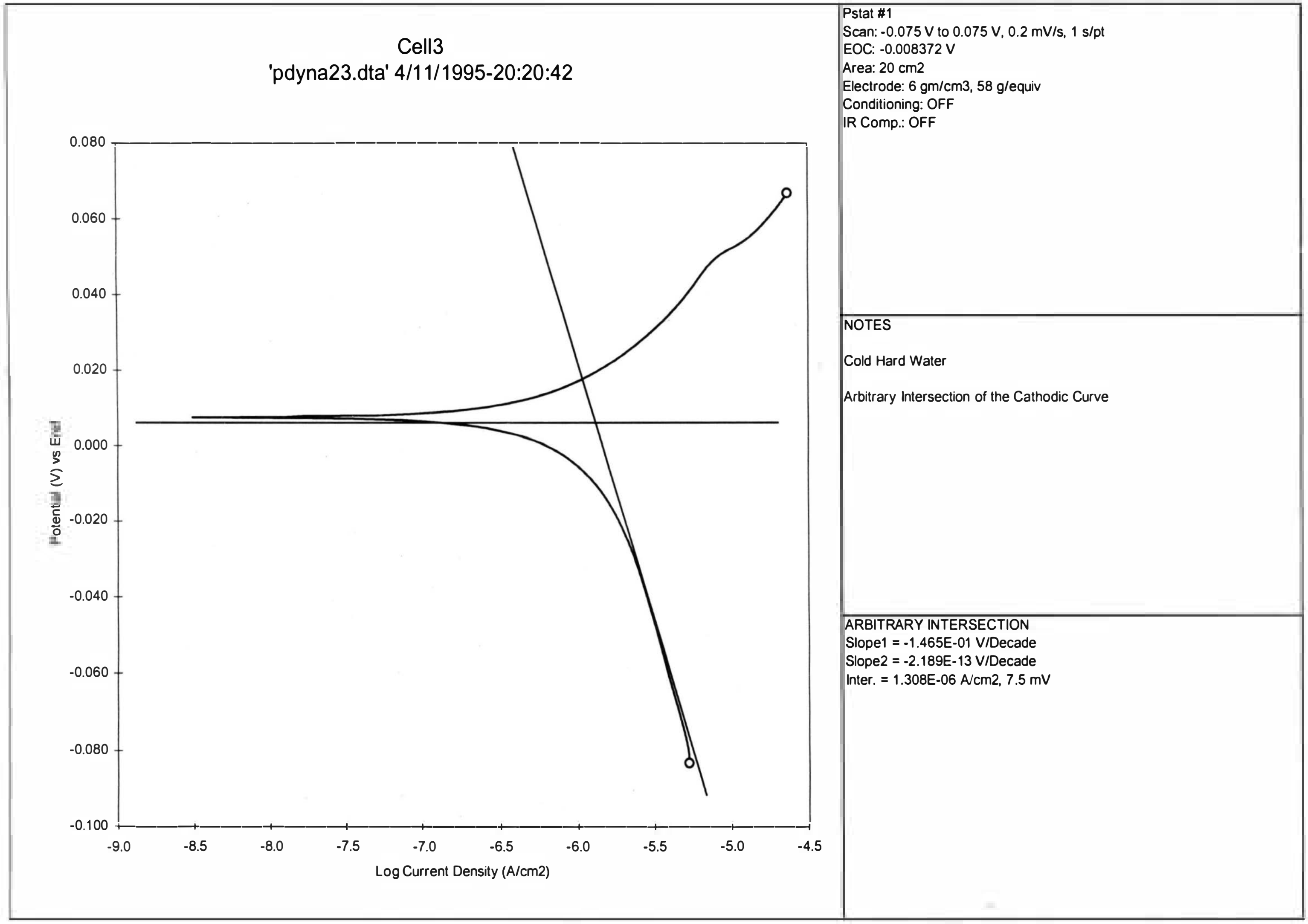
NOTES

Cold Soft Water

LOG Tafel Analysis

TAFEL RESULTS
Region = -63.6 mV to 48.1 mV
Ecorr = 7.2 mV
Icorr = 1.882E-07 A/cm2
BetaC = 72.6 mV/Decade
BetaA = 29.5 mV/Decade
Rp = 4.528E+04 Ohm cm2
CorrRate = 0.251 mpy

Figure A-2: Plot of Final Potentiodynamic Scan.



Pstat #1
Scan: -0.075 V to 0.075 V, 0.2 mV/s, 1 s/pt
EOC: -0.008372 V
Area: 20 cm2
Electrode: 6 gm/cm3, 58 g/equiv
Conditioning: OFF
IR Comp.: OFF

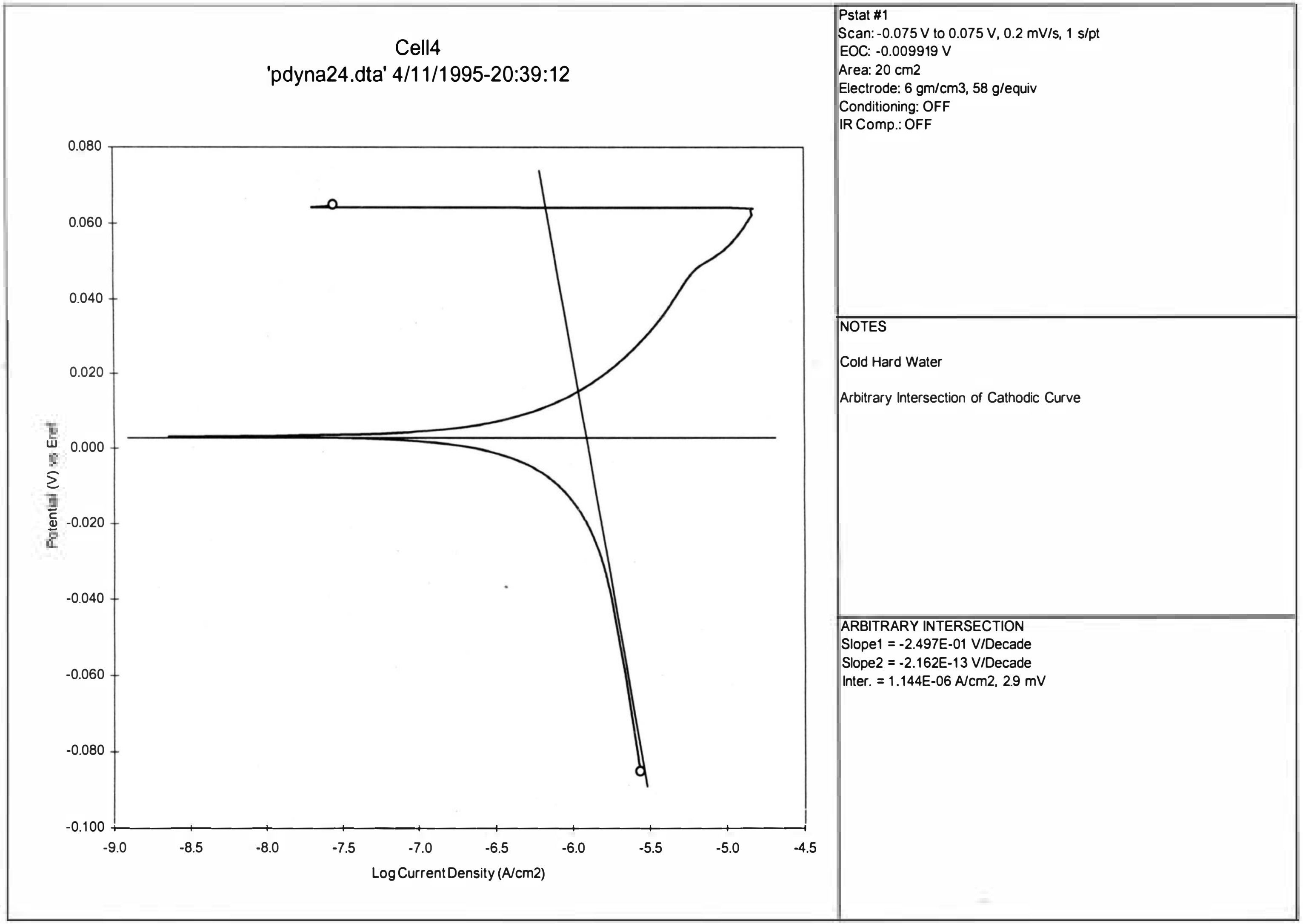
NOTES

Cold Hard Water

Arbitrary Intersection of the Cathodic Curve

ARBITRARY INTERSECTION
Slope1 = -1.465E-01 V/Decade
Slope2 = -2.189E-13 V/Decade
Inter. = 1.308E-06 A/cm2, 7.5 mV

Figure A-3: Plot of Final Potentiodynamic Scan.



Pstat #1
Scan: -0.075 V to 0.075 V, 0.2 mV/s, 1 s/pt
EOC: -0.009919 V
Area: 20 cm2
Electrode: 6 gm/cm3, 58 g/equiv
Conditioning: OFF
IR Comp.: OFF

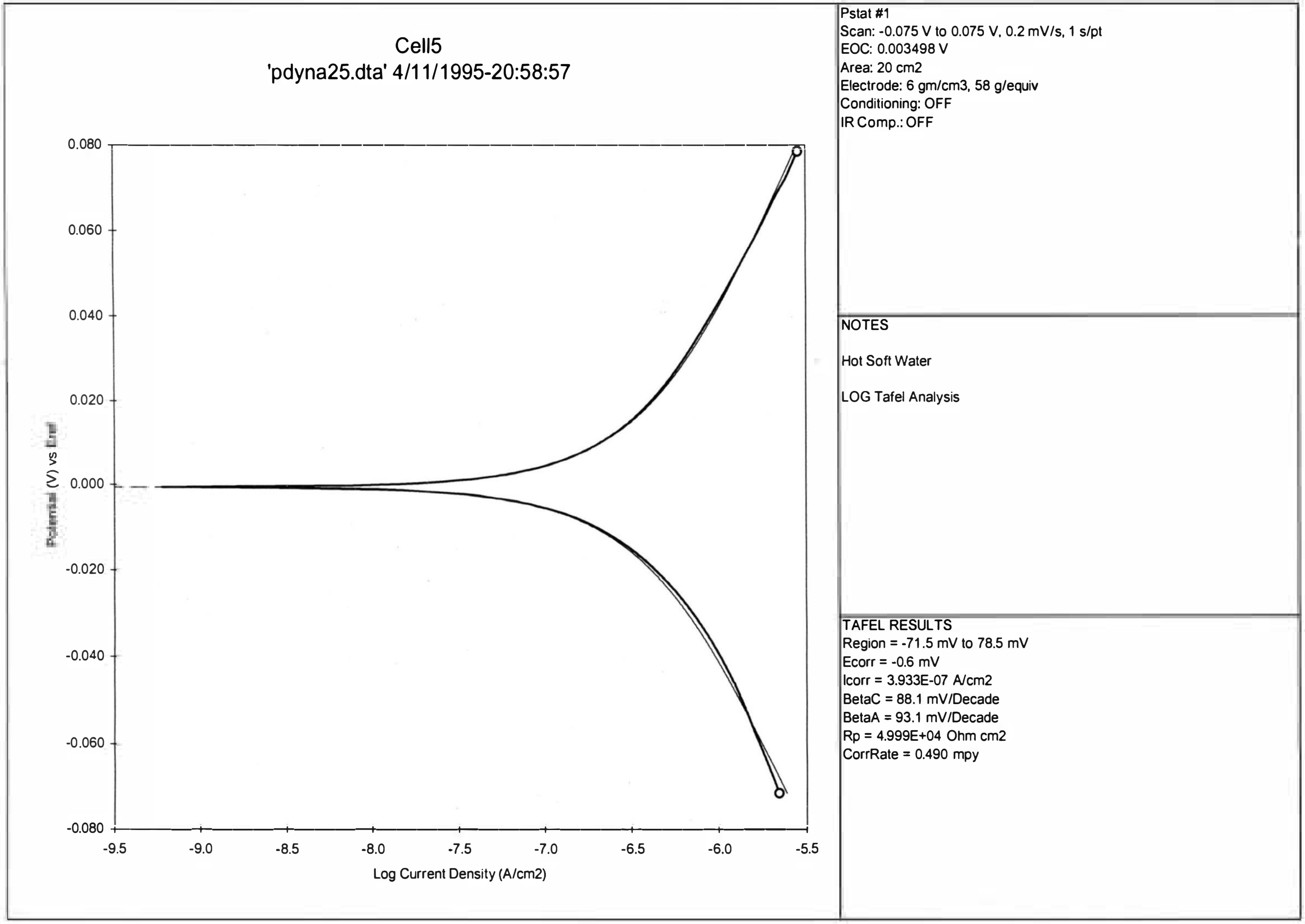
NOTES

Cold Hard Water

Arbitrary Intersection of Cathodic Curve

ARBITRARY INTERSECTION
Slope1 = -2.497E-01 V/Decade
Slope2 = -2.162E-13 V/Decade
Inter. = 1.144E-06 A/cm2, 2.9 mV

Figure A-4: Plot of Final Potentiodynamic Scan.



Pstat #1
Scan: -0.075 V to 0.075 V, 0.2 mV/s, 1 s/pt
EOC: 0.003498 V
Area: 20 cm2
Electrode: 6 gm/cm3, 58 g/equiv
Conditioning: OFF
IR Comp.: OFF

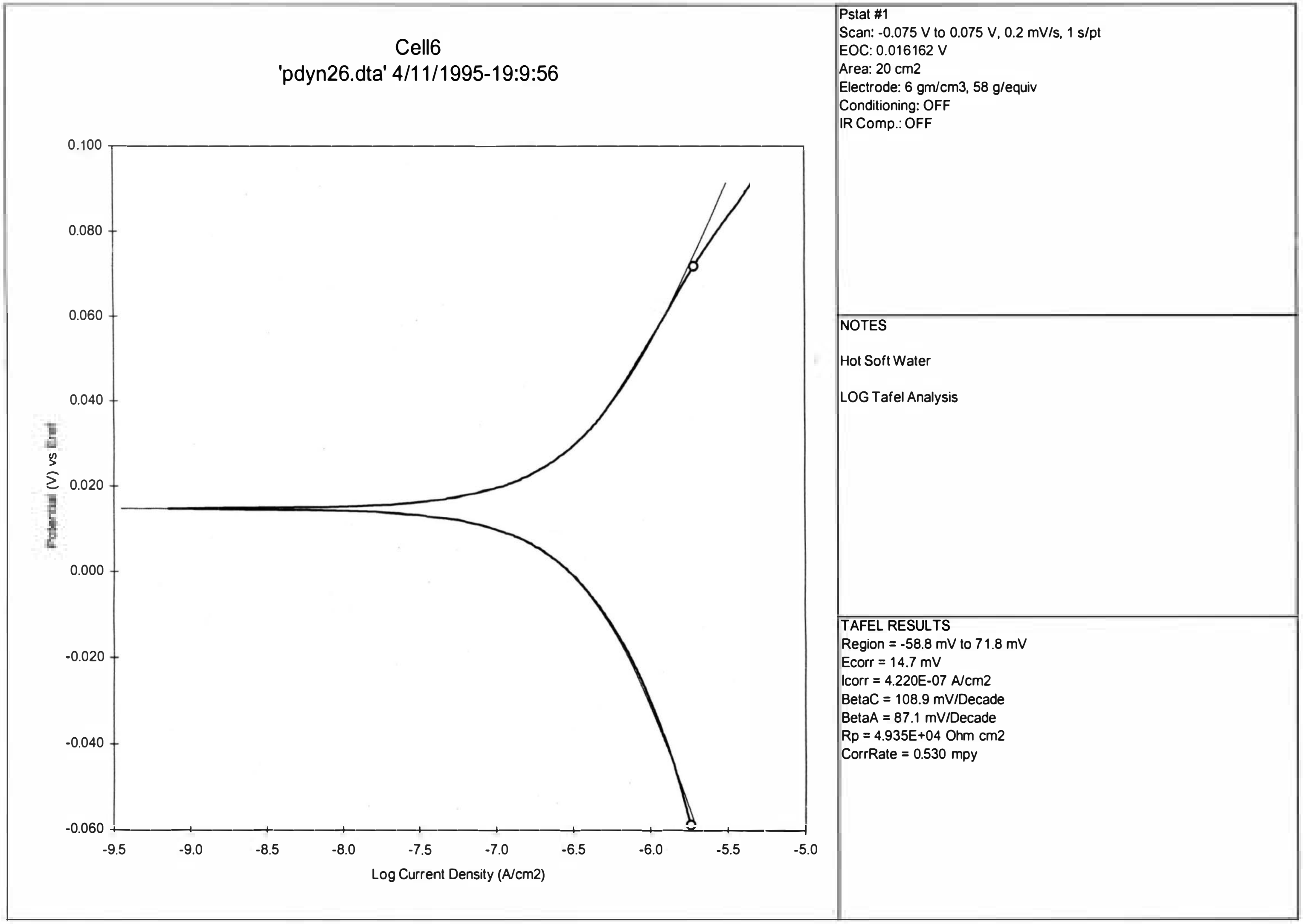
NOTES

Hot Soft Water

LOG Tafel Analysis

TAFEL RESULTS
Region = -71.5 mV to 78.5 mV
Ecorr = -0.6 mV
Icorr = 3.933E-07 A/cm2
BetaC = 88.1 mV/Decade
BetaA = 93.1 mV/Decade
Rp = 4.999E+04 Ohm cm2
CorrRate = 0.490 mpy

Figure A-5: Plot of Final Potentiodynamic Scan.



