

C.1

THE EFFECT OF PH ADJUSTMENT ON THE INTERNAL CORROSION RATE OF  
CAST IRON AND COPPER WATER DISTRIBUTION PIPES

by

LOUISE MILLETTE

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Department of Civil Engineering

University of British Columbia  
2075 Wesbrook Place  
Vancouver, Canada  
V6T 1W5

Date: December 1985

## ABSTRACT

Two experimental sessions were conducted to examine the effects of pH adjustment on internal corrosion of cast iron and copper water distribution pipes. The Greater Vancouver Regional District uses surface lakes as its potable water source. As confirmed by chemical water characteristics monitoring, the supplied tap water has several of the attributes of an aggressive water: low pH (4.9 to 5.7), low alkalinity (10 to 15 mg/L as CaCO<sub>3</sub>), low hardness (6 to 7 mg/L as CaCO<sub>3</sub>), and dissolved oxygen consistently near saturation.

Because of this aggressive nature, the tap water has a tendency to dissolve water distribution pipes, and in particular domestic copper pipes (municipal cast iron mains are cement lined for corrosion protection). This accelerated corrosion of copper pipes not only increases the maintenance costs for home owners, it also encourages high levels of copper in their tap water. This last finding was confirmed by a preliminary tap water metal concentration survey wherein, after a month of sampling of six dwellings, it was found that the recommended maximum copper level of 1.0 mg/L was exceeded in 67% of the cold water morning first flush samples.

The investigated corrosion control measure consisted of pH adjustment to target values of 6, 7 and 8, through the addition of hydrated lime (Ca(OH)<sub>2</sub>). Cast iron and copper pipe samples were exposed to pH adjusted water for durations ranging from one to twelve weeks. For the most part, the adjusted pH experimental flow-through units were gravity-fed; however, to examine the effects of the much higher normal distribution system pressure, another set of control units were maintained at system pressure.

Although it was found that the absolute winter corrosion rates were higher than the summer rates, analysis of the relative coupon weight loss variations, with

reference to the gravity control unit, lead to two major findings. The corrosion rates of cast iron were ten times those of copper and the increased pH acted to enhance these cast iron corrosion rates by approximately 15%. However, pH adjustment successfully decreased copper corrosion by 68%. The effects of the increased pressure on corrosion were different for both metals. The corrosion rates of cast iron coupons in the control pressurized cells were twice the rates of the coupons in the gravity control units. The effect of the increased pressure on copper was not as marked, but the rates were found to be slightly lower than expected from the pressurized water lower pH.

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## 1. INTRODUCTION

### 1.1 BACKGROUND INFORMATION

The City of Vancouver and its neighbouring municipalities, together called the Greater Vancouver Regional District, use two surface lakes (located in nearby, protected watersheds) as potable water sources (See Figure 1.1.1). This water has a very 'aggressive' nature, i.e. it is corrosive to metals. This is due, in part, to the fact that the hydrological system is fed by precipitation, which has a naturally acidic pH, as well as to the low buffering capacity of the soils in the catchment areas. A combination of these water characteristic contributes to the corrosiveness:

1. The low pH.

The pH of rain water is normally close to 5.5 because the dissolution of the atmospheric carbonic gas in the falling drops favors the formation of the weak carbonic acid species; this increases acidity and reduces pH. Vancouver's tap water's pH is in the acidic range, with values ranging from 4.5 to 5.5, i.e. well below the neutral pH 7 value. This pH condition increases the metals' solubility in water.

2. The low hardness and alkalinity.

These two water characteristics are indicators of the amount of ionic species in the water. Because Vancouver's water contains very little dissolved species, it tends to acquire more during transit to the household and will therefore dissolve anything it contacts, in particular the metal components of water distribution pipes.

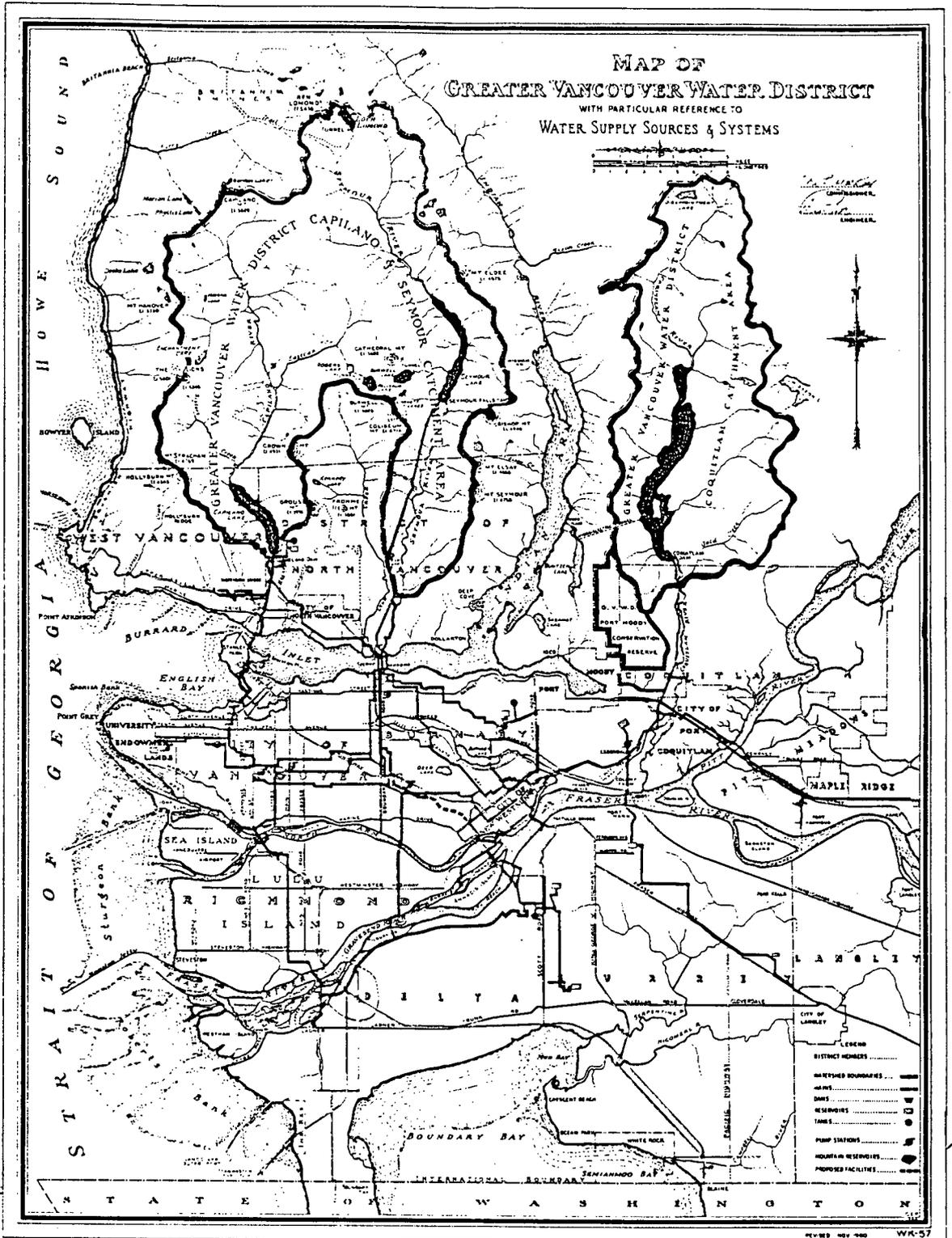


FIGURE 1.1.1 GVRD Water Supply System

### 3. The high oxygen content.

Dissolved oxygen plays an important electron acceptor role in metal corrosion. It is often viewed as a limiting factor in metal dissolution; the concentration of dissolved oxygen available controlling the rate of electron release. Vancouver's water has a high oxygen content, very near the saturation value.

The aggressive nature of drinking water may not be a concern in itself but it does become an important factor when one looks at the effects on the distribution system and the metal concentration levels in potable water.

An aggressive water tends to dissolve the distribution pipes; this produces three undesirable impacts. Firstly, the lifespan of the distribution system is reduced and failures occur more frequently. This is costly not only in dollars paid for reparation, but in loss of service and wastage of clean water.

In Metropolitan Toronto, for instance, it was estimated that over \$5 Million would be spent in 1983 for repairs to the water distribution systems. In Winnipeg, this amount jumped to \$7.7 Million (Gummov, 1984). In the United States, the annual corrosion cost in the field of water supply has been estimated at \$700 Million for 1979 (Singley, 1984). These costs estimates do not include the investment for maintenance of private home plumbing, or the extra energy cost needed to pump water in pipes where rust tubercules reduce the useful diameter. The true economic impact of corrosion in the distribution system is a serious add-on to a community's service costs.

Secondly, the increased metal oxides (or ions) in the water affects its aesthetic value, and the municipalities may have to deal with very dissatisfied citizens, either because of the stains they find in their water fixtures or because of the colour or taste of the water itself. For example, high iron content in water will cause a familiar brownish-red colour; this fairly common phenomenon was even given the name 'red-water'.

The third and last aspect is no less important, namely the health hazard associated with high metal levels in drinking water. The detrimental effects of heavy-metals such as lead or mercury have been widely discussed, but there is now a growing concern that copper, which is commonly used in domestic plumbing systems, might be toxic as well. It would act at the chronic level when the daily intakes are only slightly higher than needed. This increased dissolution of copper, by corrosive water, might be as important a factor as the cost of reduced life expectancies of the piping system.

As Begin (1982) pointed out, it is very improbable that research/development in the materials field will ever develop with a totally corrosion resistant alloy to replace the ones already in use. He therefore suggested that further research into the nature and control of corrosion might yield better solutions to any future problems in this area.

## 1.2 STATEMENT OF PURPOSE

In this research, the reduction of the corrosion rate of cast-iron and copper pipe samples in tap water was studied at room temperature. This was accomplished by increasing the tap water pH through lime addition.

Two additional preliminary studies were conducted. One looked at the effect of the distribution system pressure on the corrosion rate of pipe samples in normal tap water. The other was a first investigation of the metal concentrations at the consumer's tap, both after an overnight residence and after running freely.

## 1.3 AUDIENCE

This research and report are presented in fulfillment of the requirements for the completion of a Master of Applied Science degree with the Environmental Engineering Group of the Civil Engineering Department, University of British Columbia.

It is assumed that the reader has some background in water chemistry. A brief review of the relevant electrochemical principles will be given in Chapter 2.

#### 1.4 INFORMATION SOURCES

The experimental results presented in this report were gathered during two separate experimental sessions. The first four-week experiment was performed during January and February 1984; the second twelve-week experiment ran from June to September 1985. The four-week tap water survey took place in the Vancouver Area, in August 1985.

For the literature review, the Engineering Index, the NTIS data bank, the Engineering Meetings data bank and the Corrosion Abstracts were searched, either manually or by computer, during the Fall of 1985.

#### 1.5 WORKING DEFINITION

To facilitate the comprehension of the report, some frequently used terms are defined below.

Coupon, metallic coupon	A piece of distribution pipe used as an experimental unit
Cell	Acrylic cylinder used to contain the metal coupons for the duration of the experiment
Feed water	Tap water used for the experiment. The pH may be adjusted or left unchanged, for use as the control test
Gravity control	Set-up where the feed water flows in the cells by gravity
Pressure control	Set-up connected to the municipal water distribution system and kept at the same pressure

First-flush	Samples of water having spent the night in the distribution pipes
GVRD	Greater Vancouver Regional District

## 1.6 LIMITATIONS OF THE REPORT

Due to the complexity of the problem, only specific aspects of corrosion were examined.

The corrosion rate was assessed by the weight loss of the pipe coupons, assuming a uniform loss over the entire surface. Localized corrosion was not investigated and the increase of the metal concentration in the cell water was not examined. As well, although the weight of the corrosion product was calculated, it was not sampled and analysed.

In addition, the data was analysed looking at the overall effects on the corrosion rate. The modelling of the action of pH on the different reaction rates of corrosion, and the investigation of the electrochemical processes involved in dilute aqueous solution were not studied; they are far beyond the scope of this work.

The water sampling program was kept at a preliminary stage, looking at only six household water supplies. It should be considered as a first exploratory assessment of the situation.

## 1.7 SCOPE OF COVERAGE

This report is presented in three main parts. In the first, Chapter 2, background information on corrosion is given, and some of the most recently published works on the topic of corrosion in water distribution systems are reviewed. The second part, Chapter 3, describes the methodology used to perform the experimental analyses. The third and last part of the main body presents and discusses the results obtained

in this research.

The reader will also find a summary of the major findings and conclusions, along with the recommendations for further work, in the Conclusions and Recommendations, Chapter 5.

Because corrosion analysis by coupon weight loss generates a lot of intermediate numerical data, the calculations were done by computer. To keep this discussion as clear as possible, the cumulative weight losses and averages, and the laboratory metal concentrations are presented in Appendices C,D and E of this report. Any additional data will be supplied by the author, upon request.

## 2. BACKGROUND AND LITERATURE REVIEW

This chapter is divided into three main sections. Firstly, general notions concerning corrosion are reviewed; then, some of the recently published works on the topic of corrosion in water distribution systems are presented. Finally, the last section briefly examines some of the effects of high copper concentrations in drinking water on human health.

### 2.1 CORROSION PHENOMENON

In the region of water stability, i.e. where most human activities take place, metallic substances are not widely found as pure metals, with the exception of gold. They are found as ores (oxides or sulfides) and are transformed into their metal phase at a great expense of energy (Singley, 1978). Consequently, this useful metallic phase is not in a stable state: it is metastable. The metals will return to their ore form, in time, driven into the process by a force proportional to the energy originally invested in their extraction. The less energy required, the more 'noble' the metal and the longer it will stay in useful service. Although the situation appears to be straightforward, it is in fact a multi-faceted one. As Edeleanu and Hines (1983) stated:

"Corrosion is a process and the rate at which the process takes place, and for that matter, the manner in which it occurs, is a function of the conditions as well as the nature of the material."

Each corrosion situation has different conditions that will give rise to different corrosion patterns.

This section will present an overview of the corrosion phenomenon mechanism, and the tools available to measure and control it. Several textbooks deal with corrosion on a more in-depth basis and the reader will find further information on most of

the topics presented here in manuals such as Uhlig's (1971) or Fontana and Greene's (1978).

### 2.1.1 TYPES OF CORROSION

The literature lists several possible types of corrosion:

uniform	corrosion fatigue
electrochemical	intergranular
galvanic	fretting
concentration cell	impingement
erosion corrosion	dezincification
embrittlement	graphitization
stress corrosion	chemical reaction
filiform	

The above listed are presented in the corrosion handbook edited by Schweitzer (1983). This diversity emphasizes the many aspects that fairly well-known electrochemical processes can take.

In the aqueous corrosion situation of a distribution system, only some of these forms are encountered, according to Tromans (1983).

#### 1. Uniform attack.

The metal dissolution is uniform on the whole exposed surface. Copper, in close to neutral pH water, exhibits such behavior.

#### 2. Galvanic.

When dissimilar metals are allowed to contact, either directly or through an electrolyte solution, the metal with the greater reduction potential, i.e. the less 'noble' metal, will corrode. Very frequently, in plumbing systems, couplings or weldings will be made of a metal alloy different from the one of the connected pipes. As well, pipes of different metals may be directly connected together.

#### 3. Crevice.

When parts of the carried liquid are allowed to be trapped under overlapping joints, bolts heads, welds or any surface defects, their characteristics start to change. In general, the pH decreases as the dissolved oxygen is depleted, and chloride ions are concentrated in the liquid above the surface. This creates a set of autocatalytic corrosive conditions and the metal is locally attacked. Any joints of a plumbing system will promote such a type of corrosion.

4. Pitting.

Pits on the metal surface evolve in non-shielded areas. However, once they are initiated, the evolution of the conditions inside the pit is similar to a case of crevice corrosion. Localized corrosion (pitting and crevice) causes failure of the pipe by perforation, even if only a small amount of material is lost from the metal surface. It is therefore an undesirable situation in water distributions systems.

5. Selective leaching.

For quite an extended period of time, brass taps and fittings were widely used in domestic water appliances, especially in Europe. It is now well known that the zinc part of the alloy (the less noble metal) is released in the water stream and leaches out, leaving a porous, but apparently undisturbed, copper matrix. This selective leaching of one metal of an alloy can go unnoticed until failure of the weakened element.

6. Erosion-corrosion.

In situations where the liquid flow on the metal surface is sufficiently powerful to remove the protective corrosion products, the metal corrodes faster under the joint mechanical and electrochemical actions. In water distribution,

where the liquid is often accelerated (elbows, valves, etc) these combined effects are expected.

## 7. Stress corrosion cracking

Corrosion will cause an early failure of metal submitted to stress.

It is not easy to obtain quantitative data on localized corrosion. In this experiment, the corrosion rates are considered uniform as the weight losses are distributed over the entire coupon surface. However, visual inspection of the coupons allows for qualification of this type of corrosion.

### 2.1.2 MECHANISMS OF ACTION

"Basically, if any portion of a metal in aqueous solution is in any way different (heterogeneous) from any other portion, an electrical potential exists between them and a corrosion cell will develop." (Fox and Tate, 1983)

It is generally accepted that corrosion is an electrochemical mechanism by which electrons are transferred from a metal to an acceptor, causing the metal atoms to escape the metal structure and dissolve in the solution. These electrochemical exchanges are described by theoretical equations and potentials, which help to assess the "corrosivity" of a particular environment. The first part of this section briefly addresses the electrochemical theory of corrosion.

By simultaneous solution of the electrochemical equations for a particular system, diagrams are developed which show the regions of pH and electro-motive force (potential) where metals are passive or immune to corrosion. Although these diagrams do not give information on the actual rate of the corrosion process, they provide useful information on the situation. The Emf-pH diagrams, also called Pourbaix diagrams, are discussed in the second part of this section.

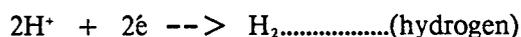
Finally, to quantify corrosion and express the rate at which it will take place, kinetics were developed. This will be the last aspect of the corrosion mechanism to be addressed here.

### 2.1.2.1 Electrochemistry

The metal portion where the ions escape the matrix is called the anode. Using 'M' as a general representation of a metal, the general anodic dissolution reaction is written:



However, the electrons cannot just 'escape' the metal, they must be accepted by an ion. This electron capture takes place at the cathode and can involve a variety of ionic species found in the solution, including metal ions. Some examples of cathodic reactions would be:



The combination of an anode and a cathode forms a galvanic cell, where chemical energy is converted to electrical energy (Uhlig, 1971).

In metallic corrosion, both of these reactions take place on the same surface. The superposition of pin-point anodes and cathodes is such that the situation can be described in terms of reactive sites rather than separate anodic and cathodic sites (Piron, 1982). The exchange taking place at the metal surface will be influenced by the metal and solution compositions, the state of the surface, the flow of the liquid on the surface, etc.

Since corrosion can only proceed if there is a complete cell formation, i.e. an anodic and cathodic reaction, a more general expression of the electron transfer is:



in which the electrons do not appear because they are accepted by the cathodic (or reduced) species.

Since this electron transfer is nothing more than an electric current, the electrical potential associated with it can be measured and calculated using the Nernst equation (Uhlig, 1971):

$$E = E^{\circ} - \frac{R T}{n F} \ln \left( \frac{(C)^c (D)^d}{(A)^a (B)^b} \right)$$

in which,

A,B,C,D : activities of the species  
 a,b,c,d : reaction coefficients  
 $E^{\circ}$  : free standard state cell potential  
 R : gas constant  
 n : number of electrons transferred  
 F : Faraday constant  
 E : potential of the cell

It is beyond the scope of this work to detail any further the theory of the Nernst equation. However, two important facts must be noted.

- To measure a potential, an electric current must flow. A potential is therefore always a relative measure involving a metal in oxidation and a particular cathode.

- For all metals, tables are constructed that list their potential with reference to a standard electrode, usually the hydrogen electrode. Table 2.1.1 lists the potential with respect to the hydrogen electrode, which is the anode. A negative sign in the potential therefore indicates that the reaction does not proceed in that way, and that the metal is the anode (i.e. it corrodes).

With the electrode potential of the metals and the Nernst equation, it is possible to calculate the resulting potential of a cell. If the result is positive, the direction of the reaction, assumed in writing the cell equation, was correct and it will proceed. Therefore, by writing the equations for all the existing species of a metal in water, it is possible to determine the conditions where the formation of a particular species is favored. These thermodynamical analyses, leading to useful tools for corrosion study, are the topic of the following section.

#### 2.1.2.2 Thermodynamics

As was mentioned previously, oxygen, hydrogen and the hydroxide ion ( $\text{OH}^-$ ) play a determining role in the electrochemistry of metal corrosion. Pourbaix, recognizing the importance of water in corrosion, devised a graphical representation of the thermodynamics of metal in water, with respect to pH (which determines the  $\text{H}^+$  and  $\text{OH}^-$  balance) and potential.

These diagrams show the various thermodynamically stable forms of a metal in water of a certain pH and potential. If the favored species is the metallic state ( $\text{M}^0$ ), its domain of existence is called the immune region; if the metal will adopt a soluble metal oxide (or hydroxide) form, the region is active and the metal will dissolve in water; if the corrosion product is insoluble, the region is called passive and the corrosion should be slowed.

Figures 2.1.1a) and b) show simplified diagram for copper and iron in water, as adapted from Pourbaix (1982).

TABLE 2.1.1 Oxidation potentials

Electromotive Force Series	
Electrode Reaction	Standard Oxidation Potential, $E^\circ$ (V), 25°C*
$\text{Li} = \text{Li}^+ + e^-$	3.05
$\text{K} = \text{K}^+ + e^-$	2.93
$\text{Ca} = \text{Ca}^{++} + 2e^-$	2.87
$\text{Na} = \text{Na}^+ + e^-$	2.71
$\text{Mg} = \text{Mg}^{++} + 2e^-$	2.37
$\text{Be} = \text{Be}^{++} + 2e^-$	1.85
$\text{U} = \text{U}^{+3} + 3e^-$	1.80
$\text{Hf} = \text{Hf}^{+4} + 4e^-$	1.70
$\text{Al} = \text{Al}^{+3} + 3e^-$	1.66
$\text{Ti} = \text{Ti}^{++} + 2e^-$	1.63
$\text{Zr} = \text{Zr}^{+4} + 4e^-$	1.53
$\text{Mn} = \text{Mn}^{++} + 2e^-$	1.18
$\text{Nb} = \text{Nb}^{+3} + 3e^-$	ca. 1.1
$\text{Zn} = \text{Zn}^{++} + 2e^-$	0.763
$\text{Cr} = \text{Cr}^{+3} + 3e^-$	0.74
$\text{Ga} = \text{Ga}^{+3} + 3e^-$	0.53
$\text{Fe} = \text{Fe}^{++} + 2e^-$	0.440
$\text{Cd} = \text{Cd}^{++} + 2e^-$	0.403
$\text{In} = \text{In}^{+3} + 3e^-$	0.342
$\text{Tl} = \text{Tl}^+ + e^-$	0.336
$\text{Co} = \text{Co}^{++} + 2e^-$	0.277
$\text{Ni} = \text{Ni}^{++} + 2e^-$	0.250
$\text{Mo} = \text{Mo}^{+3} + 3e^-$	ca. 0.2
$\text{Sn} = \text{Sn}^{++} + 2e^-$	0.136
$\text{Pb} = \text{Pb}^{++} + 2e^-$	0.126
$\text{H}_2 = 2\text{H}^+ + 2e^-$	0.000
$\text{Cu} = \text{Cu}^{++} + 2e^-$	-0.337
$\text{Cu} = \text{Cu}^+ + e^-$	-0.521
$2\text{Hg} = \text{Hg}_2^{++} + 2e^-$	-0.789
$\text{Ag} = \text{Ag}^+ + e^-$	-0.800
$\text{Pd} = \text{Pd}^{++} + 2e^-$	-0.937
$\text{Hg} = \text{Hg}^{++} + 2e^-$	-0.854
$\text{Pt} = \text{Pt}^{++} + 2e^-$	ca. -1.2
$\text{Au} = \text{Au}^{+3} + 3e^-$	-1.50

\* Standard reduction potentials,  $\phi^\circ$ , have the opposite sign.

Ref: Uhlig, 1978.

The exact diagrams are quite complex and, because they require delicate experimental measurement, are still being updated today, over fifteen years after they were first presented by Pourbaix (Silverman, 1982).

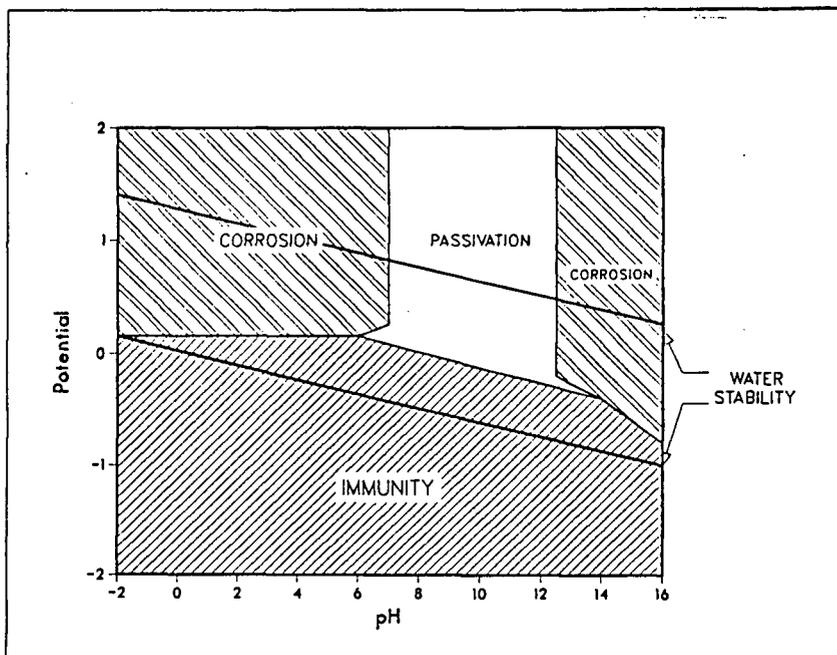


FIGURE 2.1.1a) Pourbaix diagram of copper in water

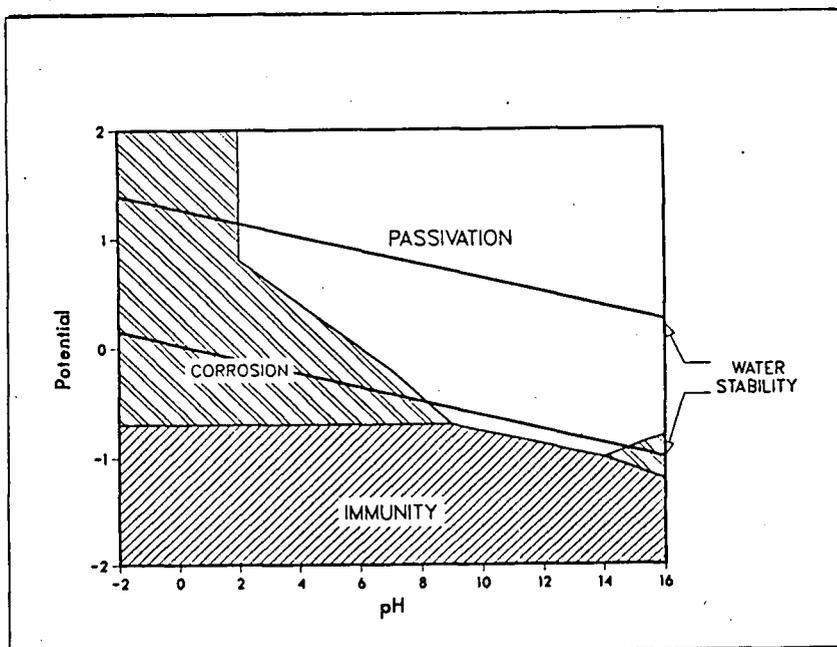


FIGURE 2.1.1b) Pourbaix diagram of iron in water

An important zone indicated on the Emf-pH diagram is delimited by two parallel lines –the region of water stability. As with any other chemical, water can be reduced or oxidized. When reduction occurs, hydrogen gas evolves; when oxidation occurs, oxygen is produced. Therefore, it is only between these two lines that water can exist in the form we know for most human activities (Mathieu, 1982).

When other ions are present in water, the metal species may differ, or exist in different zones. One diagram, then, accurately describes only one set of conditions. However, once a curve is constructed, it allows one, knowing the pH or potential, to choose the value of the other parameter and force the metal into a desired state. This is how plating is done, for example. This is also how, by impressing an outside potential on a metal, it can be forced into an immune region (where it is thermodynamically impossible for it to corrode) or into a passive region (where an insoluble corrosion product is favored). This method of protecting metals against corrosion will be briefly discussed in Section 2.1.4.

Unfortunately, in practice, although a metal may have a 'tendency' to passivate, it may not do so. The rate of formation of the protective corrosion product is sometimes so low that the protection will not occur during the useful life of the metal. To learn more about the actual corrosion rates, the kinetics of the process were developed. An overview is presented in the next section.

### 2.1.2.3 Kinetics

In the case of metallic corrosion in an aqueous solution, it was already mentioned that the free oxidation of the metal and the reduction of the cathode take place on the same metal surface. Therefore, the resulting cell potential lies somewhere between the anodic and cathodic potential, with respect to a reference electrode. Also, because the electrons given by the anode are directly accepted by the cathode, the currents of the anode and cathode are the same.

When the reactions are controlled by the movements of the ions at the metal surface, the process is said to be activation controlled. In this case, the current density (current per area) follows a logarithmic relationship with respect to the voltage impressed beyond its equilibrium potential (overvoltage). This relationship is known as the Tafel equation (Uhlig, 1971):

$$\eta_a = \beta_a \log(i/i_a)$$

where,

$\eta$  : polarizing overvoltage

( $E^{\text{applied}} - E^\circ$  (equilibrium))

$i$  : current density

$a$  : anodic subscript

$i_0$  : minimum current density needed to polarize the voltage

Figure 2.1.2 is a graphical representation of the log current relationship, known as the polarization diagram.

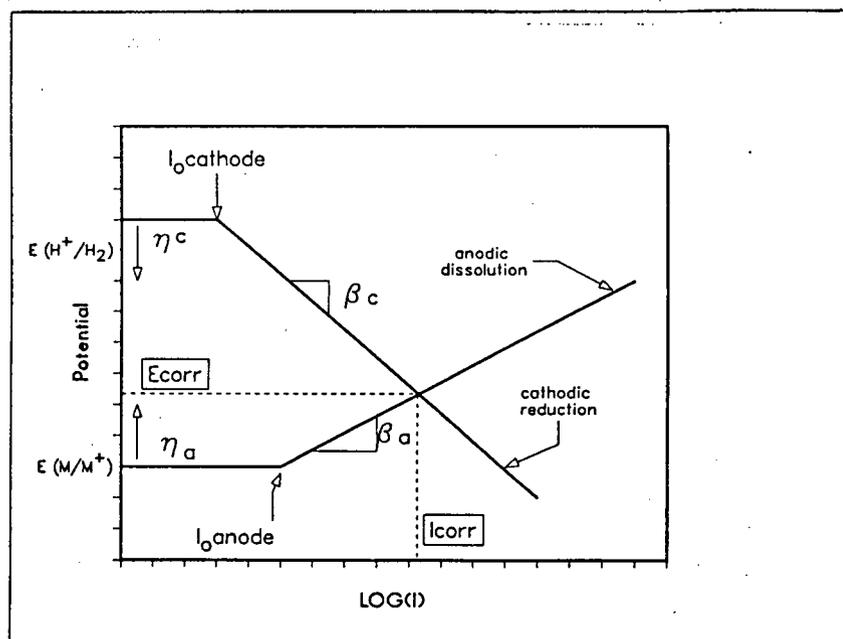


FIGURE 2.1.2 General Polarization Diagram

The important parameters are:

- $E_{\text{corr}}$  = freely corroding mixed potential  
 $I_{\text{corr}}$  = corrosion current  
 $E_{\text{M}^+/\text{M}^0}$  = equilibrium anodic potential  
 $E_{\text{H}^+/\text{H}_2}$  = equilibrium cathodic potential  
 $\beta$  = Tafel slope for (a) anode or (c) cathode  
 $\eta$  = (a) anodic or (c) cathodic overvoltage

From the obtained corrosion current and, knowing the number of electrons given by each dissolved atom of metal, it is then possible to calculate the corrosion rate, i.e. the amount of matter that will be lost in time as a result of the electrical exchange.

Figure 2.1.2 is the simplest polarization curve. Without going into great detail here, it is important to mention that, often, as the voltage increases, the metal enters a zone of the thermodynamic diagram where it cannot exist as an ion, but instead will form an insoluble corrosion product. This product does not usually allow a lot of electron transfer and, as it binds to the metal surface, causes the current to decrease. This phenomenon, called passivation, is graphically presented in Figure 2.1.3, in a simplified manner.

If the potential is raised even further and the metal goes beyond the passivation zone, the protective film starts to break down and pitting corrosion occurs. This particular behavior of metals in distribution system has been studied at various levels. Copper pitting, in particular, has been investigated by Suzuki et al., (1983), Fujii et al., (1984), and others.

The experimental determination of polarization curves and the analysis of the potential are the tools of a growing interest in the water distribution field. Unfortunately, their complexity does not allow for further discussion in this work. In addition to the above mentioned authors, Atlas et al., (1982), DiQuarto, (1985) and Okada (1984) published fundamental studies on the pitting phenomenon.

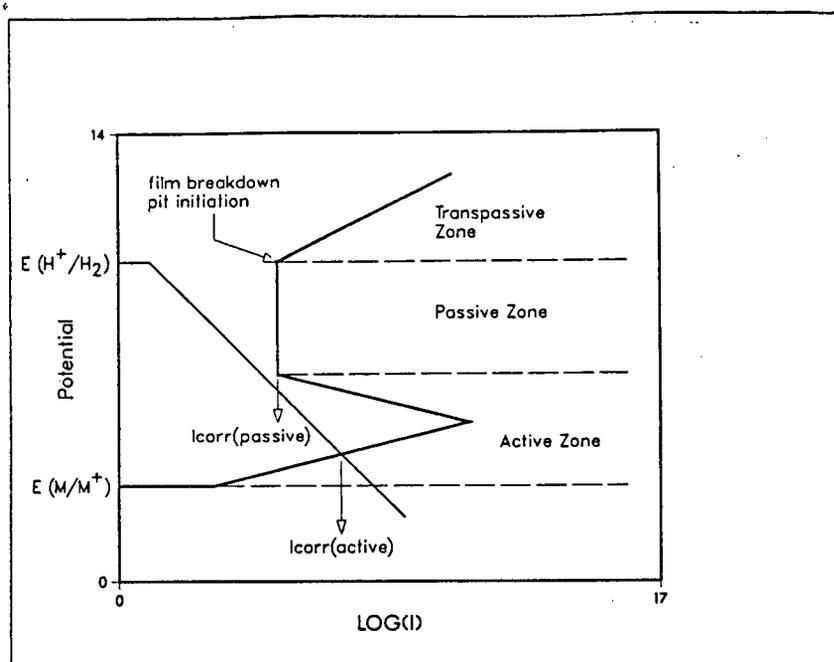


FIGURE 2.1.3 Passivation and pit initiation

### 2.1.3 MONITORING AND EVALUATION

Although the theoretical bases of corrosion are relatively well known, the in-situ monitoring and evaluation of corrosion in drinking water supply systems remains a delicate operation. Several factors complicate the procedure.