Pstat #1
Scan: -0.075 V to 0.075 V, 0.2 mV/s, 1 s/pt
EOC: 0.016162 V
Area: 20 cm2
Electrode: 6 gm/cm3, 58 g/equiv
Conditioning: OFF
IR Comp.: OFF

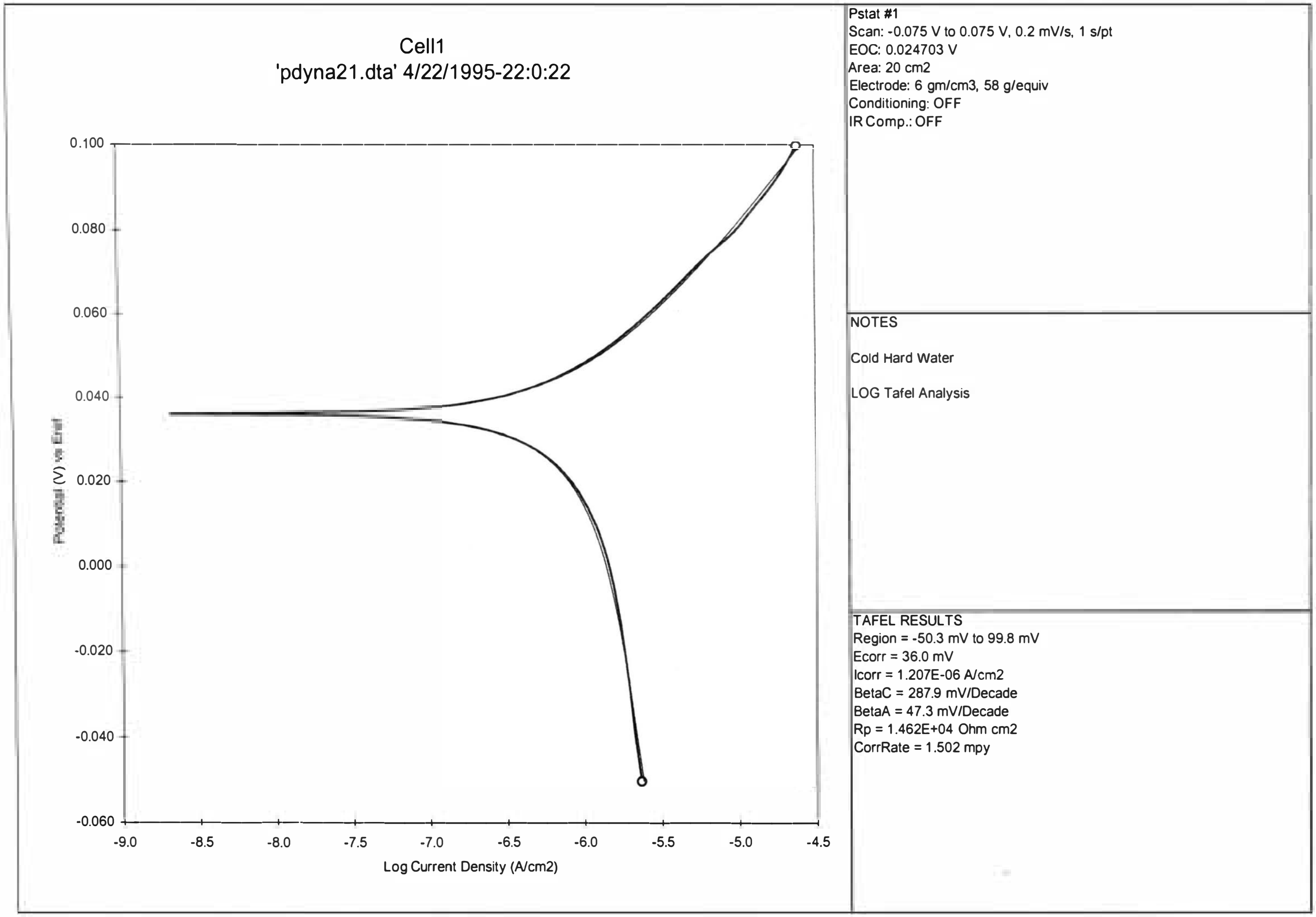
NOTES

Hot Soft Water

LOG Tafel Analysis

TAFEL RESULTS
Region = -58.8 mV to 71.8 mV
Ecorr = 14.7 mV
Icorr = 4.220E-07 A/cm2
BetaC = 108.9 mV/Decade
BetaA = 87.1 mV/Decade
Rp = 4.935E+04 Ohm cm2
CorrRate = 0.530 mpy

Figure A-6: Plot of Final Potentiodynamic Scan.



Pstat #1
Scan: -0.075 V to 0.075 V, 0.2 mV/s, 1 s/pt
EOC: 0.024703 V
Area: 20 cm2
Electrode: 6 gm/cm3, 58 g/equiv
Conditioning: OFF
IR Comp.: OFF

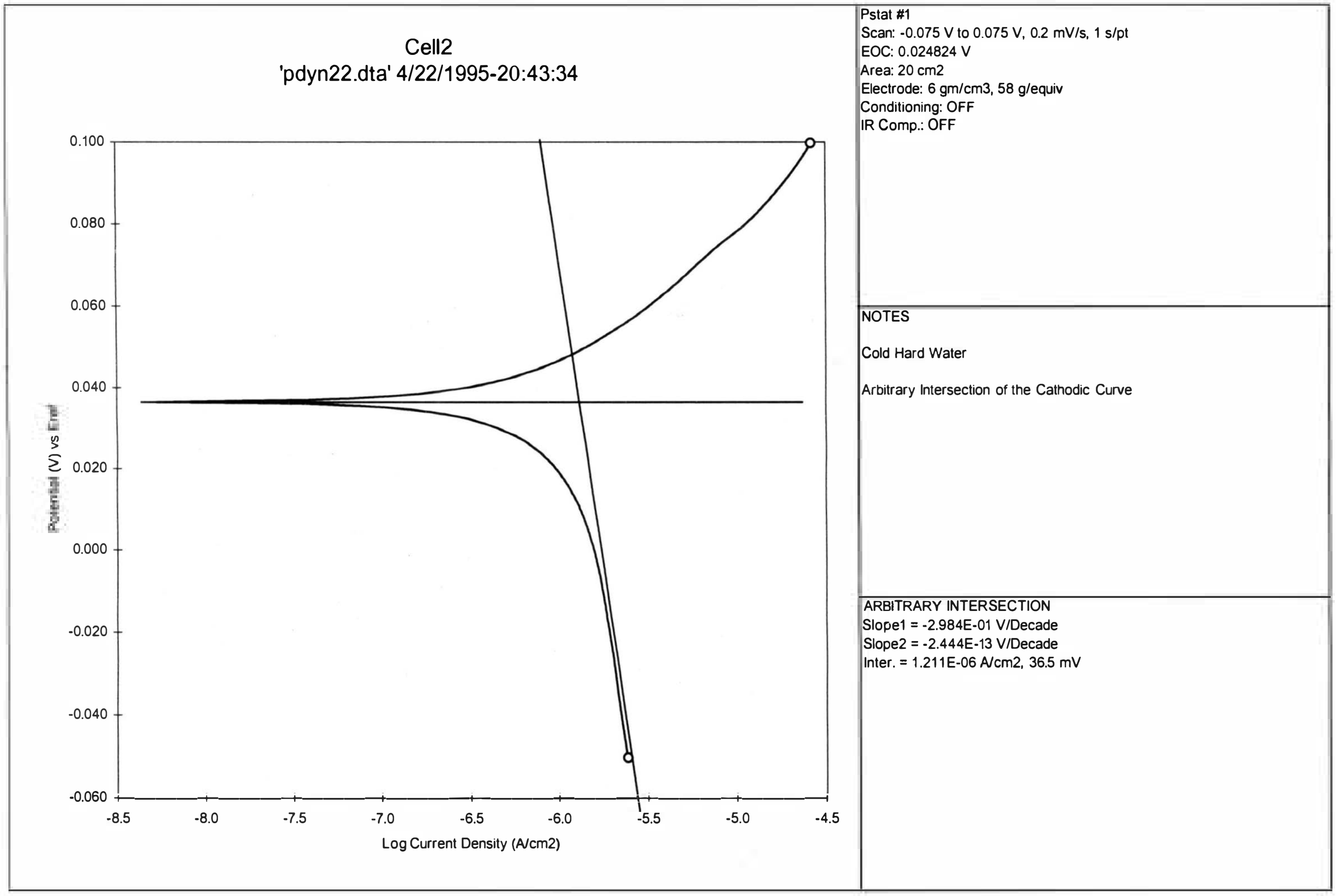
NOTES

Cold Hard Water

LOG Tafel Analysis

TAFEL RESULTS
Region = -50.3 mV to 99.8 mV
Ecorr = 36.0 mV
Icorr = 1.207E-06 A/cm2
BetaC = 287.9 mV/Decade
BetaA = 47.3 mV/Decade
Rp = 1.462E+04 Ohm cm2
CorrRate = 1.502 mpy

Figure A-7: Plot of Final Potentiodynamic Scan.



Cell2
'pdyn22.dta' 4/22/1995-20:43:34

Pstat #1
Scan: -0.075 V to 0.075 V, 0.2 mV/s, 1 s/pt
EOC: 0.024824 V
Area: 20 cm2
Electrode: 6 gm/cm3, 58 g/equiv
Conditioning: OFF
IR Comp.: OFF

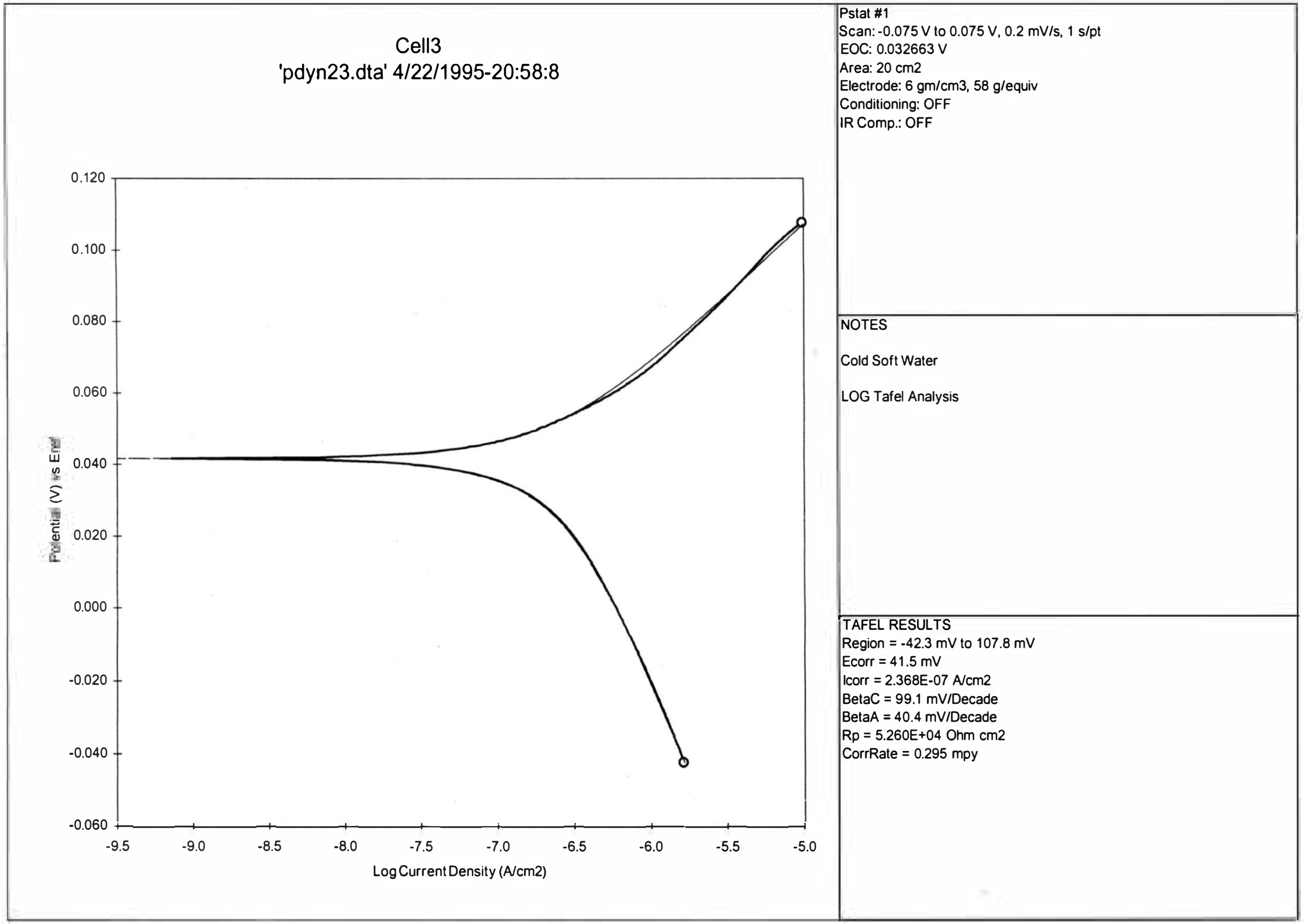
NOTES

Cold Hard Water

Arbitrary Intersection of the Cathodic Curve

ARBITRARY INTERSECTION
Slope1 = -2.984E-01 V/Decade
Slope2 = -2.444E-13 V/Decade
Inter. = 1.211E-06 A/cm2, 36.5 mV

Figure A-8: Final Potentiodynamic Scan.



Pstat #1
Scan: -0.075 V to 0.075 V, 0.2 mV/s, 1 s/pt
EOC: 0.032663 V
Area: 20 cm2
Electrode: 6 gm/cm3, 58 g/equiv
Conditioning: OFF
IR Comp.: OFF

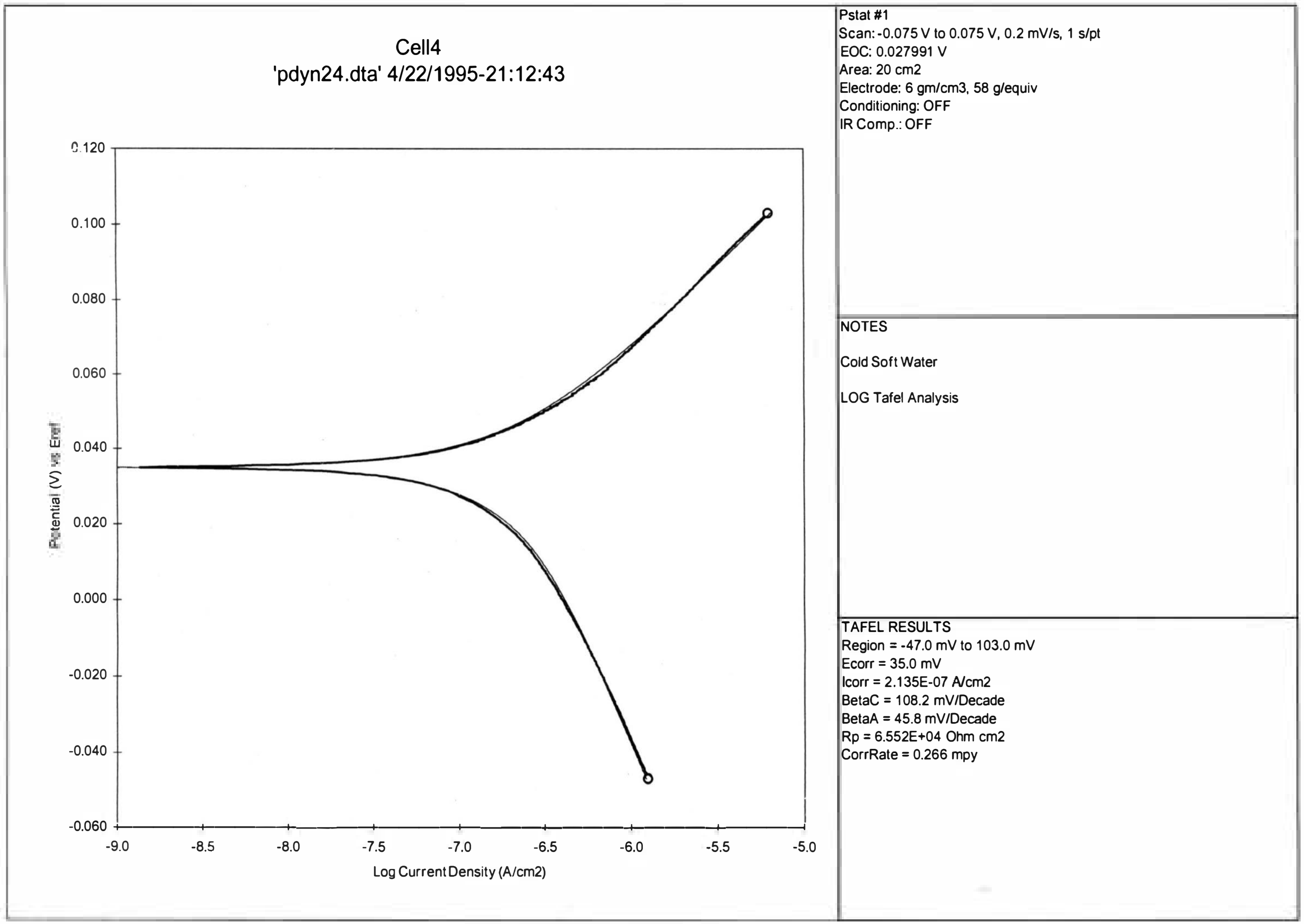
NOTES

Cold Soft Water

LOG Tafel Analysis

TAFEL RESULTS
Region = -42.3 mV to 107.8 mV
Ecorr = 41.5 mV
Icorr = 2.368E-07 A/cm2
BetaC = 99.1 mV/Decade
BetaA = 40.4 mV/Decade
Rp = 5.260E+04 Ohm cm2
CorrRate = 0.295 mpy

Figure A-9: Plot of Final Potentiodynamic Scan.


Cell4
'pdyn24.dta' 4/22/1995-21:12:43

Pstat #1
Scan: -0.075 V to 0.075 V, 0.2 mV/s, 1 s/pt
EOC: 0.027991 V
Area: 20 cm2
Electrode: 6 gm/cm3, 58 g/equiv
Conditioning: OFF
IR Comp.: OFF

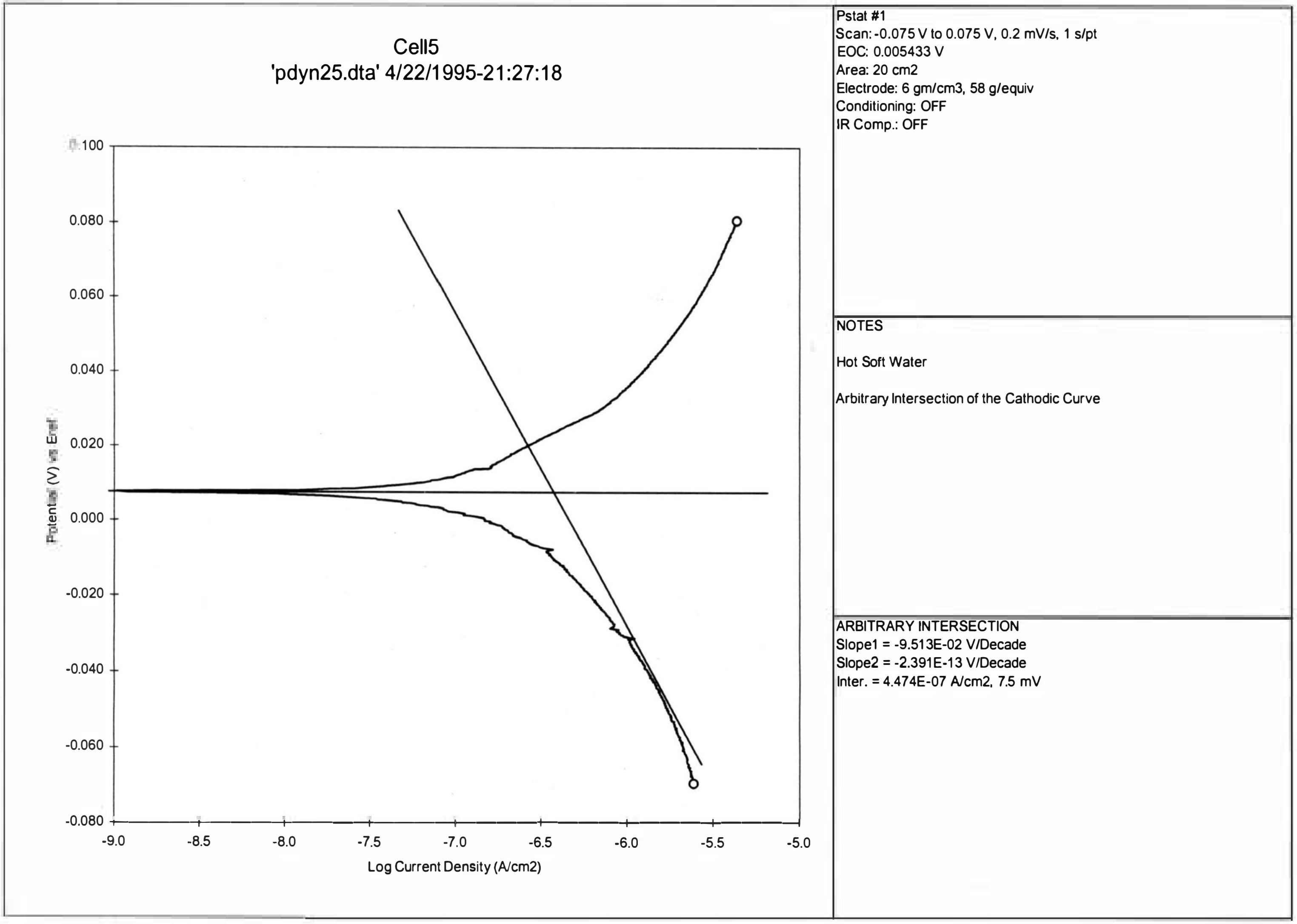
NOTES

Cold Soft Water

LOG Tafel Analysis

TAFEL RESULTS
Region = -47.0 mV to 103.0 mV
Ecorr = 35.0 mV
Icorr = 2.135E-07 A/cm2
BetaC = 108.2 mV/Decade
BetaA = 45.8 mV/Decade
Rp = 6.552E+04 Ohm cm2
CorrRate = 0.266 mpy

Figure A-10. Plot of Final Potentiodynamic Scan


Cell5
'pdyn25.dta' 4/22/1995-21:27:18

Pstat #1
Scan: -0.075 V to 0.075 V, 0.2 mV/s, 1 s/pt
EOC: 0.005433 V
Area: 20 cm2
Electrode: 6 gm/cm3, 58 g/equiv
Conditioning: OFF
IR Comp.: OFF

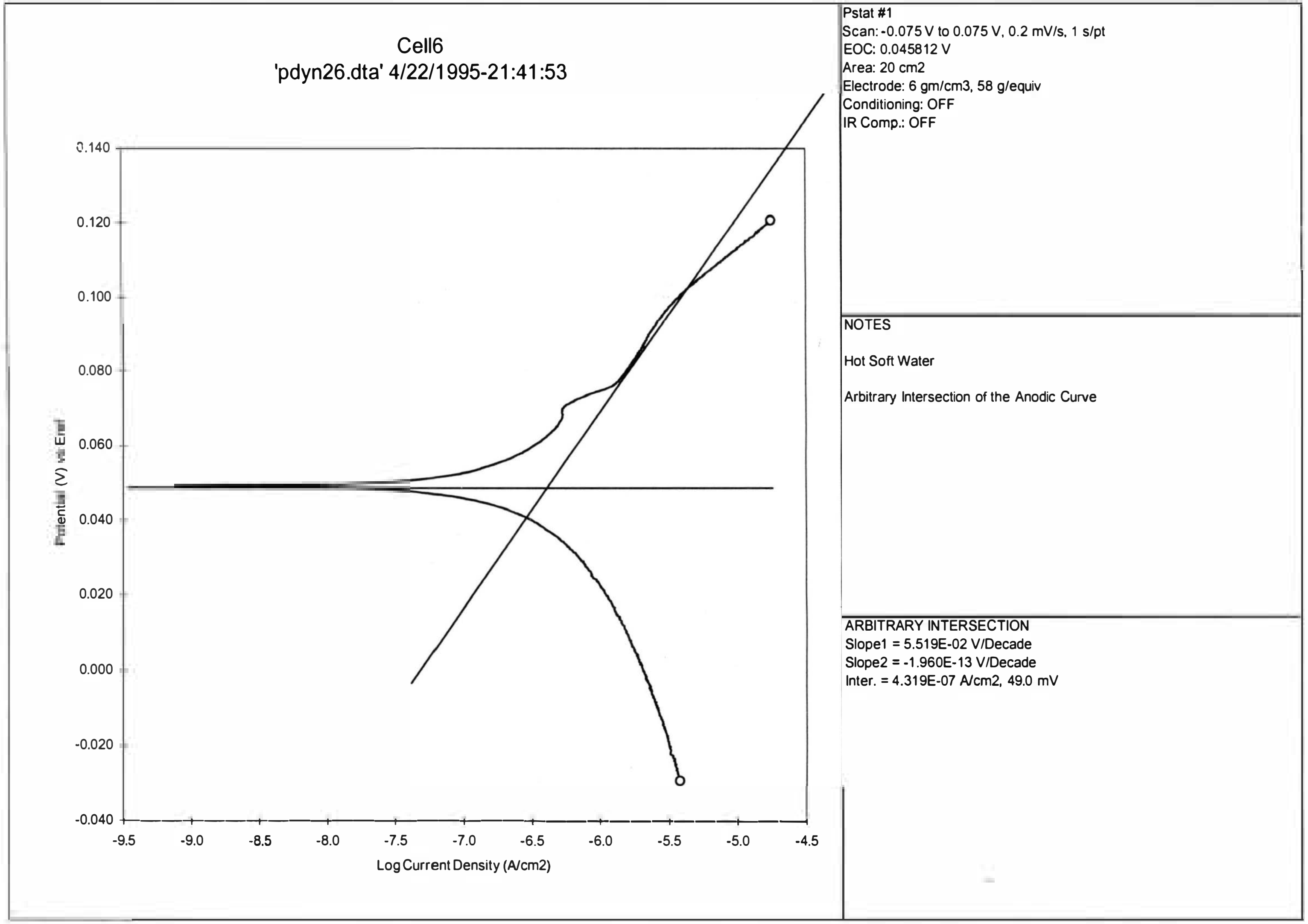
NOTES

Hot Soft Water

Arbitrary Intersection of the Cathodic Curve

ARBITRARY INTERSECTION
Slope1 = -9.513E-02 V/Decade
Slope2 = -2.391E-13 V/Decade
Inter. = 4.474E-07 A/cm2, 7.5 mV

Figure A-11. Plot of Final Potentiodynamic Scan



Pstat #1
Scan: -0.075 V to 0.075 V, 0.2 mV/s, 1 s/pt
EOC: 0.045812 V
Area: 20 cm2
Electrode: 6 gm/cm3, 58 g/equiv
Conditioning: OFF
IR Comp.: OFF

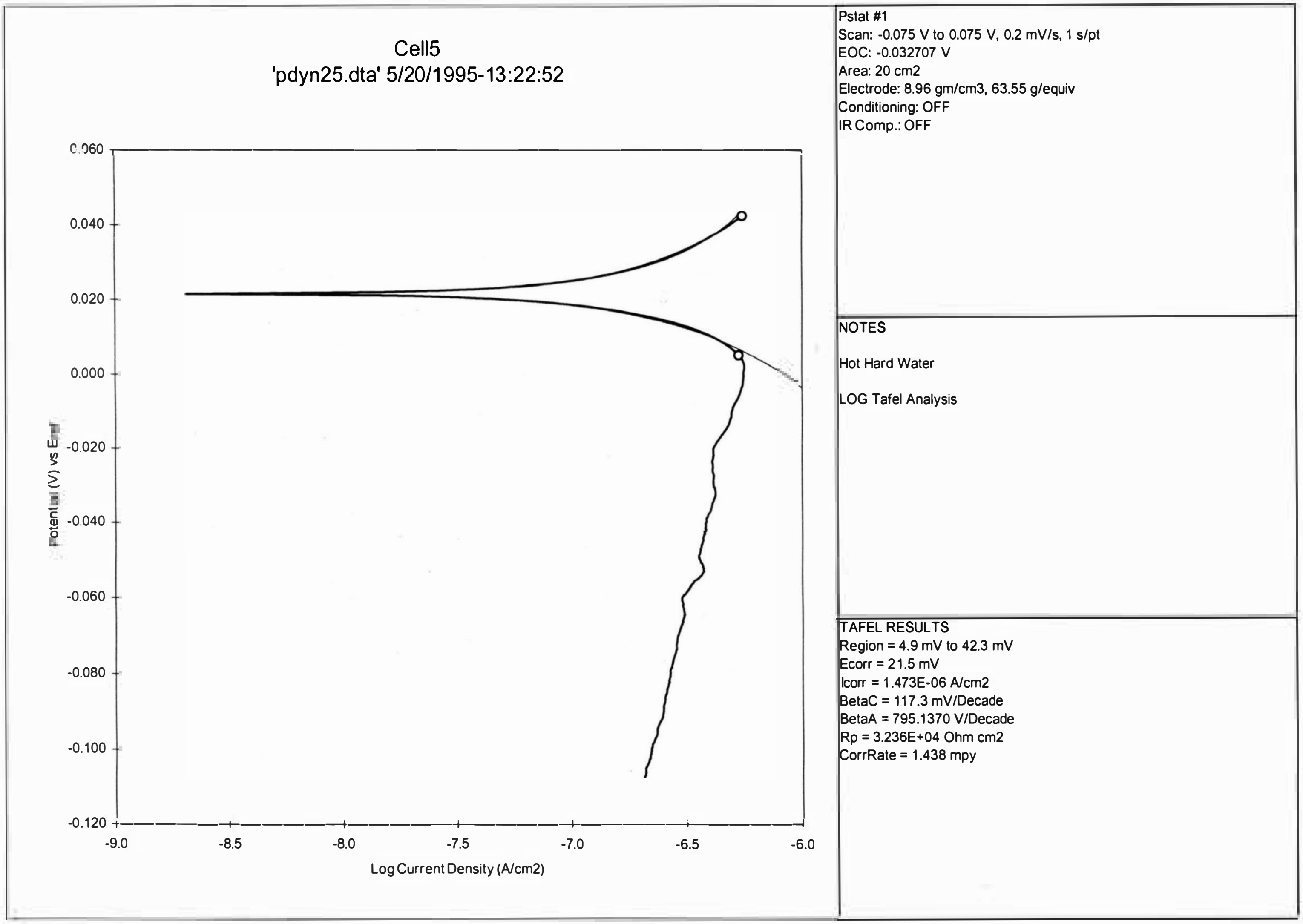
NOTES

Hot Soft Water

Arbitrary Intersection of the Anodic Curve

ARBITRARY INTERSECTION
Slope1 = 5.519E-02 V/Decade
Slope2 = -1.960E-13 V/Decade
Inter. = 4.319E-07 A/cm2, 49.0 mV

Figure A-12. Plot of Final Potentiodynamic Scan



Pstat #1
Scan: -0.075 V to 0.075 V, 0.2 mV/s, 1 s/pt
EOC: -0.032707 V
Area: 20 cm2
Electrode: 8.96 gm/cm3, 63.55 g/equiv
Conditioning: OFF
IR Comp.: OFF