Firstly, the pipes are usually buried and difficult to access. Furthermore, the domestic lines are usually much too small in diameter to allow access, or even visual inspection, of the inner surface. Secondly, the inspection of the distribution system requires an interruption of water service, which makes it even less attractive to the groups responsible for the service maintenance.

Nevertheless, now that the potential health problem associated with metals in drinking water is recognized as adding to the overall cost of corrosion, municipalities are more and more interested in monitoring the situation and several tools are available to them (Young, 1978).

Using the classification adopted by Mathieu (1982), monitoring methods can be labelled as direct, if they are based on observations of the effects of corrosion, or

indirect, if they look at the kinetic situation and its potential to encourage corrosion processes.

- Direct measures

The direct methods look at the effects of corrosion. Because of that, they are "a posteriori", or after the fact measures. Amongst others, visual inspection, ultrasonic thickness control, radiography, thermography, inside diameter evaluation, in-situ corrosion coupons weight loss and in-situ electrical probes<sup>1</sup> can be listed. They all have a common goal: recognizing corrosion by its effects on the pipes. Such effects include: weight loss, thickness reduction, cracks and pits development, corrosion product buildup or inside diameter reduction.

Two other consequences of corrosion which can successively be used to assess the problem, are the 'leaks' and 'users complaints' events. By monitoring the frequency of the pipe failures and keeping track of the red-water, black-water or bad taste reports, a water supplier can localize the problem areas, predict the state of a system segment and be prepared when it reaches the point where replacement is required (Boffardi and Schweitzer, 1984).

- Indirect measures

Corrosion can be directly monitored by looking at the environmental conditions in the pipe. Some analytical parameters which can be considered are pH, hardness and dissolved metal levels, all of which are affected by corrosion. A change in their value over the length of the water system is a corrosion indication. On site measurement of the potential, and experimental determination of the polarization curve are also available for corrosion monitoring. However, if such methods do indicate the overall corrosion potential, they supply little

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<sup>1</sup> As the filament of the probe becomes more corroded, its cross section decreases and the resistance increases.

information on localized corrosion events.

Basically, as mentioned by Mathieu (1982), Edeleanu and Hines (1983), and Filinovsky et al., (1985), one single monitoring method seldom succeeds in describing accurately a corrosion situation. Several measures should be combined to assess the phenomenon adequately.

Voyles et al., (1984) and Kirmeyer and Logsdon (1983), outlined a complete monitoring sequence for corrosion in water distribution systems. It includes, amongst other things, a water quality assessment, a public complaints survey, pipe and coupon testing and field sampling. Their work stresses the many aspects involved in the problem.

#### 2.1.4 CONTROL

Four fundamental approaches to corrosion control can be listed: physical obstruction of the electrical contact between the metal and the corrosive environment, electrical maintenance of the system in a thermodynamically safe zone, chemical alteration of the electrolyte to reduce its corrosivity and, addition of 'corrosion inhibitors' to the system (Hartley, 1982).

##### 1. Physical interference

By physically isolating the metal from the electrolyte, the corrosion process is prevented. This straightforward approach is responsible for the on-going development of coatings (polymer, metallic based or organic paints) or thicker linings (cement, mortar, rubber), that are claimed to separate completely the metal pipe from the flowing liquid. However, these surface protectants are only as good as their adherence to the metal, and for as long as their integrity is maintained. They must be insoluble, impervious and adherent over the range of conditions found in the system (Patterson, 1978).

From the polarization diagram, it can be shown that once the lining fails, the tiny surface of exposed metal, which now acts as anode for the bulk of the liquid, is under a greater corrosion rate than if the entire pipe surface was unlined. The metal of that localized area can be consumed at an accelerated rate and failure by perforation will occur. This is why coatings are seldom used by themselves, with another protection usually added to compensate for the unavoidable discontinuities in the coating.

## 2. Electrical protection

Electrical protection of metal derives from the kinetics of corrosion; it can be effectively represented on a polarization diagram. The sought after protection can be cathodic or anodic, depending on whether the impressed voltage is negative (making the metal to be protected a cathode) or positive (making the metal to be protected more 'anodic').

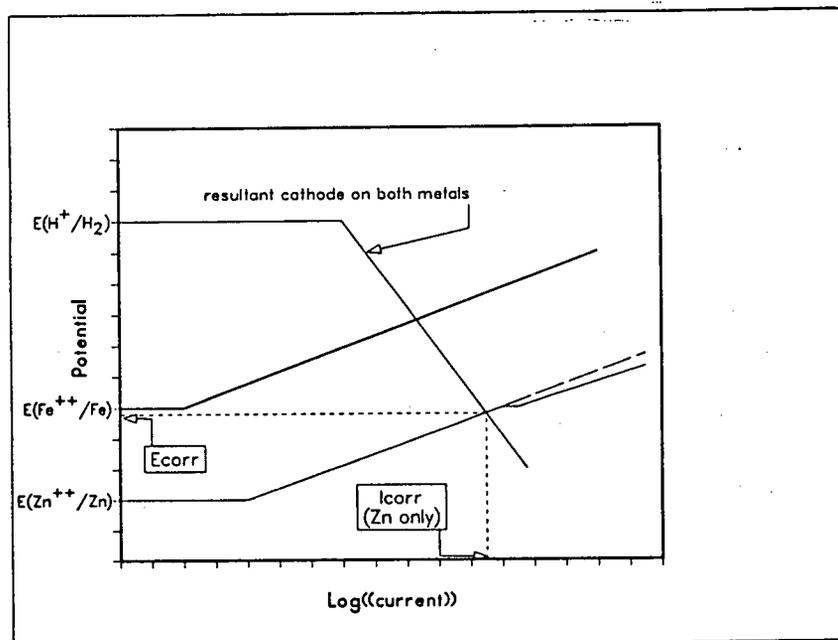


FIGURE 2.1.4 Cathodic protection by zinc addition

Figure 2.1.4 illustrates the principle of cathodic protection. The potential is decreased just below the equilibrium value for the metal and corrosion is

prevented. This decrease can be achieved by the use of an auxiliary anode and a outside electromotive force, or by 'sacrificing' a less noble metal. The zinc coating of galvanized pipes is one example of this cathodic protection.

Impressed or sacrificial cathodic protection is widely used to protect the outside of metallic pipes, usually in combination with a coating. This reduces the area needing protection and, consequently, the electrical energy or metal expenditure. As far as the internal protection of pipes is concerned, little is found in the literature. McGrath and Tighe-Ford (1984) report having found a time-dependent buildup of internal cathodic protection which challenges the belief that such a protection is not possible. Most authors, however, stress the danger of inducing internal corrosion while cathodically protecting the exterior of other pipelines, a phenomenon known as stray-current, (Bender, 1984).

Anodic protection, as shown on Figure 2.1.5, is derived both from the kinetics and thermodynamics of corrosion. By impressing an anodic current, the metal is forced to form a passive corrosion product. No mention of the use of this particular electrical protection method (in drinking water supply systems) was found in the literature.

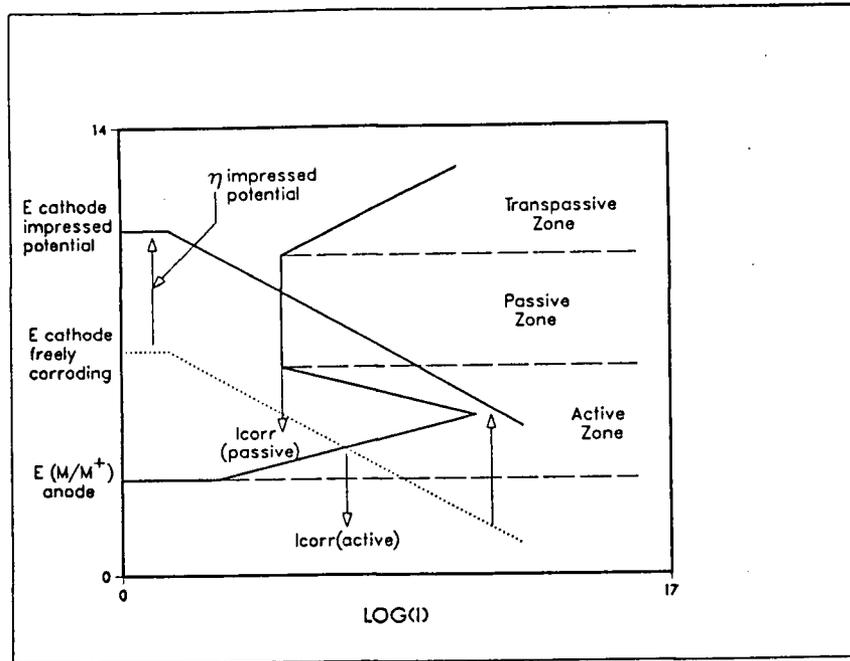


FIGURE 2.1.5 Anodic protection by impressed current

### 3. Electrolyte adjustment

If only a low number of ions in the electrolyte are available to accept the electrons released in the corrosion process, the rate of the dissolution will decrease. By deaerating water, i.e. removing the dissolved oxygen ions, maintaining its pH near neutral (same amounts of hydroxide and hydrogen ions), and removing chlorides and sulfates ions, corrosion can be controlled. However, not all these controls can be applied to drinking water, as will be discussed in Section 2.2.

### 4. Inhibitors

Corrosion inhibitors are substances that, when added in small amounts to an environment, have a marked effect on the corrosion rate. Inhibitors have many modes of action which are not always well understood. They appear to decrease the number of sites available for the electronic exchange by coating the

metal surface.

Corrosion inhibitors can be a variety of organic or inorganic compounds. Those most commonly used, and which are compatible with required water potability are: sodium phosphates and orthophosphates, zinc phosphates and orthophosphates, and various silicates.

## 2.2 CORROSION IN WATER DISTRIBUTION SYSTEMS

The escalating costs associated with corrosion damage has given rise to a growing interest in corrosion studies and control measures. As Stanley R. Saylor remarked in his opening address, for the corrosion workshop of the Fall 1985 meeting of the American Water Works Association in Seattle, Washington, "corrosion did not used to be a topic to get many people up on a Sunday morning". This new concern also produces a "feed-back" in the literature, where an increasing number of publications address the water distribution corrosion problem.

This section is a review of the most recent work published on the topic; because of the volume of material available, the author limited the investigation to the most common technical publications, mainly in the 1980's. The review follows an outline parallel to the background description, addressing first the types of corrosion and then, the respective influences of the pipes and water quality, and finishes with an overview of the control methods in use.

### 2.2.1 TYPES OF CORROSION

The metal pipes of a distribution system might exhibit many of the aqueous forms of corrosion depending on the type of metal and the water characteristics.

The long life-span of lead pipes says a lot about the uniformity <sup>2</sup> of their

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<sup>2</sup>It must be noted that perfectly uniform corrosion does not occur in real-life situations. Filinovsky et al. (1985) studied the causes of nonhomogeneous corrosion. They provided equations to calculate the corrosion rates, taking into consideration the three factors mainly responsible for non-uniform corrosion: nonhomogeneous distribution

corrosion. Lead is a noble metal which slowly dissolves into the solution. Copper is also a relatively noble metallic element and corrodes uniformly in many situations (Kirmeyer and Logsdon, 1983). However, accelerated copper pipe failure caused by pitting has been observed in some high chloride or dissolved oxygen situations (Suzuki and Ishikawa, 1983).

Galvanized iron will also corrode uniformly as long as the protective zinc coating is intact. When the film breaks down, the underlying iron surface will pit, producing characteristic iron oxide tubercles on the surface (Fujii and Kodama, 1984).

When grey cast iron corrodes, the iron going into solution leaves behind a misleading 'graphite flakes' layer (Gummov, 1984). The surface appears undisturbed when it is no longer structurally sound. This graphitization is an example of selective leaching, as is the preferred dissolution of nickel in brass fixtures, which is called dezincification (Jester, 1985).

Because the flowing water can remove the protective films of the distribution pipe surfaces, a high flow will cause impingement, i.e. erosion-corrosion (Sussman, 1978). It may also accelerate other types of corrosion by increasing the exchange rates between the bulk of the liquid and the metal surface (Hilburn, 1983).

It is not realistic to attempt to suppress all corrosion in a metallic network of pipes. Galvanic corrosion will appear at any heterogeneity of the metal surface (Fox and Tate, 1983) or when dissimilar alloys are in contact (Nielsen, 1984). However, the goal of corrosion control should be to maintain the corrosion process in a low uniform rate, to maximize the life of the materials.

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<sup>2</sup>(cont'd) of the electrochemical activity, unequal accessibility of the oxidizer supply and external thermal, electrical and magnetic (or other) fields. However, this simultaneous resolution of Laplace equations is beyond the average corrosion assessment program.

### 2.2.2 INFLUENCE OF PIPES

It has already been mentioned that the pipe material will change the corrosion situation in the water distribution system. In addition, even within a group of pipes of the same material and meeting the same quality requirements, the surface finish can be quite variable. Fox and Tate (1983) found widespread variations in the surface finish of galvanized iron pipes. Fundamental electrochemical investigations show that the physical nature of the surface (state of aggregate, crystal structure, ionic radius, etc.) will also have an effect on the behavior of copper (Raicheva, 1984).

In fact, properties other than just the bare metal surface have an important role in the corrosion exchange; for example, the metal oxides attached to the surface often play an active part in the process. Fujii et al.,(1984) found that the surface potential of copper was affected by the constitution of the surface film, in addition to the oxidizing power of the environment. Craig (1984) and DiQuarto (1985) both stressed the semi-conductivity behavior of the corrosion films, the latter on copper, the former on steel. They emphasized the activity of the films involved in the so-called 'passivation' process.

### 2.2.3 INFLUENCE OF THE WATER QUALITY

If the water carried by the pipes could be depleted of most of the electron acceptor ions, corrosion would no longer be a problem. However, this is not a realistic approach and most control efforts tend to modify the waters' ionic balance and provide a less aggressive solution, or to attempt control the flow conditions to minimize the enhancement of corrosion.

To provide data for the choice of the control parameters, several studies have looked at the influence of specific water characteristics. The results are definitely informative, although they sometimes apply to a very narrow situation and some contradictory results have been found.

In this section, after a brief review of some important aqueous equilibria, some studies of the most documented water characteristics are presented.

### 2.2.3.1 Water Stability Indexes

In a majority of the literature, natural waters with low pH, low alkalinity, low hardness and high dissolved oxygen content are reported to have an aggressive nature and cause problems in the distribution systems (Kirmeyer and Logsdon (1983), amongst others).

The carbonic acid system, (i.e. the different forms taken by atmospheric carbonic gas as it dissolves in water:  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ), is one of the main pH regulatory system for natural waters. The ionic species of this system, bicarbonates ( $\text{HCO}_3^-$ ) and carbonates ( $\text{CO}_3^{2-}$ ), usually account for the main part of alkalinity. As well, hardness is closely linked to the carbonic system

Caused by divalent metallic ions, hardness usually enters fresh waters during their contact with soils. Well water, in particular, may have been in contact with, for example, limestone, and dissolved calcium carbonate ( $\text{CaCO}_3$ ) and magnesium carbonate ( $\text{MgCO}_3$ ). In fact, the importance of the carbonic acid system is such that hardness is usually broken down into two parts: carbonate hardness (that associated with carbonate and bicarbonate anions) and non-carbonate hardness<sup>3</sup>.

Calcium is usually the most abundant of the hardness-causing cations, and the relatively insoluble calcium carbonate ( $\text{CaCO}_3$ ) plays an important role in corrosion protection. Indeed, this compound tends to precipitate when the temperature or the pH of the water increases (a phenomenon observed in water boilers in areas where hardness is high). Several attempts to provoke and control this calcium carbonate film formation on pipe surfaces to prevent corrosion have

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<sup>3</sup>The complexities of the carbonic and calco-carbonic equilibria are beyond this brief reminder. The reader will find additional information in Sawyer and McCarty, 1978, Chapters 5, 17 and 18.

been made. This is discussed further below.

Furthermore, when water treatment is required, it often 'upsets' the natural balance of calcium carbonate in the water. The finished water can either be left with too much or too little of the species, and the solution is unstable with respect to the calco-carbonic equilibrium. If the water is oversaturated, it will naturally tend to go back to the equilibrium levels, the calcium carbonate will precipitate out and the water will be said to be 'scaling'. If too little is left in the water, the chemical drive towards equilibrium will make the unsaturated water dissolve any calcium carbonate it encounters. For example, any existing deposits in the pipes might be dissolved and re-suspended. Such a water is said to be 'aggressive'.

As Rossum and Merrill (1983) noted, corrosion control engineers, in their quest to define overall water corrosivity, have often focussed on the waters' ability to precipitate (or dissolve) calcium carbonate as a global indicator. Several indexes have been developed to assess this tendency, and they have often been applied toward the decision of whether or not the water is corrosive to metals, neglecting that corrosion is more than a chemical solubility process. The same authors reviewed six widely used indexes: the Langelier Index, the Ryznar Index, the Aggressiveness Index, the Driving Force Index, the Momentary Excess and the Calcium Carbonate Precipitation Potential (CCPP). They conclude:

"...neither these nor any other index studied (except CCPP) adequately simulate  $\text{CaCO}_3$  deposition capacity over the entire range of pH values. Indeed, for the most part, the originators did not intend that they did so. However, the authors perceive a tendency within the profession to believe that these indexes are equivalent to, or somehow simulate  $\text{CaCO}_3$  deposition. This is not so."

In fact, other authors recognized that these indexes did not give reliable predictions, and attempted to develop their own indexes, often with the aid of sophisticated computer programs to allow the for the inclusion of more variables.

Ferguson (1984), after pointing out that the Langelier and Ryznar Indexes did not account for residence time in the system or the temperature effect, derived his own kinetic model for heat transfer surfaces. Singley (1985) also presented several different calculations leading to a more accurate calco-carbonic equilibrium pH. However, as Pisigan (1985) reported, when the Langelier Index is calculated using that more accurate pH, it still does not correlate with the observed corrosion rate of mild steel, as measured by coupons weight loss. Tekeu (1983), came to the same conclusions for copper and cast iron coupons. Water with positive indexes (i.e. scaling, according to the accepted interpretation) were sometimes as corrosive or more corrosive than those with negative indexes values.

Singley and Pisigan also developed a multi-variable empirical model to predict the corrosion rates, combining additional parameters with the ones of the calco-carbonic equilibrium. They report having obtained a satisfactory graphical fit to their experimental data.

It is interesting to note that the most apparently successful prediction models for metal solubility or corrosion rates involve graphical representations to describe the intricate equilibrium relationships. Schock and Gardels (1983) represented the variation in lead solubility as a function of the Total Carbonate Species (TIC) and pH, confirming that relatively low TIC (10 to 80 mg/L as  $\text{CaCO}_3$ ) and high pH (9.0), reduced lead solubility.

Similarly, to provide more efficient corrosion control by calcium carbonate deposition, graphical concentration models are recommended, as discussed in the following section.

#### 2.2.3.2 Calcium Carbonate

The method of using calcium carbonate films to protect pipes is used mostly in areas where chemicals are already added to the raw water for treatment. As an alternative to the previously discussed indexes, which will not

supply information on the required amounts of chemicals, multi-entries graphics are proposed.

Merril et al., (1978), in their handbook on  $\text{CaCO}_3$  corrosion control, began their demonstration by setting the limitations of the control measures, with respect to the water hardness content. They recommended the use of Caldwell-Lawrence diagrams to assess the conditions of the raw water, and to calculate the required amounts of chemicals. Those diagrams, set for specific total dissolved solids content and temperature, showed lines of identical Calcium, Alkalinity, pH and Alkalinity. An iterative process led to the selection of the best chemical dosages. However, Dubuc et al., (1984), mentioned that the Caldwell-Lawrence diagrams were inefficient for low-alkalinity, low-hardness waters.

Desjardins et al., (1981) demonstrated the use of Legrand-Poirier diagrams. The graphs showed, versus the calcium and total carbonic acid species, lines of calco-carbonic equilibria. Once a specific water's curve is obtained, the chemicals needed can be calculated directly from the graph. The calculations involved in generating the characteristic curve, however, are complex enough to require the use of a computer program (Millette, 1982, Dubuc, 1984).

To alleviate the complications of theoretical calculations, the calcium carbonate saturation state can be determine experimentaly by the 'marble test' (Pisigan and Singley, Technical note, 1985). In this test, the water is allowed to contact solid  $\text{CaCO}_3$ , and the changes in pH, alkalinity, and calcium concentration are monitored until they reach stable values. However, as these authors emphasized, even if the test shows that the water is supersaturated, it still does not mean that precipitation will occur. They reported studies were natural waters took 70,000 years to reach calco-carbonic equilibrium. Also, if precipitation does occur, nothing ensures that the film will be protective.

Indeed, prediction of calcium carbonate deposition is only one part of the procedure leading to pipe protection. Other requirements must be fulfilled. The protective films, as discussed in section 2.2.2, participate in the corrosion process differently, depending on their composition. As Merrill et al., (1978), explained, to be protective, the film must be dense, tenacious and uniform. These authors gave five recommendations to enhance the production of a 'good' film, pertaining to degree of oversaturation, calcium and alkalinity levels, alkalinity to chlorides+sulfates ratio, pH and water velocity. As they pointed out, these aspects are not well documented. Pisigan and Singley (1985), also mentioned this film 'quality' requirement but, although they stated that it was related to water composition (calcium, alkalinity and pH), they did not specify how.

#### 2.2.3.3 Ions, Dissolved Gases and pH

In addition to the species of the carbonic system, natural waters usually contain other dissolved ions, some of which play an important role in corrosion.

Chloride ions ( $\text{Cl}^-$ ), which are found in all fresh waters, affect corrosion. Figure 2.2.1, from Uhlig, (1971), shows the effect of sodium chloride on the relative corrosion rate of iron. It can be seen that the rate first increases (up to about 3% NaCl), and then decreases. Since 3% NaCl is the concentration of seawater, it can be concluded that in drinking water, which falls below this concentration, chlorides will enhance the corrosion rates.

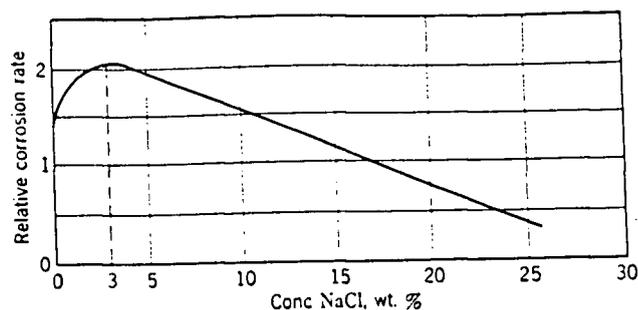


Fig. 14. Effect of sodium chloride concentration on corrosion of iron in aerated solutions, room temperature (composite of data, several investigations).

#### FIGURE 2.2.1 Effect of sodium chloride on the corrosion rate of iron

DiQuarto (1985), found that chloride ions noticeably enhanced the corrosion of copper electrodes. Tekeu (1983) studied the effects of several ionic species on the corrosion rates of copper and cast iron coupons. He found that the three determining ions were: sulfates ( $\text{SO}_4^{2-}$ ), nitrates ( $\text{NO}_3^-$ ) and chlorides ( $\text{Cl}^-$ ), with sulfates being the most aggressive. He observed an increase in cast iron corrosion rates with an increase in the concentration of the ions, up to a maximum value.

Ions are also observed to have synergistic actions on the corrosion rate. Bjorndahl and Nobe (1984), found dissolved oxygen increased the corrosion rate of copper in the presence of chlorides. On the other hand, Atlas et al., (1982), observed that dissolved oxygen played only a minor role in copper pipe corrosion, if residual chlorine was found in the drinking water. Fujii et al., (1982), noticed that, in fact, dissolved oxygen did have the major oxidating role for the initial copper corrosion, but that residual chlorine took over to cause pitting of the pipes and acceleration of the failure. This was confirmed by the studies of Suzuki and Ishikawa (1983), who found that chlorite ions affected the formation of cuprous oxide layers, thereby reducing the pit initiation time and accelerating the pitting process thereafter, by concentrating in the oxide film.

More recent work by the same authors (1984) showed that pH affected the resistance of the copper film to pitting by chlorine. They also confirmed that chloride ( $\text{Cl}^-$ ) reduced copper resistance to corrosion but that sulfates increased the protectiveness of the film.

It is not the purpose here to confuse the reader, only to illustrate how each water situation is different, and to show that corrosion rates are determined by the interactions of several elements, at different stages of the process. As Hilburn (1983, 1985) observed, uniform corrosion of copper is characterized as a "heterogeneous rate process composed of metal oxidation and oxide film growth, interfacial chemical reactions, and mass transport in the liquid phase". Although he recognized that each rate was influenced by a distinct set of environmental variables, he isolated the effects of pH and temperature on the overall corrosion rate. For the Seattle Tolt River treatment, he recommended a pH increase of 6.3 to 8.0.

In fact, altering the pH affects all the chemical equilibria, changes the proportions of the various ionic species and alters the gases' solubility. The overall effect being difficult to model, a laboratory experiment becomes a viable alternative, as it provides data on the global effects of water characteristics modifications. This approach was chosen by the author in this present work and also by Desjardins et al. (1983), in similar studies. Those authors found that an increased pH decreased the corrosion rate of ductile cast iron in the low hardness, low alkalinity and high dissolved oxygen conditions of their test water.

Non-chemical water characteristics are also known to influence corrosion rates; these are discussed in the next section.

#### 2.2.3.4 Temperature and Flow Velocity

Temperature will affect corrosion rates because chemical activity varies with the water temperature. Hilburn (1983, 1985) found that all three rates of

the copper corrosion mechanism were increased as the temperature changed from 5°C to 25°C; Uhlig (1971), reported that the corrosion rate of copper in tropical climates increased by 1.5 to 2.0 times over that in more temperate climates.

In some cases, however, water may become protective as the temperature increases. Desjardins et al., (1983), described the shift in the upper part of the Legrand-Poirier stability curve with an increased temperature. They showed that the higher temperature, reducing the solubility of calcium carbonate, will cause a well balanced, or even corrosive, cold water to become scaling in hot water pipes.

The flow velocity in the pipes will also affect corrosion rates. A high flow will favor the transfer between metal and solution and, possibly, disturb the protective film. Hilburn (1983,1985) found a great increase in copper corrosion with high flow velocities; Singley and Lee (1984), studying black steel, noted that "corrosion rates were inversely proportional to the pipe size and thus directly proportional to the velocity of flow within the velocity range tested". Sussman (1978) reported a case of impingement pitting in a building's copper pipes after a new, more powerful, circulation pump was installed.

However, if high flows are detrimental, so too can be very very low flows or stagnant conditions, such as those encountered at the dead ends of water distribution lines. Under the effect of corrosion, the limited exchange between some parts of the liquid and the bulk fluid will allow their characteristics to change towards a more acidic state as the metal and chloride ions concentrate near the metal surface. Those autocatalytic zones will lead to a localized attack of the pipe (Tromans, 1983). Also leading to increased corrosion rates, the sediments will be allowed to accumulate in the stagnant zones and, possibly, will support a bacterial population. This biological aspect of corrosion in

water distribution systems is discussed below.

### 2.2.3.5 Bacterial Growth

Although the vast majority of potable waters receive some disinfection treatment before entering the distribution system, it appears unavoidable that the pipe surface will, in time, support some bacterial population. O'Connor and Banerji (1984), studied bacterial impact on corrosion with a pipe-loop system; they could not maintain it bacteria-free despite repeated disinfections with high doses of chlorine. By adding some of their pipe-loop microorganisms to a cast iron stirred corrosion reactor, they observed an increased corrosion rate and more localized pitting. These authors also conducted a survey of five Missouri water supply systems and found that, generally, higher bacterial plate counts were observed in locations where water quality complaints were more frequent.

Victoreen (1978, 1984) studied the corrosion of cast iron mains and concluded that rust production and turbidity could be reduced by reducing the bacterial population. The author stressed the danger of overestimating chemical corrosion by neglecting the bacterial involvement in the process.

Another aspect of bacteria and corrosion control, emphasized by several authors, is the possible contradictory effects of disinfection and corrosion control measures. Can corrosion control lead to a higher bacterial survival rate, leading in turn to higher required chlorine doses (which increases corrosion), offsetting the effects of corrosion control, both in costs and effects?

Nakhjiri et al., (1984), studied this aspect for the Seattle distribution system corrosion control program. They found that, indeed, the new water conditions (higher pH and alkalinity) would be more favorable to bacteria. However, even if the corrosion rate of copper increased by 70% when free chlorine residual changed from 0 to 1.0 mg/L, the authors stated that the corrosion control measures would still be beneficial. The actual chlorine dose of

0.20 mg/L produced sufficient bacterial kill in the new conditions, and no additional disinfection costs were predicted.

Desjardins et al., (1981), studied the problems encountered in a Quebec municipality where the calco-carbonic equilibrium pH of the treated water was near 8.8, causing disinfection problems in the water distribution system<sup>4</sup>. For corrosion control, they reduced the equilibrium pHs by changing the chemical treatment dosages and achieved, at the same time, a better disinfection. Chemical costs were reduced at both levels, adding to the savings generated by corrosion reduction.

O'Connor et al., (1984), found the same bacterial counts on steel, copper and PVC pipes, which suggest identical potentials for microbial activities. However, the other authors dealing with biologically mediated corrosion usually refer only to steel pipe occurrences. In fact, in natural waters, "copper is one of the very few metals that remains free of fouling organisms, normal corrosion being sufficient to release copper ions in concentrations which poison marine life" (Uhlir, 1971). Nevertheless, if increased doses of chlorine are needed to protect the steel pipes of the system, this will in turn affect copper in the ways discussed previously, and it must be accounted for.

#### 2.2.4 EXTERNAL INFLUENCES

Up to this point, the discussed corrosion parameters were more or less 'controllable' by the water supplier. Water composition is determined by the raw water source but it can be adjusted with chemicals. Pipe surface defects and galvanic connections may result from a manufacturing flaw, but they can be detected through inspection. In this section, some of the more 'uncontrollable' corrosion causes are

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<sup>4</sup>High pH favors the decomposition of chlorine into hypochlorite ions ( $\text{OCl}^-$ ), the chlorine species with a lower disinfecting capacity. The required chlorine doses increase as pH increases.

reviewed.

#### 2.2.4.1 Stray Current

According to Uhlig's (1971) definition, "stray electric currents are those that follow paths other than the intended circuit, or they may be any extraneous currents in the earth". The 'earth' type is of rare occurrence and is usually of small magnitude and duration. The first type, however, is frequent in cities where electric currents intended for various utilities, criss-cross in every direction.

For example, the returning current of electric street railways may use a buried watermain as a return path, if the rails are poorly insulated and the resistance is lower in the pipe than in the ground.

In general, the stray current will cause corrosion of the exterior of the pipe, which is an economical concern but not a water quality one. It will not be discussed here. However, Bender (1984), reports a case where stray current caused the internal corrosion of a large diameter water pipe. A combination of conditions caused the cathodic protection intended for four buried utility lines to find its way into the pipe and accelerate the corrosion rate dramatically. As the author states, such an occurrence might be rare but corrosion-involved engineers should be aware of it.

In fact, if the suggestion of internal cathodic protection for pipes put forth by McGrath and Tighe-Ford (1984) finds practical application, other problems of electrical corrosion control will have to be considered. A last example is presented by Haney (1981). The author reported that the protection potential of a sacrificial zinc anode increased with time to a point where it no longer acted as the anode but as the cathode, actually increasing the corrosion of the 'protected' pipe. Fortunately, it appears that this situation can be rectified by placing gypsum around the zinc anode. The aggressive sulfate ions found in gypsum help the anodic reaction to proceed in the right direction.

#### 2.2.4.2 Users

The owners of domestic plumbing systems attached to the municipal supply may sometimes be responsible for their own increased corrosion rates.

Voyles et al., (1984), and Sussman, (1978), studied the corrosivity of zero hardness water produced by domestic water softeners, especially when the supplied water already had a low hardness content. Sussman also mentioned the "thousands of failures of aluminium, galvanized steel and iron pipes installed downstream of copper pipe systems".

Rossum, (1978), reported cases of copper pitting failures which occurred because new dwellings were left unoccupied several months after construction. The pipes were not used after installation and the manufacturing debris, left in the pipes, initiated pits on the lower half of the horizontal pipe sections. The problem could have been avoided by thoroughly flushing the new pipes daily, for the first three days after installation.

From these examples, it can be seen that the water utilities have at least one good tool to prevent such events from deteriorating drinking water quality: information.

#### 2.2.4.3 Acid Precipitation

The effect of acid precipitation (rain, snow, dry fallouts) on drinking water is a new concern. The March 1984 issue of the Journal American Water Works Association presented the first studies addressing this topic. Perry (1984) summarized the situation:

"The most serious aspect of water supply contamination related to acidic deposition could be increased corrosivity of water supplied to the distribution system."

This author emphasized the potential for metallic contaminants to enter the drinking water when in contact with metal surfaces, the worst situation being the one

of small distribution systems depending on roof catchments for water supply. Reed and Henningson (1984) also advanced similar conclusions. Leibfried et al., (1984), stressed the fact that, in their study of a Pennsylvania water system, the supplier could not meet the recommended pH values for drinking water (6.5 to 8.5), and that the situation worsened substantially during the runoff following a storm. Taylor and Symons (1984), studying water systems of New England, found the water to be aggressive, and the maximum contaminant levels for lead and copper to be exceeded in 7% and 29% of their first flush samples. They attributed at least part of the problem to acid deposition in the poorly buffered soil of the region.

More recent studies by McDonald (1985) also focused on the possible metal increase in water due to acid rain and the possible health effect, depending on the amount ingested daily<sup>5</sup>.

Although acid deposition studies were presented separately due to the 'uncontrollable' and 'evolutive' nature of the sources, the problems associated with pH decrease in water supply were the same as the one previously mentioned, and could be controlled chemically.

### 2.2.5 CONTROL MEASURES

Throughout the previous section, as the effects of various water characteristics were reviewed, it was mentioned in which direction they should be modified to reduce corrosion. Many authors present, in the literature, the results of pilot or full-scale corrosion control strategy implementations, involving those aforementioned modifications.

One of the better documented studies is the Seattle distribution system corrosion control study. In the preliminary internal corrosion report (Kennedy Engineers, 1978), the use of lime, sodium bicarbonate and sodium silicates were recommended. It was established that the corrosion protection cost would be \$7.50 per residence, leading to

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<sup>5</sup>The effect of high metals levels in drinking water is briefly covered in Section 2.3.

an excellent benefit to cost ratio of 5.4:1.

The actual study is composed of seven volumes (Kennedy Engineers, 1979 to 1983). The first volume is summarized by Hoyt et al., (1982), and reports on the Cedar River pilot plant study. It was recommended that 1.7 mg/L of quick lime (CaO) be added to raise the pH to 8.3 and the alkalinity to 19 mg/L. Herrera and Hoyt (1984) present the sister study for the Tolt River pilot plant. The slightly different conditions required the addition of 2.0 mg/L of lime and 9 mg/L of sodium bicarbonate. The third volume of the series deals specifically with the treatment effects on tin/antimony solder (Herrera et al., 1982).

The full-scale implementation of the recommended treatment is studied in Volume IV. It was found that the chemical dosages must be applied gradually to prevent the sloughing of corrosion products from older pipes, which gave rise to red-water consumer complaints. The target values could be reached in 42 days without problem<sup>6</sup>.

Other cities apply corrosion control measures although, as mentioned by Reed and Henningson (1984), it is only a small percent of those having corrosive waters. Costello, (1978), reported on the use of lime for water stabilization in the 4200 miles of Chicago's distribution system. In Boston, sodium hydroxide lead to satisfactory results at a low annual cost of \$0.59 per person (Karalekas et al., 1983). Zinc orthophosphate inhibitor was also tried in Boston for a period of seven months, but was discontinued because it did not adequately control lead corrosion and enhanced algae growth in the storage reservoirs.

This detrimental side effect of zinc orthophosphate is also reported by Haskew (1978) in Weehawken, New Jersey. Nelson and Kingery (1978), however, report a successful use of zinc orthophosphate in Pinellas county water systems, when used with sodium hydroxide for pH control. Sanders (1978) mentioned the lack of success

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<sup>6</sup>Volumes V and VI, dealing with disinfection, and copper corrosion rate parameters were discussed previously. Volume VII was not available at the time of writing.

obtained with glassy polyphosphate and zinc polyphosphate in Sioux Falls, South Dakota, when dealing with a bacterial induced cast iron corrosion situation. On the other hand, Swayze (1983), described the satisfying use of zinc phosphate in Carbondale, Illinois. They abandoned the use of sodium hydroxide (for pH control) for the use of the corrosion inhibitor, which was less expensive and safer to manipulate.

The list of individual adjustment and/or inhibitor addition permutations could go on and on, without sketching a clearer general solution. In fact, all waters are different and must be investigated individually. Boffardi and Schweitzer (1984) discussed the effects of several inhibitors, but emphasized the necessity of a monitoring program, both to assess the corrosion situation and the efficiency of control measures. A coupon lab test can provide data on the situation and permit the selection of a set of control measures, but the in-situ monitoring must be an on-going process. "Customer satisfaction is the most important monitoring technique available to the water utilities" (Boffardi and Schweitzer, 1984).

### 2.3 COPPER LEVELS IN DRINKING WATER

The vast majority of the previously mentioned authors list possible health hazards as one of the problems associated with high corrosion rates. The toxicity of lead has been documented sufficiently and will not be detailed here. However, secondary contaminants, such as copper, are now a concern.

Demayo and Taylor, (1981), prepared an extensive literature review on copper toxicity for Environment Canada's Guidelines for surface water series. They stated that, although copper is one of the essential elements, ingested in milligram quantities, it will induce vomiting and diarrhea<sup>7</sup>. McDonald, (1985), also mentioned this effect of copper and suggested that, because of the obvious symptoms, copper should not be a acute problem. It will induce vomiting at levels above 15 mg/L, but will cause the

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<sup>7</sup>This may occur when acidic food or drink (vinegar, carbonate beverages, citrus juice) has been in prolonged contact with metal (e.g. soft drinks in dispensing machines).

water to be unpalatable at much lower levels. McDonald reported the taste detection level to be between 5 and 7.5 mg/L, but Sims and Raible (1983), mentioned a case of localized copper corrosion that came to their attention after several bad taste complaints; the levels were between 1.5 and 2 mg/L.

Although acute copper intoxication might not be a problem because of the low taste threshold, chronic problems could be associated with a high daily intake. Children and infants consume a greater amount of water, with respect to their body weight, than adults. They would be the first ones affected (McDonald, 1985). Although copper intake can be assessed by blood levels (Subramania and Meranger, 1983), the analysis is not easy and such a sampling could hardly fit into a routine corrosion monitoring program.

Zoeteman and Haring (1978) found a general increase in copper, zinc and lead levels in drinking water in the Netherlands, after distribution. To assess the ingested amount of contaminants, they suggested the use of a 'proportional sampling' device. Installed on a tap, it would collect a daily composite sample by diverting a fixed percent of the flow, each time the tap was used. From a study involving 400 people, these authors reported that 74% of the users took the morning first flush to prepare coffee or tea, and that 73% never flushed the tap if the water was intended for cooking or beverage preparation. This points to the importance of controlling the first-flush metal levels.

On the other hand, Sherlock et al., (1983), studied dietary copper intake and found water to be a small contributor to the total quantity ingested. The weekly adult intake ranged between 10.2 and 21 mg; there appeared to be little difference between participants from households with lead pipes and those from households with copper pipes.

It remains a fact that copper has some potential chronic effects. Pulmonary deposition, fibrosis, granulomas and malignant liver tumors have been reported by

Demayo and Taylor (1981). Although the U.S. EPA (in Demayo and Taylor, 1981) sets an upper limit of 1 mg/L for copper in drinking water, these authors suggested that the above mentioned potential chronic health effects warranted a maximum raw water level of 0.50 mg/L.

### 3. METHODOLOGY

#### 3.1 INTRODUCTION

This study on corrosion required three distinct facets of experimental procedures: laboratory water characteristics monitoring, metal samples preparation and drinking water sampling program. The outline of the laboratory set up is given in this chapter, followed by a description of the experimental and analytical procedures used in each aspect of the research.

#### 3.2 LABORATORY SET-UP

The purpose of the laboratory experiment was to examine the effect of an increase in the pH of drinking water on the corrosion rate of two types of distribution pipes: cast-iron and copper.

The corrosion rate was assessed using the weight loss of metallic coupons exposed, for various lengths of time, to a low flow of water. Simultaneously, separate groups of coupons were exposed to different pHs. Further, to investigate the effect of the distribution system pressure on corrosion, two different series of cells were used: one receiving its feed water by gravity, the other directly connected to the water distribution system and, therefore, pressurized.

Because of the different pressures inside the cells, the two groups required slightly different experimental set-ups, as described below.

##### 3.2.1 GRAVITY CELLS

To prepare feed water at different pHs, the water was first drawn from one tap and stored in 90-liter containers where its pH could be adjusted. A lime solution ( $\text{Ca}(\text{OH})_2$ ), was added to increase the pH to the target value on a daily basis. The feed basins were installed 0.64 meter above the bench top and, from there, the water

was allowed to flow, by gravity, into the two attached cells, one containing copper samples, the other cast iron coupons, as shown on Figure 3.2.1.

In the first experiment, six cells were part of the "gravity" group. In addition to a gravity-fed control basin (pH not adjusted), pH 7 and pH 8 were studied. Three experimental conditions for two metals required six different cells. In the second experiment, eight cells were fed by gravity; a pH 6 basin was added to the study.

To prevent contamination, only non-metal components were used in the plumbing connections. PVC bulk-head fittings were installed at the bottom of the basins and fitted with plastic valves. Tygon tubing was used to distribute the flow to the acrylic cells.

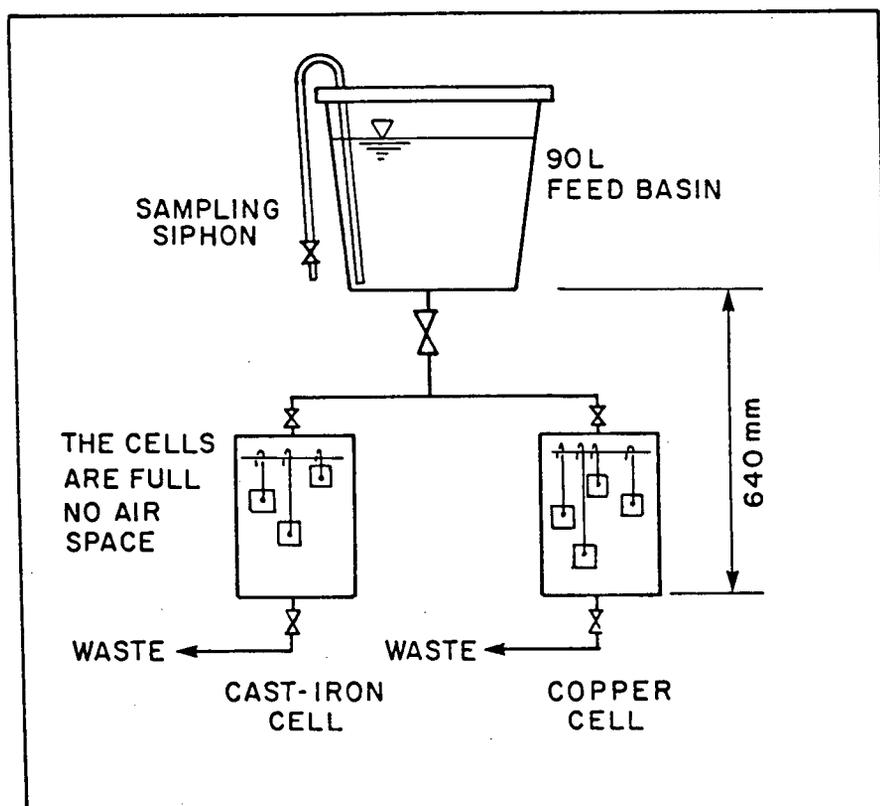


FIGURE 3.2.1 Gravity Cells

The body of the cells was made of 16.5 cm (6.5 inch) inside diameter, 0.64 cm (0.25 inch) thick, clear acrylic tubing, and the top and bottom were of 0.64 cm (0.25 inch) acrylic sheet. The bottom and hanging bars were glued on; the top cover was held in place with nylon threaded rods and PVC nuts. PVC welding rod was used to make the hooks needed to suspend the metal coupons in the cells, as shown on Figure 3.2.2.

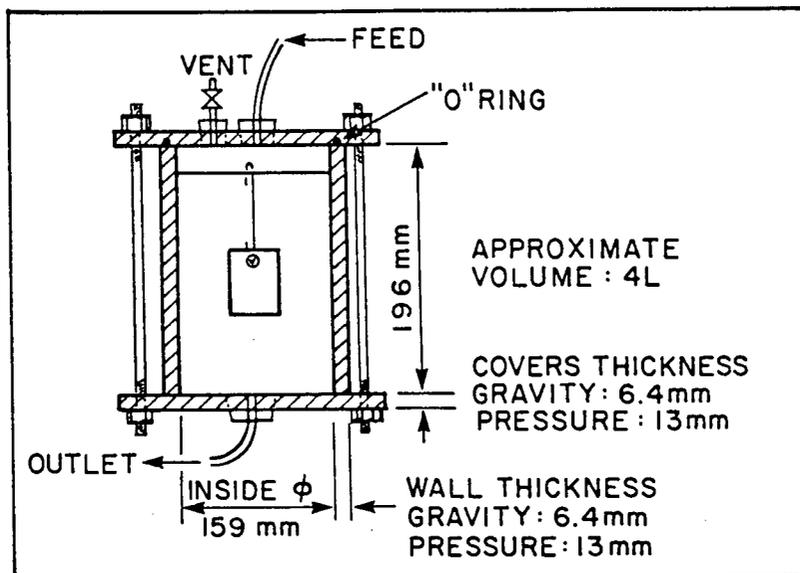


FIGURE 3.2.2 Cell Dimensions

The basins were filled approximately once per week and the effluent from the cells was sent to waste. An approximate average flow of 200 ml/hour was maintained by adjusting the outlet clamps of the cells. Although this method allowed large daily variations in the flowrates, it is still believed, according to Tekeu (1983), to be a sufficient water flow to avoid any significant changes in the water characteristics inside the cells.

### 3.2.2 PRESSURIZED CELLS

The municipal water distribution system is usually maintained at a pressure near 60 PSI. However, since the metal samples in the gravity-fed cells were subjected to a much lower pressure, it was decided to investigate the effects of a higher normal pressure on the corrosion rate, by using a set of "pressured control" cells. Two cells, one containing copper samples and one cast-iron samples, were connected directly to the laboratory plumbing system by means of PVC pipes. No adjustment of the feedwater pH was done in these cells, thus explaining the pressure control appellation.

Because of the increased stress on these cells, thicker acrylic was required, both for the body and covers. A stainless steel plate was added on top of the acrylic cover and the cells were assembled with stainless steel threaded rods and nuts. Although these were metallic components, they were not considered to have any contamination potential because they were not in contact with the water or metal samples. The flow-through in these cells was kept at the same low levels as that in the gravity-fed cells.

### 3.3 WATER QUALITY MONITORING

In this experiment, the pH was the only water characteristic modified. However, many other parameters were monitored to ensure that the feed-water variations with time were minimal.

In this section, the water sampling procedures are described and the experimental methods outlined.

#### 3.3.1 SAMPLING PROCEDURE

The water samples for the gravity cells were taken out of the feed basins. For the pressure cells, the combined effluents were used for analysis.

In the first experiment, all the samples were taken on the filling day, one set before filling and one set after filling. However, because the nitrogen and metals analyses showed very little change between the 'before' and 'after' samples, the 'after' set of samples was left out for the second experiment.

The basin contents were completely mixed and the samples were drawn from the bottom with a siphon tube. The samples for metals and nitrogen analyses were stored in acid washed plastic bottles. The dissolved oxygen samples were taken directly into standards 300 ml BOD bottles.

One litre brown glass bottles were used to store sufficient sample for the remaining analyses.

### 3.3.2 ANALYTICAL PROCEDURES

Unless otherwise specified, all tests were performed according to Standard Methods for the Examination of Water and Wastewater ( A.P.H.A., 1980).

#### 1. Chloride

The chloride ion ( $\text{Cl}^-$ ) concentration was determined using the ASTM Standards Colorimetric Method (ASTM method D512c, 1983) for water containing 0.10 to 10 mg/l chloride ion.

In this method, solutions of ferric ammonium sulfate and mercuric thiocyanate are added to a 25 ml sample. A red complex is formed and the chloride ion concentration is determined by comparing the intensity of the sample colour, after ten minutes of development, with the colour of prepared standards.

The colour comparison was done at a wavelength of 463 nm. In the first experiment, a Bausch & Lomb spectrophotometer (Spectronic 88) was used with a one-cm cell. In the second experiment, the SP8-100 Ultraviolet Spectrophotometer of Pye Unicam was used with a ten-cm cell until September 6. The last three series of samples were analysed on the Spectronic 88, with a

five-cm cell.

## 2. Dissolved Oxygen

The dissolved oxygen content was analysed using the Azide Modification of the Winkler (or iodometric) method (A.P.H.A. 1980, Section 421B). The dissolved oxygen oxidizes under strong alkaline conditions and the manganese, in return, oxidizes iodine under acid conditions. The amount of free iodine is then equivalent to the original content of dissolved oxygen and is measured by titration with sodium thiosulfate using a starch indicator.

In this experiment, a 0.0375N thiosulfate solution was used to titrate a whole 300 ml BOD bottle, rather than the standard 0.025N thiosulfate used for a 200 ml aliquot.

## 3. Hardness (Total and Calcium)

The Total and Calcium hardness were measured by the EDTA titration, using a 10 ml microburet and the recommended indicators (Hydroxynaphthol blue and Calmagite) in an undiluted 100 ml sample (A.P.H.A. 1980, Section 314B).

## 4. Metals

A Jarrell Ash atomic absorption spectrophotometer (model 810) was used for the metals analyses. Undiluted and unfiltered samples were acidified for preservation and analysed within three months of sampling. Acetylene ( $C_2H_2$ ) was used as fuel and air as oxidant. The standards were diluted in 0.57% nitric acid ( $HNO_3$ ); dilution water and acid blanks were run. The method of determination is described in U.S. EPA procedure (1979).

The samples were analysed for Calcium, Copper, Iron, Magnesium, Potassium, Sodium and Zinc.

## 5. Nitrate and Nitrite

A Technicon Autoanalyser II was used for the determination of the nitrate ( $NO_3$ ) and nitrite ( $NO_2$ ) concentration. According to the Technicon Method

100-70W (1973), the nitrates in the sample are reduced to nitrites and the total amount is stabilized into a reddish-purple complex. The concentration is determined by photometric comparison with prepared standards.

#### 6. pH and pH adjustment

In the first experiment, pH was measured on a Fisher Accumet Model 320 expanded scale research pH meter, with combined glass reference electrode (Orion 91-06). For the second experiment, the pH meter unit (Fisher Electrometer Model 380) of a Fisher Titrimeter II auto-titration system was used. Until day 10, the pH meter was equipped with an Orion probe. It was then replaced by a VWR Scientific Inc 0-14 combination probe. In both experiments, pH was adjusted according to the following procedure.

After mixing of the basin contents, a one-liter sample was drawn into a glass beaker and the pH raised slightly above the target value by addition of a lime solution (1 mg/ml concentration). The amount of lime solution required to adjust the pH of the remaining volume of water in the basin was then mixed into the feed.

#### 7. Sulfate

In both experiments, sulfates ( $\text{SO}_4$ ) were analysed using the Turbidimetric Method (A.P.H.A. 1980, Section 426C). According to this method, the sulfates are precipitated by barium chloride in the presence of an acetic acid buffer. The  $\text{SO}_4$  ion concentration is determined by comparison of the absorbance after 5 minutes development, with those one of prepared standards, at a wavelength of 420nm.

In the first experiment, 250 ml of sample was evaporated down to 25 ml, then filtered on Whatman #541 Ashless paper to remove any suspended material<sup>8</sup>. The sulfate concentration was then determined on a Bausch & Lomb

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<sup>8</sup>The heavy rainfalls of the 1983-84 winter caused sediments releases in the watershed area and, consequently, in the drinking water of the Greater Vancouver Area. The

spectrophotometer (Spectronic 88) with a one-cm cell. In the second experiment, 50 ml samples were directly analysed using the SP8-100 Ultraviolet Spectrophotometer of Pye Unicam, with a ten-cm cell.

#### 8. Temperature and Volume

The feed water basin temperature was measured with a  $-50$  to  $+50^{\circ}\text{C}$  thermometer, on a daily basis. The volume was evaluated by measuring the liquid height in the feed basins.

#### 9. Total Alkalinity

According to Standard Methods (A.P.H.A. 1980, Section 403), any alkalinity lower than  $20\text{ mg/l}$  as  $\text{CaCO}_3$  should be reported only if it was determined by Method 4d, Potentiometric Titration of Low Alkalinity. However, in this experiment,  $200\text{ ml}$  samples were titrated to colour change, according to method 4a. The choice of the colorimetric method over the potentiometric method was dictated by the considerable time needed for the pH meter to equilibrate in dilute solutions (10 to 20 minutes) and the number of samples to analyse. The results lower than  $20\text{ mg/l}$  Alk. as  $\text{CaCO}_3$  are given for information only.

For the first three quarters of the test run, Phenolphthalein and Methyl Orange indicators were used for alkalinity titrations (A.P.H.A. 1980). The rest of the titrations were performed using the indicators recommended by the 16th edition of Standards Methods (A.P.H.A. 1985), i.e. Bromocresol Green (to replace Phenolphthalein) and Metacresol Purple (to replace Methyl Orange).

The Total Alkalinity is the sum of the Phenolphthalein and Methyl Orange Alkalinities.

#### 10. Total Acidity

The Acidity was measured by colorimetric titration (A.P.H.A. 1980, Section 402a), a procedure identical to the one described in the Section 9, on alkalinity

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<sup>8</sup>(cont'd) suspended matter was removed to avoid interference in the absorbance readings.

measurement.

### 3.4 METAL SAMPLES MANIPULATIONS

The corrosion rate (gram of metal lost per square meter per day of exposure) was determined by weighing the pipe samples before and after their exposure to the water.

The identified metal coupons received a very specific treatment to ensure two things: first, that they were given a standard treatment that would allow the results to be comparable, and second, that their interaction with the studied environment would be maximized. The preparation, handling and analytical procedures used for the pipe samples are described in this section.

#### 3.4.1 CUTTING AND IDENTIFICATION

To guarantee that the metal coupons would closely approximate the characteristics of water distribution pipe materials, actual pieces of pipe were used as samples. Due to the differences between the two metals, the cutting methods varied between copper and cast iron. However, the resulting coupons were approximately of

the same dimensions (see Figure 3.4.1), and weights (10 to 12 grams).

NOTE: Approximate dimensions

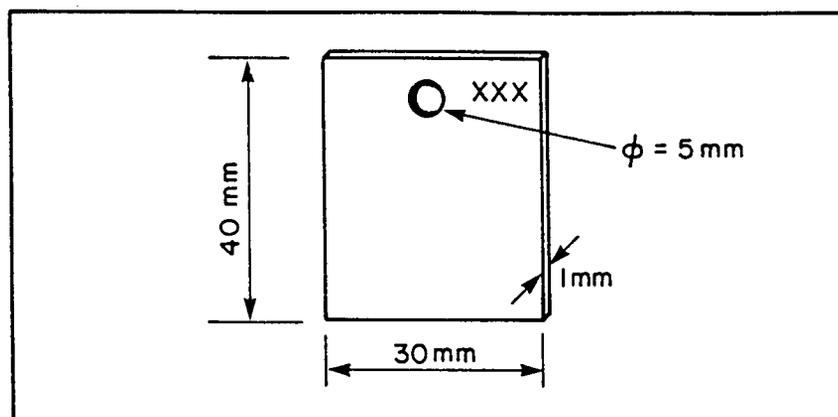


FIGURE 3.4.1 A Metallic Coupon

## 1. Copper

The copper coupons were cut out of a 19 mm (3/4 inch) diameter, type L, semi-hard Noranda copper pipe. This particular type was selected both for its easy handling characteristics and because it is widely used in domestic plumbing systems.

The pipe was first cut into 40 mm lengths with a saw; the pieces were then cut open with a tinsnip and flattened. The tinsnip was then used to cut the pieces to a 30 mm width. A 5 mm (3/16 inch) hole was pierced at approximately 6 mm of the top of the plate, in the center. A three-digit number was stamped in the upper-right corner to identify the coupon<sup>9</sup>.

## 2. Cast-Iron

<sup>9</sup> For the first experiment, the copper coupons used were provided by the Section Protection de l'Environnement of the Civil Engineering Department of l'Ecole Polytechnique de Montreal. Although fundamentally identical to the ones prepared for this experiment, they could be recognized by the '1' appearing in their upper left corner. For the remaining experiments, coupons were prepared locally.

The ductile cast-iron pipes used in the Greater Vancouver Regional District's water distribution system have a cement-lined inner surface. This same type of pipe was used to cut out the samples used in this research, although the lining was removed during the preparation process.

The 159 mm (6.5 inch) pipe was cut in 40 mm rings with a water cooled diamond blade saw. The rings were then roughly cut to size with an XLO milling machine. The final dimensions and thickness were obtained with a Favretto TA60 surface grinder. Special attention was given to metal cooling during the cutting, to avoid any change in the metal structure due to temperature increase.

A 4 mm (5/32 inch) hole was drilled in the upper edge of the plate and identification numbers were stamped on the upper right corner, in the same way as was done for copper<sup>10</sup>. However, for two thirds of the second experiment cast-iron coupons, an alternative identification method was used because it was found, in the first experiment, that the numbers did not show well after a four-week exposure period. For the coupons needed for six, eight, ten and twelve-week exposure, an 'edge-clipping' code was developed.

As can be seen from Figure 3.4.2, six 'clipping-sites' were chosen. These included the four corners, the left edge and the bottom edge. To provide a sufficient number of different combinations, the hole was also included in the identification pattern by making it either round or oval in shape. The plate 'numbers' were composed as follow: first, a '0' or '1' depending on the shape of hole, then, the letter(s) corresponding to the 'clipped' sites. The minimum 'number' comprised a single hole-character and the maximum one, a hole character and six site characters.

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<sup>10</sup>As with Copper, the plates used for the first experiment were provided by l'Ecole Polytechnique de Montreal. They also bear a '1' in the upper left corner.

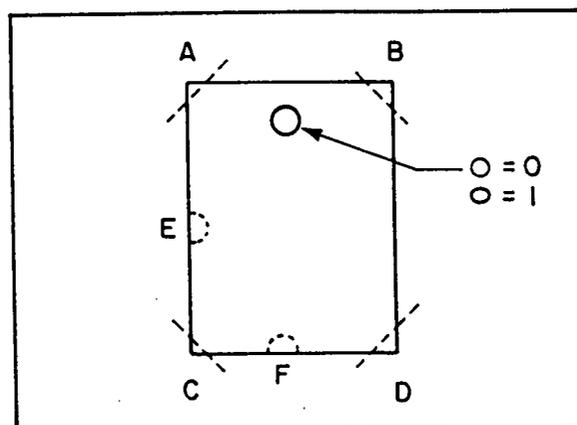


FIGURE 3.4.2 'Edge-clipping' Sites

The major problem with this identification method was that it made the surface of the coupons irregular and, therefore, complicated the corrosion rate calculations. This problem was solved by calculating, for each set of plates, a specific weight per area and using this weight, along with the clean weight, to evaluate the surface area. The details of the calculations are given in Appendix A.

### 3.4.2 CHEMICAL PREPARATION

After cutting and tagging, the metal coupons are unavoidably smeared with finger-prints and cutting lubricants; as well, if allowed to stand in open air they will start to corrode. Before starting the experiment, they must therefore be cleaned to ensure a good uniformity in the results and maximize their interaction with the studied environment.

The procedure presented here is a modification of the one used by Larson and King (1954) and was proven effective by the work of Tekeu (1983). The same steps were repeated prior to each new weighing.

## 1. Method description

The cleaning procedure requires the plates to be dipped successively into nine washing baths, as listed in Table 3.4.1.

TABLE 3.4.1 Content of Washing Baths

BATH #	SOLUTION CONTENT
1	Carbon tetrachloride (CCl <sub>4</sub> )
2	2.5% HNO <sub>3</sub> and HCl acids
3	Concentrated HCl acid
4	Distilled water
5	Sodium carbonate, 1N (Na <sub>2</sub> CO <sub>3</sub> )
6	Distilled water
7	Distilled water
8	Acetone (CH <sub>3</sub> COCH <sub>3</sub> )
9	Acetone

As a coupon progresses through the series, different impurities are removed from its surface.

The first bath removes greases and oils (e.g. cutting, lubricants, finger-prints, etc) which are soluble in organic solvent.

The following three baths give the metal an acid treatment, removing any metal oxide already formed on the surface. All remaining traces of acid are then neutralized by the weak base solution and the plates are rinsed thoroughly in distilled water.

Finally, the water is removed by two successive acetone washes. The clean plates are then stored in a dessicator for at least twelve hours before weighing and use.

## 2. Coupon handling

For the cleaning operations, the coupons were strung by groups of 25 to 30 on a triple length of twine (50% cotton - 50% polyester) as shown in Figure 3.4.3.

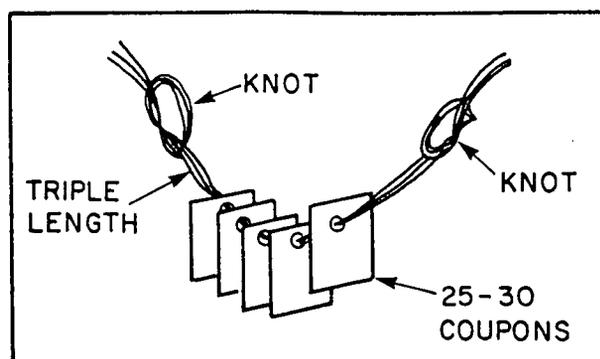


FIGURE 3.4.3 One String of Coupons

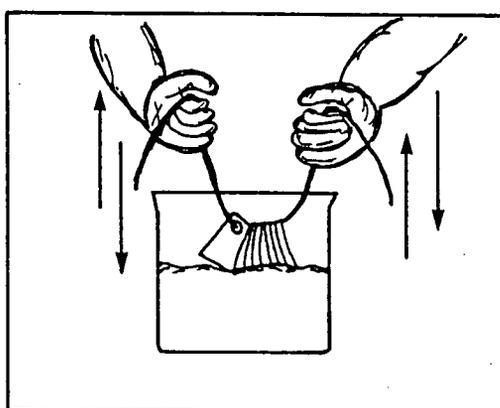


FIGURE 3.4.4 Washing Motion

The up-and-down motion in the wash bath (Figure 3.4.4), must be brisk, approximately 2 strokes per minute, to provide a good contact between the metal and the solution. The samples must not be touched with bare hands after washing and each metal must be stored isolated from other types of metal.

### 3.4.3 SAMPLING PROCEDURES AND SCHEDULES

The PVC hooks used to suspend the coupons in the cells were identified with coloured tape according to the exposure period required by the supported coupon. At

any one time, a maximum of 18 plates could fit in a cell, given the inner space available. However, these plates would have been put in at different times and/or removed at different times, according to the experimental schedule.

The plates were taken out of the cells and put to dry overnight at 104°C before being returned to the dessicator for storage. They were then weighed, cleaned again, and the final corroded weight was be used in the calculation of the corrosion rate.

In the first experiment, triplicates were used for all exposure times; three plates went in and out of the cells together. However, because the data analysis showed that the variations within a triplet were very small, the second experiment used only duplicates for each exposure.

1. First experiment

As shown in Figure 3.4.5a), the first plates went in on January 23rd 1984. The experiment was run for four weeks, with the last plates being removed on February 20th 1984.

2. Second experiment

As shown in Figure 3.4.5b), the second experiment started on Tuesday, June 18, 1985 and ended September 10th, 1985. One duplicate was exposed for the 1.0, 1.5, 2.0, and 4.0-week periods, therefore repeating the observations of the first experiment. For the additional 6, 8,10 and 12-week exposures, two sets of duplicates (i.e. four plates) were used, repeating the 'two-series' pattern of the shorter period of exposure.

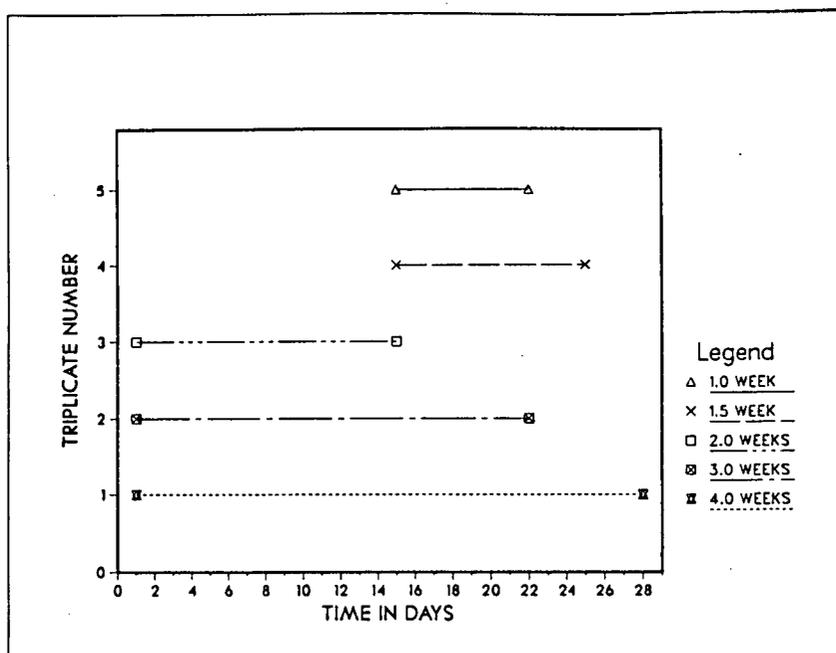


FIGURE 3.4.5a) First Experimental Schedule

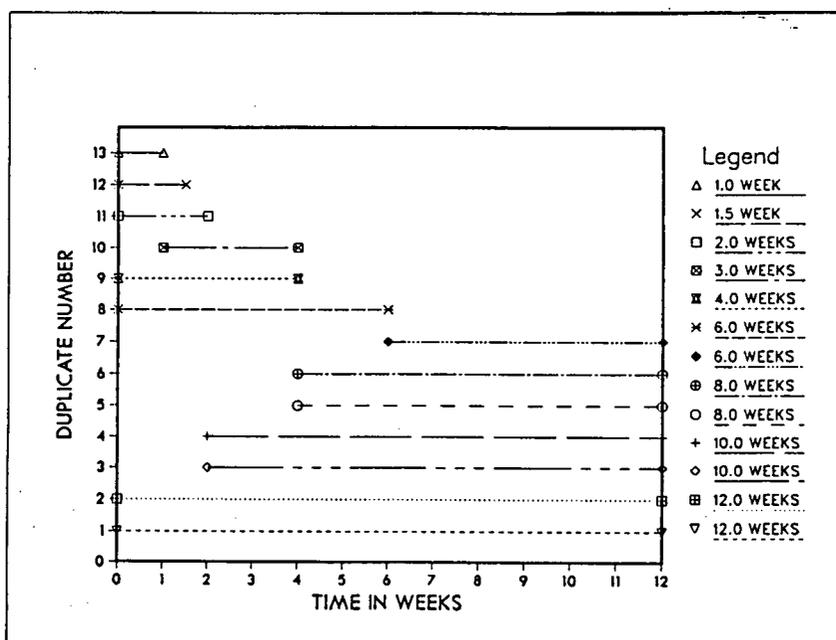


FIGURE 3.4.5b) Second Experimental Schedule

### 3.4.4 CORROSION RATE CALCULATIONS

The corrosion rate is the amount of metal lost per surface area per day of exposure. In this experiment the units are grams of metal lost per square meter of

surface per day. The data relative to the plates of a triplicate (or duplicate) was averaged and treated as one independent variable. The surface areas were calculated using the clean weight and a 'specific weight per area', which was calculated for each group of plates, using the dimensions of a sample of plates. The calculations are detailed in Appendix A. The 'rusted weight' was measured before the final cleaning but it does not enter the corrosion rate calculations. It is given for reference only.

A Digital Mettler AC100 ME-41373 analytical scale was used for all weight measurements.

### 3.5 PRIVATE DWELLING TAP WATER SURVEY

To provide the data for a preliminary assessment of the tap water metal content, the residents of six private dwellings in the Greater Vancouver Area were asked to sample their home water during the month of August 1985. The sampling sites and methodology, and the related analytical procedures are described in the following section.

#### 3.5.1 SAMPLING SITES AND METHODOLOGY

The sampling sites were selected to represent one of the six chosen types of housing in this survey: old and new single family house, and low-rise and high-rise dwelling. Another important selection parameter was the availability of the house resident to sample during August 1985.

In Table 3.5.1, the sampled buildings characteristics are summarized, according to the information provided by the residents themselves. Figure 3.5.1 points out the location of the sampling points, although this was not a selection criteria.