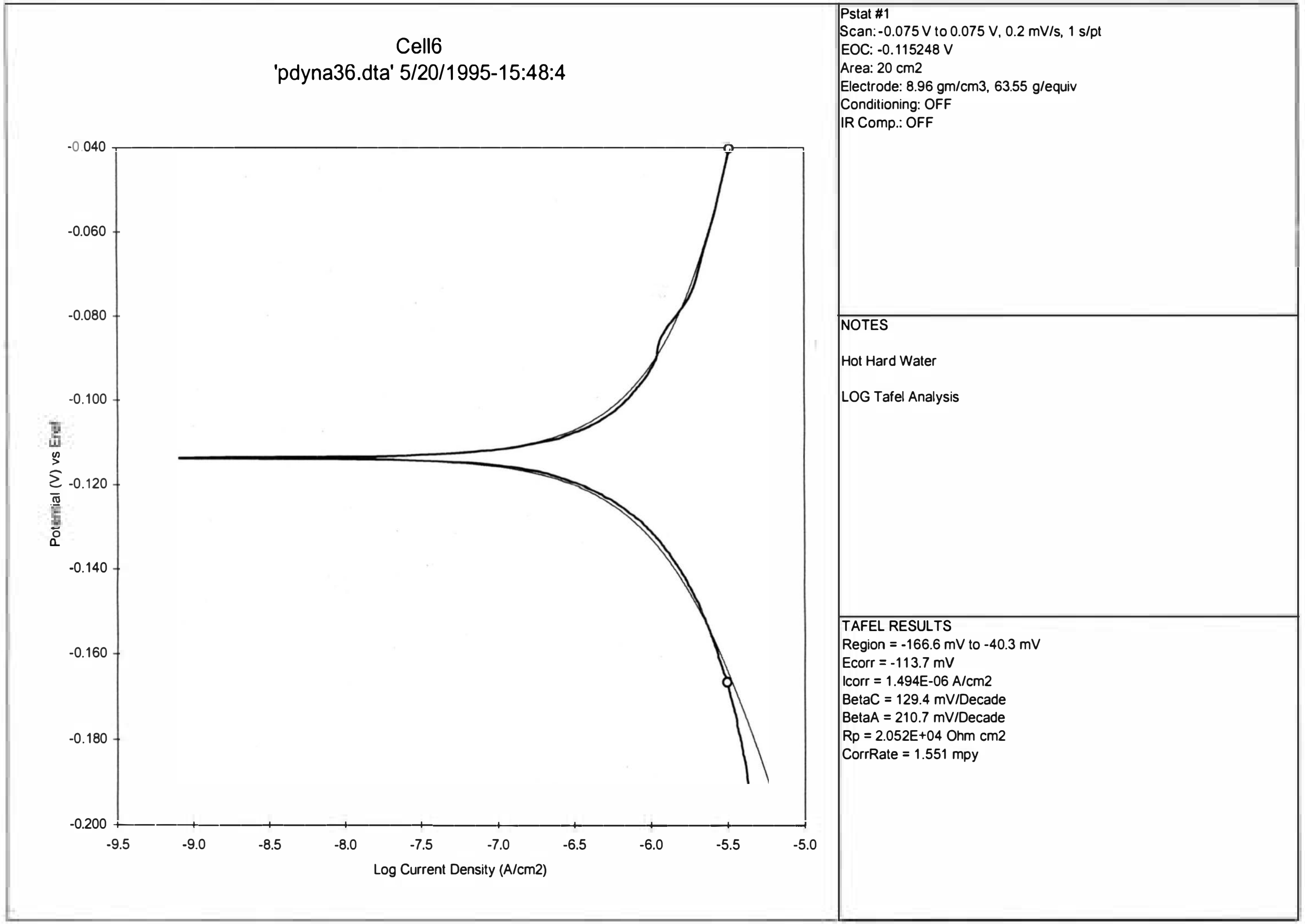
NOTES

Hot Hard Water

LOG Tafel Analysis

TAFEL RESULTS
Region = 4.9 mV to 42.3 mV
Ecorr = 21.5 mV
Icorr = 1.473E-06 A/cm2
BetaC = 117.3 mV/Decade
BetaA = 795.1370 V/Decade
Rp = 3.236E+04 Ohm cm2
CorrRate = 1.438 mpy

Figure A-13. Plot of Final Potentiodynamic Scan



Cell6
'pdyna36.dta' 5/20/1995-15:48:4

Pstat #1
Scan: -0.075 V to 0.075 V, 0.2 mV/s, 1 s/pt
EOC: -0.115248 V
Area: 20 cm2
Electrode: 8.96 gm/cm3, 63.55 g/equiv
Conditioning: OFF
IR Comp.: OFF

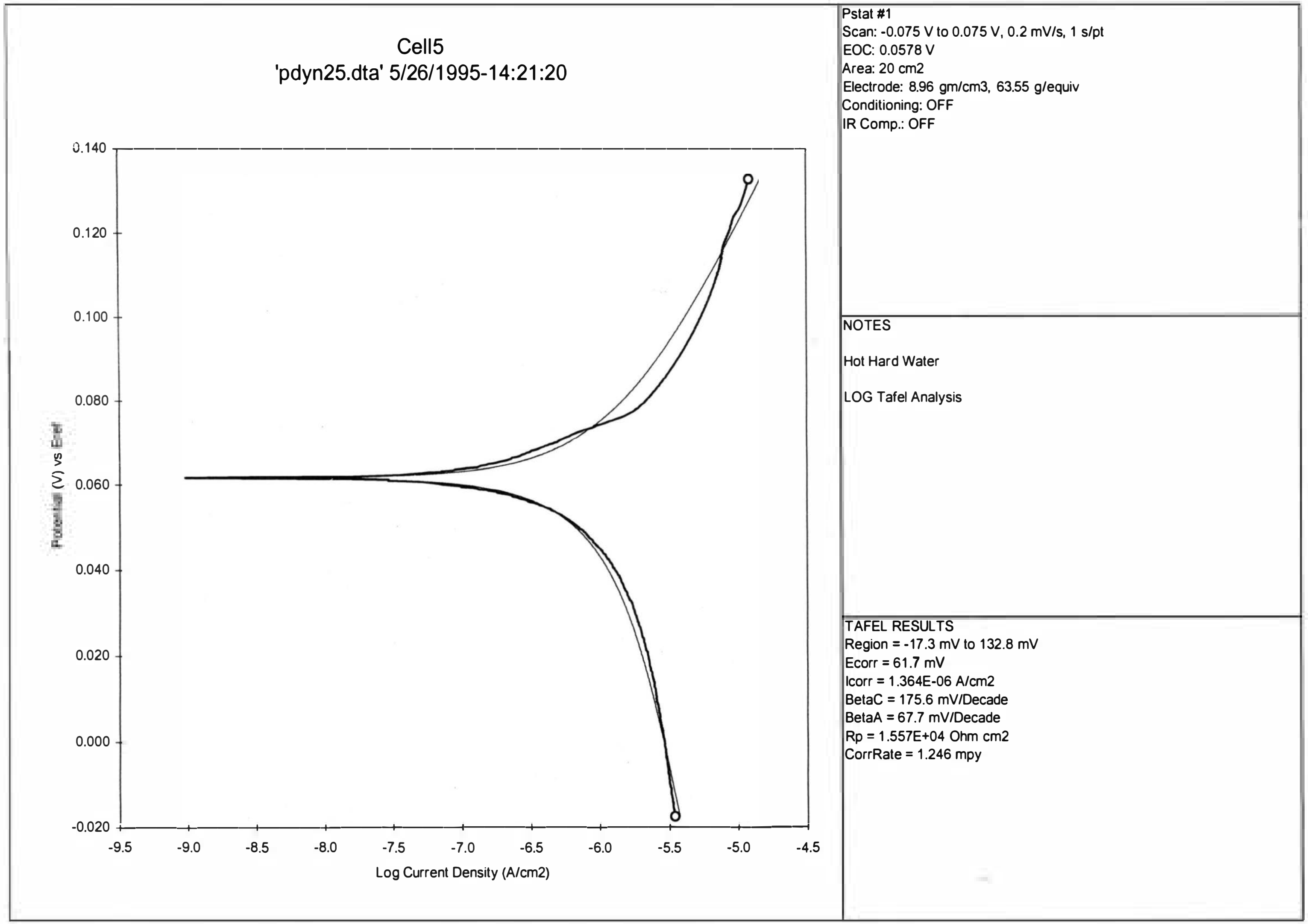
NOTES

Hot Hard Water

LOG Tafel Analysis

TAFEL RESULTS
Region = -166.6 mV to -40.3 mV
Ecorr = -113.7 mV
Icorr = 1.494E-06 A/cm2
BetaC = 129.4 mV/Decade
BetaA = 210.7 mV/Decade
Rp = 2.052E+04 Ohm cm2
CorrRate = 1.551 mpy

Figure A-14. Plot of Final Potentiodynamic Scan



Cell5
'pdyn25.dta' 5/26/1995-14:21:20

Pstat #1
Scan: -0.075 V to 0.075 V, 0.2 mV/s, 1 s/pt
EOC: 0.0578 V
Area: 20 cm2
Electrode: 8.96 gm/cm3, 63.55 g/equiv
Conditioning: OFF
IR Comp.: OFF

NOTES

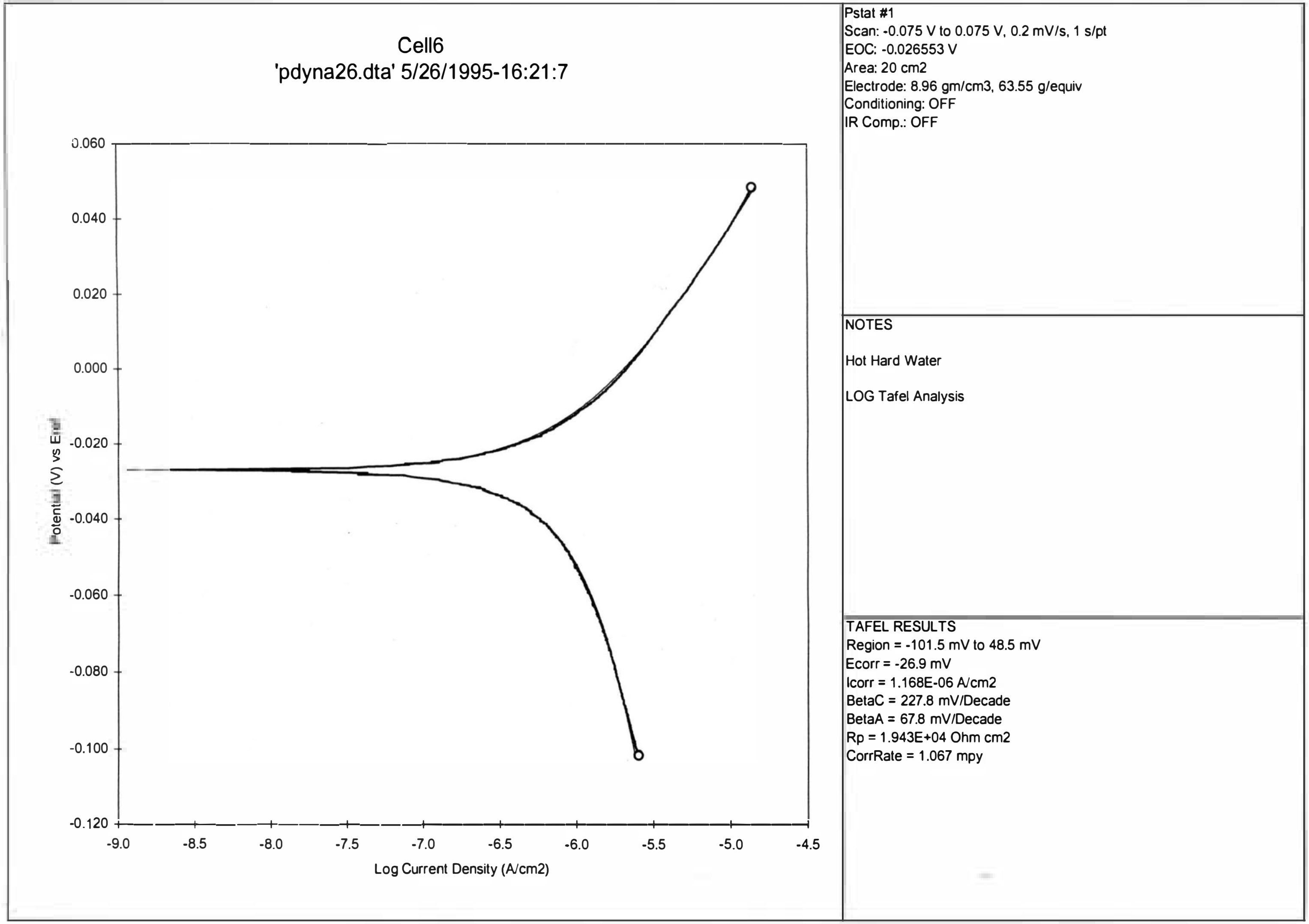
Hot Hard Water

LOG Tafel Analysis

TAFEL RESULTS
Region = -17.3 mV to 132.8 mV
Ecorr = 61.7 mV
Icorr = 1.364E-06 A/cm2
BetaC = 175.6 mV/Decade
BetaA = 67.7 mV/Decade
Rp = 1.557E+04 Ohm cm2
CorrRate = 1.246 mpy

Figure A-15. Plot of Final Potentiodynamic Scan

Cell6
'pdyna26.dta' 5/26/1995-16:21:7



Pstat #1
Scan: -0.075 V to 0.075 V, 0.2 mV/s, 1 s/pt
EOC: -0.026553 V
Area: 20 cm2
Electrode: 8.96 gm/cm3, 63.55 g/equiv
Conditioning: OFF
IR Comp.: OFF

NOTES

Hot Hard Water

LOG Tafel Analysis

TAFEL RESULTS
Region = -101.5 mV to 48.5 mV
Ecorr = -26.9 mV
Icorr = 1.168E-06 A/cm2
BetaC = 227.8 mV/Decade
BetaA = 67.8 mV/Decade
Rp = 1.943E+04 Ohm cm2
CorrRate = 1.067 mpy

Figure A-16. Plot of Final Potentiodynamic Scan

APPENDIX A, Continued.

STATISTICAL ANALYSIS OF ELECTROCHEMICAL TESTING

Table A-9: Statistical Comparison of Experimental Results from Electrochemical Testing Using Duncans New Multiple Range.

Completely Random Design

Treatment	Treatment Mean	Treatment Total	Replicate 1	Replicate 2	Replicate 3	Replicate 4	
Hot Hard	1.375	5.499	1.473	1.494	1.364	1.168	
Hot Soft	0.409	1.636	0.393	0.400	0.411	0.432	
Cold Soft	0.211	0.843	0.204	0.188	0.237	0.214	
Cold Hard	1.151	4.605	1.094	1.100	1.207	1.204	
Replicate Totals			3.164	3.182	3.219	3.018	12.583

r = 4
T = 4
n = 16

CF = 9.896
TSS = 3.893
TrtSS = 3.812
EES = 0.081

ANOVA

Source	df	SS	MS	F
Treatments	3	3.812	1.271	189.050
Error	12	0.081	0.007	
Total	15	3.893		

$F_{tab(3,12)\ 0.05}$ 3.49
$F_{tab(3,12)\ 0.01}$ 5.95

$S_x = 0.041$
$LSD_{.05} = 0.126$
$t_{(12)\ 0.05}$ 2.18
$t_{(12)\ 0.01}$ 3.06

$S_D = 0.058$
$LSD_{.01} = 0.177$

APPENDIX A, Continued.