TABLE 3.5.1 Private Dwellings Sampled for Tap Water

TYPE OF DWELLING	NO. OF STORIES	YEAR BUILT	LOCATION	TYPE OF PIPE
House (A)	3	1982	Ptarmigan Place North Vancouver	Copper
House (B)	1	1930	Canada Way Burnaby	Copper
Low-rise (A)	3	1955	Oak Street Vancouver	Galvanized Iron
Low-rise (B)	3	1965	West 5th Avenue Vancouver	Copper
High-rise (A)	18	1978	Maywood Street Burnaby	n/a
High-rise (B)	13	1970	Allison Road Vancouver	Copper

The water was sampled eight times during the month of August 1985, more or less on the Mondays and Thursdays of each week. The residents were provided with 32 pre-labelled bottles and an instruction sheet<sup>11</sup>. They were asked to fill four different bottles on each sampling day. One for the first-flush of the hot water tap, one for the first-flush of the cold water tap, one after running the hot water tap until hot and one after running the cold water tap until cold. For preservation, the 60 ml nalgene bottles contained approximately 2 ml of concentrated nitric acid (HNO<sub>3</sub>), the sampling 'kit' therefore included a pair of protective plastic gloves.

### 3.5.2 ANALYTICAL PROCEDURES

The house samples were analysed only for metals concentrations. The same procedure as described in 3.3.2.d) was used. The samples were analysed within a month for Calcium, Copper, Iron, Magnesium, Potassium, Sodium and Zinc. A set of combined standards was used.

<sup>11</sup>A copy of the sampling methodology and questionnaire is given in Appendix B.

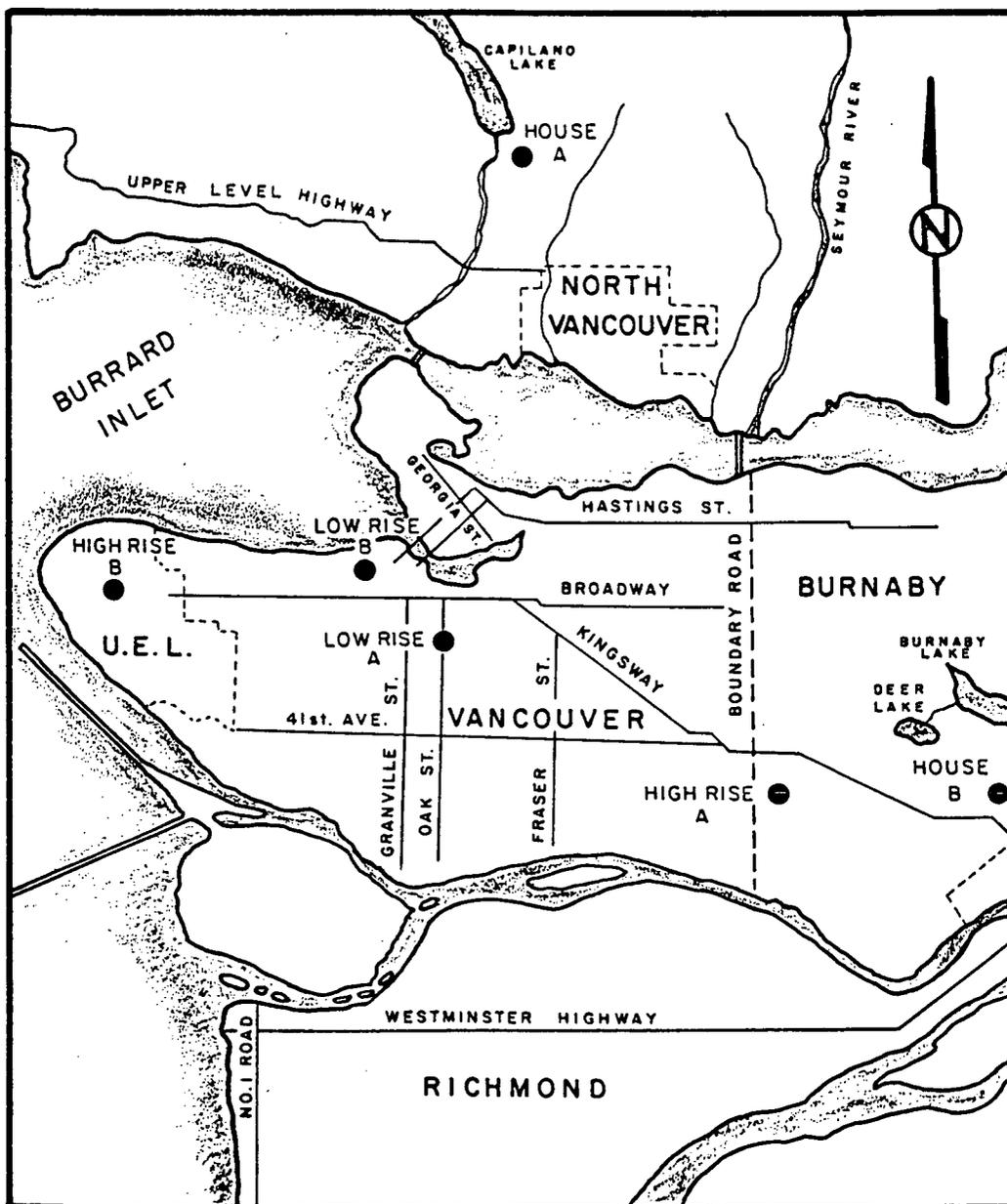


FIGURE 3.5.1 Location of Sampled Private Households

#### 4. RESULTS AND DISCUSSION

The data gathered during both laboratory experiments and tap water survey are presented in this chapter. The first section covers the laboratory water characteristics. pH, and other water parameters which were modified by the addition of lime are discussed first; the remaining monitored water characteristics are presented in the second half of the section.

Section 2 summarizes the coupon weight loss data and the observed corrosion rates. Following the outline of section one, the 1984 experimental results are discussed first, followed by the 1985 observations. These findings are then compared and discussed. In the last and third section, the data collected in the private household tap water survey are summarized and discussed. Some trends in metal concentrations, with respect to the type of dwelling and the water residence time in the pipes, are outlined.

##### 4.1 LABORATORY WATER CHARACTERISTICS

Throughout the experiments, several water parameters were monitored, both in the raw tap water and in each of the adjusted feed-basins. By adding lime ( $\text{Ca(OH)}_2$ ), to adjust the pH, four water characteristics other than pH were also modified: acidity, alkalinity, hardness and calcium concentration. The results pertaining to these five parameters are discussed in the first part of this section.

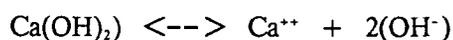
The remaining water characteristics were not deliberately altered in the experiment. However, to ensure that the tap water composition did not change abruptly during the course of the experiment, they were regularly measured. These results are presented in the second part of this section.

#### 4.1.1 PH, HARDNESS, ALKALINITY, ACIDITY AND CALCIUM

As mentioned previously, some of the typical characteristics of a corrosive water are: low pH, low hardness and low alkalinity. With a median pH between 4.9 and 5.5, average hardness between 6 and 7 mg/L as CaCO<sub>3</sub>, and average alkalinity between 10 and 15 mg/l as CaCO<sub>3</sub>, the tap water supplied by the GVRD's distribution system definitely meets corrosive standards.

In this study, lime (Ca(OH)<sub>2</sub>), was added to increase the pH and reduce the water's aggressive nature. The choice of this particular chemical was dictated by its low cost, widespread use in the water and wastewater field, and ease of manipulation and availability. Lime is a fairly insoluble substance in water but the dilute solution used (1 mg/ml), allowed for ease of handling and almost complete dissolution (since this concentration was only slightly greater than saturation).

The dissociation reaction of lime in water is:



The released hydroxide ion (OH<sup>-</sup>) reduces the hydrogen ion (H<sup>+</sup>) concentration by forming water; pH is therefore increased and the water becomes less acidic.

This change in pH, as discussed in the previous chapter, has several effects, both on corrosion rates and on various water species' solubilities. The mechanisms of this action were not investigated here, but the overall resulting impacts on alkalinity and acidity are presented below. The effect of pH adjustment on corrosion rates is the topic of Section 4.2.

The other ion resulting from lime dissociation is calcium (Ca<sup>++</sup>), one of the hardness causing cations and an element of the calco-carbonic equilibrium. The changes in hardness and calcium concentrations are also presented below.

## 4.1.1.1 First Experimental Sequence (1984)

Table 4.1.1 shows the average ( $\mu$ ) and standard deviation ( $\sigma$ ) values<sup>12</sup> for total acidity, total alkalinity, total hardness and calcium for the first experiment. Because pH is a logarithm, the median value is presented instead of the average, and the interval containing 33% of the values instead of the standard deviation.

From these cumulative results, it can be seen that the values, although low, followed the expected trend with lime addition. pH, alkalinity, hardness and calcium, increased with the amount of lime; acidity decreased. A more detailed analysis is presented in Table 4.1.1 for each parameter.

TABLE 4.1.1 Summary of pH Related Data - First Experiment

Parameter (units)		Gravity Control	Goal pH 7	Goal pH 8	Pressure Control
pH (pH units)	median 33% x	5.30 5.20 - 5.35	7.30 6.90 - 7.50	8.10 7.85 - 8.20	4.92 4.90 - 4.98
Total Acidity (mg/L as CaCO <sub>3</sub> )	$\mu$ $\sigma$	2.28 0.31	0.88 0.21	0.39 0.58	2.35 0.85
Total Alkalinity (mg/L as CaCO <sub>3</sub> )	$\mu$ $\sigma$	14.35 5.63	16.85 4.68	19.40 4.65	13.56 4.06
Total Hardness (mg/L as CaCO <sub>3</sub> )	$\mu$ $\sigma$	6.98 2.03	11.38 2.03	13.45 3.43	5.92 1.89
Calcium Conc. (mg/L)	$\mu$ $\sigma$	0.79 0.43	2.49 0.59	2.81 1.17	0.69 0.16

## 1. pH

<sup>12</sup>The average and standard deviation were calculated according to Geller, 1971.

$$\mu = \sum x/n \text{ and } \sigma^2 = \sum (x-\mu)^2/(n-1)$$

where n is the number of values x.

Figure 4.1.1a) shows pH variations with time. The typical jagged pattern is a result of the once-daily pH adjustment method. Lime was added, causing the pH to increase but, as it was neutralized by the carbonic acid system, pH slowly decreases until the next adjustment, and so on.

Figure 4.1.1b) is a bar diagram of pH value frequency distribution. The median values for Goal pH 7 and 8 are clearly visible on the figure, but the gravity and pressure controls median values are more difficult to separate. However, the pressure control consistently displayed a somewhat lower pH, which was expected since the higher system pressure allows more carbonic acid to dissolve in the water, therefore decreasing the pH.

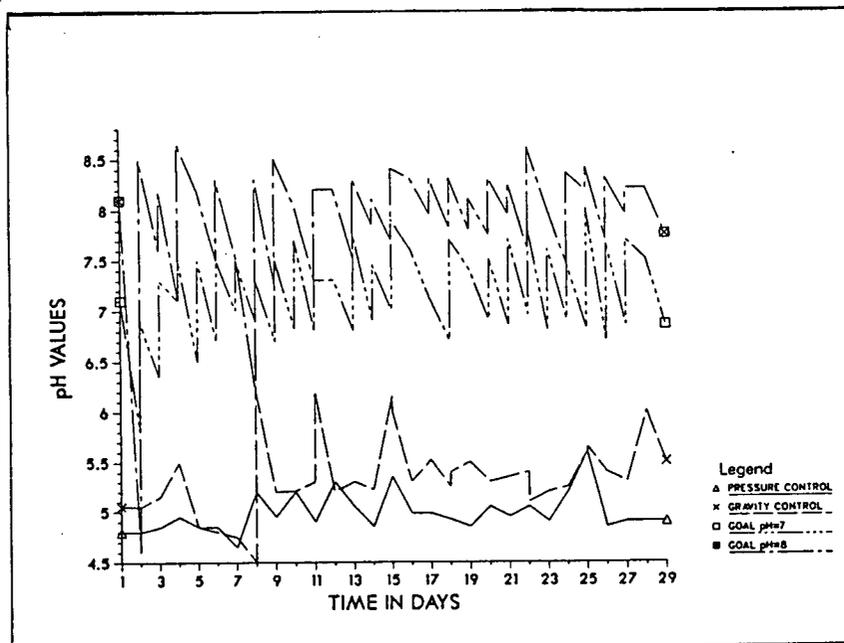


FIGURE 4.1.1a) pH Values versus Time - First Experiment

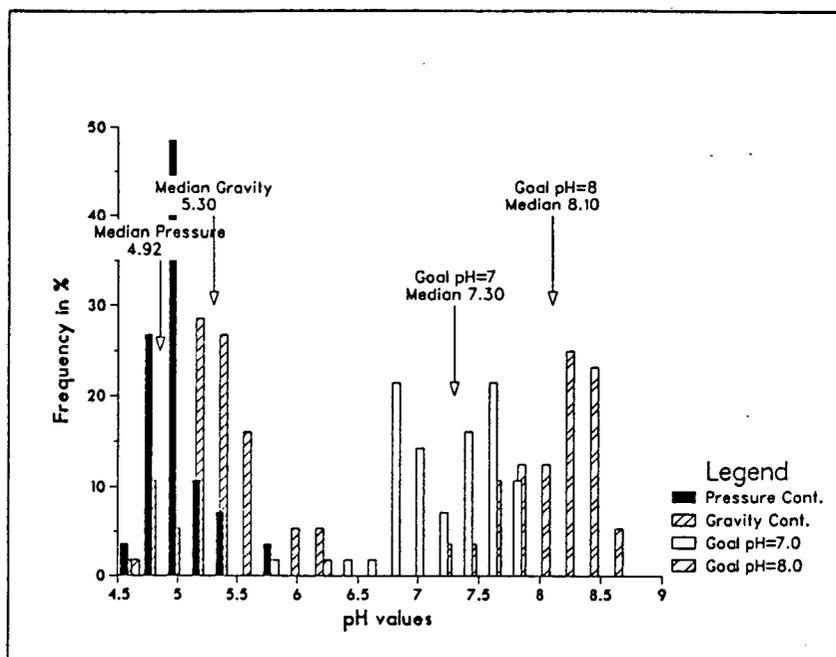


FIGURE 4.1.1b) Frequency Distribution of pH - First Experiment

## 2. Acidity

As defined in Standard Methods (A.P.H.A., 1985), acidity is an 'aggregated' property of water and is caused by several substances. Strong mineral acids (such as  $\text{FeCl}_3$ ), ferrous or aluminium sulfates, and weak acids (such as carbonic acid), contribute to acidity. It is, by definition, the capacity of the water to neutralize a strong base.

According to Sawyer and McCarty, (1978), the range of carbonic acidity extends from pH 4.5 to pH 8.5; the presence of the other components of acidity usually causes pH to drop to lower values. Therefore, in this experiment, the tap water's acidity can be assumed to be entirely carbonic; this was expected, since the water did not drain from mines or ore dumps (where the stronger mineral acidity is usually uptaken).

However, with Standard Methods (A.P.H.A., 1985), setting the standard deviation of acidity near 1.8 mg/L as  $\text{CaCO}_3$ , care must be taken

in interpreting the very low measured obtained. One possible conclusion is that the buffering capacity of this water is very low. Lime addition apparently decreased acidity, which can be interpreted as beneficial; Standard Methods and Sawyer and McCarty both mention the link between acidity and water corrosiveness.

Figure 4.1.2 shows acidity versus time and pH values. Here again, the jagged pattern resulting from the method of lime addition is seen, although acidity was only measured on filling day.

### 3. Alkalinity

Alkalinity is the opposite of acidity; it is the capacity of the water to neutralize a strong acid. As mentioned in Section 3.3.2, the results presented here were not obtained by potentiometric titration and are presented only for information. The difficulties in reproducing alkalinity measurements are also reflected in the large daily variations in the values.

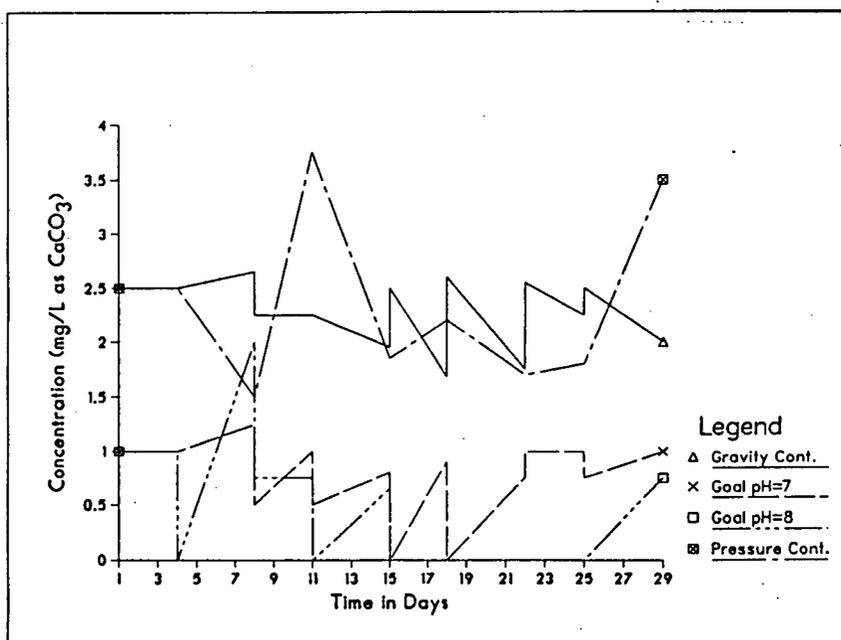


FIGURE 4.1.2 Acidity versus Time - First Experiment

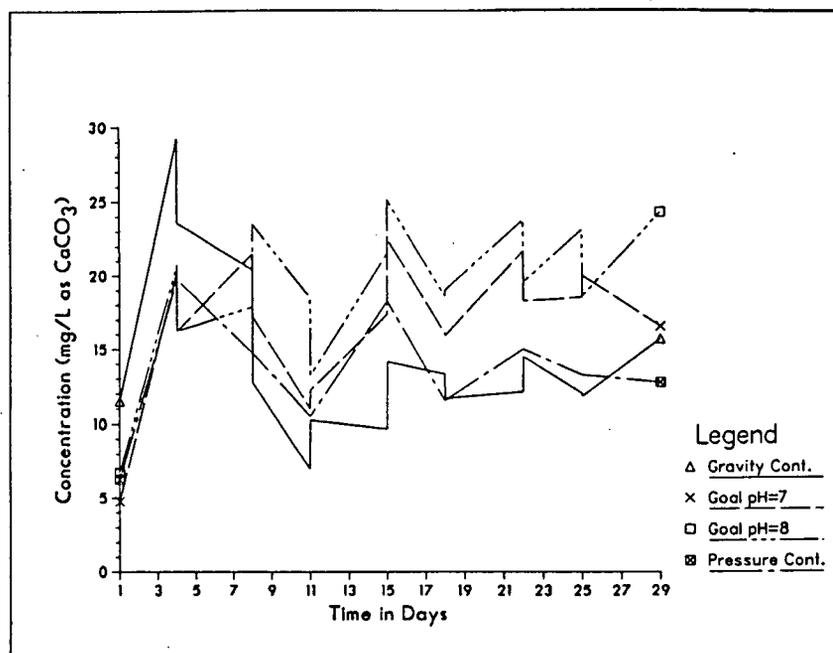


FIGURE 4.1.3 Alkalinity versus Time – First Experiment

Nevertheless, the expected trend of alkalinity increase with lime addition is visible from Figure 4.1.3. Here also, the low values tend to reflect the low buffering capacity of the water. According to Sawyer and McCarty (1978), most of the alkalinity in these samples was due to bicarbonate ions ( $\text{HCO}_3^-$ ), since the pH were lower than 8.3<sup>13</sup>.

#### 4. Hardness

Table 4.1.2 shows the common water hardness classifications, according to Sawyer and McCarty (1978).

<sup>13</sup>In some cases, the Goal pH 8 water, after adjustment, contained small amounts of carbonate ( $\text{CO}_3^{2-}$ ) alkalinity.

TABLE 4.1.2 Degree of Hardness

mg/L as CaCO <sub>3</sub>	Degree of Hardness
0 - 75	Soft
75 - 150	Moderately Hard
150 - 300	Hard
more than 300	Very Hard

From Figure 4.1.4, it can be seen that the tap water was definitely in the lower soft range, even after lime addition. According to Standard Methods (A.P.H.A., 1985), these values also fall in the lower range of the test sensitivity, which would account, in part, for the variability of the results.

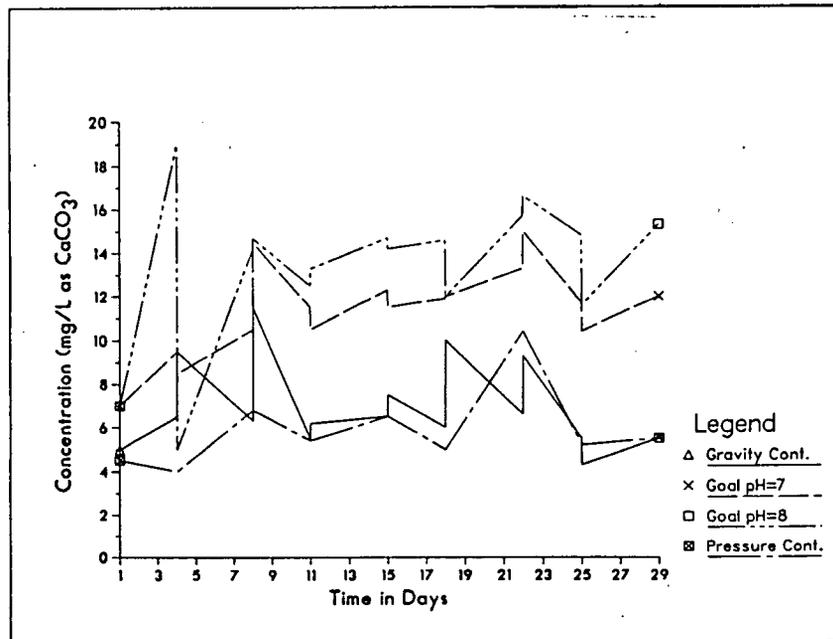


FIGURE 4.1.4 Hardness versus Time - First Experiment

Because total hardness was always lower than total alkalinity, the hardness can be considered as entirely carbonate. This carbonate hardness is the component known to precipitate when temperature is elevated, and was called 'temporary hardness' for that reason. However, the quantities involved here are too low to be the source of any scaling problems.

## 5. Calcium

Calcium was measured by Atomic Absorption and is, therefore, the most accurately determined of the above mentioned water characteristics. As expected, the water calcium content increased with pH, reflecting the amount of lime added.

Figure 4.1.5 shows the variations in calcium concentration with time, for all basins and the tap water. For this parameter, two samples were taken on each filling day, one from the water remaining in the basin, and the other from the new water after filling and pH adjustment. This last sample, the 'after' sample, was uniformly lower in calcium content than the 'before' sample. This was caused by the extra lime added between fillings, at each daily pH adjustment.

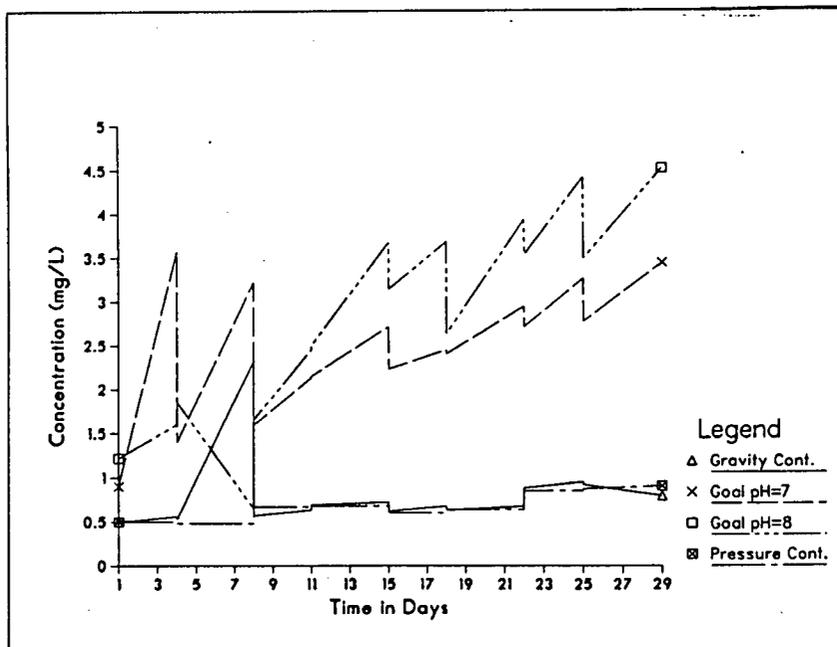


FIGURE 4.1.5 Calcium versus Time - First Experiment

Table 4.1.3 details the variations in calcium concentrations between the gravity control and the adjusted pH basins, the expected calculated hardness variations and the measured hardness variations, as well as a

comparison between the basins.

TABLE 4.1.3 Variations in Calcium and Hardness - First Experiment

Variation	Control to pH 7	Control to pH 8
in Calcium (mg/L Ca)	1.70	2.02
Equivalence in CaCO <sub>3</sub>	4.25	5.05
in Measured Hardness (mg/L as CaCO <sub>3</sub> )	4.40	6.47
Difference as % of Calcium value	4%	28%

The correlation between the values is within the precision for both measurements, as expressed by the standard deviations, Table 4.1.1. In the case of pH 8, the measured calcium concentrations  $\sigma$  were already as high as 40%, reflecting the difficulties of adding the same amount of lime to maintain the pH as close to the target value as possible.

#### 4.1.1.2 Second Experimental Sequence (1985)

This section follows the same format as Section 4.1.1.1; the corresponding tables and figures presented for the first experiment are shown here for the second one. Since the discussion of the individual parameters would be identical to the discussion for the first experiment's results, it will not be repeated and one may refer to the first results.

TABLE 4.1.4 Summary of pH Related Data - Second Experiment

Parameter (units)		Gravity Control	Goal pH 6	Goal pH 7	Goal pH 8	Pressure Control
pH (pH units)	median	5.65	6.10	7.05	8.05	5.55
	33% x	5.55 -	6.05 -	6.95 -	7.95 -	5.45 -
		5.70	6.20	7.25	8.15	5.65
Total Acidity (mg/L as CaCO <sub>3</sub> )	$\mu$	2.33	1.64	1.01	0.07	3.12
	$\sigma$	0.76	0.51	0.29	0.25	0.79
Total Alkalinity (mg/L as CaCO <sub>3</sub> )	$\mu$	11.52	14.53	18.29	23.15	10.93
	$\sigma$	2.21	2.95	2.40	3.79	2.26
Total Hardness (mg/L as CaCO <sub>3</sub> )	$\mu$	6.58	10.74	14.03	18.18	7.89
	$\sigma$	1.76	2.60	2.46	3.04	3.07
Calcium Conc. (mg/L)	$\mu$	1.14	2.42	4.38	6.64	1.19
	$\sigma$	0.11	0.29	0.34	0.67	0.22

As shown in Table 4.1.4, the tap water, in Summer 1985, had the same low pH, acidity, alkalinity and hardness characteristics as in Winter 1984.

### 1. pH

In Figures 4.1.6a) and b), one can recognize the typical jagged pattern of daily pH adjustment. Goal pH 6 was added to complete the studied range of pH, and the median value appears quite clearly on Figure 4.1.6b). In this second experiment, the gravity and pressure controls are difficult to differentiate from each other; however the pressure median pH is still lower than the gravity median pH, for the overall experiment.

### 2. Acidity

As expected, acidity decreased from an already low value, as pH was increased. Figure 4.1.7 shows the values of acidity versus time and

pH.

### 3. Alkalinity

Lime addition increased alkalinity to a value near 23 mg/L as  $\text{CaCO}_3$ . As is seen from Figure 4.1.8, the higher pH resulted in a greater variation in the alkalinity values (although all readings were quite variable).

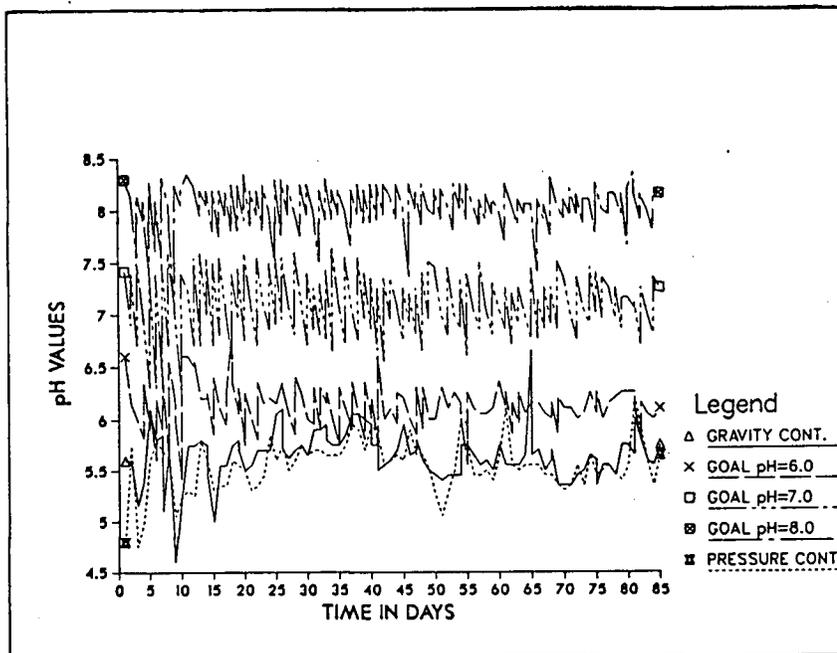


FIGURE 4.1.6a) pH Values versus Time - Second Experiment

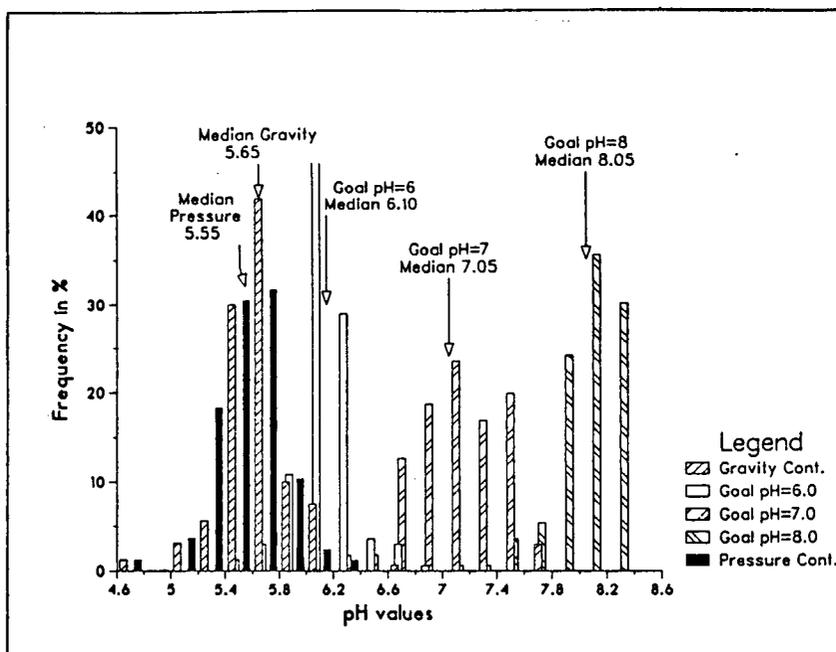


FIGURE 4.1.6b) Frequency Distribution of pH - Second Experiment

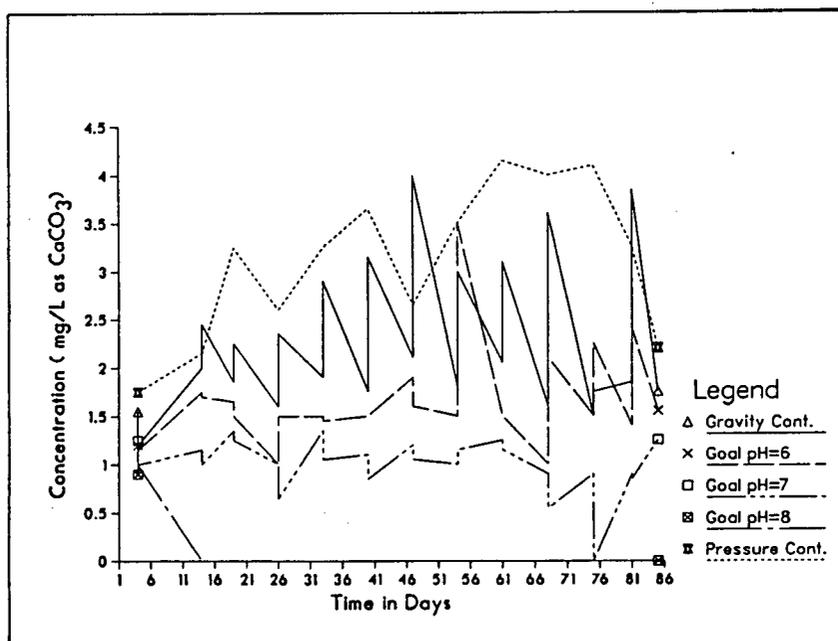


FIGURE 4.1.7 Acidity versus Time - Second Experiment

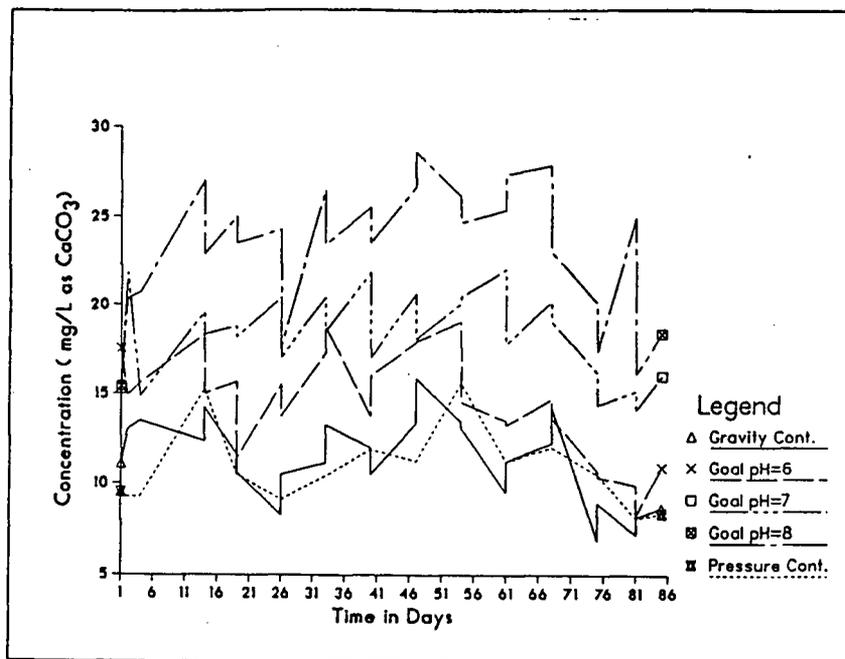


FIGURE 4.1.8 Alkalinity versus Time - Second Experiment

#### 4. Hardness

Although the hardness was increased by almost 300% by adjusting the pH to 8, the value remained in the low hardness range of natural waters. Total hardness was entirely carbonate hardness. Figure 4.1.9 presents the hardness data.

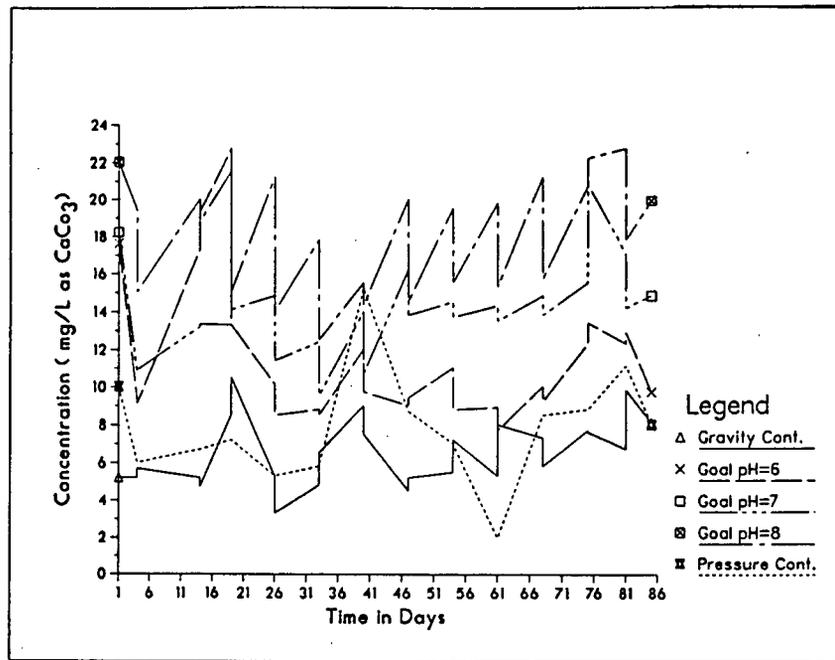


FIGURE 4.1.9 Hardness versus Time - Second Experiment

## 5. Calcium

In the second experiment, the water metal samples were taken only after filling. The calcium concentration pattern of Figure 4.1.10 does not display the previously seen jagged pattern, because the 'before' values are not included.

Table 4.1.5 shows the correlation between the calcium and hardness increases with pH adjustment.

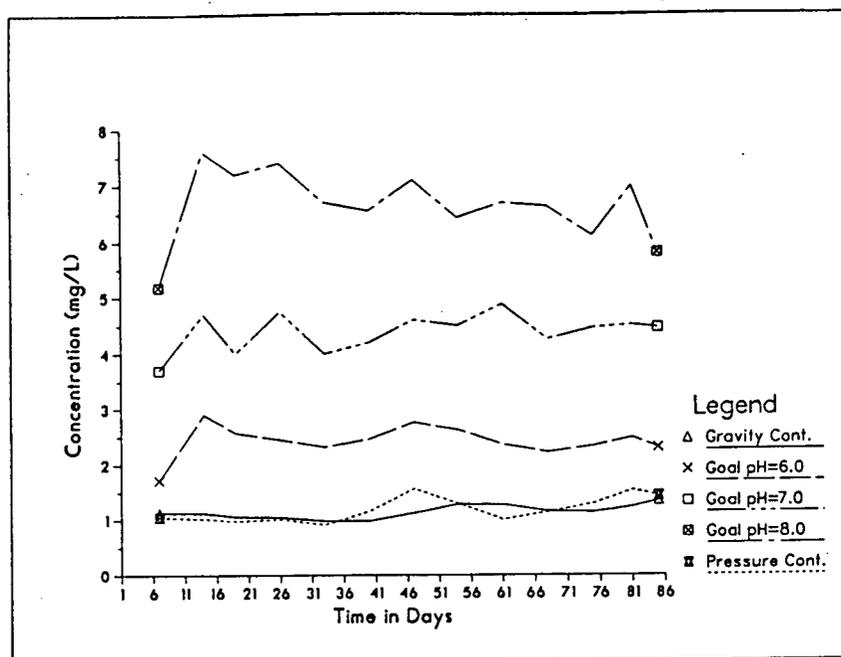


FIGURE 4.1.10 Calcium versus Time - Second Experiment

TABLE 4.1.5 Variations in Calcium and Hardness - Second Experiment

Variation	Control to pH 6	Control to pH 7	Control to pH 8
in Calcium (mg/L Ca)	1.28	3.24	5.50
Equivalence in CaCO <sub>3</sub>	3.20	8.10	13.75
in Measured Hardness (mg/L as CaCO <sub>3</sub> )	4.16	7.45	11.60
Difference as % of Calcium value	30%	8%	6%

#### 4.1.1.3 Comparison and Discussion

To assess the significance of the variations in water characteristics between the two experimental sessions, the means were compared using a Student t test, with a confidence limit interval of 95% (Geller, 1974). This standard t test allows one to evaluate whether, within the chosen probability, the averages belong to different populations, or cannot be considered as distinct from each other. The test applies to samples of less than 30, which was the case in these

experiments.

The t test results are presented for acidity, alkalinity, hardness and calcium in the second half of this section. However, pH values could not be statistically compared because of the logarithmic nature of the measurement. The comparison presented here, therefore, looks at the 33% interval value for the various measurements. It is presented in the first part of this section.

#### 1. pH

In comparing the median pH values given in Tables 4.1.1 and 4.1.4, one will notice two distinct trends. First, the gravity control and pressure control pH values were significantly lower in the first experiment. In fact, the 33% intervals of the 1984 un-adjusted waters do not intersect those from 1985. Second, a totally different trend applies to the adjusted pH values. In both experiments, the pH median values are close to each other and their intervals overlap completely.

This second trend is easily explained, since pH adjustment was the purpose of lime addition. Any other occurrence would have been unsatisfactory because the target values were identical. The fluctuations in the un-adjusted pH, however, were not in the control of the experimenter. Since, in both experiments, the same laboratory set-ups and techniques were used, and the water was drawn from the same tap, the explanations must lie in some external factor. In fact, the main difference between the 1984 and 1985 experiments is a 'seasonal' one. Indeed, the 1984 tests took place in January and February, two winter months which, in these regions, receive heavy rainfall. On the other hand, the 1985 experiment ran from June to September, dryer summer months, during which precipitation is

only a fraction of the winter precipitation<sup>14</sup>. This situation would be similar to that described by Liebfried et al., (1984), wherein the drinking water pH was found to decrease significantly after stormwater runoff.

Although such differences between control experimental units are less than ideal, they are part of the problems associated with 'real life' factors. Additional seasonal water pH comparisons should be included in future works. For the purpose of this analysis, however, the difference should be kept in mind, but the data will be analysed under the assumption that this variation is not significant. A pilot-plant corrosion study mentioned by Treweek (1985), showed that the seasonal water quality variations did not significantly influence the corrosion rates of black iron, galvanized steel, copper, lead-tin-solder-coated copper, lead and asbestos-cement pipes.

## 2. Acidity, Alkalinity, Hardness and Calcium

The t test is based on the hypothesis that, if the two averages ( $\mu_1$ ,  $\mu_2$ ), are significantly different at a 95% confidence level, their difference  $d = \mu_1 - \mu_2$ , will be greater than  $t_{0.05} S_d$ , where:

$$t_{0.05} = 95\% \text{ Student } t$$

$$S_d = \sigma_e \sqrt{1/n_1 + 1/n_2}$$

$$\sigma_e = \sqrt{(n_1\sigma_1^2 + n_2\sigma_2^2) / (n_1 + n_2 - 2)}$$

and  $n_1, n_2 =$  number of cases

Table 4.1.6 summarizes the  $d$  and  $t_{0.05} S_d$  values for acidity, alkalinity, hardness and calcium concentration between the two experimental sessions.

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<sup>14</sup>The summer of 1985 was the fifth driest summer on record at the Climate Data Service of Environment Canada. Total precipitation for this time period was less than 30 mm, while in January and February 1984, it was above 300 mm (Penny, 1985).

TABLE 4.1.6 Student t variations, Acid., Alk., Hard., Calcium

Parameter	Gravity Control	Goal pH=7	Goal pH=8	Pressure Control
Acidity d	0.05	0.13	0.32*	0.77
$t_{0.05}S_d$	0.41	0.18	0.26	0.80
Alkalinity d	2.83*	1.44	3.75*	2.63
$t_{0.05}S_d$	2.44	2.23	2.64	2.88
Hardness d	0.40	2.65*	4.73*	1.97
$t_{0.05}S_d$	1.19	1.48	2.04	2.48
Calcium d	0.35*	1.89*	3.83*	0.50*
$t_{0.05}S_d$	0.28	0.45	0.88	0.19

An asterisk indicates that  $d > t_{0.05} S_d$ , i.e. where the averages can be considered significantly different within a 95% confidence interval.

The reader will note that more than 50% of the results appear to be significantly different, especially all values of calcium and all values for pH=8. However, some additional considerations make the interpretation less straightforward than it first appears to be. This type of comparison is significant only if all conditions other than the studied one remained equal. In this case, for the second experiment, because a fifth series of cells was added for pH=6, the amount of work involved on each filling day increased, and thus the filling days became further apart in time; the basins were allowed to get almost totally empty before refilling. As a result, although the flows were quite similar in both experiments, a greater amount of lime was added to the water in the second experiments, because more daily pH adjustment were performed on one fill of water. It is therefore normal that hardness, alkalinity and calcium be higher in the second series of measurements.

Acidity, alkalinity and hardness, for the two control units, cannot be considered significantly different in 66% of the cases. This similarity can be considered as satisfying, especially taking into account the fact that the tests results were at the limit of the methods' sensitivity.

In conclusion, the water characteristics modified by lime addition were sufficiently similar in the two experiments to allow comparison, especially the studied adjusted pH values. It is assumed that the seasonal variations did not affect the corrosion rate to a significant extent, although further research on these variations is indicated.

#### 4.1.2 DISSOLVED OXYGEN, CHLORIDES, NITRATES+NITRITES AND SULFATES

Tekeu (1982), studied the corrosion of ductile cast iron and copper pipe coupons in water of varying composition. He found the ductile cast iron corrosion rate increased with sulfate concentration up to 40 mg/L  $\text{SO}_4^{2-}$ , as well as with nitrate concentrations up to a value between 100 and 200 mg/L  $\text{NO}_3^-$ , depending on the contact time. This author also observed increased corrosion rate with an increased chloride concentration, up to a value of 390 mg/L  $\text{Cl}^-$ . A further increase in the concentration of  $\text{Cl}^-$  caused a corrosion inhibition phenomenon to occur (also reported by Uhlig, 1971). Tekeu did not find dissolved oxygen concentrations between 6.40 and 9.60 mg/L to have a significant effect on the corrosion of copper and ductile cast iron.

Because of the possible effects of all these above mentioned ions on corrosion, their concentrations were monitored throughout both experiments. The results are compared and discussed below.

##### 4.1.2.1 First Experimental Sequence (1984)

Table 4.1.7 shows the average ( $\mu$ ) and the standard deviation ( $\sigma$ ) values of dissolved oxygen, chlorides, nitrates+nitrites and sulfates concentration for the

first experiment. With the exception of dissolved oxygen, which was very high throughout the experiments, the ions were found in low concentrations. A more detailed examination of each of those parameters follows.

TABLE 4.1.7 Summary of DO,  $CL^-$ ,  $NO_3 + NO_2$ , and  $SO_4^{2-}$  - First Experiment

Parameter (units)		Gravity Control	Goal pH 7	Goal pH 8	Pressure Control
Dissolved $O_2$ (mg/L)	$\mu$	10.26	10.32	10.45	12.17
	$\sigma$	1.28	1.01	1.12	0.39
Chloride conc. (mg/L)	$\mu$	1.35	1.16	1.24	1.08
	$\sigma$	0.50	0.28	0.22	0.16
$NO_3 + NO_2$ (mg/L as N)	$\mu$	0.14	0.18	0.16	0.12
	$\sigma$	0.04	0.08	0.07	0.03
Sulfate Conc. (mg/L)	$\mu$	1.80	1.38	1.38	1.58
	$\sigma$	1.04	0.51	0.52	0.48

#### 1. Dissolved Oxygen

Figure 4.1.11 shows the variation in dissolved oxygen with time. Typically, for Gravity Control, Goal pH=7 and Goal pH=8, the jagged patten produced by the bi-weekly basin filling is observed. Since cooler tap water contains more dissolved oxygen (as can be seen from the Pressure Control curve), the oxygen content of the basin water peaked on filling day and decreased as the water gradually warmed to room temperature.

During this first experiment, the tap water average temperature was  $8.94^\circ C$  which, according to Standard Methods (A.P.H.A., 1985), allows for a maximum dissolved oxygen content of 11.58 mg/L (saturation value). Therefore, it can be calculated that the tap water had an average oxygen saturation of 100%. The room temperature basins had lower average oxygen concentrations but, as shown in Table 4.1.8, they were all very close to

their own saturation value, depending on their average temperatures<sup>15</sup>.

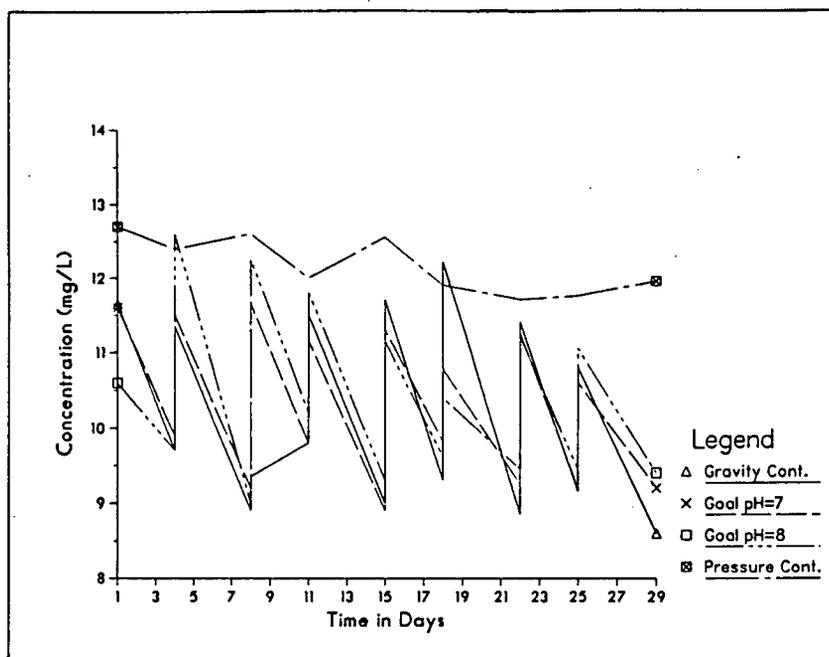


FIGURE 4.1.11 Dissolved Oxygen Concentration with time - First Experiment

TABLE 4.1.8 Percent Dissolved Oxygen Saturation - First Experiment

Experimental Unit	Average Temperature °C	Oxygen Saturation Value (mg/L)	Average % Saturation
Gravity Cont.	16.75	9.70	100
Goal pH=7	17.04	9.64	100
Goal pH=8	16.50	9.75	100
Pressure Cont.	8.94	11.58	100

## 2. Chloride

Figure 4.1.12 shows the variation in chloride concentration with time. Putting aside the last point of the Gravity Control curve, which can be neglected as an outlier, the reader will notice the absence of any definite trend in the concentration variation, both in time and between the experimental units. The measured amounts are also very low for drinking

<sup>15</sup> A saturation value of 100% reflect the method of calculating the average DO, by taking all the 'before' and 'after' results. In fact, the 'after' value does not apply for half the time; however, since DO was not continually monitored, no intermediate values were available.

water, where a maximum value of 250 mg/l can be tolerated before a 'salty' taste makes the water unpalatable (Sawyer and McCarty, 1978).

Most of the variation observed in the values probably resulted from experimental fluctuations. Chloride is a very common contaminant and, although extra care was taken to keep the glassware as clean as possible, chloride could have been introduced at any point of an analysis by contact with the skin or gloves of the experimenter.

### 3. Nitrate+Nitrite

As reported by Sawyer and McCarty (1978), high nitrate ( $\text{NO}_3^-$ ) concentrations in drinking water can cause methemoglobinemia, an oxygen transfer deficiency, in infants. For that reason, the nitrate level of drinking water must not exceed 10 mg/L (B.C. guidelines, in Purdon, 1983).

As one can see from the previously mentioned Table 4.1.7 values, the total nitrogen concentrations were consistently lower than 0.20 mg/L as N, which corresponds to 0.89 mg/L as  $\text{NO}_3^-$ , i.e. less than 10% of the recommended upper value. Figure 4.1.13 shows the expected absence of any trend in nitrate+nitrite concentration, both in time and between experimental units. The initial high values probably resulted from experimental fluctuations. The values measured in the potable water of this research were so much lower than the ones routinely measured in wastewater that some time was required to adjust the test sensitivity in that lower range.

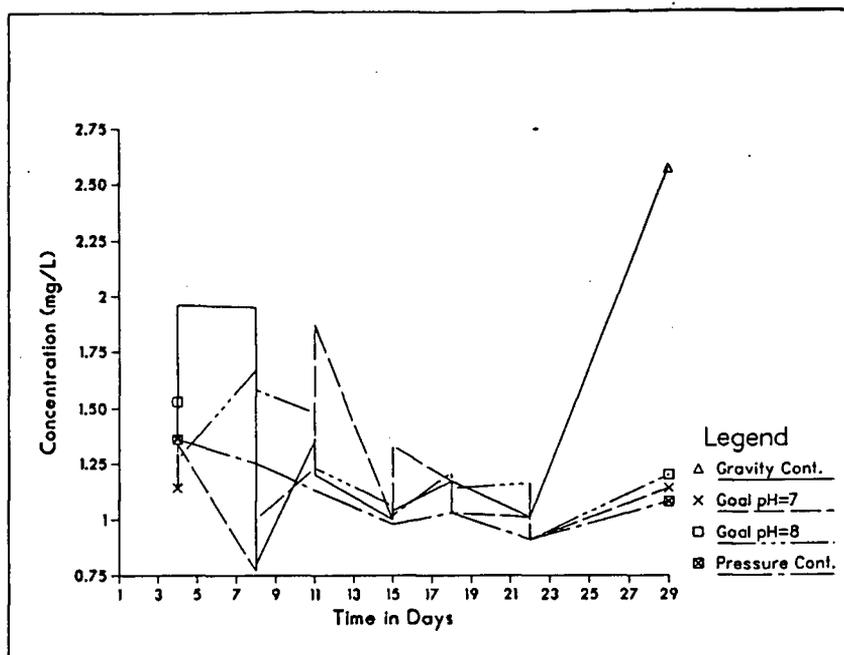


FIGURE 4.1.12 Chloride Concentration with Time - First Experiment

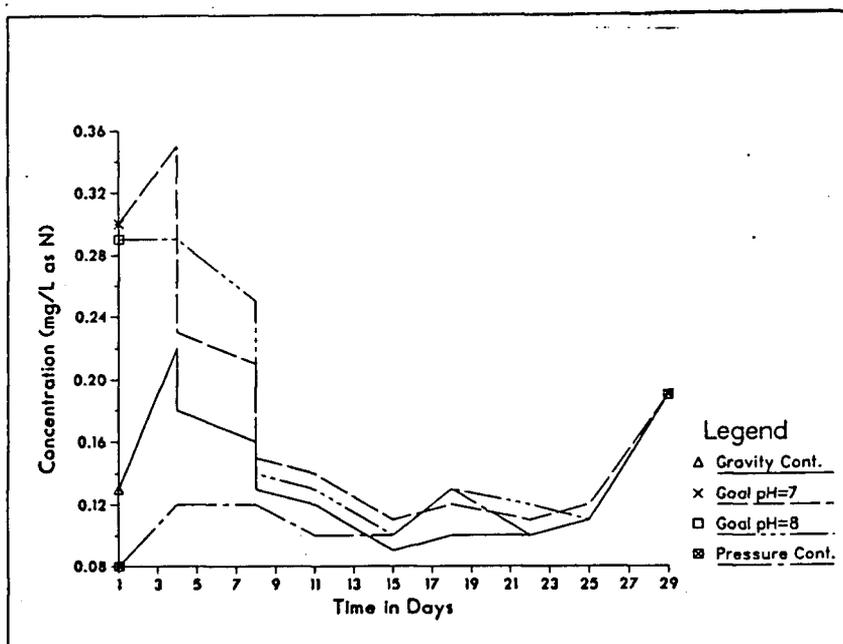


FIGURE 4.1.13 Nitrate+Nitrite Concentration with Time - First Experiment

#### 4. Sulfate

As shown in Figure 4.1.14, the sulfate concentration with time was consistently low, and no definite trend allows differentiation between the experimental units. As reported by Sawyer and McCarty (1978), the

maximum suitable level for sulfate in drinking water is 250 mg/L<sup>16</sup> The reader will note that the values were all less than 10% of this value, i.e. below 25 mg/L. The last Gravity Control data point is outstandingly high, which confirms the contamination already suspected by the unusually high chloride content of the same sample.

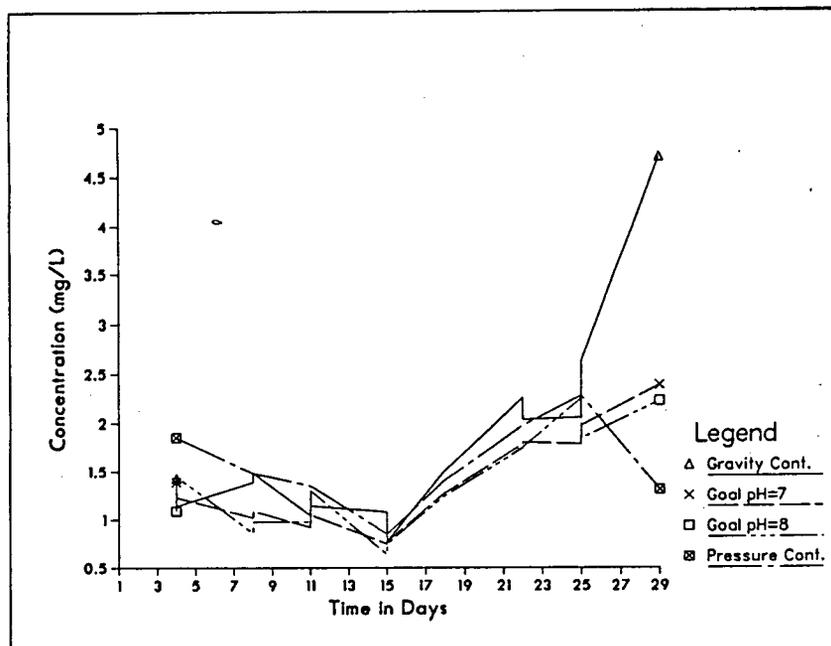


FIGURE 4.1.14 Sulfate Concentration with Time - First Experiment

#### 4.1.2.2 Second Experimental Sequence (1985)

This section follows an outline parallel to that of Section 4.1.2.1. The same tables and figures will be presented below, summarizing the 1985 data.

In Table 4.1.8, one will note that the dissolved oxygen levels were lower in the second experiment but that all the other ions were in a same low concentration range.

<sup>16</sup>British Columbia maximum acceptable concentration is 500 mg/L (Purdon, 1983).

TABLE 4.1.9 Summary of DO,  $Cl^-$ ,  $NO_3^- + NO_2^-$ , and  $SO_4^{2-}$  - Second Experiment

Parameter (units)		Gravity Control	Goal pH 6	Goal pH 7	Goal pH 8	Pressure Control
Dissolved $O_2$ (mg/L)	$\mu$	8.97	8.96	9.03	8.81	9.19
	$\sigma$	0.84	0.84	0.78	0.58	1.20
Chloride conc. (mg/L)	$\mu$	1.09	1.08	1.07	1.06	0.98
	$\sigma$	0.15	0.08	0.09	0.07	0.14
$NO_3^- + NO_2^-$ (mg/L as N)	$\mu$	0.09	0.09	0.10	0.10	0.08
	$\sigma$	0.03	0.02	0.03	0.03	0.03
Sulfate Conc. (mg/L)	$\mu$	2.69	2.74	2.43	2.61	2.65
	$\sigma$	0.42	0.46	0.49	0.39	0.52

### 5. Dissolved Oxygen

Figure 4.1.15 shows the variation in dissolved oxygen during the course of the second experiment. The descending pattern is a result of an increase in both the ambient room and water temperatures, during the month of August (starting on day 45).

Figure 4.1.16 shows, for comparison, the tap water temperature during the experiment. The average value of  $17.7^\circ C$  corresponds to a dissolved oxygen saturation content of 9.53 mg/L (Standard Methods, A.P.H.A., 1985). The average percent D.O. saturation in the pressure control was therefore 96.4%. For the gravity control and other basins, the average temperatures were higher, as summarized in Table 4.1.10. As expected, all the saturation percent values were still uniformly high.

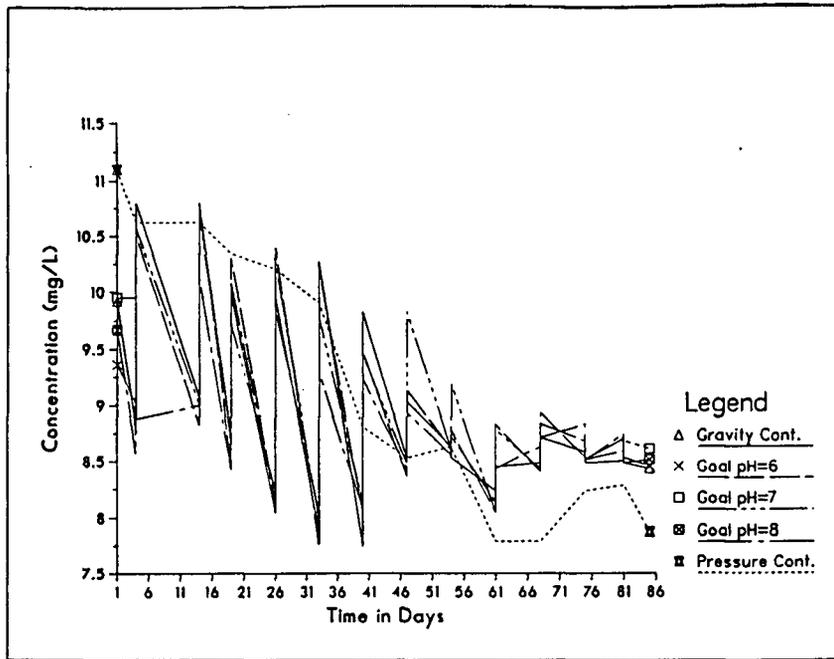


FIGURE 4.1.15 Dissolved Oxygen Concentration with time - Second Experiment

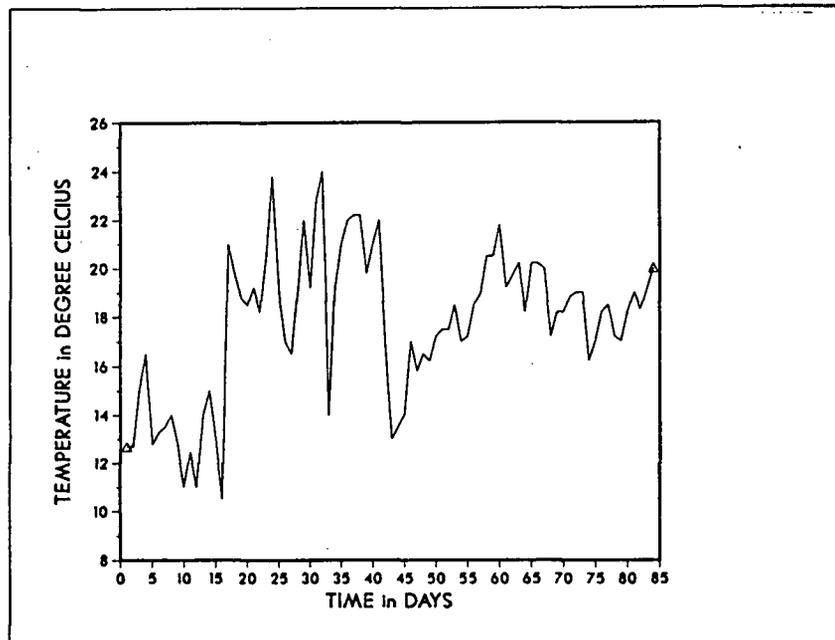


FIGURE 4.1.16 Tap Water Temperature - Second Experiment

TABLE 4.1.10 Percent Dissolved Oxygen Saturation - Second Experiment

Experimental Unit	Average Temperature °C	Oxygen Saturation Value (mg/L)	Average % Saturation
Gravity Cont.	20.5	9.00	99.6
Goal pH=6	20.0	9.09	98.6
Goal pH=7	20.1	9.07	99.6
Goal pH=8	20.3	9.04	97.5
Pressure Cont.	17.7	9.53	96.4

## 6. Chloride

Although the values were all in the 1 mg/L range, Figure 4.1.17 shows an unexpected jagged pattern in Chloride concentration with time. This suggests that there might have been some chloride contamination in the lime solution during this particular experiment. However, this trend seems to subside into the background variation after day 36 of the experiment, and no significant difference separated the various experimental units.

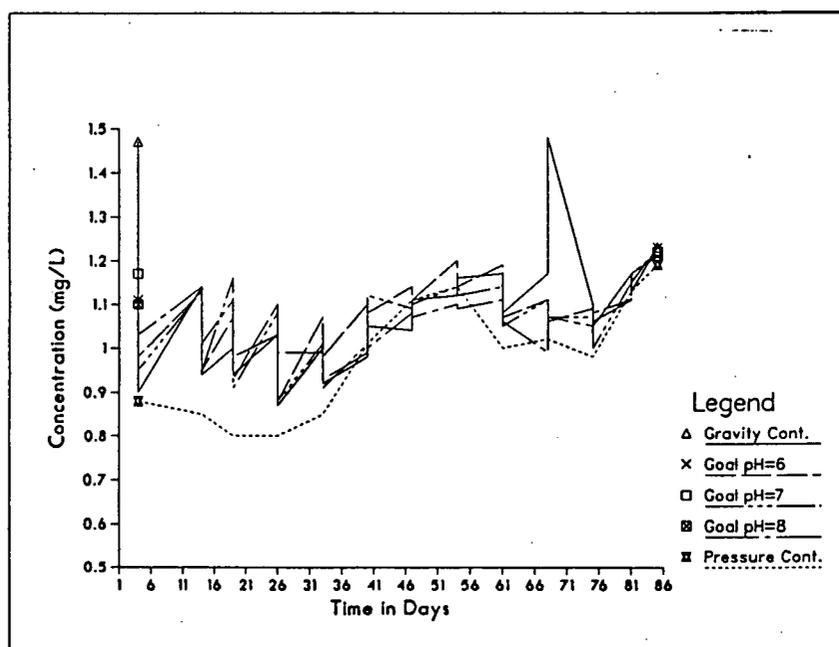


FIGURE 4.1.17 Chloride Concentration with Time - Second Experiment

## 7. Nitrate+ Nitrite

Figure 4.1.18 shows the nitrate+nitrite concentration variations with time. There is very little difference between the concentrations of the various waters, with all the variations being within 0.15 mg/L, as can be seen from the ordinate.

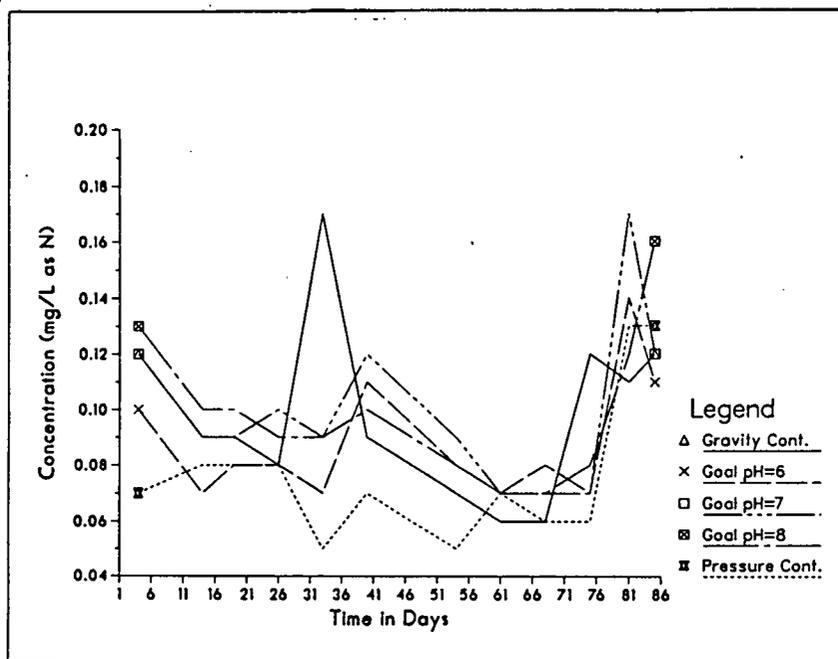


FIGURE 4.1.18 Nitrate+Nitrite Concentration with Time - Second Experiment

## 8. Sulfate

Figure 4.1.19 shows the absence of any definite trends in the variations of sulfates concentrations, both with time and between the different waters.

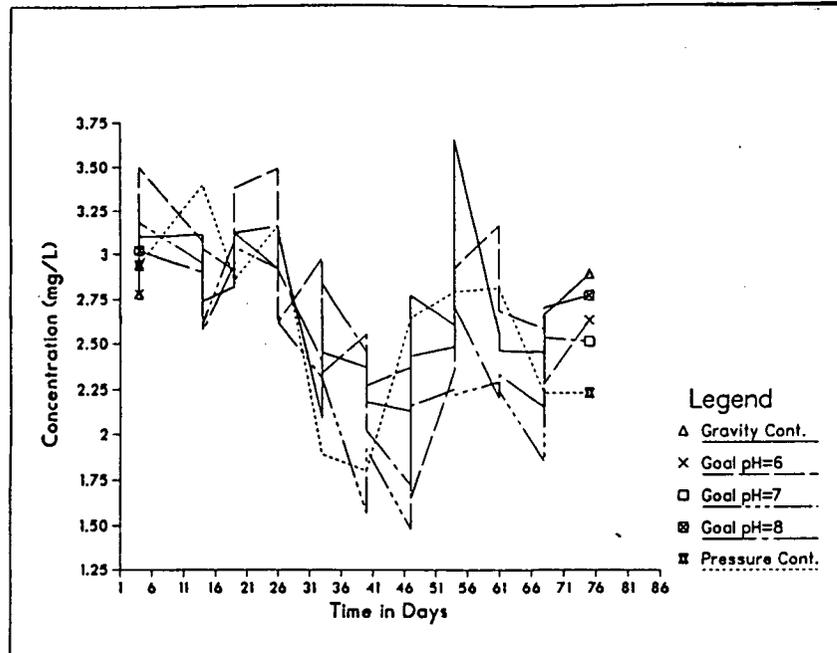


FIGURE 4.1.19 Sulfate Concentration with Time - Second Experiment

#### 4.1.2.3 Comparison and Discussion

A t test was used to evaluate the significance of the variations in water characteristics between the two experimental sessions. The results are summarized in Table 4.1.11, where an asterisk indicates the cases when  $d > t_{0.05} S_d$ , i.e. when the averages can be assumed to belong to different populations, with a confidence interval of 95%.