Table A-9, Continued

Duncans Multiple Range

Means	2	3	4
$SSR_{.05}$	3.082	3.225	3.313
$SSR_{.01}$	4.320	4.504	4.622
$LSR_{.05}$	0.126	0.132	0.136
$LSR_{.01}$	0.177	0.185	0.189

Rank of Means

Cold Soft	Hot Soft	Cold Hard	Hot Hard
0.211	0.409	1.151	1.375

	# Means	Mean Difference	LSR		LSD	
			0.05	0.01	0.05	0.01
Largest - Smallest						
Hot Hard - Cold Soft	4	1.164	●	●	●	●
Cold Hard - Cold Soft	3	0.941	●	●	●	●
Hot Soft - Cold Soft	2	0.198	●	●	●	●
Largest - 2nd Smallest						
Hot Hard - Hot Soft	3	0.966	●	●	●	●
Cold Hard - Hot Soft	2	0.742	●	●	●	●
Largest - 2nd Largest						
Hot Hard - Cold Hard	2	0.224	●	●	●	●

APPENDIX A, Continued

Table A-10: Equilibrium System Calculations Electrochemical Corrosion Testing. (Cold Hard Water)

Water Analysis

		pH =	**8.12**	
Temp., C =	**12**	**Alkalinity =**	**164**	mg/l as $CaCO_3$
Temp., K =	285.15	**Alkalinity =**	0.00328	meq/l

		mg/l	**Mol. wt**	**mmol/l**	**meq/l**	z	cz^2
Cations	**Ca^{++}**	**87**	40.1	2.170	4.339	2	0.00868
	Mg^{++}	**39**	24.3	1.605	3.210	2	0.00642
	Na^{+}	**9**	23.0	0.391	0.391	1	0.00039
	K^{+}	**0**	39.1	0.000	0.000	1	0.00000
	Fe^{++}	**0**	55.8	0.000	0.000	2	0.00000
Anions	**HCO_3^-**	**0**	61.0	0.000	0.000	1	0.00000
	$CO_3^=$	**0**	60.0	0.000	0.000	2	0.00000
	Alk, $CaCO_3$	**164**	100.0	1.640	3.280	2	0.00656
	$SO_4^=$	**241**	96.1	2.508	5.016	2	0.01003
	Cl^-	**11**	35.5	0.310	0.310	1	0.00031
	NO_3^-	**0**	62.0	0.000	0.000	1	0.00000
	F^-	**0**	19.0	0.000	0.000	1	0.00000

Sum Cations = 7.94 meq/l   Sum cz^2 = 0.03239

Sum Anions = 8.61 meq/l

Total Hardness = 377 mg/l as $CaCO_3$ (Ca & Mg)

Ionic Strength Calculations

E	A	I	log g_m	log g_d	g_m	g_d
83.011	0.5011	0.0162	-0.0550	-0.2198	0.8811	0.6028

Equilibrium Constant Calculations

Water Equilibrium Calculations

(corrected for temperature and ionic strength)

K_1	K_2	K_w	K_s
4.62E-07	5.38E-11	4.12E-15	1.19E-08

$[H^+]$	$[OH^-]$
8.61E-09	4.79E-07

Acidity Calculations

p	s	t	Acidity, eq/l
1.0373	-4.70E-07	1.0125	0.00336

Buffer Intensity Calculations

a_1	equiv/unit pH.I
0.9757	0.00019

Carbonate System Calculations

Component	mol/l	mg/l as $CaCO_3$	meq/l
H_2CO_3	0.000060	6.039	0.121
HCO_3^-	0.003239	161.951	3.239
$CO_3^=$	0.000020	2.025	0.041

Langelier Index = 0.5722

CCPP = 13.373

APPENDIX A, Continued

Table A-11: Equilibrium System Calculations
Electrochemical Corrosion Testing.
(Cold Soft Water)

Water Analysis **pH =** **8.25**

Temp., C = **13** **Alkalinity =** **164** mg/l as $CaCO_3$

Temp., K = 286.15 **Alkalinity =** 0.00328 meq/l

		mg/l	Mol. wt	mmol/l	meq/l	z	cz^2
Cations	**Ca^{++}**	**1**	40.1	0.025	0.050	2	0.00010
	Mg^{++}	**0.1**	24.3	0.004	0.008	2	0.00002
	Na^+	**157**	23.0	6.826	6.826	1	0.00683
	K^+	**0**	39.1	0.000	0.000	1	0.00000
	Fe^{++}	**0**	55.8	0.000	0.000	2	0.00000
Anions	**HCO_3^-**	**0**	61.0	0.000	0.000	1	0.00000
	$CO_3^=$	**0**	60.0	0.000	0.000	2	0.00000
	Alk, $CaCO_3$	**164**	100.0	1.640	3.280	2	0.00656
	$SO_4^=$	**202**	96.1	2.102	4.204	2	0.00841
	Cl^-	**11**	35.5	0.310	0.310	1	0.00031
	NO_3^-	**0**	62.0	0.000	0.000	1	0.00000
	F^-	**0**	19.0	0.000	0.000	1	0.00000

Sum Cations = 6.88 meq/l Sum cz^2 = 0.02222

Sum Anions = 7.79 meq/l

Total Hardness = 3 mg/l as $CaCO_3$ (Ca & Mg)

Ionic Strength Calculations

E	A	I	log g_m	log g_d	g_m	g_d
82.633	0.5019	0.0111	-0.0467	-0.1870	0.8980	0.6502

Equilibrium Constant Calculations **Water Equilibrium Calculations**

(corrected for temperature and ionic strength)

K_1	K_2	K_w	K_s
4.54E-07	5.13E-11	4.33E-15	1.02E-08

$[H^+]$	$[OH^-]$
6.26E-09	6.92E-07

Acidity Calculations

p	s	t	Acidity, eq/l
1.0276	-6.85E-07	1.0164	0.00331

Buffer Intensity Calculations

a_1	equiv/unit pH.I
0.9785	0.00016

Carbonate System Calculations

Component	mol/l	mg/l as $CaCO_3$	meq/l
H_2CO_3	0.000045	4.452	0.089
HCO_3^-	0.003226	161.323	3.226
$CO_3^=$	0.000026	2.643	0.053

Langelier Index = -1.1815

CCPP = -9.233

APPENDIX A, Continued

Table A-12: Equilibrium System Calculations
Electrochemical Corrosion Testing.
(Hot Hard Water)

Water Analysis

		pH =	**8.16**
Temp., C =	**55**	**Alkalinity =**	**162** mg/l as $CaCO_3$
Temp., K =	328.15	**Alkalinity =**	0.00324 meq/l

		mg/l	Mol. wt	mmol/l	meq/l	z	cz^2
Cations	**Ca^{++}**	**75**	40.1	1.870	3.741	2	0.00748
	Mg^{++}	**44**	24.3	1.811	3.621	2	0.00724
	Na^+	**19**	23.0	0.826	0.826	1	0.00083
	K^+	**0**	39.1	0.000	0.000	1	0.00000
	Fe^{++}	**0**	55.8	0.000	0.000	2	0.00000
Anions	**HCO_3^-**	**0**	61.0	0.000	0.000	1	0.00000
	$CO_3^=$	**0**	60.0	0.000	0.000	2	0.00000
	Alk, $CaCO_3$	**162**	100.0	1.620	3.240	2	0.00648
	$SO_4^=$	**218**	96.1	2.268	4.537	2	0.00907
	Cl^-	**11**	35.5	0.310	0.310	1	0.00031
	NO_3^-	**0**	62.0	0.000	0.000	1	0.00000
	F^-	**0**	19.0	0.000	0.000	1	0.00000

Sum Cations = 8.19 meq/l Sum cz^2 = 0.03141
Sum Anions = 8.09 meq/l

Total Hardness = 368 mg/l as $CaCO_3$ (Ca & Mg)

Ionic Strength Calculations

E	A	I	log g_m	log g_d	g_m	g_d
68.300	0.5439	0.0157	-0.0589	-0.2355	0.8732	0.5815

Equilibrium Constant Calculations
(corrected for temperature and ionic strength)

K_1	K_2	K_w	K_s
6.71E-07	1.15E-10	8.80E-14	6.00E-09

Water Equilibrium Calculations

$[H^+]$	$[OH^-]$
7.92E-09	1.11E-05

Acidity Calculations

p	s	t	Acidity, eq/l
1.0236	-1.11E-05	1.0290	0.00320

Buffer Intensity Calculations

a_1	equiv/unit pH.l
0.9744	0.00022

Carbonate System Calculations

Component	mol/l	mg/l as $CaCO_3$	meq/l
H_2CO_3	0.000037	3.702	0.074
HCO_3^-	0.003138	156.890	3.138
$CO_3^=$	0.000046	4.555	0.091

Langelier Index = 1.1662
CCPP = 31.510

APPENDIX A, Continued

Table A-13: Equilibrium System Calculations Electrochemical Corrosion Testing. (Hot Soft Water)

Water Analysis

		pH =	**8.27**
Temp., C =	**56**	**Alkalinity =**	**165** mg/l as $CaCO_3$
Temp., K =	329.15	**Alkalinity =**	0.0033 meq/l

		mg/l	Mol. wt	mmol/l	meq/l	z	cz^2
Cations	**Ca^{++}**	**1**	40.1	0.025	0.050	2	0.00010
	Mg^{++}	**0.1**	24.3	0.004	0.008	2	0.00002
	Na^+	**167**	23.0	7.261	7.261	1	0.00726
	K^+	**0**	39.1	0.000	0.000	1	0.00000
	Fe^{++}	**0**	55.8	0.000	0.000	2	0.00000
Anions	**HCO_3^-**	**0**	61.0	0.000	0.000	1	0.00000
	$CO_3^=$	**0**	60.0	0.000	0.000	2	0.00000
	Alk, $CaCO_3$	**165**	100.0	1.650	3.300	2	0.00660
	$SO_4^=$	**196**	96.1	2.040	4.079	2	0.00816
	Cl^-	**12**	35.5	0.338	0.338	1	0.00034
	NO_3^-	**0**	62.0	0.000	0.000	1	0.00000
	F^-	**0**	19.0	0.000	0.000	1	0.00000

Sum Cations =	7.32 meq/l	Sum cz^2 =	0.02247
Sum Anions =	7.72 meq/l		

Total Hardness = 3 mg/l as $CaCO_3$ (Ca & Mg)

Ionic Strength Calculations

E	A	I	$\log g_m$	$\log g_d$	g_m	g_d
67.992	0.5451	0.0112	-0.0510	-0.2041	0.8892	0.6251

Equilibrium Constant Calculations

(corrected for temperature and ionic strength)

K_1	K_2	K_w	K_s
6.46E-07	1.08E-10	8.98E-14	5.05E-09

Water Equilibrium Calculations

$[H^+]$	$[OH^-]$
6.04E-09	1.49E-05

Acidity Calculations

p	s	t	Acidity, eq/l
1.0187	-1.49E-05	1.0357	0.00322

Buffer Intensity Calculations

a_1	equiv/unit pH.I
0.9735	0.00023

Carbonate System Calculations

Component	mol/l	mg/l as $CaCO_3$	meq/l
H_2CO_3	0.000030	2.967	0.059
HCO_3^-	0.003172	158.597	3.172
$CO_3^=$	0.000057	5.660	0.113

Langelier Index = -0.5365

CCPP = -3.805

APPENDIX A, Continued.

Table A-14: Visual Scale Observations for Electrochemical Testing.

Treatment	Reiber Cell #	Date	Visual Observations
Cold Hard	3	4/7/95	Uniform light yellow-brownish color
Cold Hard	4	4/7/95	Uniform light yellow-brownish color
Cold Hard	1	4/18/95	Uniform light yellow-brownish color
Cold Hard	2	4/18/95	Uniform light yellow-brownish color
Cold Soft	1	4/7/95	overlying a dark brown-reddish surface
Cold Soft	2	4/7/95	Uniform light yellow-brownish film overlying a dark brown-reddish surface
Cold Soft	3	4/18/95	Uniform light yellow-brownish film overlying a dark brown-reddish surface
Cold Soft	4	4/18/95	Uniform light yellow-brownish film overlying a dark brown-reddish surface
Hot Hard	5	5/16/95	Uniform light blue-greenish film over a tarnished brown background
Hot Hard	6	5/16/95	Uniform light blue-greenish film over a tarnished brown background
Hot Hard	5	5/22/95	Uniform light blue-greenish film over a tarnished brown background
Hot Hard	6	5/22/95	Uniform light blue-greenish film over a tarnished brown background
Hot Soft	5	4/7/95	Uniform yellow-blue precipitate overlying a dark brown-reddish surface
Hot Soft	6	4/7/95	Uniform yellow-blue precipitate overlying a dark brown-reddish surface
Hot Soft	5	4/18/95	Uniform yellow-blue precipitate overlying a dark brown-reddish surface
Hot Soft	6	4/18/95	Uniform yellow-blue precipitate overlying a dark brown-reddish surface

APPENDIX B

Table B-1: Soluble and Total Copper Concentrations after 3-day Intervals for By-product Release Testing.

Date	Soluble Copper			Total Copper			Date	Soluble Copper			Total Copper		
	Loop 1	Loop 2	Loop 3	Loop 1	Loop 2	Loop 3		Loop 4	Loop 5	Loop 6	Loop 4	Loop 5	Loop 6
9/30/95	0.292	0.495	0.786	0.403	0.806	0.903	1/16/96	1.527	0.9	0.908	1.627	0.99	1.052
10/03/95	0.296	0.460	0.601	0.344	0.626	0.710	1/19/96	0.802	1.304	0.819	0.867	1.393	0.933
10/06/95	0.254	0.405	0.668	0.309	0.527	0.766	1/22/96	0.711	1.37	0.873	0.792	1.467	0.966
10/09/95	0.488	0.412	0.708	0.523	0.515	0.815	1/25/96	0.863	1.458	0.943	0.959	1.617	1.056
10/12/95	0.281	0.383	0.434	0.332	0.539	0.539	1/28/96	1.115	1.114	1.312	1.209	1.222	1.312
10/15/95	0.484	0.522	0.656	0.538	0.661	0.785	1/31/96	1.195	1.226	1.354	1.285	1.313	1.419
10/18/95	0.516	0.475	0.676	0.555	0.651	0.765	2/03/96	0.817	1.115	0.923	0.897	1.181	1.000
10/21/95	0.341	0.367	0.439	0.400	0.542	0.528	2/06/96	1.451	1.356	1.346	1.568	1.462	1.439
10/24/95	0.387	0.449	0.473	0.426	0.533	0.573	2/09/96	1.442	1.535	0.986	1.545	1.632	1.357
10/27/95	0.394	0.436	0.466	0.440	0.642	0.555	2/12/96	0.983	1.922	0.893	1.057	2.005	0.941
10/30/95	0.462	0.377	0.573	0.506	0.522	0.671	2/15/96	1.353	1.189	1.240	1.416	1.313	1.305
11/02/95	0.381	0.431	0.498	0.441	0.548	0.608	2/18/96	0.532	0.805	0.512	0.617	0.966	0.576
11/05/95	0.372	0.420	0.474	0.435	0.716	0.586	2/21/96	1.293	0.774	1.118	1.357	0.899	1.200
11/08/95	0.380	0.460	0.497	0.438	0.664	0.593	2/24/96	0.541	1.074	0.540	0.644	1.154	0.642
11/11/95	0.367	0.454	0.512	0.443	0.803	0.648	2/27/96	1.238	1.084	1.131	1.299	1.170	1.189
11/14/95	0.389	0.537	0.495	0.437	0.723	0.609	3/01/96	1.298	1.093	1.198	1.348	1.132	1.312
11/17/95	0.398	0.488	0.546	0.459	0.716	0.652	3/04/96	0.742	1.194	0.747	0.830	1.228	0.813
11/20/95	0.389	0.469	0.573	0.461	0.700	0.694	3/07/96	0.824	1.042	0.775	0.889	1.121	0.818
11/23/95	0.304	0.451	0.600	0.363	0.786	0.557	3/10/96	1.155	0.867	1.035	1.204	0.958	1.098
11/26/95	0.328	0.510	0.582	0.384	0.690	0.727	3/13/96	1.212	1.020	1.030	1.293	1.055	1.109
11/29/95	0.343	0.626	0.648	0.396	0.774	0.827	3/16/96	0.905	1.057	0.825	1.006	1.133	0.933
Average	0.374	0.458	0.567	0.430	0.652	0.672	**Average**	1.048	1.167	0.977	1.129	1.258	1.070

Loop 1 - Hot Hard Water (Continuously Recirculated)

Loop 2 - Hot Soft Water (Continuously Recirculated)

Loop 3 - Hot Hard Water (Intermittently Recirculated)

Loop 4 - Cold Hard Water (Continuously Recirculated)

Loop 5 - Cold Soft Water (Continuously Recirculated)

Loop 6 - Cold Hard Water (Intermittently Recirculated)

APPENDIX B, Continued.

Table B-2: Temperature (°C) Data Collected During By-product Release Testing.

Date	Loop 1	Loop 2	Loop 3	Date	Loop 4	Loop 5	Loop 6
9/30/95	55	55	55	1/16/96	15	15	15
10/03/95	55	55	56	1/19/96	15	15	15
10/06/95	55	55	58	1/22/96	17	17	17
10/09/95	56	56	56	1/25/96	17	17	17
10/12/95	55	55	55	1/28/96	18	18	18
10/15/95	55	55	55	1/31/96	16	16	16
10/18/95	56	56	56	2/03/96	16	16	16
10/21/95	55	55	55	2/06/96	16	16	16
10/24/95	54	54	54	2/09/96	16	16	16
10/27/95	56	56	56	2/12/96	16	16	16
10/30/95	55	55	55	2/15/96	16	16	16
11/02/95	54	54	54	2/18/96	17	17	17
11/05/95	55	55	55	2/21/96	17	17	17
11/08/95	55	55	55	2/24/96	17	17	17
11/11/95	55	55	55	2/27/96	16	16	16
11/14/95	56	56	56	3/01/96	16	16	16
11/17/95	55	55	55	3/04/96	16	16	16
11/20/95	55	55	55	3/07/96	17	17	17
11/23/95	55	55	55	3/10/96	16	16	16
11/26/95	54	54	54	3/13/96	18	18	18
11/29/95	55	55	55	3/16/96	18	18	18
Average	55	55	55	**Average**	16	16	16

Loop 1 - Hot Hard Water (Continuously Recirculated)

Loop 2 - Hot Soft Water (Continuously Recirculated)

Loop 3 - Hot Hard Water (Intermittently Recirculated)

Loop 4 - Cold Hard Water (Continuously Recirculated)

Loop 5 - Cold Soft Water (Continuously Recirculated)

Loop 6 - Cold Hard Water (Intermittently Recirculated)

APPENDIX B, Continued.