TABLE 4.1.11 Student t variations, DO, Chlorides, Nitrates+ Nitrites, Sulfates

Parameter	Gravity Control	Goal pH=7	Goal pH=8	Pressure Control
Dissolved O <sub>2</sub> d	1.29*	1.29*	1.64*	2.98*
$t_{0.05}S_d$	0.66	0.56	0.53	0.90
Chloride d	0.26*	0.09	0.18*	0.10
$t_{0.05}S_d$	0.21	0.12	0.10	0.12
NO <sub>2</sub> +NO <sub>3</sub> d	0.05*	0.08*	0.06*	0.04*
$t_{0.05}S_d$	0.03	0.05	0.05	0.03
Sulfate d	0.89*	1.05*	1.23*	1.07*
$t_{0.05}S_d$	0.50	0.36	0.31	0.56

The statistical test showed that 14 of the 16 comparisons (87.5%), were significantly different at 95% confidence limit. The significance of such variation in this research is discussed below for each parameter.

#### 9. Dissolved Oxygen

Because the first experiment took place in winter, the raw water was cooler and, therefore, contained more dissolved oxygen. By comparing the percent saturations of Tables 4.1.8 and 4.1.10, however, one will notice that the water was, in all cases, at more than 96% of its maximum content. This shows clearly that throughout the year, the tap water remained almost completely oxygen saturated.

The maximum absolute concentration variation was observed between the pressure controls, where the difference in DO concentrations was almost 3 mg/L, as the DO levels decreased from 12 mg/L in the winter to 9 mg/L in the summer. Tekeu (1982) studied the influence of dissolved oxygen concentration changes, from 6.4 to 9.6 mg/L, i.e. a maximum of 3.2 mg/L variation. He did not find a significant change in the corrosion rates of cast-iron or copper. This finding, suggests that, even though his

studied range was different from the variation range in the present study, the 3 mg/L fluctuation in the upper concentration levels might not have a significant influence on corrosion rates.

Because the dissolved oxygen concentration did not change significantly from one set of cells to the other within one experiment, the oxygen level probably did not affect the relative corrosion rates in that experiment. Therefore, the relative changes in corrosion rates (between the various pH values), should compare favourably from one experiment to the other. However, any comparison between the absolute corrosion rates of the two experiments should be analysed with care. Although Tekeu's findings do not confirm it, it is possible that the greater amount of dissolved oxygen in the first experiment's water might have encouraged higher corrosion rates for that session.

#### 10. Chloride

Chloride was significantly different in 50% of the cases, but stayed below 1.5 mg/L, with the maximum concentration change being lower than 0.30 mg/L. In Tekeu's studies of the influence of chloride ions on the corrosion rates of copper and ductile cast iron, the chloride concentration was varied in increments of 10 mg/L, or greater, to a maximum value of 390 mg/L. From his results, a variation of 0.30 mg/L in chloride, would not lead to a significant change in corrosion rate. Therefore, for the purpose of this discussion, the chloride concentrations were close enough to compare.

#### 11. Nitrate+Nitrite

The nitrate+nitrite concentrations are shown to be statistically different in all cases but, in both experiments, the absolute values stayed below 0.20 mg/L as N. In Tekeu's work, nitrate ( $\text{NO}_3$ ) was varied in

increments of 7 mg/L as  $\text{NO}_3$ , which corresponds to a change of 1.6 mg/L, when expressed as N, as it is in the present experiment<sup>17</sup>. From Tekeu's work, it is doubtful that the change in nitrate between the 1984 and 1985 experiment had an influence on the corrosion rates.

## 12. Sulfate

From Tables 4.1.7 and 4.1.8, it can be seen that the sulfate concentration during the second experiment was, on average, 75% higher than the 1984 concentration. This observation is confirmed by the statistical test results indicating that, in all cases, the compared averages were significantly different. The maximum absolute concentration difference was found between the Goal pH=8 basins, and had a value of 1.23 mg/L (The measured concentrations were all lower than 4 mg/L).

Again, from Tekeu's work, it appears doubtful that such a small change in the already low concentration will have any influence on the corrosion rates. Moreover, the results of the first experiment, as can be seen from the relatively large standard deviations, cannot be considered to be as reliable as those from the second experiment. Indeed, for the first series of measures, a less sensitive determinative test was used, and the water samples had to be concentrated ten times and filtered before analysis. During the sample preparation, some sulfate might have been lost, which could totally account for the difference between the two experimental sessions. Looking at the combination of observations, it appears that the sulfate concentration changes are not significant in this study.

From the observations of the above mentioned parameters, it is obvious that no abrupt change in water quality occurred between the two experimental

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<sup>17</sup> Although the sum of nitrate and nitrite was measured in this experiment, nitrite ( $\text{NO}_2$ ) usually accounts for a very small percent of the total, and is neglected for this comparison (Sawyer and McCarty, 1978).

sessions. If some significant water composition changes were observed between 1984 and 1985, they were too small in magnitude to have a significant influence on the corrosion rates except, possibly, in the case of oxygen.

The changes in dissolved oxygen content, due to seasonal variations in water temperature, might have affected the corrosion rates within one experiment. This fact will be taken into consideration in the rest of the analysis. Additional seasonal water quality assessments should be included in future work.

## 4.2 WEIGHT LOSS AND CORROSION RATE

In this section, the specific weight loss (weight loss per surface area), and the corrosion rate of the metallic coupons are presented. In keeping with the previous structure, the results of the 1984 experiment are presented first, followed by the results of 1985. The two sets of data are then compared and discussed.

The fourth and last part of this section contains a very brief discussion regarding the metal concentrations in the laboratory tap water.

### 4.2.1 FIRST EXPERIMENTAL SEQUENCE (1984)

The first part of the discussion will concern the specific weight losses for cast iron and copper; the corrosion rates for both metals will be discussed later.

#### 1. Specific Weight Loss

Figures 4.2.1a) and 4.2.1b) show the specific weight losses ( $\text{g}/\text{m}^2$ ) for cast iron and copper coupons. As expected, the weight loss increased with contact time and, although this first experiment lasted only four weeks, the rate of weight change already appeared to start decreasing after the first two weeks.

By comparing the two metals, several dissimilarities can be noted; for example, the magnitude of the total weight changes, in which the ordinate scale of the cast iron graph is ten times that of copper. This larger metal loss from

cast iron was expected since copper is a more noble metal than cast iron and, in general, is more resistant in corrosive environments. This difference was directly noticeable by inspection of the corrosion product deposited on the coupon surface; it was much more abundant for cast iron.

Tekeu (1983), in experiments with contact times up to 2.5 weeks, observed specific weight losses between 20 and 30 g/m<sup>2</sup> for cast iron and between 1 and 2 g/m<sup>2</sup> for copper, the quantities varying with the water composition. These cast iron results are in the same range as the values measured in this experiment for the gravity-fed cells. For copper, however, the results obtained in the present work were significantly higher (as much as five times, in the case of the gravity control samples). Desjardins et al. (1983), measured, for cast iron after 4 weeks of immersion at pH 7, specific weight losses between 60 and 65 g/m<sup>2</sup>. These results are very close to the values measured here. These authors' unpublished results for copper under the same conditions, showed weight losses between 8 and 16 g/m<sup>2</sup> (after 4 weeks contact time). Figure 4.2.1b) shows that the weight losses in the present experiment were slightly lower, ranging between 4 and 14 g/m<sup>2</sup>.

Figure 4.2.1b) shows that, in the case of copper, outstandingly large weight losses were found in the gravity control cell. This weight loss curve is higher and clearly apart from the other curves, which are grouped in the lower part of the diagram. For cast iron, the maximum weight loss curve was found for the pressure control cell, with all the gravity curves being in the same general area of the graph, and lower on the axis.

As mentioned in Chapter 1, the pressure control cells were added in an attempt to correlate the actual corrosion rates observed in the pressurized pipes of the distribution system, with the rates found in the un-pressurized coupon weight loss experiment. Interestingly, for this first experiment, it can be seen

from these figures that the pressure effect was different for different metals.

While it greatly increased cast iron corrosion, pressure decreased the weight loss of copper.

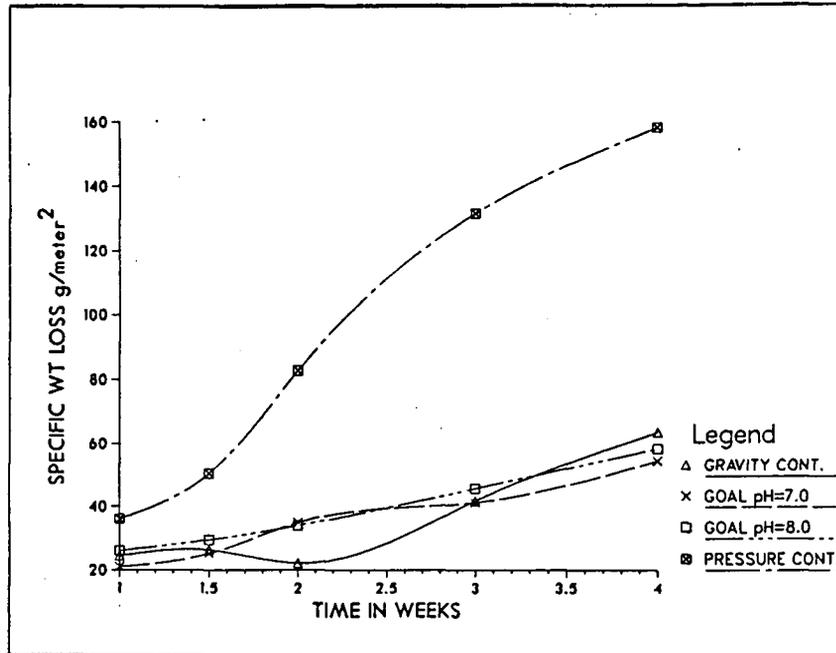


FIGURE 4.2.1a) Specific Weight Losses of Cast Iron - First Experiment

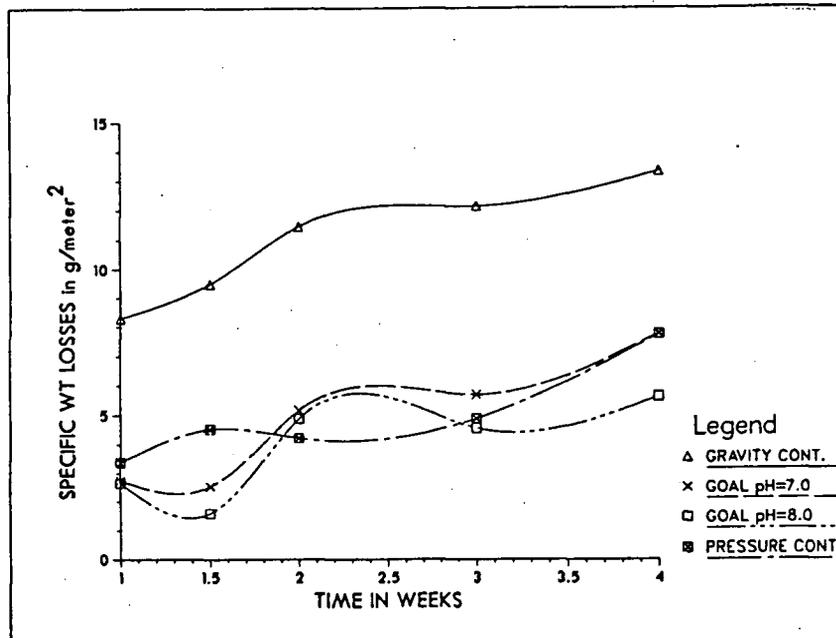


FIGURE 4.2.1b) Specific Weight Losses of Copper - First Experiment

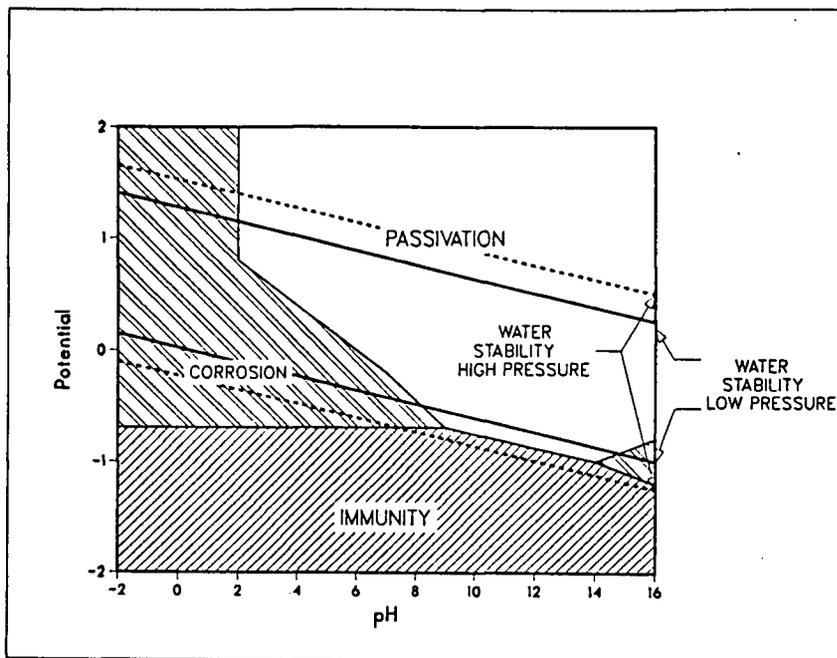


FIGURE 4.2.2a) Effect of High Pressure on Iron Noble Behavior

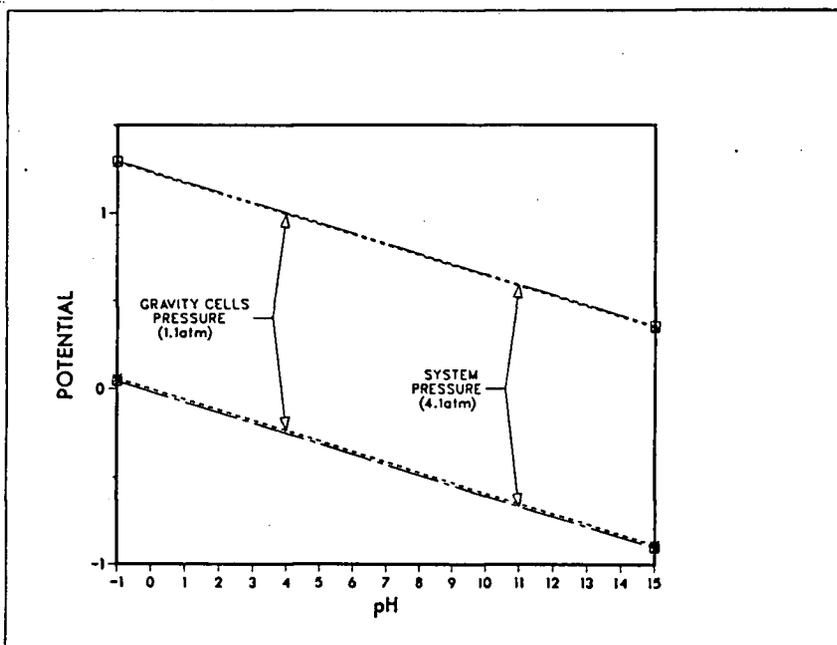


FIGURE 4.2.2b) Effect of System Pressure on Water Stability Region

No mention of this particular effect of the system pressure was found in the reviewed literature. In section 4.1, it was noted that the increased-pressure cells had a slightly lower pH, higher acidity and a cooler temperature. However, these changes of water characteristics do not appear to account for the opposite

effects on copper and cast iron corrosion rates, nor do they fall into the general pH pattern of the gravity cells.

It is known, however, that pressure alters the thermodynamics of corrosion. Higher pressures expand the water stability region and, as shown on Figure 4.2.2a), derived from data presented by Pourbaix (1982), if the increase is sufficient, a metal could start displaying a 'noble' behavior not usually possible in normal pressure conditions. For example, on Figure 4.2.2a) it can be seen that, under the high pressure conditions, iron can exhibit an immune behavior in water, in a very narrow potential region, between pH 9 and 14.

However, as shown on Figure 4.2.2b), the difference in pressure between the gravity-fed cells (1.1 atmosphere) and the system-pressured cells (60 psi = 4.1 atm.), was not sufficient to significantly alter the thermodynamic conditions. The reason behind these varying effects of pressure probably depends on the alteration of other corrosion limiting factors, or on the modification of their synergistic actions. Additional data needed to document this new aspect of the problem resulted in the pressurized cells being maintained for the second experimental sequence.

From Figure 4.2.1a), it is not possible to distinguish a pattern in the effect of pH on the weight loss of cast iron. The curves are more or less merged together and no clear trend is visible. On the other hand, putting aside the pressure control curve<sup>18</sup>, one can see from the copper weight loss (Figure 4.2.1b)), a steady decrease in the total weight loss as pH increases from the unadjusted median value of 5.30 to the goal pH value of 8.

From both sets of curves, as previously mentioned, it appeared that the rate of weight changes was already decreasing as the contact time increased. This

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<sup>18</sup>It is interesting to note, however, that the pressure curve, with a median pH value of 4.92, would have been expected to lie higher than the gravity control curve, a pattern it does not follow.

analysis of the corrosion rates is discussed below.

## 2. Corrosion Rates

Figures 4.2.3a) and 4.2.3b) show that, indeed, the corrosion rates decreased with contact time and appeared to reach a constant value around the third week of immersion. Desjardins et al. (1983), has noted that this limit for corrosion rates can be attained during the second week of contact, which is slightly faster than the result observed here.

The pressure control cast iron curve, however, does not follow the overall pattern and the corrosion rates seemed to maintain the high initial value until the end of the experiment. In fact, cast iron did not display the behavior expected from the findings of Desjardins et al., where it was seen that no significant decrease of corrosion rates with increased pH occurred. Copper, on the other hand, showed a decrease in corrosion rates with increased pH, and this effect appeared to be somewhat more noticeable as the contact time increased. The effect of pH adjustment can be better seen in Figures 4.2.4a) and 4.2.4b), whereby the pressure curves have been left out of the corrosion rates diagram.

Although the copper results appeared to suggest a reduction of copper corrosion with increased pH, the lack of trends in the cast iron results and the unexplained effects of pressure again stressed the need to repeat these tests, as part of the second experiment.

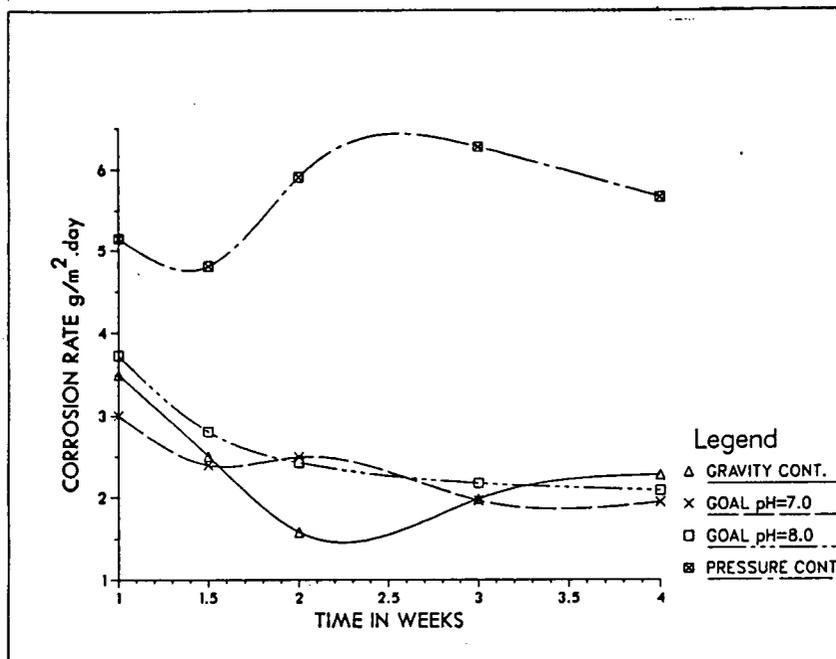


FIGURE 4.2.3a) Corrosion Rates of Cast Iron - First Experiment

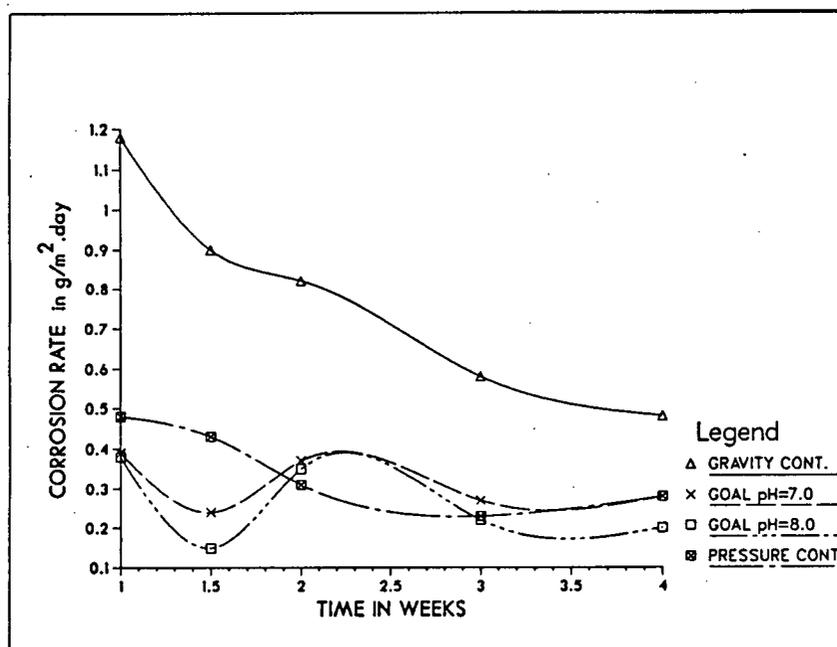


FIGURE 4.2.3b) Corrosion Rates of Copper - First Experiment

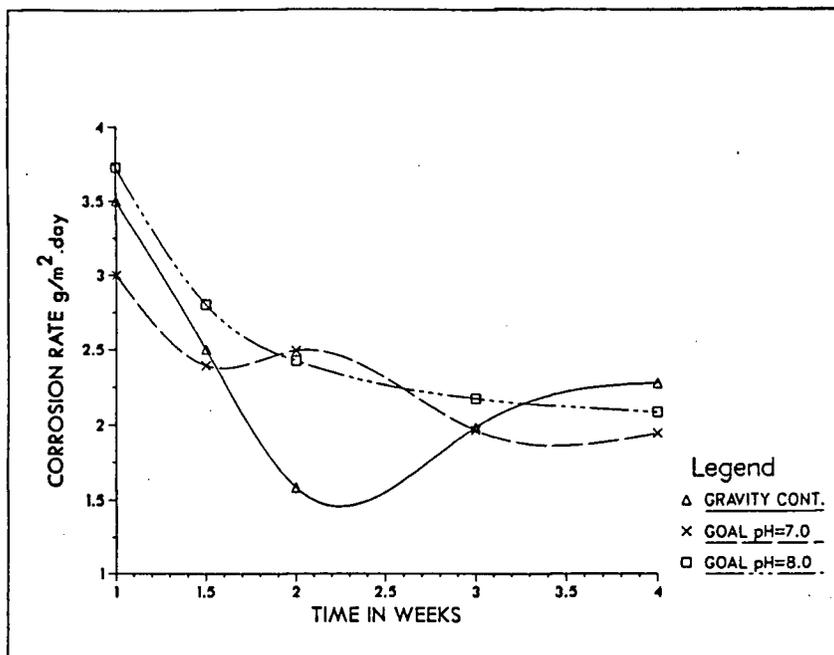


FIGURE 4.2.4a) Gravity Corrosion Rates of Cast Iron - First Experiment

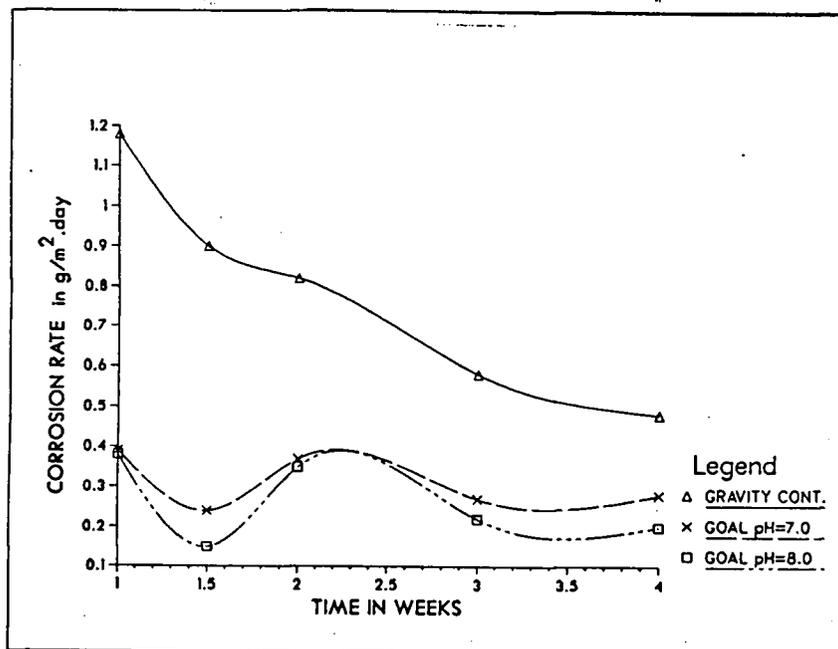


FIGURE 4.2.4b) Gravity Corrosion Rates of Copper - First Experiment

#### 4.2.2 SECOND EXPERIMENTAL SEQUENCE (1985)

It was decided that the second experimental session should be supplemented by the addition of a goal pH 6 basin. Also, the contact times were increased to periods

up to 12 weeks. The pH 6 basin, it was hoped, would supply data to cover the range of pH between the control cells and the Goal pH=7 cells. The longer contact times would act to confirm the long-term corrosion rates stabilization and show if the pH effect was still marked after twelve weeks of immersion.

Following the same structure used in Section 4.2.1, the specific weight loss results are presented first, followed by the corrosion rate results.

#### 1. Specific Weight Loss

Figures 4.2.5a) and 4.2.5b) show the specific weight losses of cast iron and copper with time and pH. The weight changes of the cast iron samples were, on average, ten times greater than the values measured for the copper coupons, reaching a maximum value of approximately 200 g/m<sup>2</sup> in the pressure control. All the gravity-fed cell cast iron samples had losses, after twelve weeks of immersion, between 75 and 105 g/m<sup>2</sup>, i.e. less than 50% of the amount lost under pressure.

Copper, as shown on Figure 4.2.5b), displayed a maximum weight loss pattern for both control cells, reaching a final 12-week value of between 20 and 25 g/m<sup>2</sup>. Desjardins et al.'s (1983), unpublished copper results of a 1982 experiment, showed weight losses between 20 and 30 g/m<sup>2</sup>, after twelve weeks contact. These values are in the same range as the results obtained here.

Pressure greatly enhanced cast iron corrosion, while it appeared to have no particular effect on copper; it is seen that the two control curves are very similar to each other.

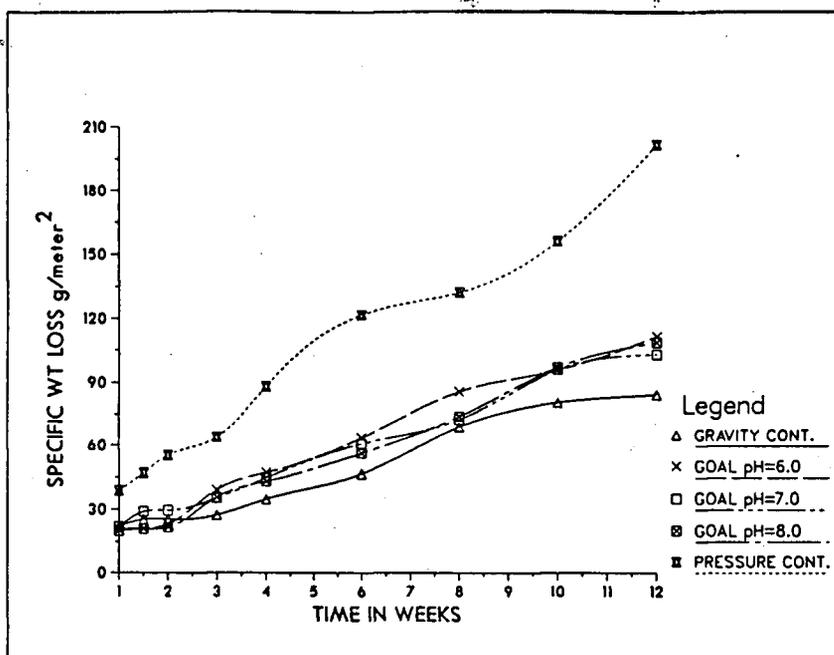


FIGURE 4.2.5a) Specific Weight Losses of Cast Iron - Second Experiment

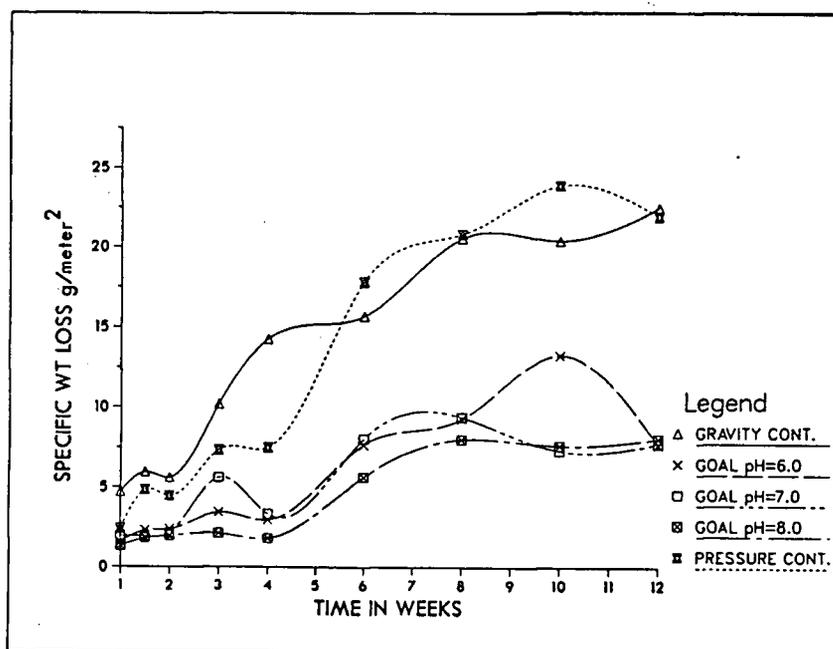


FIGURE 4.2.5b) Specific Weight Losses of Copper - Second Experiment

Increased pH did not result in a marked change in the weight losses of cast iron. In fact, aside from the markedly different pressure control curve, the gravity control curve is the only one noticeably isolated from the others. These

samples also showed the smallest weight losses of the group.

The copper coupons, on the other hand, displayed, at least until the tenth week, reduced weight losses at higher pH. The twelfth week values of goal pH 6,7 and 8 were almost identical, a result that did not continue the previously mentioned trend with increased pH.

The weight loss increase appeared to be smaller as the contact time increased, indicating that corrosion was faster in the first few days of immersion. This pattern is more clearly noticeable from the corrosion rates diagrams, shown in Figures 4.2.6a) and b).

## 2. Corrosion Rates

Figure 4.2.6a) and 4.2.6b) show the corrosion rates versus time and pH for both metals. From these two groups of curves, it can be seen that the constant corrosion rate was reached between the fourth and fifth weeks, although, in the case of copper, the corrosion rates for the pressure and gravity controls did not really show a steady, constant value. The shape of these curves suggest that the limit value might still be lower than those attained after twelve weeks.

The effect of pH increase was apparently opposite on the two metals. Figures 4.2.7a) and 4.2.7b), in which the pressure curves were left out for greater clarity, emphasize the opposing pH trends. For copper, the lowest corrosion rates were observed in the goal pH 8 cells, while for cast iron, the lowest rate was found in the gravity control cells, where the median pH was 5.65.