Table B-3: pH Data Collected During By-product Release Testing.

Date	Hot Hard	Hot Soft	Date	Loop 1	Loop 2	Loop 3	Date	Cold Hard	Cold Soft	Date	Loop 4	Loop 5	Loop 6
9/27/95	7.92	8.17	9/30/95	8.71	8.61	8.26	1/13/96	8.10	8.46	1/16/96	8.29	8.57	8.27
9/30/95	7.93	8.18	10/03/95	8.54	8.35	8.28	1/16/96	8.21	8.35	1/19/96	8.37	8.16	8.21
10/03/95	7.91	8.18	10/06/95	8.76	8.73	8.30	1/19/96	8.14	8.22	1/22/96	8.36	8.35	8.20
10/06/95	8.05	8.16	10/09/95	8.25	8.50	8.25	1/22/96	8.12	8.14	1/25/96	8.33	8.27	8.17
10/09/95	8.02	8.31	10/12/95	8.43	8.44	8.37	1/25/96	8.04	8.45	1/28/96	8.31	8.50	8.12
10/12/95	7.97	8.41	10/15/95	8.28	8.46	8.36	1/28/96	8.02	8.35	1/31/96	8.32	8.41	8.09
10/15/95	7.94	8.29	10/18/95	8.18	8.38	8.22	1/31/96	8.20	8.24	2/03/96	8.37	8.18	8.20
10/18/95	8.02	8.39	10/21/95	8.30	8.48	8.36	2/03/96	8.00	8.18	2/06/96	8.05	8.27	8.05
10/21/95	7.94	8.27	10/24/95	8.25	8.38	8.26	2/06/96	7.98	8.10	2/09/96	8.10	8.24	8.02
10/24/95	7.90	8.23	10/27/95	8.31	8.55	8.42	2/09/96	8.23	8.04	2/12/96	8.24	8.25	8.20
10/27/95	7.91	8.43	10/30/95	8.28	8.56	8.32	2/12/96	8.06	8.46	2/15/96	8.08	8.39	8.04
10/30/95	7.97	8.32	11/02/95	8.23	8.42	8.25	2/15/96	8.45	8.36	2/18/96	8.44	8.43	8.39
11/02/95	8.02	8.21	11/05/95	8.26	8.39	8.32	2/18/96	8.02	8.34	2/21/96	8.14	8.54	8.09
11/05/95	8.02	8.32	11/08/95	8.23	8.32	8.27	2/21/96	8.36	8.24	2/24/96	8.39	8.37	8.31
11/08/95	7.96	8.13	11/11/95	8.25	8.32	8.24	2/24/96	8.13	8.14	2/27/96	8.12	8.25	8.08
11/11/95	7.91	8.44	11/14/95	8.18	8.53	8.25	2/27/96	8.02	8.13	3/01/96	8.10	8.22	8.04
11/14/95	7.90	8.28	11/17/95	8.23	8.48	8.24	3/01/96	8.24	8.06	3/04/96	8.24	8.17	8.14
11/17/95	8.09	8.24	11/20/95	8.23	8.40	8.26	3/04/96	8.24	8.06	3/07/96	8.18	8.20	8.13
11/20/95	8.00	8.18	11/23/95	8.25	8.26	8.25	3/07/96	8.04	8.28	3/10/96	8.14	8.38	8.12
11/23/95	7.92	8.17	11/26/95	8.26	8.37	8.18	3/10/96	8.12	8.24	3/13/96	8.14	8.35	8.10
11/26/95	7.90	8.14	11/29/95	8.23	8.32	8.14	3/13/96	8.22	8.10	3/16/96	8.22	8.21	8.14
Average	7.96	8.26	**Average**	8.32	8.44	8.28	**Average**	8.14	8.24	**Average**	8.23	8.32	8.15

Loop 1 - Hot Hard Water (Continuously Recirculated)

Loop 2 - Hot Soft Water (Continuously Recirculated)

Loop 3 - Hot Hard Water (Intermittently Recirculated)

Loop 4 - Cold Hard Water (Continuously Recirculated)

Loop 5 - Cold Soft Water (Continuously Recirculated)

Loop 6 - Cold Hard Water (Intermittently Recirculated)

APPENDIX B, Continued.

Table B-4: Alkalinity (mg/L as $CaCO_3$) Data Collected During By-product Release Testing.

Date	Hot Hard	Hot Soft	Date	Loop 1	Loop 2	Loop 3	Date	Cold Hard	Cold Soft	Date	Loop 4	Loop 5	Loop 6
9/27/95	177	168	9/30/95	197	194	196	1/13/96	212	206	1/16/96	221	202	216
9/30/95	187	192	10/03/95	182	168	186	1/16/96	162	204	1/19/96	161	203	168
10/03/95	191	201	10/06/95	203	203	196	1/19/96	164	186	1/22/96	166	192	170
10/06/95	170	172	10/09/95	196	192	200	1/22/96	166	184	1/25/96	164	174	160
10/09/95	166	160	10/12/95	160	177	162	1/25/96	184	186	1/28/96	186	190	186
10/12/95	219	204	10/15/95	196	198	196	1/28/96	190	186	1/31/96	193	190	192
10/15/95	192	178	10/18/95	198	176	182	1/31/96	164	180	2/03/96	168	188	168
10/18/95	168	160	10/21/95	160	158	156	2/03/96	190	178	2/06/96	190	180	192
10/21/95	154	172	10/24/95	150	180	160	2/06/96	190	188	2/09/96	196	190	194
10/24/95	168	182	10/27/95	174	184	172	2/09/96	158	190	2/12/96	164	194	164
10/27/95	168	166	10/30/95	168	164	172	2/12/96	186	190	2/15/96	186	190	186
10/30/95	160	166	11/02/95	166	162	158	2/15/96	158	156	2/18/96	156	166	156
11/02/95	156	162	11/05/95	160	162	162	2/18/96	190	180	2/21/96	190	182	190
11/05/95	164	166	11/08/95	166	164	160	2/21/96	156	178	2/24/96	156	190	162
11/08/95	158	158	11/11/95	168	166	166	2/24/96	190	192	2/27/96	190	192	190
11/11/95	162	180	11/14/95	167	182	164	2/27/96	186	184	3/01/96	190	190	186
11/14/95	168	184	11/17/95	166	188	166	3/01/96	164	186	3/04/96	164	192	158
11/17/95	162	164	11/20/95	162	169	169	3/04/96	156	184	3/07/96	166	188	166
11/20/95	158	160	11/23/95	156	166	162	3/07/96	194	194	3/10/96	186	186	190
11/23/95	174	184	11/26/95	158	178	170	3/10/96	194	190	3/13/96	198	196	196
11/26/95	166	180	11/29/95	168	186	168	3/13/96	158	166	3/16/96	156	180	164
Average	171	174	**Average**	172	177	173	**Average**	177	185	**Average**	178	188	179

Loop 1 - Hot Hard Water (Continuously Recirculated)

Loop 2 - Hot Soft Water (Continuously Recirculated)

Loop 3 - Hot Hard Water (Intermittently Recirculated)

Loop 4 - Cold Hard Water (Continuously Recirculated)

Loop 5 - Cold Soft Water (Continuously Recirculated)

Loop 6 - Cold Hard Water (Intermittently Recirculated)

APPENDIX B, Continued.

Table B-5: Calcium (mg/L) Data Collected During By-product Release Testing.

Date	Hot Hard	Hot Soft	Date	Loop 1	Loop 2	Loop 3	Date	Cold Hard	Cold Soft	Date	Loop 4	Loop 5	Loop 6
9/27/95	82.7	0.4	9/30/95	72.2	0.7	75.1	1/13/96	76.9	0.14	1/16/96	73.9	0.2	76.0
9/30/95	83.2	0.3	10/03/95	88.5	0.7	84.2	1/16/96	87.0	0.14	1/19/96	78.5	0.5	78.4
10/03/95	75.1	1.0	10/06/95	77.5	0.9	76.1	1/19/96	78.4	0.12	1/22/96	79.1	0.8	79.5
10/06/95	75.2	1.4	10/09/95	75.0	1.4	75.1	1/22/96	79.3	0.12	1/25/96	76.6	13.6	88.1
10/09/95	84.1	0.8	10/12/95	85.4	0.9	84.0	1/25/96	70.5	0.12	1/28/96	73.7	0.8	70.9
10/12/95	77.0	0.7	10/15/95	76.1	0.7	76.0	1/28/96	83.2	0.14	1/31/96	73.0	0.2	74.2
10/15/95	76.3	1.3	10/18/95	75.8	1.3	75.7	1/31/96	80.9	0.13	2/03/96	81.7	0.6	81.5
10/18/95	85.3	1.2	10/21/95	85.8	1.2	82.5	2/03/96	76.5	0.14	2/06/96	78.5	4.1	82.4
10/21/95	81.0	2.4	10/24/95	82.8	2.3	82.7	2/06/96	74.2	0.12	2/09/96	77.3	2.5	72.4
10/24/95	71.5	0.9	10/27/95	70.8	0.9	71.0	2/09/96	81.4	0.14	2/12/96	82.5	0.2	81.6
10/27/95	81.2	0.3	10/30/95	69.5	0.4	69.5	2/12/96	78.1	0.24	2/15/96	74.6	0.5	81.1
10/30/95	88.6	0.3	11/02/95	87.1	0.3	91.6	2/15/96	84.2	0.23	2/18/96	81.6	0.3	81.6
11/02/95	87.2	0.3	11/05/95	84.6	0.5	93.7	2/18/96	72.6	0.22	2/21/96	71.6	0.2	72.0
11/05/95	89.4	0.4	11/08/95	93.8	0.4	90.0	2/21/96	91.6	0.21	2/24/96	83.2	0.2	84.1
11/08/95	92.2	0.4	11/11/95	89.0	0.5	94.5	2/24/96	69.8	0.18	2/27/96	72.6	0.2	71.7
11/11/95	92.9	0.3	11/14/95	91.9	0.3	98.2	2/27/96	81.6	0.59	3/01/96	90.9	0.6	71.8
11/14/95	82.0	0.2	11/17/95	87.7	0.3	83.7	3/01/96	106.8	0.44	3/04/96	82.5	0.7	84.7
11/17/95	85.0	0.3	11/20/95	87.1	0.3	81.0	3/04/96	86.9	0.50	3/07/96	79.4	0.5	80.6
11/20/95	87.2	0.3	11/23/95	87.8	0.3	87.3	3/07/96	73.3	0.42	3/10/96	72.3	1.3	73.0
11/23/95	79.3	0.2	11/26/95	80.0	0.2	80.4	3/10/96	73.1	0.42	3/13/96	72.3	0.4	74.1
11/26/95	76.2	0.2	11/29/95	76.0	0.2	76.6	3/13/96	93.7	0.45	3/16/96	93.0	0.5	82.0
Average	82.5	0.6	Average	82.1	0.7	82.3	Average	81.0	0.25	Average	78.5	1.4	78.2

Loop 1 - Hot Hard Water (Continuously Recirculated)

Loop 2 - Hot Soft Water (Continuously Recirculated)

Loop 3 - Hot Hard Water (Intermittently Recirculated)

Loop 4 - Cold Hard Water (Continuously Recirculated)

Loop 5 - Cold Soft Water (Continuously Recirculated)

Loop 6 - Cold Hard Water (Intermittently Recirculated)

APPENDIX B, Continued.

Table B-6: Magnesium (mg/L) Data Collected During By-product Release Testing.

Date	Hot Hard	Hot Soft	Date	Loop 1	Loop 2	Loop 3	Date	Cold Hard	Cold Soft	Date	Loop 4	Loop 5	Loop 6
9/27/95	41.5	0.12	9/30/95	38.9	0.21	38.1	1/13/96	37.0	0.05	1/16/96	35.8	0.06	34.8
9/30/95	38.4	0.09	10/03/95	44.5	0.77	44.2	1/16/96	37.5	0.05	1/19/96	41.4	0.27	44.5
10/03/95	39.1	0.66	10/06/95	38.7	0.69	37.9	1/19/96	44.3	0.05	1/22/96	43.5	0.38	42.4
10/06/95	47.9	0.74	10/09/95	38.4	0.65	38.4	1/22/96	42.9	0.04	1/25/96	42.5	7.62	39.3
10/09/95	47.0	0.68	10/12/95	48.7	0.67	49.2	1/25/96	35.4	0.04	1/28/96	34.9	0.39	37.1
10/12/95	38.1	0.36	10/15/95	38.3	0.38	37.9	1/28/96	32.2	0.04	1/31/96	34.9	0.05	34.8
10/15/95	37.3	0.90	10/18/95	38.1	0.89	37.9	1/31/96	42.7	0.04	2/03/96	41.9	0.36	42.0
10/18/95	49.1	0.75	10/21/95	47.5	0.78	47.5	2/03/96	34.2	0.04	2/06/96	32.8	2.33	32.7
10/21/95	47.1	1.69	10/24/95	47.8	1.68	47.0	2/06/96	34.7	0.03	2/09/96	33.8	1.30	37.3
10/24/95	37.4	0.46	10/27/95	38.9	0.47	38.6	2/09/96	42.3	0.03	2/12/96	42.1	0.07	42.7
10/27/95	42.1	0.20	10/30/95	36.9	0.18	37.5	2/12/96	33.1	0.08	2/15/96	35.0	0.15	32.9
10/30/95	46.4	0.13	11/02/95	46.2	0.14	46.5	2/15/96	42.6	0.04	2/18/96	42.8	0.06	43.7
11/02/95	47.1	0.13	11/05/95	45.0	0.17	44.6	2/18/96	35.5	0.03	2/21/96	36.8	0.05	36.7
11/05/95	45.6	0.13	11/08/95	47.8	0.15	47.5	2/21/96	40.4	0.04	2/24/96	44.9	0.04	44.5
11/08/95	46.0	0.13	11/11/95	48.8	0.14	49.7	2/24/96	35.6	0.03	2/27/96	36.6	0.54	35.8
11/11/95	46.2	0.09	11/14/95	46.6	0.09	46.7	2/27/96	32.1	0.03	3/01/96	32.7	0.52	37.3
11/14/95	42.2	0.07	11/17/95	46.6	0.08	45.4	3/01/96	46.5	0.21	3/04/96	47.0	0.36	46.7
11/17/95	49.4	0.11	11/20/95	41.5	0.10	44.7	3/04/96	43.3	0.19	3/07/96	43.4	0.25	45.6
11/20/95	48.8	0.12	11/23/95	46.8	0.12	47.0	3/07/96	37.0	0.21	3/10/96	37.1	0.66	37.6
11/23/95	41.3	0.07	11/26/95	42.5	0.08	42.4	3/10/96	36.4	0.21	3/13/96	36.4	0.23	36.1
11/26/95	39.4	0.07	11/29/95	40.0	0.08	39.5	3/13/96	36.7	0.26	3/16/96	40.6	0.28	44.3
Average	43.69	0.37	**Average**	43.26	0.41	43.25	**Average**	38.2	0.08	**Average**	38.9	0.76	39.5

Loop 1 - Hot Hard Water (Continuously Recirculated)

Loop 2 - Hot Soft Water (Continuously Recirculated)

Loop 3 - Hot Hard Water (Intermittently Recirculated)

Loop 4 - Cold Hard Water (Continuously Recirculated)

Loop 5 - Cold Soft Water (Continuously Recirculated)

Loop 6 - Cold Hard Water (Intermittently Recirculated)

APPENDIX B, Continued.

Table B-7: Sodium (mg/L) Data Collected During By-product Release Testing.

Date	Hot Hard	Hot Soft	Date	Loop 1	Loop 2	Loop 3	Date	Cold Hard	Cold Soft	Date	Loop 4	Loop 5	Loop 6
9/27/95	13.5	168.2	9/30/95	13.6	166.5	13.4	1/13/96	14.44	184.0	1/16/96	13.6	162.7	12.9
9/30/95	15.6	168.7	10/03/95	21.0	202.9	20.5	1/16/96	23.16	165.8	1/19/96	22.0	13.0	21.1
10/03/95	14.4	164.9	10/06/95	14.7	168.3	14.6	1/19/96	22.97	171.4	1/22/96	22.6	174.0	22.6
10/06/95	21.9	202.4	10/09/95	14.6	191.3	14.7	1/22/96	22.09	167.9	1/25/96	20.5	152.6	21.5
10/09/95	22.7	204.8	10/12/95	22.5	204.4	22.4	1/25/96	13.66	156.6	1/28/96	13.8	169.5	13.8
10/12/95	13.7	165.9	10/15/95	13.8	166.5	13.7	1/28/96	13.63	164.7	1/31/96	13.7	167.6	13.5
10/15/95	13.7	152.0	10/18/95	13.8	151.0	13.7	1/31/96	21.93	176.1	2/03/96	21.6	49.2	22.1
10/18/95	22.2	201.0	10/21/95	21.4	198.2	21.3	2/03/96	13.27	166.9	2/06/96	13.0	173.5	13.5
10/21/95	20.9	148.5	10/24/95	20.9	148.1	20.8	2/06/96	13.60	166.0	2/09/96	14.5	162.5	14.3
10/24/95	14.3	154.0	10/27/95	14.3	154.0	14.4	2/09/96	22.02	168.4	2/12/96	21.3	171.9	22.1
10/27/95	20.3	216.7	10/30/95	13.7	213.9	13.9	2/12/96	14.37	160.8	2/15/96	13.9	168.5	14.1
10/30/95	22.0	205.0	11/02/95	21.8	204.2	21.7	2/15/96	24.57	189.1	2/18/96	23.2	183.4	24.0
11/02/95	22.9	208.7	11/05/95	22.9	205.4	22.9	2/18/96	13.66	172.1	2/21/96	14.1	169.7	13.7
11/05/95	22.9	208.6	11/08/95	22.9	209.4	23.1	2/21/96	22.78	181.4	2/24/96	22.7	168.3	22.0
11/08/95	22.9	208.3	11/11/95	23.0	208.8	22.9	2/24/96	13.56	153.6	2/27/96	13.7	157.2	13.9
11/11/95	22.5	159.8	11/14/95	22.7	159.9	22.8	2/27/96	13.87	157.1	3/01/96	14.3	161.4	14.1
11/14/95	19.9	155.8	11/17/95	21.8	158.7	21.9	3/01/96	21.62	163.8	3/04/96	24.3	172.5	24.5
11/17/95	22.5	195.2	11/20/95	20.4	189.8	20.4	3/04/96	23.83	176.3	3/07/96	22.0	173.1	23.1
11/20/95	22.8	200.2	11/23/95	22.7	209.5	22.9	3/07/96	16.32	176.3	3/10/96	15.7	177.6	15.7
11/23/95	18.8	163.9	11/26/95	19.2	166.7	19.6	3/10/96	14.83	170.7	3/13/96	15.4	178.7	15.5
11/26/95	16.9	158.6	11/29/95	17.6	166.9	17.6	3/13/96	24.61	196.3	3/16/96	23.9	193.4	24.2
Average	19.4	181.5	**Average**	19.0	183.1	19.0	**Average**	18.32	170.7	**Average**	18.1	157.2	18.2

Loop 1 - Hot Hard Water (Continuously Recirculated)

Loop 2 - Hot Soft Water (Continuously Recirculated)

Loop 3 - Hot Hard Water (Intermittently Recirculated)

Loop 4 - Cold Hard Water (Continuously Recirculated)

Loop 5 - Cold Soft Water (Continuously Recirculated)

Loop 6 - Cold Hard Water (Intermittently Recirculated)

APPENDIX B, Continued.

Table B-8: Chloride (mg/L) Data Collected During By-product Release Testing.

Date	Hot Hard	Hot Soft	Date	Loop 1	Loop 2	Loop 3	Date	Cold Hard	Cold Soft	Date	Loop 4	Loop 5	Loop 6
9/27/95	11.6	11.4	9/30/95	12.6	12.3	12.8	1/13/96	12.6	12.2	1/16/96	12.7	12.4	12.6
9/30/95	11.6	11.4	10/03/95	12.1	11.2	11.9	1/16/96	12.8	12.4	1/19/96	13.0	12.6	12.7
10/03/95	11.9	12.1	10/06/95	11.5	11.4	11.5	1/19/96	13.6	12.4	1/22/96	13.5	13.0	13.3
10/06/95	11.3	10.7	10/09/95	11.8	11.5	11.7	1/22/96	13.3	12.0	1/25/96	13.3	13.5	13.4
10/09/95	10.9	10.9	10/12/95	11.5	11.4	11.4	1/25/96	11.6	11.5	1/28/96	11.5	11.8	11.6
10/12/95	11.6	11.6	10/15/95	11.8	11.8	11.8	1/28/96	11.1	11.2	1/31/96	11.4	11.2	11.5
10/15/95	11.7	11.4	10/18/95	11.6	11.6	11.8	1/31/96	12.5	11.8	2/03/96	12.7	12.1	12.4
10/18/95	11.1	11.1	10/21/95	11.4	11.5	11.4	2/03/96	11.0	11.4	2/06/96	11.5	12.6	11.5
10/21/95	11.4	11.6	10/24/95	11.8	12.2	11.7	2/06/96	11.3	11.4	2/09/96	11.7	11.8	9.7
10/24/95	11.9	12.0	10/27/95	12.0	12.3	12.2	2/09/96	12.5	11.9	2/12/96	12.6	12.8	12.7
10/27/95	11.6	13.7	10/30/95	11.8	18.5	11.9	2/12/96	11.3	14.5	2/15/96	11.7	16.0	11.5
10/30/95	11.6	11.3	11/02/95	11.6	11.7	12.4	2/15/96	11.8	11.4	2/18/96	11.7	12.3	11.5
11/02/95	10.9	11.0	11/05/95	11.0	11.0	10.9	2/18/96	11.5	11.2	2/21/96	11.9	11.5	11.5
11/05/95	10.9	10.9	11/08/95	11.0	12.0	11.0	2/21/96	11.3	11.4	2/24/96	11.4	12.1	11.4
11/08/95	11.2	12.0	11/11/95	11.0	11.5	11.1	2/24/96	11.5	11.3	2/27/96	11.7	11.9	11.6
11/11/95	11.1	15.5	11/14/95	11.2	15.7	11.0	2/27/96	11.1	11.0	3/01/96	11.4	11.6	11.5
11/14/95	11.0	11.3	11/17/95	11.0	11.5	11.0	3/01/96	12.5	11.7	3/04/96	12.6	11.9	12.7
11/17/95	12.0	11.6	11/20/95	11.4	11.8	11.4	3/04/96	13.4	11.8	3/07/96	13.2	11.6	13.4
11/20/95	12.4	12.1	11/23/95	12.5	13.9	12.3	3/07/96	11.7	11.8	3/10/96	12.0	12.0	12.0
11/23/95	11.8	11.4	11/26/95	12.3	11.4	12.5	3/10/96	11.4	11.3	3/13/96	11.4	11.4	11.4
11/26/95	11.8	11.6	11/29/95	12.0	12.8	12.0	3/13/96	12.9	12.2	3/16/96	13.5	12.4	13.4
Average	11.5	11.7	**Average**	11.7	12.3	11.7	**Average**	12.0	11.8	**Average**	12.2	12.3	12.1

Loop 1 - Hot Hard Water (Continuously Recirculated)

Loop 2 - Hot Soft Water (Continuously Recirculated)

Loop 3 - Hot Hard Water (Intermittently Recirculated)

Loop 4 - Cold Hard Water (Continuously Recirculated)

Loop 5 - Cold Soft Water (Continuously Recirculated)

Loop 6 - Cold Hard Water (Intermittently Recirculated)

APPENDIX B, Continued.

Table B-9: Sulfate (mg/L) Data Collected During By-product Release Testing.

Date	Hot Hard	Hot Soft	Date	Loop 1	Loop 2	Loop 3	Date	Cold Hard	Cold Soft	Date	Loop 4	Loop 5	Loop 6
9/27/95	229.8	267.3	9/30/95	149.4	162.9	144.3	1/13/96	133.8	164.8	1/16/96	138.0	148.5	140.0
9/30/95	178.7	165.4	10/03/95	240.5	266.4	223.1	1/16/96	270.1	145.1	1/19/96	259.6	138.0	236.7
10/03/95	175.5	200.2	10/06/95	135.8	135.2	143.1	1/19/96	236.2	169.0	1/22/96	228.0	165.6	234.0
10/06/95	229.3	243.1	10/09/95	152.8	209.2	146.5	1/22/96	232.5	163.4	1/25/96	222.7	224.3	227.0
10/09/95	238.5	249.7	10/12/95	257.6	260.9	268.7	1/25/96	204.8	160.6	1/28/96	153.7	165.4	148.7
10/12/95	182.4	156.0	10/15/95	153.1	152.5	150.5	1/28/96	188.7	165.6	1/31/96	158.0	154.6	160.8
10/15/95	168.6	210.1	10/18/95	147.8	164.2	152.7	1/31/96	249.7	213.6	2/03/96	245.8	179.2	247.7
10/18/95	267.8	249.4	10/21/95	227.5	254.2	233.4	2/03/96	193.4	186.8	2/06/96	163.7	222.2	169.6
10/21/95	221.8	137.3	10/24/95	233.2	143.7	241.5	2/06/96	224.2	217.9	2/09/96	177.1	177.5	187.0
10/24/95	163.4	148.5	10/27/95	146.5	132.7	152.1	2/09/96	272.9	225.2	2/12/96	256.6	222.5	242.8
10/27/95	214.9	260.6	10/30/95	147.3	262.6	153.0	2/12/96	206.6	166.8	2/15/96	169.0	177.5	179.7
10/30/95	244.4	240.9	11/02/95	249.2	256.2	244.2	2/15/96	261.2	264.6	2/18/96	274.9	270.6	272.2
11/02/95	258.1	262.8	11/05/95	248.0	263.2	257.9	2/18/96	204.6	207.3	2/21/96	152.6	200.0	149.7
11/05/95	257.4	259.4	11/08/95	252.5	263.2	259.2	2/21/96	269.4	208.6	2/24/96	257.9	174.6	264.4
11/08/95	246.9	333.3	11/11/95	255.0	247.9	268.4	2/24/96	200.5	173.1	2/27/96	140.9	150.0	158.8
11/11/95	265.4	147.3	11/14/95	270.0	149.9	283.6	2/27/96	207.7	166.6	3/01/96	163.0	160.5	163.3
11/14/95	212.5	153.3	11/17/95	248.3	149.3	243.1	3/01/96	256.0	185.6	3/04/96	257.7	164.0	251.1
11/17/95	267.3	246	11/20/95	231.1	222.3	230.0	3/04/96	258.8	175.3	3/07/96	253.5	153.3	231.3
11/20/95	279.1	266.8	11/23/95	277.1	268.1	270.6	3/07/96	210.8	155.5	3/10/96	163.0	155.5	161.0
11/23/95	216.8	165.5	11/26/95	234.6	164.7	226.4	3/10/96	201.6	194.8	3/13/96	166.6	150.3	151.4
11/26/95	197.3	151.6	11/29/95	210.9	171.3	205.5	3/13/96	249.6	206.1	3/16/96	264.4	195.6	249.3
Average	224.6	215.0	**Average**	212.8	204.8	214.2	**Average**	225.4	186.5	**Average**	203.2	178.6	201.3

Loop 1 - Hot Hard Water (Continuously Recirculated)

Loop 2 - Hot Soft Water (Continuously Recirculated)

Loop 3 - Hot Hard Water (Intermittently Recirculated)

Loop 4 - Cold Hard Water (Continuously Recirculated)

Loop 5 - Cold Soft Water (Continuously Recirculated)

Loop 6 - Cold Hard Water (Intermittently Recirculated)

APPENDIX B, Continued.

Table B-10: Orthophosphate (mg/L-P) Data Collected During By-product Release Testing.

Date	Hot Hard	Hot Soft	Date	Cold Hard	Cold Soft
9/27/95	0.09	0.08	1/13/96	0.03	0.03
9/30/95	0.06	0.06	1/16/96	0.06	0.04
10/03/95	0.11	0.05	1/19/96	0.06	0.05
10/06/95	0.06	0.04	1/22/96	0.06	0.05
10/09/95	0.07	0.06	1/25/96	0.03	0.03
10/12/95	0.12	0.06	1/28/96	0.03	0.03
10/15/95	0.16	0.08	1/31/96	0.07	0.04
10/18/95	0.17	0.06	2/03/96	0.03	0.04
10/21/95	0.16	0.04	2/06/96	0.04	0.04
10/24/95	0.24	0.08	2/09/96	0.04	0.04
10/27/95	0.10	0.06	2/12/96	0.03	0.03
10/30/95	0.29	0.08	2/15/96	0.02	0.03
11/02/95	0.19	0.06	2/18/96	0.03	0.03
11/05/95	0.12	0.05	2/21/96	0.04	0.03
11/08/95	0.14	0.09	2/24/96	0.03	0.03
11/11/95	0.17	0.05	2/27/96	0.03	0.03
11/14/95	0.15	0.05	3/01/96	0.05	0.03
11/17/95	0.08	0.13	3/04/96	0.05	0.03
11/20/95	0.17	0.06	3/07/96	0.04	0.03
11/23/95	0.13	0.04	3/10/96	0.05	0.04
11/26/95	0.17	0.05	3/13/96	0.06	0.04
Average	0.15	0.06	Average	0.04	0.04

Loop 1 - Hot Hard Water (Continuously Recirculated)

Loop 2 - Hot Soft Water (Continuously Recirculated)

Loop 3 - Hot Hard Water (Intermittently Recirculated)

Loop 4 - Cold Hard Water (Continuously Recirculated)

Loop 5 - Cold Soft Water (Continuously Recirculated)

Loop 6 - Cold Hard Water (Intermittently Recirculated)

APPENDIX B, Continued.

STATISTICAL ANALYSIS OF BY-PRODUCT RELEASE TESTING

Table B-11: Analysis of Variance for Statistical Comparison of Experimental Results from Loops 1 and 2.

Anova: Single Factor *Using Analysis ToolPak in Excel 5.0

SUMMARY

Treatments	*Count*	*Sum*	*Average*	*Variance*
Loop 1	21	7.846	0.374	0.005
Loop 2	21	9.627	0.458	0.004

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit 90%*	*F crit 95%*	*F crit 99%*
Treatments	0.076	1	0.076	17.584	0.00015	2.835	4.085	7.314
Experimental Error	0.172	40	0.004					
Total	0.247	41						

Table B-12: Analysis of Variance for Statistical Comparison of Experimental Results from Loops 1 and 3.

Anova: Single Factor *Using Analysis ToolPak in Excel 5.0

SUMMARY

Treatments	*Count*	*Sum*	*Average*	*Variance*
Loop 1	21	7.846	0.374	0.005
Loop 3	21	11.905	0.567	0.009

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit 90%*	*F crit 95%*	*F crit 99%*
Treatments	0.392	1	0.39227	54.734	5.26E-09	2.835	4.085	7.314
Experimental Error	0.287	40	0.00717					
Total	0.679	41						

APPENDIX B, Continued.

Table B-13: Analysis of Variance for Statistical Comparison of Experimental Results from Loops 1 and 4.

Anova: Single Factor *Using Analysis ToolPak in Excel 5.0

SUMMARY

Treatments	*Count*	*Sum*	*Average*	*Variance*
Loop 1	21	7.846	0.374	0.005
Loop 4	21	21.999	1.048	0.091

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit 90%*	*F crit 95%*	*F crit 99%*
Treatments	4.769	1	4.769	99.551	2.1E-12	2.835	4.085	7.314
Experimental Error	1.916	40	0.048					
Total	6.686	41						

Table B-14: Analysis of Variance for Statistical Comparison of Experimental Results from Loops 1 and 5.

Anova: Single Factor *Using Analysis ToolPak in Excel 5.0

SUMMARY

Treatments	*Count*	*Sum*	*Average*	*Variance*
Loop 1	21	7.846	0.374	0.005
Loop 5	21	24.499	1.167	0.071

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit 90%*	*F crit 95%*	*F crit 99%*
Treatments	6.603	1	6.603	174.586	3.5E-16	2.835	4.085	7.314
Experimental Error	1.513	40	0.038					
Total	8.116	41						

APPENDIX B, Continued

Table B-15: Analysis of Variance for Statistical Comparison of Experimental Results from Loops 1 and 6.

Anova: Single Factor *Using Analysis ToolPak in Excel 5.0

SUMMARY

Treatments	*Count*	*Sum*	*Average*	*Variance*
Loop 1	21	7.846	0.374	0.005
Loop 6	21	20.508	0.977	0.057

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit 90%*	*F crit 95%*	*F crit 99%*
Treatments	3.817	1	3.817	123.767	8.2E-14	2.835	4.085	7.314
Experimental Error	1.234	40	0.031					
Total	5.051	41						

Table B-16: Analysis of Variance for Statistical Comparison of Experimental Results from Loops 2 and 3.