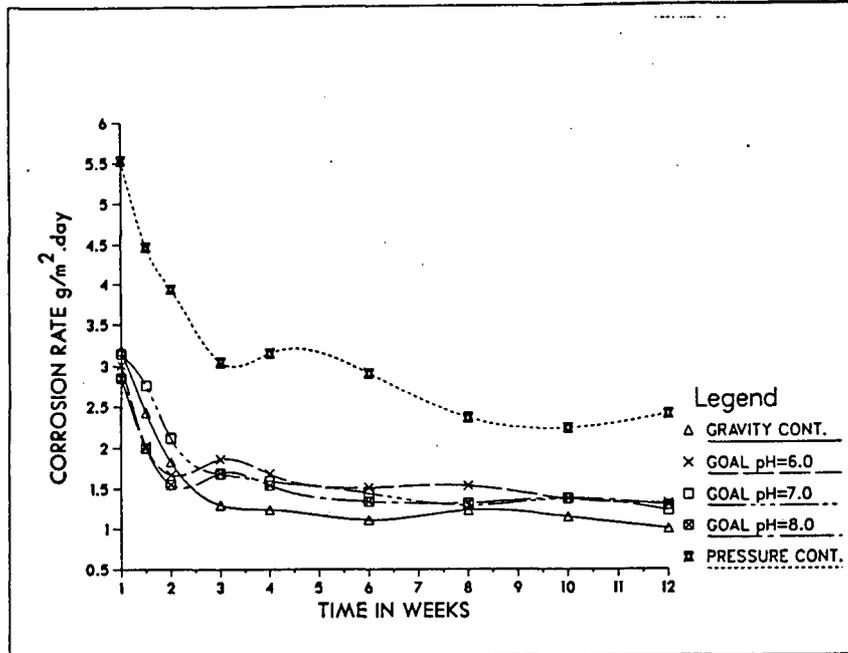


FIGURE 4.2.6a) Corrosion Rates of Cast Iron - Second Experiment

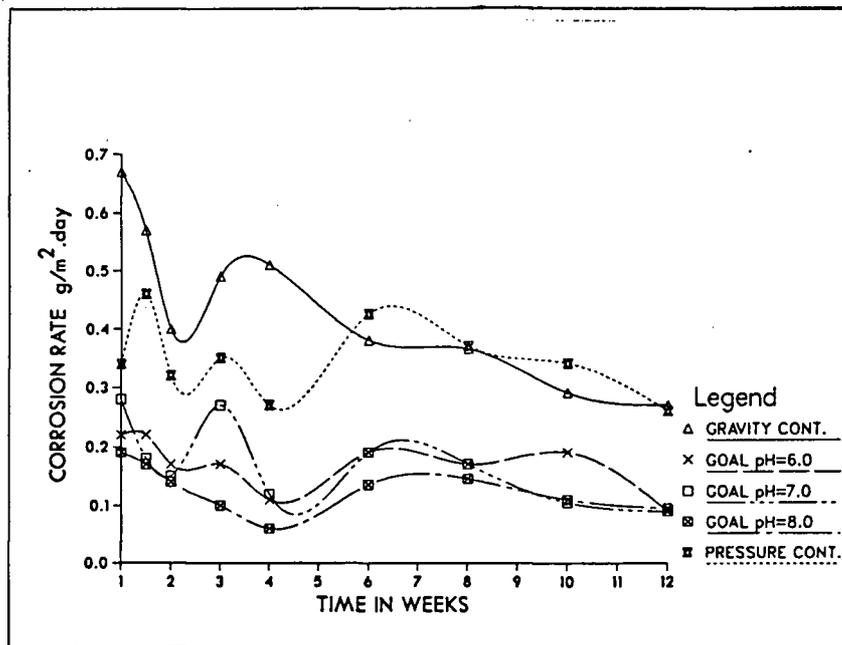


FIGURE 4.2.6b) Corrosion Rates of Copper - Second Experiment

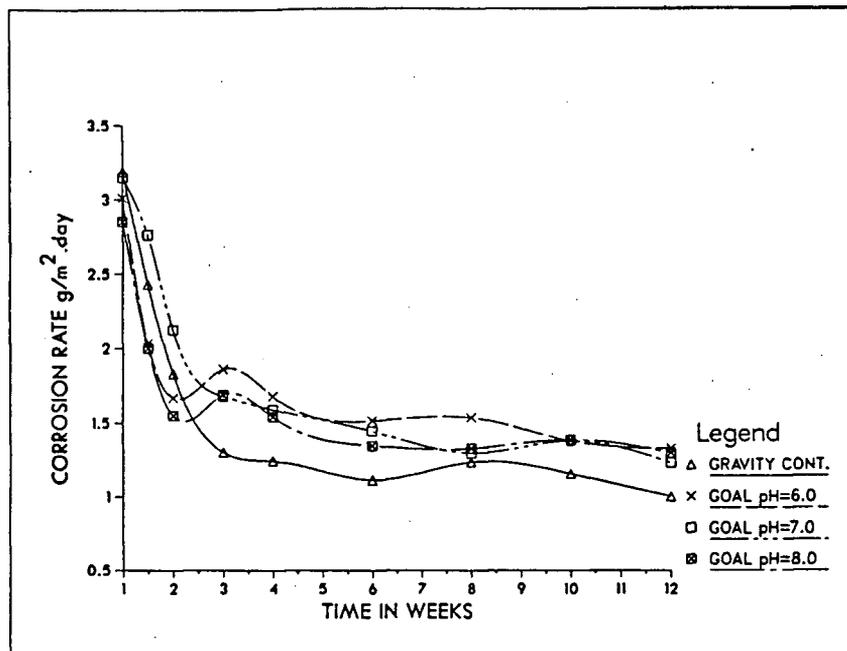


FIGURE 4.2.7a) Gravity Corrosion Rates of Cast Iron - Second Experiment

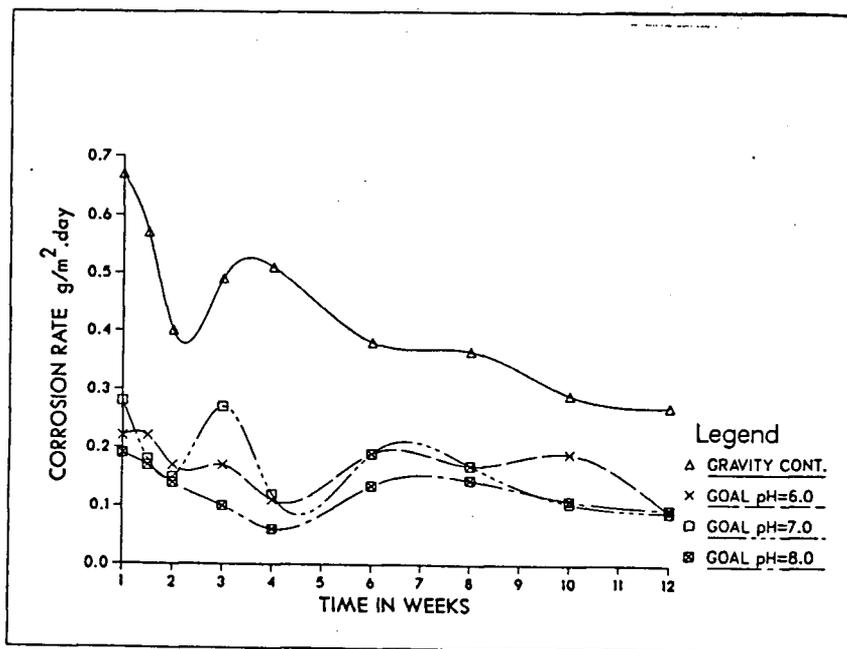


FIGURE 4.2.7b) Gravity Corrosion Rates of Copper - Second Experiment

### 4.2.3 COMPARISON AND DISCUSSION

From the comparison of the water characteristics in Section 4.1, it was concluded that some significant seasonal changes had occurred between the 1984 and

1985 experiments: i.e. in particular temperature, dissolved oxygen and pH. Since the effects of these changes on the absolute corrosion rates are not fully known, caution is used in comparing the corrosion results between the experiments.

Tables 4.2.1a) and Table 4.2.1b) summarize the corrosion rates for contact times up to four weeks, for both experiments. The ratio of the 1984 values over the 1985 values is given to quantify the differences in the results.

TABLE 4.2.1a) Comparison of Corrosion Rates - Cast Iron

Exposure (Weeks)	Year	Gravity Control	Goal pH=7	Goal pH=8	Pressure Control
1.0	1984	3.50 <sup>1</sup>	3.00	3.73	5.15
	1985	3.19	3.15	2.85	5.53
	ratio	1.10	0.95	1.31	0.93
1.5	1984	2.50	2.39	2.80	4.80
	1985	2.43	2.76	2.00	4.47
	ratio	1.03	0.87	1.40	1.07
2.0	1984	1.58	2.49	2.42	5.90
	1985	1.83	2.12	1.55	3.93
	ratio	0.86	1.18	1.56	1.50
3.0	1984	1.98	1.96	2.17	6.26
	1985	1.30	1.68	1.69	3.04
	ratio	1.52	1.17	1.28	2.06
4.0	1984	2.27	1.94	2.08	5.65
	1985	1.24	1.59	1.54	3.15
	ratio	1.83	1.22	1.35	1.79

<sup>1</sup>Corrosion rate in g/m<sup>2</sup>d

TABLE 4.2.1b) Comparison of Corrosion Rates - Copper

Exposure (Weeks)	Year	Gravity Control	Goal pH=7	Goal pH=8	Pressure Control
1.0	1984	1.18 <sup>1</sup>	0.39	0.38	0.48
	1985	0.67	0.28	0.19	0.34
	ratio	1.76	1.39	2.00	1.41
1.5	1984	0.90	0.24	0.15	0.43
	1985	0.57	0.18	0.17	0.46
	ratio	1.58	1.33	0.88	0.94
2.0	1984	0.82	0.37	0.35	0.30
	1985	0.40	0.15	0.14	0.32
	ratio	2.05	2.47	2.50	0.94
3.0	1984	0.58	0.27	0.22	0.23
	1985	0.49	0.27	0.10	0.35
	ratio	1.19	1.00	2.20	0.66
4.0	1984	0.48	0.28	0.20	0.28
	1985	0.51	0.12	0.06	0.27
	ratio	0.94	2.33	3.33	1.04

<sup>1</sup>Corrosion rate in g/m<sup>2</sup>d

From Table 4.2.1a), the average ratio 1984/1985 corrosion rate for cast iron is found to be 1.30, with a standard deviation of 0.30. For copper, Table 4.2.1b) values yield an average ratio of 1.60, and a higher deviation of 0.71. Both these comparisons show that the corrosion rates were higher in the first experimental session than in the second.

It is difficult, at this point, to explain these differences by a single factor change. However, it appears, as suspected, that the combination of lower pH, higher dissolved oxygen and carbon dioxide created a more corrosive situation in the first experiment. The absolute corrosion rates will therefore not be compared, with only the relative changes in corrosion rates caused by pH adjustment or pressure discussed.

For cast iron, in both cases, pressure greatly enhanced the corrosion process and the observed corrosion rates were, on average, 100% higher in pressurized

conditions. This effect was more prominent in the first experiment, with the pressure possibly having a synergistic effect on the already more aggressive conditions. As well, it is quite obvious from both sets of cast iron results that increased pH did not reduce corrosion: in fact, corrosion of cast iron, in general, was slightly higher under pH controlled conditions.

As for copper, the effect of pressure did not have as dramatic an effect on corrosion as that observed for cast iron. In both sets of copper results (see Figure 4.2.6b), it can be noted that pressurized samples displayed lower corrosion rates than samples in gravity control and, therefore, these rates were lower than the rates expected from their low pH conditions (in both cases, the pressure control had the lowest pH of all the cells). The percent changes, i.e. the difference between corrosion rates in a pH adjusted cell and the gravity control cell, expressed as a percent of the gravity control value are presented in Table 4.2.2a) for cast iron and Table 4.2.2b) for copper<sup>19</sup>.

TABLE 4.2.2a) Percent Changes in Corrosion Rate with pH - Cast Iron

Exposure (Weeks)	Year	Goal pH=6	Goal pH=7	Goal pH=8
1.0	1984	-	-14.3	+6.6
	1985	-5.6	-1.25	-10.7
1.5	1984	-	-4.4	+12.0
	1985	-16.5	+13.6	-17.7
2.0	1984	-	+57.6	+53.2
	1985	-8.7	+15.8	-15.3
3.0	1984	-	-1.0	+9.6
	1985	+43.1	+29.2	+30.0
4.0	1984	-	-14.5	-8.4
	1985	+35.5	+28.2	+24.2
6.0	1985	+36.0	+29.7	+20.7
8.0	1985	+24.0	+4.9	+7.3
10.0	1985	+19.1	+19.1	+20.0
12.0	1985	+32.0	+23.0	+29.0
	Average	+17.7	+13.3	+11.5

<sup>19</sup>The percent change calculation is:

$$\frac{(\text{adjusted pH corrosion rate}) - (\text{gravity control corrosion rate})}{(\text{gravity control corrosion rate})} \times 100\%$$

The cast iron data shows a small difference in the percent increase from pH 6 to pH 8; as such, it cannot be concluded which of the pH levels really caused the highest increase in corrosion. It is, however, notable that corrosion did increase overall by approximately 15%, although no plausible explanation has been found to this point.

TABLE 4.2.2b) Percent Changes in Corrosion Rates with pH - Copper

Exposure (Weeks)	Year	Goal pH=6	Goal pH=7	Goal pH=8
1.0	1984	-	-66.9	-67.8
	1985	-67.2	-58.2	-71.6
1.5	1984	-	-73.3	-83.3
	1985	-61.4	-68.4	-70.2
2.0	1984	-	-54.9	-57.3
	1985	-57.5	-62.5	-65.0
3.0	1984	-	-53.4	-62.1
	1985	-67.3	-44.9	-79.6
4.0	1984	-	-41.7	-58.3
	1985	-78.4	-76.5	-88.2
6.0	1985	-50.7	-49.3	-64.0
8.0	1985	-53.4	-53.4	-60.3
10.0	1985	-34.5	-63.8	-62.1
12.0	1985	-66.7	-66.7	-64.8
	Average	-59.7	-59.6	-68.2

The copper data shows trends closer to those one might expect with pH adjustment. For pH 6 and 7, the decreases were almost identical. The slowest rates were measured for the samples of the pH 8 basins, in which the average corrosion reduction was calculated as 68.2%, over the gravity control value.

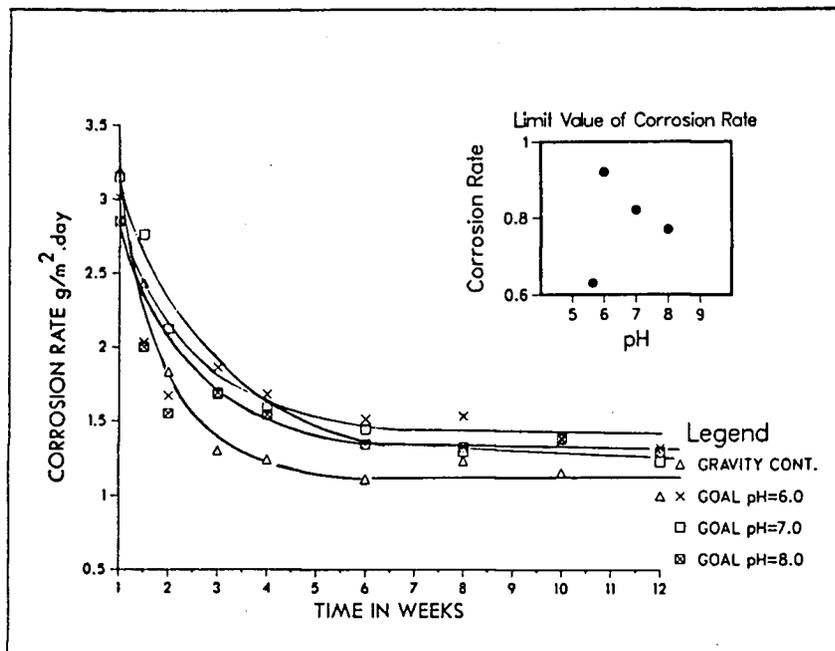


FIGURE 4.2.8a) Effect of pH on Corrosion Rates of Cast Iron

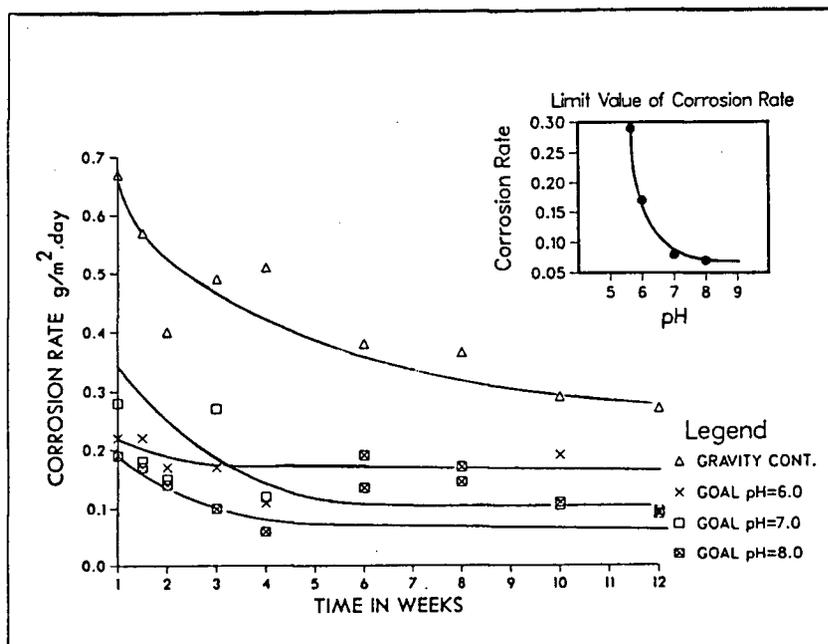


FIGURE 4.2.8b) Effect of pH on Corrosion Rates of Copper

Figures 4.2.8a) and 4.2.8b) show manually fitted curves for corrosion rates versus time and pH, based on the 1985 results only. The effect of pH adjustment is clearly visible from these curves. The insert diagrams, which correlate the limit corrosion rate value with pH, complement these observations. With this limited number

of data points, it appears that the beneficial effect of pH increase on long-term corrosion rates, is the same at pH 7 and 8. However, further work would be needed to corroborate this observation.

Use of this limit value of corrosion rate should control the concentration of metal introduced into the water through the distribution network, given that the conditions remained unchanged for long periods of time. At the same time, corrosion was stabilized at the limit asymptotic corrosion rate value. The next discussion concerns some observations gathered during both experiments on the concentrations of metal in laboratory tap water.

#### 4.2.4 LABORATORY WATER METAL CONTENT

Seven metals were monitored throughout both experiments, for all feed-waters. The curves, showing the concentrations of magnesium, potassium, sodium and zinc, do not suggest any special trends of concentrations with time or pH. They are presented in Appendix F.

Figures 4.2.9a) and 4.2.9b) show the variation of iron content in the feed-water, for both experiments; Figures 4.2.10a) and 4.2.10b), show similar curves for copper concentration<sup>20</sup>. These two metals are presented since they are especially susceptible to change during transportation in the pipes, either domestic copper pipes or, cement-lined municipal cast-iron mains.

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<sup>20</sup>Calcium was discussed in Section 4.1.

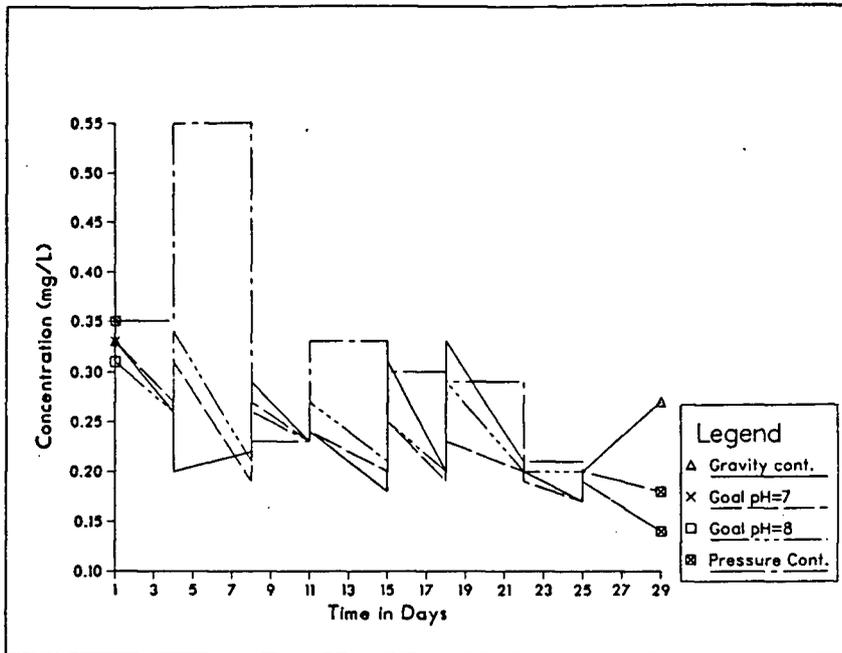


FIGURE 4.2.9a) Iron Concentration vs Time - First Experiment

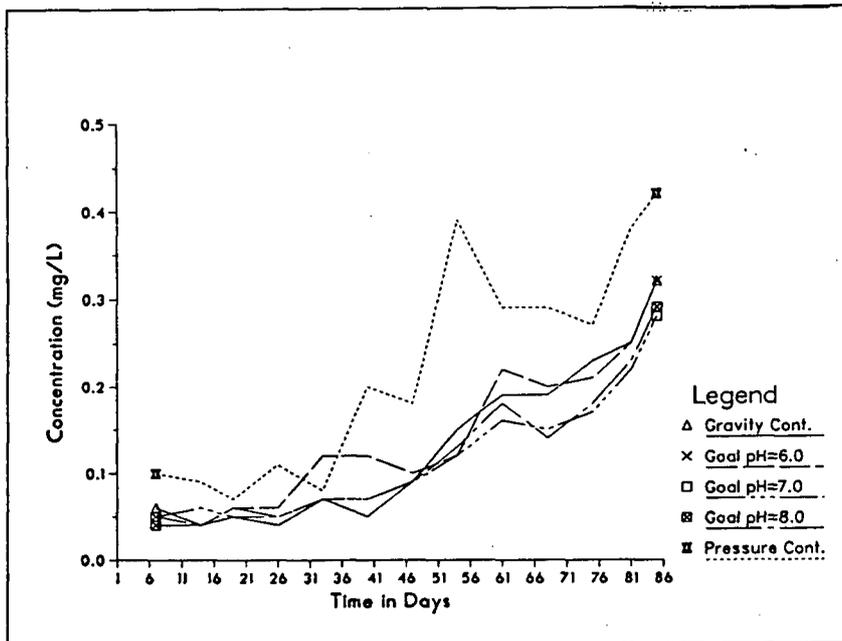


FIGURE 4.2.9b) Iron Concentration vs Time - Second Experiment

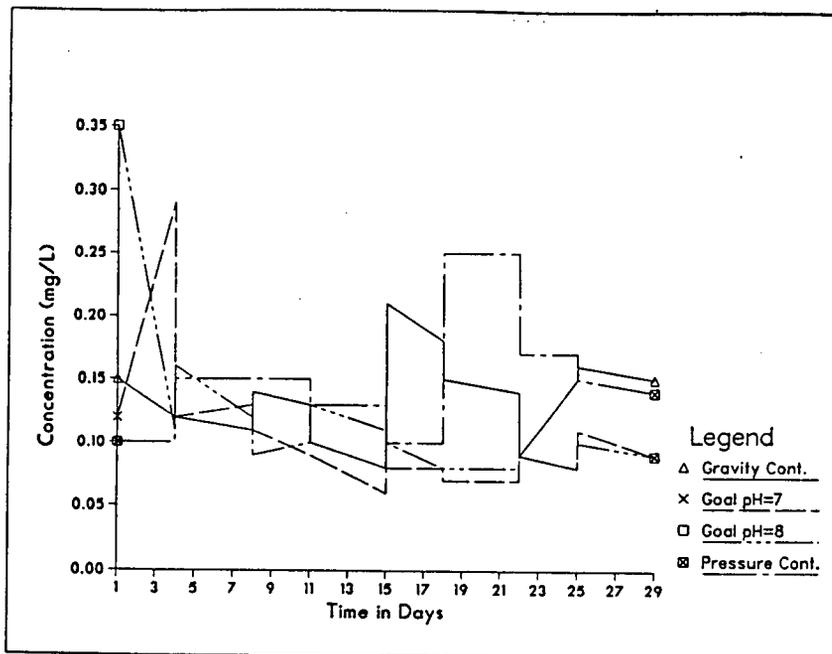


FIGURE 4.2.10a) Copper Concentration vs Time - First Experiment

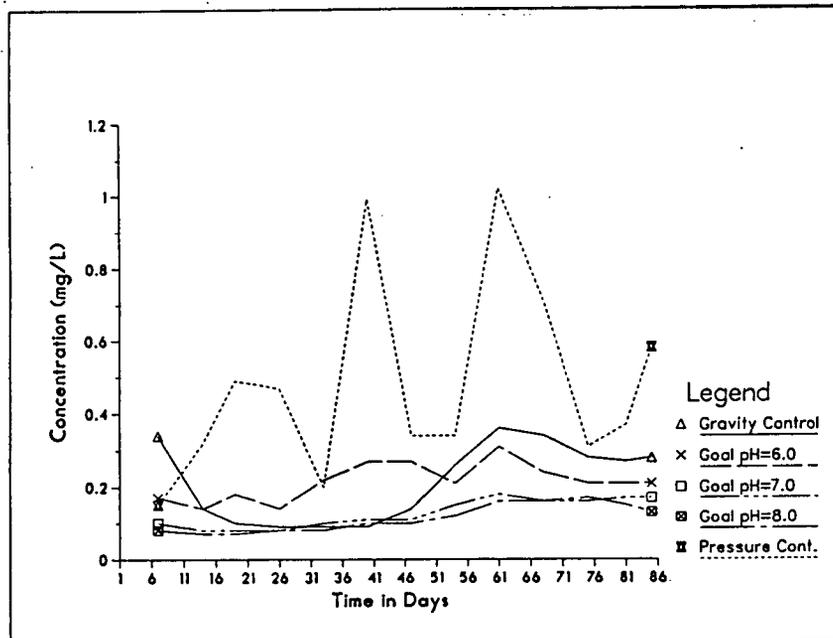


FIGURE 4.2.10b) Copper Concentration vs Time - Second Experiment

The GVRD regularly analyses water quality at the intake point of the distribution system raw water. In 1982, the analyses showed an average iron concentration of 0.13 mg/L, and an average copper concentration below detection, i.e.  $<0.001$  mg/L (Personnal communication, Bob Jones, Greater Vancouver Water District,

1983). The values presented in Figures 4.2.9 and 4.2.10 show that, for both experiments, the tap water concentrations of cast iron varied between 0.05 and 0.35 mg/L, and copper concentrations varied between 0.10 and 0.40 mg/L<sup>21</sup>.

Comparing the laboratory results and the intake water data, it is quite obvious, especially in the case of copper, that the metal content increased during distribution; most of the time, however, metal concentrations remained below the British Columbia maximum recommended values of 0.30 mg/L for iron and 1.0 mg/L for copper (Purdon, 1983). The iron concentration also appeared to increase steadily during the course of the second experiment, although no explanation was found for this phenomenon. The other metals did not show any particular pattern with time.

The tap used to fill the basins of the experimental set-up was regularly flushed. The metal concentrations were found to be quite uniform at this particular location. However, when the water is allowed to remain in the pipes for a longer time, or when the pipe surface is disturbed by flow variations, the measured values can be quite variable. Table 4.2.3 shows the various metal concentrations measured in a tap water sample collected from a frequently used faucet in the UBC Environmental Engineering Laboratory, on September 26, 1984. For comparison, the averages values of a September 10, 1985 gravity control sample are given.

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<sup>21</sup> These values do not take into consideration the pressure control concentrations, because for this particular set-up, the water samples had to be taken downstream of the cells due to rigid plumbing connections. Therefore, those particular samples always contained more metal.

TABLE 4.2.3 Sept. 26, 1984 Turbid Tap Water Sample Metal Content

Metal content (mg/L)	Sept 10, 1985 Gravity basin	Sept 26, 1984 Turbid tap
Calcium	1.34	0.25
Copper	0.28	n/a
Iron	0.32	17.98
Magnesium	0.15	2.57
Potassium	0.18	1.27
Sodium	0.56	1.28
Zinc	0.01	0.06

This sample was taken because the water had a brownish colour, which is an uncommon occurrence. As evidenced by the change in metal concentrations, some disturbance in the distribution system had resulted in a release of high metal content sediments into the water.

This particular, single event is presented here to demonstrate that the water quality might be altered before it reaches the consumer's tap. In this case, the problem was so obvious from the change in the water's esthetic value, that there was little risk of someone consuming that water. However, some less noticeable changes in metal concentrations have been noted by several authors (Koch et al., 1977, Zoeteman and Haring, 1978, amongst others) after overnight residence of the water in the pipes. This aspect of metal release, which is not covered in the coupon testing, where the flows are kept constant, prompted the decision to conduct a preliminary tap water sampling program of six private dwellings in the GVRD. The results are presented in the following section.

#### 4.3 TAP WATER SURVEY PROGRAM

Six private dwellings sampled their kitchen faucets eight times during August 1985, each time collecting four different samples: morning first flush, hot and cold, and running water, hot and cold<sup>22</sup>. The concentrations of seven metals were measured

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<sup>22</sup>The sampling methodology has been discussed in Chapter 3.

in these samples; the results are presented in this section.

In the first part, a graphical representation of some metal concentrations is presented to supplement the average values tabulated in Appendix E. The concentrations are discussed with respect to the recommended maximum values by the British Columbian and Canadian governments. In the second and third parts of this section, the average concentrations are compared between dwellings, between residence times and between sample temperatures. Because of the limited number of samples, the comparisons are more qualitative than quantitative, and only the most obvious trends are mentioned. A general discussion concludes and summarizes this section.

#### 4.3.1 AVERAGE CONCENTRATION

Tables E.1 to E.6 of Appendix E summarize, for each dwelling, the average concentrations measured for the studied metals, in each type of sample. An asterisk indicates the concentrations which exceeded the maximum recommended values for British Columbia or Canada. The acceptable maximum levels are listed in Table 4.3.1.

TABLE 4.3.1 Maximum Acceptable Metals Concentration

Metal	Concentration (mg/L)
Ca	n/a
Cu	1.0 (B.C.)
Fe	0.3 (B.C.)
Mg	n/a
K	n/a
Na	20.0* (Canada)
Zn	5.0 (Canada)

\* Value at which inspection is recommended

The maximum acceptable calcium and magnesium concentrations are not explicitly given, but the authorities, while not setting an absolute upper level,

recommend that, for drinking purposes, water with less than 200 mg/L Total Hardness as  $\text{CaCO}_3$  be used. From the measured values of calcium ( $<1.5$  mg/L) and magnesium ( $<1.0$  mg/L) in this survey, these two metals did not stand out as potential problems.

From the tabulated values of Appendix E, the maximum acceptable copper level (1.0 mg/L) was exceeded in 5 of the 24 samples, with two occurrences exceeding the level by as much as 100% (Figure 4.3.1 graphically shows the copper levels in the samples; the maximum acceptable concentration is indicated by a dashed line). If one were to use the 0.50 mg/L maximum recommended level of Demayo and Taylor (1981), it would be exceeded in half of the samples.

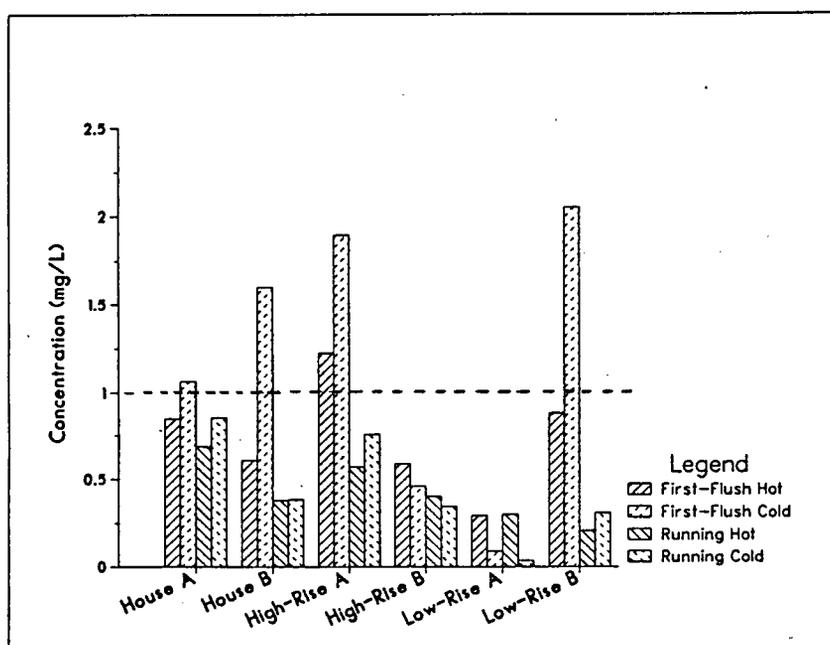


FIGURE 4.3.1 Copper Concentration in GVRD Private Dwellings

Figure 4.3.2 shows that iron was in excess of the recommended value (dashed line) in 4 of the 24 samples. However, these particular events were all observed in the same dwelling, and the reason behind these high levels will be discussed in more depth in the next section. From the six other dwellings' samples, iron does not appear to be a problem metal.

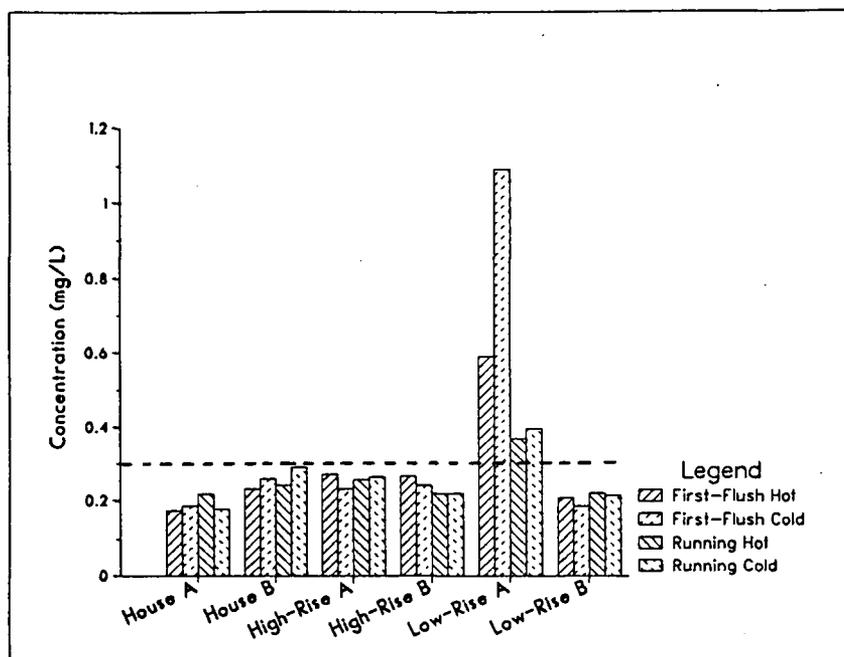


FIGURE 4.3.2 Iron Concentration in GVRD Private Dwellings

Since neither governmental authority sets maximum acceptable levels for potassium, it has to be concluded that this metal is not considered a problem metal. The average concentrations measured in this survey were below 0.6 mg/L.

The value given in Table 4.3.1 for sodium, as indicated in the table footnote, is not a maximum level. It is the value at which the environmental authorities should be consulted about the quality of the water supply. Sodium can be consumed by normal adults in quantities of up to 10 grams per day; as well, the water dietary contribution usually represents a very small percent of the total ingested quantity (Environment Canada, 1978). However, because many people, suffering from high blood pressure, require low sodium diets, the water content of this metal should be controlled to prevent it from becoming a health hazard to this segment of the population; hence, the recommended 20 mg/L value.

The values measured in this survey indicate a uniform sodium concentration of between 0.42 and 0.48 mg/L in all samples, indicating no problem with this metal level in the GVRD water system.

For zinc, the maximum level of 5 mg/L was never attained; 23 of the 24 samples were below 10% of this value.

From this preliminary survey, it appears that most metals stayed in low concentration ranges, regardless of the type of dwelling or type of sample, with a few notable exceptions. Copper was found in excess in a relatively large number of samples and in every type of dwelling; iron was found in excess in all the samples of one dwelling only. The following two sections outline the relationship between these concentration variations and the type of building or the type of sample (as influenced by residence time and temperature).