Anova: Single Factor *Using Analysis ToolPak in Excel 5.0

SUMMARY

Treatments	*Count*	*Sum*	*Average*	*Variance*
Loop 2	21	9.627	0.458	0.004
Loop 3	21	11.905	0.567	0.009

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit 90%*	*F crit 95%*	*F crit 99%*
Treatments	0.124	1	0.124	19.070	8.7E-05	2.835	4.085	7.314
Experimental Error	0.259	40	0.006					
Total	0.383	41						

APPENDIX B, Continued

Table B-17: Analysis of Variance for Statistical Comparison of Experimental Results from Loops 2 and 4.

Anova: Single Factor *Using Analysis ToolPak in Excel 5.0

SUMMARY

Treatments	*Count*	*Sum*	*Average*	*Variance*
Loop 2	21	9.627	0.458	0.004
Loop 4	21	21.999	1.048	0.091

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit 90%*	*F crit 95%*	*F crit 99%*
Treatments	3.644	1	3.644	77.181	7E-11	2.835	4.085	7.314
Experimental Error	1.889	40	0.047					
Total	5.533	41						

Table B-18: Analysis of Variance for Statistical Comparison of Experimental Results from Loops 2 and 5.

Anova: Single Factor *Using Analysis ToolPak in Excel 5.0

SUMMARY

Treatments	*Count*	*Sum*	*Average*	*Variance*
Loop 2	21	9.627	0.458	0.004
Loop 5	21	24.499	1.167	0.071

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit 90%*	*F crit 95%*	*F crit 99%*
Treatments	5.266	1	5.266	141.819	9.9E-15	2.835	4.085	7.314
Experimental Error	1.485	40	0.037					
Total	6.751	41						

APPENDIX B, Continued

Table B-19: Analysis of Variance for Statistical Comparison of Experimental Results from Loops 2 and 6.

Anova: Single Factor *Using Analysis ToolPak in Excel 5.0

SUMMARY

Treatments	*Count*	*Sum*	*Average*	*Variance*
Loop 2	21	9.627	0.458	0.004
Loop 6	21	20.508	0.977	0.057

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit 90%*	*F crit 95%*	*F crit 99%*
Treatments	2.819	1	2.819	93.483	5.1E-12	2.835	4.085	7.314
Experimental Error	1.206	40	0.030					
Total	4.025	41						

Table B-20: Analysis of Variance for Statistical Comparison of Experimental Results from Loops 3 and 4.

Anova: Single Factor *Using Analysis ToolPak in Excel 5.0

SUMMARY

Treatments	*Count*	*Sum*	*Average*	*Variance*
Loop 3	21	11.905	0.567	0.009
Loop 4	21	21.999	1.048	0.091

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit 90%*	*F crit 95%*	*F crit 99%*
Treatments	2.426	1	2.426	48.430	2.1E-08	2.835	4.085	7.314
Experimental Error	2.004	40	0.050					
Total	4.430	41						

APPENDIX B, Continued

Table B-21: Analysis of Variance for Statistical Comparison of Experimental Results from Loops 3 and 5.

Anova: Single Factor *Using Analysis ToolPak in Excel 5.0

SUMMARY

Treatments	*Count*	*Sum*	*Average*	*Variance*
Loop 3	21	11.905	0.567	0.009
Loop 5	21	24.499	1.167	0.071

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit 90%*	*F crit 95%*	*F crit 99%*
Treatments	3.776	1	3.776	94.399	4.4E-12	2.835	4.085	7.314
Experimental Error	1.600	40	0.040					
Total	5.377	41						

Table B-22: Analysis of Variance for Statistical Comparison of Experimental Results from Loops 3 and 6.

Anova: Single Factor *Using Analysis ToolPak in Excel 5.0

SUMMARY

Treatments	*Count*	*Sum*	*Average*	*Variance*
Loop 3	21	11.905	0.567	0.009
Loop 6	21	20.508	0.977	0.057

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit 90%*	*F crit 95%*	*F crit 99%*
Treatments	1.762	1	1.762	53.357	7.1E-09	2.835	4.085	7.314
Experimental Error	1.321	40	0.033					
Total	3.083	41						

APPENDIX B, Continued

Table B-23: Analysis of Variance for Statistical Comparison of Experimental Results from Loops 4 and 5.

Anova: Single Factor *Using Analysis ToolPak in Excel 5.0

SUMMARY

Treatments	*Count*	*Sum*	*Average*	*Variance*
Loop 4	21	21.999	1.048	0.091
Loop 5	21	24.499	1.167	0.071

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit 90%*	*F crit 95%*	*F crit 99%*
Treatments	0.149	1	0.149	1.843	0.182	2.835	4.085	7.314
Experimental Error	3.230	40	0.081					
Total	3.379	41						

Table B-24: Analysis of Variance for Statistical Comparison of Experimental Results from Loops 4 and 6.

Anova: Single Factor *Using Analysis ToolPak in Excel 5.0

SUMMARY

Treatments	*Count*	*Sum*	*Average*	*Variance*
Loop 4	21	21.999	1.048	0.091
Loop 6	21	20.508	0.977	0.057

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit 90%*	*F crit 95%*	*F crit 99%*
Treatments	0.053	1	0.053	0.718	0.402	2.835	4.085	7.314
Experimental Error	2.951	40	0.074					
Total	3.004	41						

APPENDIX B, Continued

Table B-25: Analysis of Variance for Statistical Comparison of Experimental Results from Loops 5 and 6.

Anova: Single Factor *Using Analysis ToolPak in Excel 5.0

SUMMARY

Treatments	*Count*	*Sum*	*Average*	*Variance*
Loop 5	21	24.499	1.167	0.071
Loop 6	21	20.508	0.977	0.057

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit 90%*	*F crit 95%*	*F crit 99%*
Treatments	0.379	1	0.379	5.955	0.019	2.835	4.085	7.314
Experimental Error	2.547	40	0.064					
Total	2.926	41						

APPENDIX B, Continued.

STATISTICAL ANALYSIS OF BY-PRODUCT RELEASE TESTING

Table B-26: Summary of Results From Statistical Analysis.

Loop	Treatment	Average Concentration	Mean Difference	F value	Confidence Level
1	Hot Hard CR	0.374	0.084	17.584	99
2	Hot Soft CR	0.458			
4	Cold Hard CR	1.048	0.119	1.843	80
5	Cold Soft CR	1.167			
1	Hot Hard CR	0.374	0.674	99.551	99
4	Cold Hard CR	1.048			
2	Hot Soft CR	0.458	0.709	141.819	99
5	Cold Soft CR	1.167			
1	Hot Hard CR	0.374	0.193	54.734	99
3	Hot Hard IR	0.567			
4	Cold Hard CR	1.048	0.071	0.718	None
6	Cold Hard IR	0.977			
3	Hot Hard IR	0.567	0.41	53.357	99
6	Cold Hard IR	0.977			

APPENDIX B, Continued

Table B-27: Equilibrium System Calculations By-product Release Testing. (Cold Hard Water)

Water Analysis **pH =** **8.14**

Temp., C = 15 **Alkalinity =** 177 mg/l as $CaCO_3$

Temp., K = 288.15 **Alkalinity =** 0.00354 meq/l

		mg/l	Mol. wt	mmol/l	meq/l	z	cz^2
Cations	**Ca^{++}**	**81**	40.1	2.020	4.040	2	0.00808
	Mg^{++}	**38**	24.3	1.564	3.128	2	0.00626
	Na^{+}	**18**	23.0	0.783	0.783	1	0.00078
	K^{+}	**0**	39.1	0.000	0.000	1	0.00000
	Fe^{++}	**0**	55.8	0.000	0.000	2	0.00000
Anions	**HCO_3^-**	**0**	61.0	0.000	0.000	1	0.00000
	$CO_3^=$	**0**	60.0	0.000	0.000	2	0.00000
	Alk, $CaCO_3$	**177**	100.0	1.770	3.540	2	0.00708
	$SO_4^=$	**225**	96.1	2.341	4.683	2	0.00937
	Cl^-	**12**	35.5	0.338	0.338	1	0.00034
	NO_3^-	**0**	62.0	0.000	0.000	1	0.00000
	F^-	**0**	19.0	0.000	0.000	1	0.00000

Sum Cations = 7.95 meq/l Sum cz^2 = 0.03190

Sum Anions = 8.56 meq/l

Total Hardness = 358 mg/l as $CaCO_3$ (Ca & Mg)

Ionic Strength Calculations

E	A	I	log g_m	log g_d	g_m	g_d
81.883	0.5035	0.0160	-0.0549	-0.2194	0.8813	0.6033

Equilibrium Constant Calculations **Water Equilibrium Calculations**

(corrected for temperature and ionic strength)

K_1	K_2	K_w	K_s
4.90E-07	5.83E-11	5.33E-15	1.16E-08

$[H^+]$	$[OH^-]$
8.22E-09	6.49E-07

Acidity Calculations

p	s	t	Acidity, eq/l
1.0336	-6.41E-07	1.0142	0.00361

Buffer Intensity Calculations

a_1	equiv/unit pH.l
0.9767	0.00019

Carbonate System Calculations

Component	mol/l	mg/l as $CaCO_3$	meq/l
H_2CO_3	0.000059	5.855	0.117
HCO_3^-	0.003490	174.493	3.490
$CO_3^=$	0.000025	2.475	0.049

Langelier Inde: 0.6390

CCPP = 15.700

APPENDIX B, Continued

Table B-28: Equilibrium System Calculations
By-product Release Testing.
(Cold Soft Water)

Water Analysis

Temp., C =	**15**	**Alkalinity =**	**185**	mg/l as $CaCO_3$
Temp., K =	288.15	**Alkalinity =**	0.0037	meq/l
		pH =	**8.24**	

		mg/l	Mol. wt	mmol/l	meq/l	z	cz^2
Cations	**Ca^{++}**	**0.3**	40.1	0.007	0.015	2	0.00003
	Mg^{++}	**0.1**	24.3	0.004	0.008	2	0.00002
	Na^+	**171**	23.0	7.435	7.435	1	0.00743
	K^+	**0**	39.1	0.000	0.000	1	0.00000
	Fe^{++}	**0**	55.8	0.000	0.000	2	0.00000
Anions	**HCO_3^-**	**0**	61.0	0.000	0.000	1	0.00000
	$CO_3^=$	**0**	60.0	0.000	0.000	2	0.00000
	Alk, $CaCO_3$	**185**	100.0	1.850	3.700	2	0.00740
	$SO_4^=$	**187**	96.1	1.946	3.892	2	0.00778
	Cl^-	**12**	35.5	0.338	0.338	1	0.00034
	NO_3^-	**0**	62.0	0.000	0.000	1	0.00000
	F^-	**0**	19.0	0.000	0.000	1	0.00000

Sum Cations = 7.46 meq/l

Sum Anions = 7.93 meq/l

Sum cz^2 = 0.02300

Total Hardness = 1 mg/l as $CaCO_3$ (Ca & Mg)

Ionic Strength Calculations

E	A	I	log g_m	log g_d	g_m	g_d
81.883	0.5035	0.0115	-0.0476	-0.1905	0.8962	0.6450

Equilibrium Constant Calculations

(corrected for temperature and ionic strength)

K_1	K_2	K_w	K_s
4.74E-07	5.45E-11	5.16E-15	1.02E-08

Water Equilibrium Calculations

$[H^+]$	$[OH^-]$
6.42E-09	8.04E-07

Acidity Calculations

p	s	t	Acidity, eq/l
1.0271	-7.97E-07	1.0170	0.00374

Buffer Intensity Calculations

a_1	equiv/unit pH.I
0.9784	0.00019

Carbonate System Calculations

Component	mol/l	mg/l as $CaCO_3$	meq/l
H_2CO_3	0.000049	4.929	0.099
HCO_3^-	0.003637	181.872	3.637
$CO_3^=$	0.000031	3.089	0.062

Langelier Inde: -1.6369

CCPP = -9.910

APPENDIX B, Continued

Table B-29: Equilibrium System Calculations By-product Release Testing. (Hot Hard Water)

Water Analysis

		pH =	**7.96**
Temp., C =	**55**	**Alkalinity =**	**171** mg/l as $CaCO_3$
Temp., K =	328.15	**Alkalinity =**	0.00342 meq/l

		mg/l	**Mol. wt**	**mmol/l**	**meq/l**	**z**	**cz²**
Cations	**Ca^{++}**	**83**	40.1	2.070	4.140	2	0.00828
	Mg^{++}	**44**	24.3	1.811	3.621	2	0.00724
	Na^{+}	**19**	23.0	0.826	0.826	1	0.00083
	K^{+}	**0**	39.1	0.000	0.000	1	0.00000
	Fe^{++}	**0**	55.8	0.000	0.000	2	0.00000
Anions	**HCO_3^-**	**0**	61.0	0.000	0.000	1	0.00000
	$CO_3^=$	**0**	60.0	0.000	0.000	2	0.00000
	Alk, $CaCO_3$	**171**	100.0	1.710	3.420	2	0.00684
	$SO_4^=$	**225**	96.1	2.341	4.683	2	0.00937
	Cl^-	**12**	35.5	0.338	0.338	1	0.00034
	NO_3^-	**0**	62.0	0.000	0.000	1	0.00000
	F^-	**0**	19.0	0.000	0.000	1	0.00000

Sum Cations = 8.59 meq/l Sum cz^2 = 0.03289

Sum Anions = 8.44 meq/l

Total Hardness = 388 mg/l as $CaCO_3$ (Ca & Mg)

Ionic Strength Calculations

E	A	I	log g_m	log g_d	g_m	g_d
68.300	0.5439	0.0164	-0.0600	-0.2401	0.8709	0.5753

Equilibrium Constant Calculations **Water Equilibrium Calculations**

(corrected for temperature and ionic strength)

K_1	K_2	K_w	K_s
6.75E-07	1.16E-10	8.85E-14	6.13E-09

$[H^+]$	$[OH^-]$
1.26E-08	7.03E-06

Acidity Calculations

p	s	t	Acidity, eq/l
1.0373	-7.02E-06	1.0185	0.00347

Buffer Intensity Calculations

a_1	equiv/unit pH.I
0.9729	0.00023

Carbonate System Calculations

Component	mol/l	mg/l as $CaCO_3$	meq/l
H_2CO_3	0.000062	6.250	0.125
HCO_3^-	0.003351	167.555	3.351
$CO_3^=$	0.000031	3.094	0.062

Langelier Inde: 1.0279

CCPP = 33.641

APPENDIX B, Continued

Table B-30: Equilibrium System Calculations
By-product Release Testing.
(Hot Soft Water)

Water Analysis

		pH =	**8.26**	
Temp., C =	**55**	**Alkalinity =**	**174**	mg/l as $CaCO_3$
Temp., K =	328.15	**Alkalinity =**	0.00348	meq/l

		mg/l	Mol. wt	mmol/l	meq/l	z	cz^2
Cations	**Ca^{++}**	**0.6**	40.1	0.015	0.030	2	0.00006
	Mg^{++}	**0.4**	24.3	0.016	0.033	2	0.00007
	Na^{+}	**182**	23.0	7.913	7.913	1	0.00791
	K^{+}	**0**	39.1	0.000	0.000	1	0.00000
	Fe^{++}	**0**	55.8	0.000	0.000	2	0.00000
Anions	**HCO_3^-**	**0**	61.0	0.000	0.000	1	0.00000
	$CO_3^=$	**0**	60.0	0.000	0.000	2	0.00000
	Alk, $CaCO_3$	**174**	100.0	1.740	3.480	2	0.00696
	$SO_4^=$	**215**	96.1	2.237	4.475	2	0.00895
	Cl^-	**12**	35.5	0.338	0.338	1	0.00034
	NO_3^-	**0**	62.0	0.000	0.000	1	0.00000
	F^-	**0**	19.0	0.000	0.000	1	0.00000

Sum Cations = 7.98 meq/l Sum cz^2 = 0.02429

Sum Anions = 8.29 meq/l

Total Hardness = 3 mg/l as $CaCO_3$ (Ca & Mg)

Ionic Strength Calculations

E	A	I	log g_m	log g_d	g_m	g_d
68.300	0.5439	0.0121	-0.0527	-0.2107	0.8858	0.6157

Equilibrium Constant Calculations **Water Equilibrium Calculations**

(corrected for temperature and ionic strength)

K_1	K_2	K_w	K_s		$[H^+]$	$[OH^-]$
6.53E-07	1.09E-10	8.55E-14	5.35E-09		6.20E-09	1.38E-05

Acidity Calculations

p	s	t	Acidity, eq/l
1.0190	-1.38E-05	1.0350	0.00340

Buffer Intensity Calculations

a_1	equiv/unit pH.l
0.9737	0.00024

Carbonate System Calculations

Component	mol/l	mg/l as $CaCO_3$	meq/l
H_2CO_3	0.000032	3.184	0.064
HCO_3^-	0.003349	167.447	3.349
$CO_3^=$	0.000059	5.864	0.117

Langelier Inde: -0.7687

CCPP = 9.427