#### 4.3.2 DWELLING COMPARISON

At the end of this section, the reader will find Figures 4.3.3a) to 4.3.3g), graphical representations of the various cumulative metal concentrations from each samples and for each dwelling, with respect to the individual metals. When referring to these particular graphs, it should be remembered that the ordinate units of mg/L are cumulative, and do not indicate what were the average sample concentrations. For example, from the first figure, one can see that, for House A, all four samples had more or less an equal calcium concentration of 1.3 mg/L. No sample had a concentration of 5.2 mg/L, where the top of the bar lies.

From these Figures, it is quite evident that calcium, potassium and sodium did not differ significantly from one dwelling to the other. This is not a surprising observation, since all units had the same raw water supply, and these so-called 'light' metals would not normally be introduced to the water during distribution.

Copper, on the other hand, varied significantly between individual dwellings, but did not show clear trends between type of dwelling. For example, it was expected that the hot water samples of both High Rises would contain some of the higher copper levels, because their hot water is continually circulated to keep it warm, and, therefore,

contacts a larger pipe surface area. As shown on Figure 4.3.3b), High Rise A did have high copper levels, but High Rise B had the second lowest copper concentrations. The Low Rise A samples also contained very little copper ( $\leq 0.30$  mg/L). Since most of the plumbing of this old building is galvanized steel pipes (see Table 3.5.1), there is little surprise in this observation, nor in the comparatively high levels of iron (Figure 4.3.3c)) and zinc (Figure 4.3.3g)) also measured in these samples.

As for the effect of building age on copper release, no strong trend was seen. House B and High Rise B were the oldest of their group, but it cannot be confirmed that the slightly higher copper levels in these samples was age related, or, indeed, even significant enough to make mention of.

For iron, aside from the very high values of High Rise A samples, (due to the galvanized steel pipes), there is no strong trend in concentration changes, either between household types or within one type. Magnesium also showed little variation in all values, with the exception of House B concentrations. As shown in Figure 4.3.3d), House B's hot water samples contained almost three times the average magnesium amounts. Although the interviewed house owner did not mention being aware of any problem, this metal most probably leached out of the sacrificial anode in the hot water tank. The increased concentration might indicate a failure in the tank lining, leading to a greater protection demand on the sacrificial anode (see Chap 2, Section 2.1.4 on electrical protection).

Zinc, as shown in Figure 4.3.3g), was quite high in the building with galvanized steel pipes, but lower in all other dwellings. House A samples contained the second highest zinc concentration but, as shown in Table E.1, that high value had a poor reproducibility ( $\mu = 0.44$  mg/L,  $\sigma = 0.38$ ), which suggests that caution be used in interpreting this result. This new house, built in 1982, could be displaying larger corrosion rates because the corrosion limit values may not be attained yet. In that case, the increased zinc concentration would reflect the greater anodic current required

for the increased corrosion protection. On the other hand, the fluctuation could simply be due to experimental error. The small number of samples does not allow for a reliable answer to this question.

At this point of the study, the limited information does not permit one to relate the various water metal contents to a specific type or age of dwelling. The only significant dwelling-related factor found in this survey is the type of pipe used for domestic plumbing, as demonstrated by the variations in Low Rise A values. However, when referring to Figures 4.3.3a)-g), the reader may notice that some metals did not have the same concentrations in all four sample-types (first flush hot and cold, running hot and cold). These comparisons between samples, with different temperatures and different residence times, are covered in the following section.

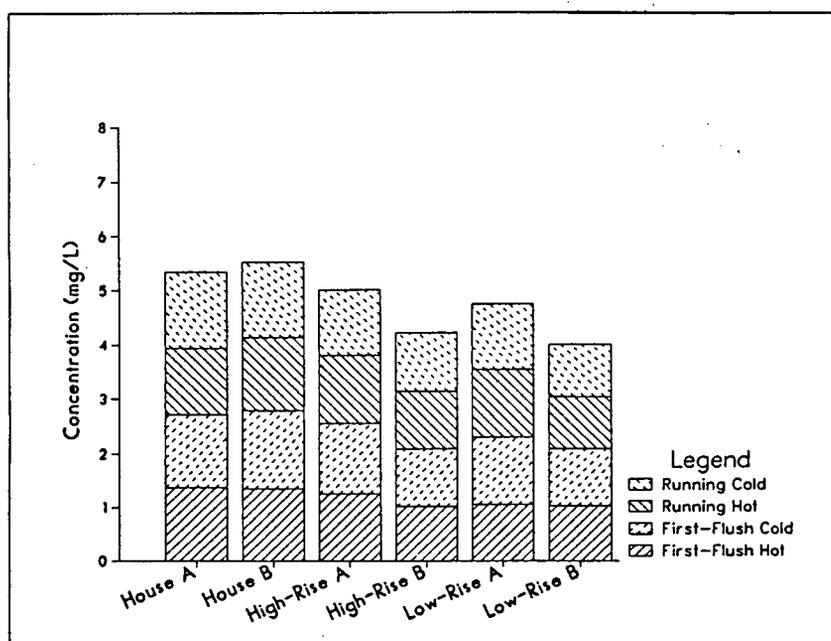


FIGURE 4.3.3a) Cumulative Dwellings Water Calcium Content

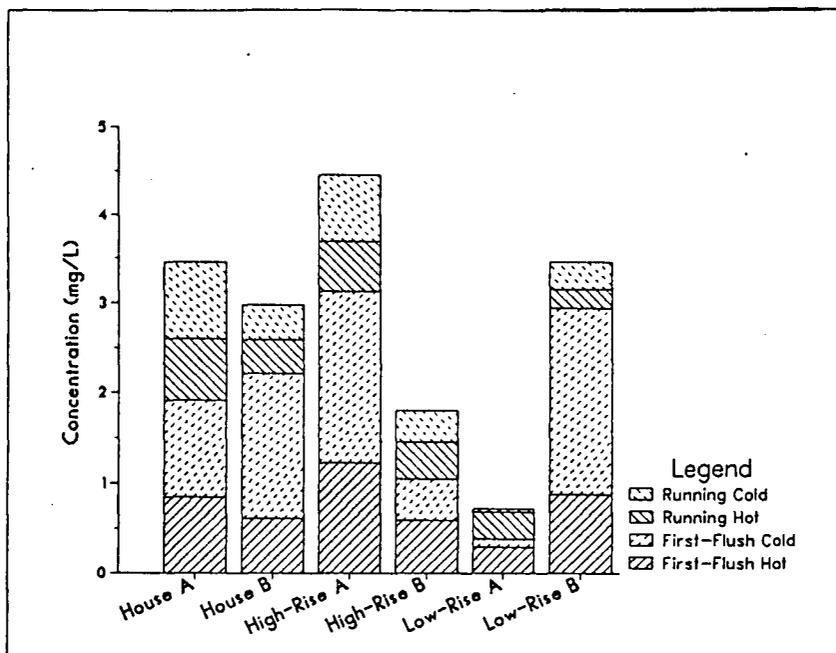


FIGURE 4.3.3b) Cumulative Dwellings Water Copper Content

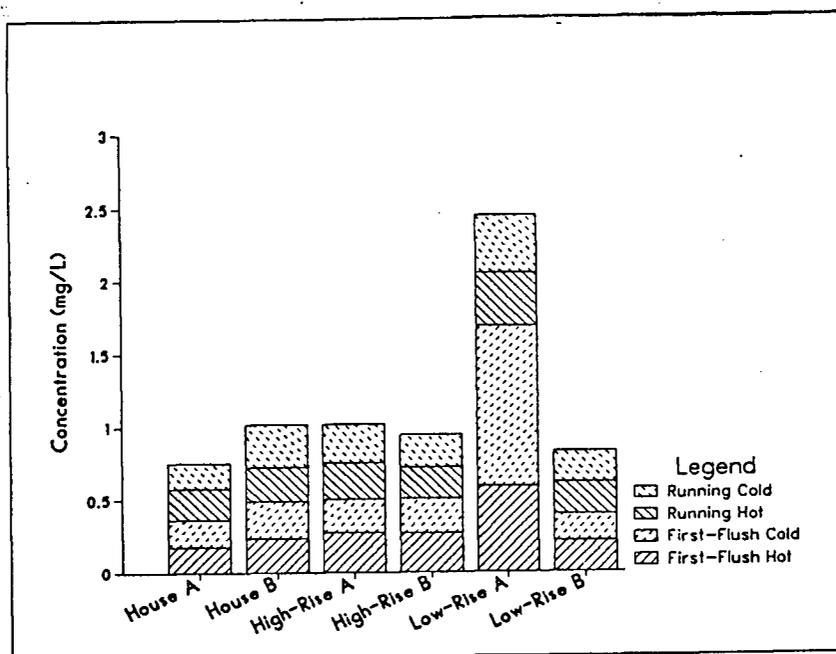


FIGURE 4.3.3c) Cumulative Dwellings Water Iron Content

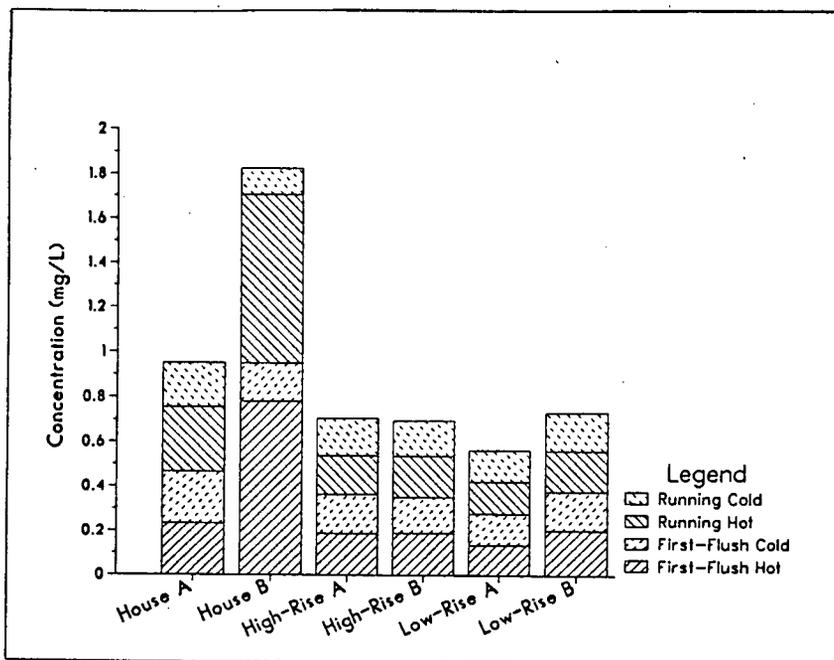


FIGURE 4.3.3d) Cumulative Dwelling Water Magnesium Content

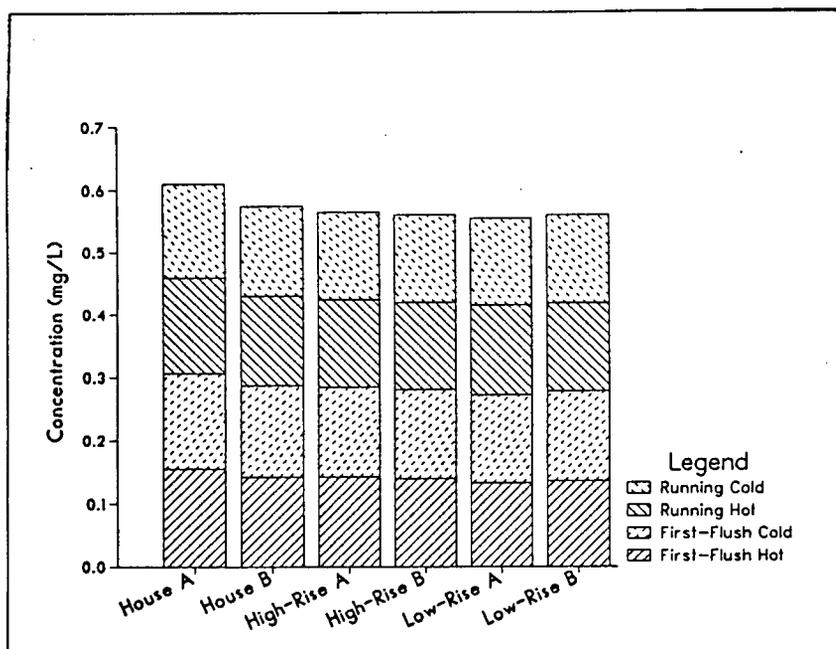


FIGURE 4.3.3e) Cumulative Dwelling Water Potassium Content

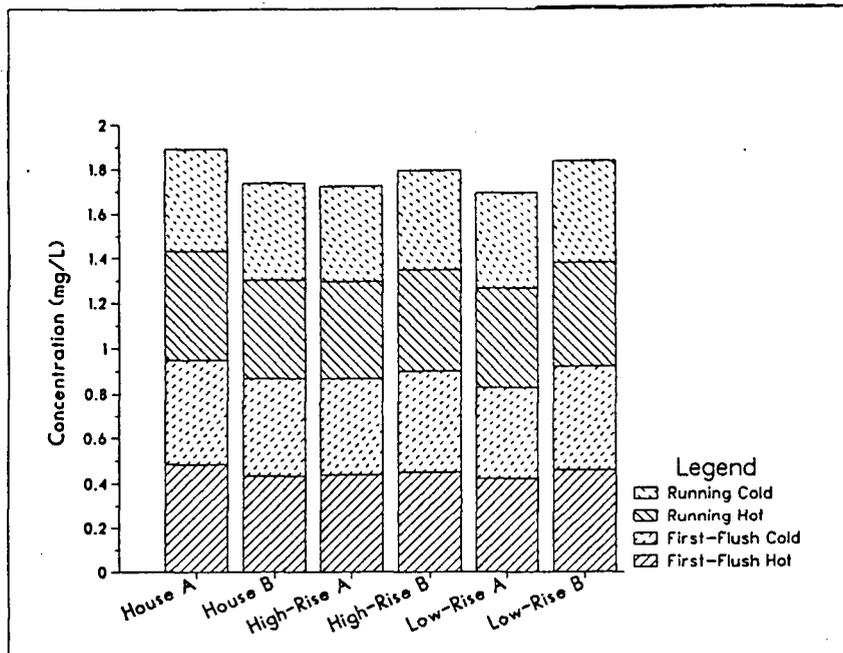


FIGURE 4.3.3f) Cumulative Dwellings Water Sodium Content

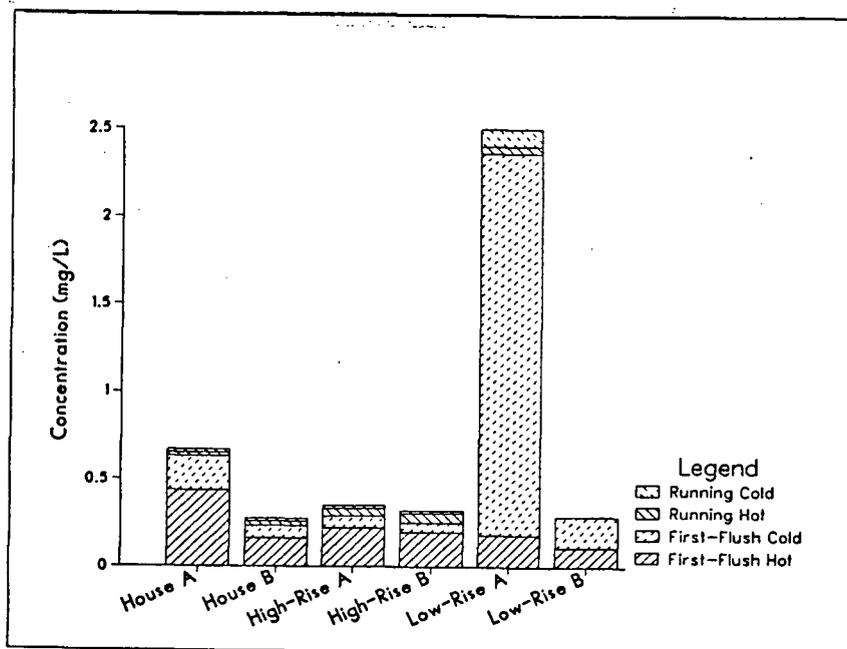


FIGURE 4.3.3g) Cumulative Dwellings Water Zinc Content

4.3.3 TEMPERATURE AND RESIDENCE TIME COMPARISONS

Figures 4.3.3a) to g) will again be used to illustrate the differences in metal concentrations, with reference to temperatures (hot or cold water samples), and

residence times (first-flush or running sample). Temperature will be discussed first, followed by residence time.

### 1. Temperature

When temperature effects were discussed in Chapter 2, it was noted that a temperature increase could have two opposing effects. On the one hand, it could increase the rate of most electrochemical processes, therefore increasing corrosion. On the other hand, it could lower the gases' solubilities, which would reduce corrosion, if these gases were limiting electron acceptors, as it sometimes the case for oxygen and chlorine.

In Figures 4.3.3a) to g), cold water samples have a dashed-line pattern, while the corresponding hot water samples have a solid-line pattern. From the figures for calcium, potassium and sodium, it appears that temperature clearly did not influence their solubility at any significant level<sup>23</sup>. In the copper diagram, Figure 4.3.3b), the dashed areas are more prominent in all units but one, indicating that more copper was found at the cold water faucet than at the hot water faucet. Although these are preliminary findings only, this result suggests that the overall water temperature increase reduced copper corrosion. This finding should, however, be confirmed in further laboratory studies, since it is difficult to ensure that the water collected actually originated totally from one side (hot or cold) (the line clearing time of 2 seconds was only an approximate value). Nevertheless, the reproducibility was acceptable (see appendix E), and these preliminary findings should be considered carefully in further studies.

One final observation concerning Figure 4.3.3b) is that, in the case of the building with galvanized pipes (Low Rise A), the copper concentration, although

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<sup>23</sup>It was already mentioned that the solubility of calcium carbonate decreases when temperature increases, and that calcium might precipitate out of solution in water heaters. This phenomenon, however, can only be observed if sufficient amounts of calcium and carbonates are present, which is not the case in this low-hardness, low-alkalinity water.

low, was much higher in the hot water samples than in the cold samples, therefore conflicting with the general trend. This discrepancy became easily explainable after an inspection of the building's piping system. It was revealed that a small part of the original hot water line had been replaced, and copper tubing had been used instead of the galvanized steel in the rest of the system, thus explaining the presence of small amounts of copper in the hot water samples.

In Figure 4.3.3c), for all buildings except Low Rise A, the dashed and solid areas occupy approximately the same overall area, which indicates there was no marked effect of water temperature on iron uptake. For the special case of Low Rise A's greater concentrations, iron levels were higher in the cold samples. This would tend to indicate that in cases of accelerated corrosion, an increased temperature decreased the corrosion of iron. This is supported by the fact that, because of the presence of copper in the hot water line, one would have expected to find greater amounts of iron in the hot water samples, due to an accelerated corrosion of the iron, in contact with copper, in the hot water line. However, this was not observed.

Magnesium was higher in most of the hot water samples, for all dwellings, as evidenced by the larger solid-line area in Figure 4.3.3d). These increased concentrations cannot, however, be attributed to an accelerated corrosion rate of magnesium in hot water, because the water on the cold line simply does not have the opportunity to uptake magnesium (never being in contact with the water heater's sacrificial anode). The difference in magnesium concentration might be significant, but it is not a temperature effect; rather, it is a design-related effect.

Zinc concentrations (Figure 4.3.3g)) were significantly higher in the hot water samples when all samples contained little of it. However, in Low Rise A,

where concentrations were five times the average, cold water samples contained more zinc than hot water samples. This difference in temperature effects between the situations of low and high total zinc contents, suggests that the variations might not be temperature related in the case of low concentration. With the concentration increase in the cold water samples of Low Rise A being so extreme, it suggests a reduction of zinc corrosion in hot water, as in the case of copper.

TABLE 4.3.2 Hot Water Temperature in Dwellings

Dwelling	Temperature (°C)
House A	51.0
House B	53.5
High Rise A	57.5
High Rise B	66.0
Low Rise A	55.0
Low Rise B	60.0

Table 4.3.2 lists the hot water temperatures measured by the tenants. From this data, it is not possible to significantly link the temperature to the magnitude of the change of metal content, since other variations were already occurring between dwellings, and the temperature effects could not be isolated. However, from these temperature values, one can see that there is quite a large variation in the temperature values, which suggests that temperature control could be a way of reducing the corrosion of some metals (magnesium, for example), since its corrosion takes place in hot water lines.

## 2. Residence Time

Most of the first-flush samples collected water that had spent at least eight hours (overnight) in the pipes. From some previously cited work (Zoeteman and Haring, 1978, amongst others), it was expected that the first flush samples of the present survey would contain higher metal levels.

In Figures 4.3.3a) to g), the first flush samples are shaded with a diagonal pattern at a 45° angle, i.e. from the lower left corner to the upper right corner. Inspection of the figures shows, as was the case for the two other comparisons, that calcium, potassium and sodium did not display any special concentration variations with residence time. The four other metals, however, were found in larger concentrations in the first flush samples, in 17 of the 24 cases, i.e. in 71% of the observations. The increase in concentration was more consistent for copper and zinc, where it was noted in all dwellings. Half the units had higher magnesium concentrations in the first flush samples, and only a third displayed this accumulation for iron. For this last metal, however, it can be seen from Figure 4.3.3c), that for Low Rise A, where the total concentration was larger, the two first flush samples totalled more than twice the content of the 'running' samples, illustrating a greater uptake for longer contact times.

These preliminary results indicate quite strongly that higher metal levels are found in overnight water, which, in some cases, might lead to concentrations higher than the recommended maximum values. This was found to be the case for copper, for which two thirds of first flush cold samples contained more than 1.0 mg/L, a concentration sufficient to give water a unpalatable taste, according to Sims and Raible (1983).

#### 4.3.4 DISCUSSION

This exploratory survey of metal concentrations at the consumer tap did not yield sufficient data to outline an effect of building age, or type, on metal content, but it did show that some samples, especially for copper and iron, exceeded the recommended maximum values in several occasions. The metal concentrations were found to be significantly higher in morning first flush samples, at least for copper, zinc and magnesium.

These preliminary results confirmed the need for additional work in this area. A broader, more systematic sampling program would yield enough data to establish the statistical significance of parameters such as: residence time, number of stories or hot water temperature. This field data could be relevantly supplemented with laboratory studies, where the conditions can be more rigidly controlled.

The problem metals, in this survey, appeared to be copper and iron. To assess the health implications of their high concentrations, a second level of sampling would be required. In this second investigation, a systematic effort should be made to evaluate the actual metal ingestion, rather than solely the water concentrations.

The proposed studies would allow the water supplier to assess whether or not the good quality of the raw water also includes the characteristics needed for this quality to be maintained during distribution. When disinfection dosages are chosen, for example, great care is taken to ensure that they are sufficient for the water to reach the consumer, before having had time to re-establish a bacterial population. Similarly, the aggressive nature of the raw water should be controlled to prevent it from introducing high levels of potentially dangerous metal in the water, thereby reducing its quality. One of the steps towards achieving this control is the establishment of what the in-situ conditions are, and how they affect the population at large.

## 5. CONCLUSIONS AND RECOMMENDATIONS

In this final chapter, the reader will find a brief summary of this report's content, organized in three sections.

In the first one, the major findings of this work are outlined, with respect to the literature review, water characteristics monitoring, metallic coupon testing and tap water survey. The main conclusions drawn from these observations are presented in the second section, followed by recommendations for future work in the third section.

### 5.1 SUMMARY OF FINDINGS

1. From the review of some of the most recently published work on water distribution pipe internal corrosion, it was found that:
  - a. Corrosion is a multi-rate, multi-variable phenomenon and one situation cannot be assessed simply by the use of traditional calco-carbonic (or water aggressivity) indexes, such as the Langelier Index or the Ryznar Index.
  - b. Although most of the monitored water characteristics (pH, acidity, alkalinity, hardness, chloride, sulfate, nitrate, temperature, dissolved oxygen, etc) were found, by one or another author, to affect corrosion, their effects varied with the specific situation and levels of other parameters.
  - c. Several references were found on the use of pH adjustment for corrosion control, where the metal leaching was successfully reduced. However, the choice of type of chemicals and dosages were specific to one water situation.
2. The monitoring of the laboratory water characteristics, for the duration of the two experiments, led to two major findings:
  - a. The water supplied by the GVRD, at the laboratory tap, consistently displayed typical aggressive water characteristics, i.e. high dissolved oxygen,

- low pH, low alkalinity and low hardness.
- b. Between the 1984 Winter experiment and the 1985 Summer experiment, a significant change in water temperature and dissolved oxygen content encouraged overall higher corrosion rates in the winter situation, when the average water temperature was lower, and the oxygen content higher.
3. The main body of this research consisted of two cast iron and copper coupon weight loss laboratory experiments. These experiments led to four findings:
    - a. Cast iron corroded approximately ten times faster than copper in tap water, at room temperature.
    - b. Cast iron coupons, exposed to the same pressure conditions as those of the water distribution network, displayed greatly enhanced corrosion rates, usually twice the values measured in gravity-fed conditions, where the pressure was only slightly higher than normal atmospheric pressure.
    - c. Increased pressure had a different effect on copper; there was a slight decrease in copper corrosion rates, with reference to the corresponding gravity-fed cells.
    - d. Addition of hydrated lime ( $\text{Ca}(\text{OH})_2$ ), to increase the water pH from the naturally occurring 5.30–5.65 values to 8.05–8.10 values, reduced the corrosion rate of copper coupons in gravity-fed cells by 68%, but apparently increased the cast iron rates by 15%.
  4. After analysis of the metal concentrations in tap water from six private dwellings, it was found that:
    - a. Copper levels in the first flush cold water samples exceeded the recommended maximum values in 67% of the cases.
    - b. First flush samples were noticeably higher in copper, zinc and magnesium. In most cases, the results suggested higher metal uptake in cold water rather than in hot water.

- c. Calcium, potassium and sodium concentrations were found to be uniform in all samples, regardless of dwelling type, temperature and water residence time.
  - d. One sampled building equipped with galvanized steel pipes, had iron concentrations in excess of the maximum acceptable values in all samples, demonstrating the importance of the type of pipes used in domestic plumbing systems.
5. Finally, from both the laboratory water characteristics monitoring and the tap water survey, it was found that copper, iron and zinc concentrations showed marked increases between the raw water intake and the tap, indicating that the aggressive nature of the GVRD water is causing dissolution of the metal distribution pipes.

## 5.2 MAJOR CONCLUSIONS

Three major conclusions can be drawn from the above mentioned findings:

1. Aqueous corrosion is a complex process in which the many species involved have synergistic and antagonistic actions. Therefore, each water situation is different and requires a 'personalized' treatment. The corrosion situation, and the impact of control measures, can only be adequately assessed with the help of laboratory coupon testing and in-situ sampling and monitoring.
2. Although pH adjustment by lime addition was found to reduce the corrosion of copper coupons significantly, the unexpected effect of pressure on corrosion rates, as well as the limited replicate data available, prevented the prediction of actual in-situ corrosion rates for the distribution system, and the determination of required full-scale control measures.
3. The preliminary tap water sampling program confirmed the relevance of studying copper corrosion, since copper was found in unacceptably high levels in several

water samples, regardless of the type of dwelling.

### 5.3 RECOMMENDATIONS FOR FUTURE STUDIES

In light of these first findings, it is recommended that the water supplier (the GVRD, in this situation) monitor the alteration of the water quality, in terms of metal concentrations, throughout its distribution system, from the raw water intake to the furthest consumer's tap. Corrosion coupons should be installed in various points of the system to monitor the corrosiveness of the environment. The collection of pipe samples, in different locations of the distribution network, would also contribute to a better understanding of the situation.

It was shown that a pH increase was a valuable approach to reducing corrosion, but additional studies would be needed before implementing any control measures. Amongst them can be listed:

1. Repeating the work presented here to gather enough data to perform significant statistical analyses.
2. Studying the isolated effects of dissolved oxygen, temperature and residence time, to understand better the seasonal and time-related corrosion changes.
3. Continuing studies of corrosion in pressurized conditions with a better control of the water characteristics, to allow side by side comparisons with gravity tests and prediction of in-situ corrosion rates.
4. Testing the effects of other chemicals, alone or in combination. Special attention should be given to chemicals such as sodium bicarbonate, that would allow a greater increase of the water buffering capacity and less variation in the target adjusted pH. The different efficient dosages should be compared in terms of costs and handling.
5. Comparing the coupon-sample results with pipe-loop test results, in which the effects of internal pressure, residence time and flow variations can be studied.

Because of the complexity of the corrosion phenomenon and the impact this process can have, both on the costs of maintaining a water supply and the maintenance of water quality in distribution, a wide field of study is open. In conclusion, the comment of Begin (1982), appears again very appropriate. He said:

"Since it is highly improbable that research/development will ever develop a totally corrosion resistant alloy, further studies in the field of corrosion control are needed to solve the upcoming future problems".

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**APPENDICES**

## A. SURFACE AREA AND CORROSION RATE CALCULATIONS EXAMPLE

### 1. Specific Weight Calculations

The calculation of the corrosion rate requires the division of the weight losses of the coupons by their exposed surface area and the time of contact. It is therefore of the utmost importance that the surface area of each coupon be evaluated accurately.

Because the metallic coupons were cut by hand, there was unavoidable variations in their dimensions. Furthermore, the tagging of the long-term exposure cast-iron coupons caused their surfaces to be irregular and even more difficult to measure. It was therefore very impractical to rely on the actual sizing of the metal plates for the calculation of their surface area. However, because the thickness was uniform within a group of coupons, it was possible to calculate, for a particular group, an average weight per area, referred to as 'specific weight'. By dividing the weight of a coupon by this constant, the area was easily obtained.

Table A.1 summarizes the results obtained for each group. The dimensions of the plates in the sample group were measured to the hundredth of mm with a digital-display vernier: NSK Max Cal Electronic Digital Caliper. In this research, the specific weight units are grams per square meter.

### 2. Corrosion rate calculations example

The corrosion rate is the amount of metal lost per surface area per day of exposure.

Using the data of two cast-iron plates of a duplicate having been exposed to pH 7 water during six weeks, we get:

The weight data (in grams):

Plate number	Clean weight	Final weight	Weight loss
# 0EF	11.2763	11.1168	0.1595
# 1ABDEF	11.2024	11.0769	0.1255

From TABLE A.1, we obtain that the specific weight for the second experiment cast iron plates is: 5195 g/m<sup>2</sup>.

Therefore, the calculated surface areas are:

# 0EF	= 11.2763g/5195g/m <sup>2</sup>	= 2.17 X 10 <sup>-3</sup> m <sup>2</sup> (2170 mm <sup>2</sup> )
# 1ABDEF	= 11.2024g/5195g/m <sup>2</sup>	= 2.16 X 10 <sup>-3</sup> m <sup>2</sup> (2157 mm <sup>2</sup> )

Weight loss per area:

# 0EF	= 0.1595g/2.17 X 10 <sup>-3</sup> m <sup>2</sup>	= 73.48 g/m <sup>2</sup>
# 1ABDEF	= 0.1255g/2.16 X 10 <sup>-3</sup> m <sup>2</sup>	= 58.20 g/m <sup>2</sup>
	AVERAGE	= 65.84 g/m <sup>2</sup>

From the exposure time being six weeks, i.e. 42 days, we obtain:  
CORROSION RATE = 1.57 g/day.m<sup>2</sup>

TABLE A.1 Specific weights related data

TYPE OF PLATE	NUMBER USED	SPECIFIC WEIGHT	STANDARD DEVIATION
First experiment Cast-iron	17	4819	233
First experiment Copper	21	4742	43
Second experiment Cast-iron	40	5195	55
Second experiment Copper	21	4620	48

B. WATER SAMPLING METHODOLOGY AND RESIDENT QUESTIONNAIRE

Drinking water sampling -- Master's research UBC

Background information

Name of person sampling: \_\_\_\_\_

Address of building: \_\_\_\_\_  
 \_\_\_\_\_

Number of stories: \_\_\_\_\_

Level on which the sampled tap is located: \_\_\_\_\_

Approximate year of building construction: \_\_\_\_\_

Type of tap sampled (kitchen or other): \_\_\_\_\_

Type of pipes (copper, galvanized iron, PVC or other):  
 \_\_\_\_\_

If the original piping system was replaced, indicate the date:  
 \_\_\_\_\_

Sampling Dates:

Comments:

Monday, Aug. 5	.....
	.....
Thursday, Aug. 8	.....
	.....
Monday, Aug. 12	.....
	.....
Thursday, Aug. 15	.....
	.....
Monday, Aug. 19	.....
	.....
Thursday, Aug. 22	.....
	.....
Monday, Aug. 26	.....
	.....
Thursday, Aug. 29	.....
	.....

FIGURE B.2 Resident Questionnaire Sheet

C. LABORATORY WATER AVERAGE METAL CONCENTRATION

TABLE C.1 Metal Concentrations in mg/L - First Experiment

Sample	Ca ± 0.03	Cu ± 0.01	Fe ± 0.02	Mg ± 0.01	K ± 0.02	Na ± 0.03	Zn ± 0.01	Value
Gravity Before	0.92 0.58	0.13 0.03	0.22 0.04	0.21 0.02	0.23 0.03	0.59 0.02	<0.01	$\mu$ $\sigma$
Gravity After	0.67 0.16	0.14 0.04	0.26 0.06	0.22 0.04	0.23 0.04	0.59 0.03	<0.01	$\mu$ $\sigma$
Goal pH7 Before	2.97 0.50	0.11 0.08	0.20 0.04	0.22 0.03	0.22 0.02	0.57 0.02	<0.01	$\mu$ $\sigma$
Goal pH7 After	2.02 0.66	0.10 0.02	0.25 0.05	0.23 0.03	0.22 0.03	0.57 0.02	<0.01	$\mu$ $\sigma$
Goal pH8 Before	3.12 1.40	0.10 0.02	0.21 0.03	0.22 0.02	0.22 0.04	0.59 0.04	<0.01	$\mu$ $\sigma$
Goal pH8 After	2.50 0.87	0.14 0.09	0.26 0.05	0.24 0.03	0.22 0.03	0.58 0.03	<0.01	$\mu$ $\sigma$
Pressure Control	0.69 0.16	0.15 0.05	0.29 0.11	0.22 0.04	0.22 0.03	0.58 0.02	<0.01	$\mu$ $\sigma$

TABLE C.2 Metal Concentrations in mg/L - Second Experiment

Sample	Ca ± 0.03	Cu ± 0.01	Fe ± 0.02	Mg ± 0.01	K ± 0.02	Na ± 0.03	Zn ± 0.01	Value
Gravity	1.14	0.21	0.13	0.16	0.17	0.52	0.01	$\mu$
Control	0.11	0.11	0.01	0.01	0.01	0.02	0.01	$\sigma$
Goal	2.42	0.21	0.14	0.17	0.20	0.55	0.01	$\mu$
pH=6	0.29	0.05	0.09	0.01	0.03	0.03	0.01	$\sigma$
Goal	4.38	0.13	0.12	0.17	0.19	0.55	0.01	$\mu$
pH=7	0.34	0.04	0.07	0.01	0.02	0.02	0.01	$\sigma$
Goal	6.64	0.11	0.12	0.18	0.18	0.53	0.01	$\mu$
pH=8	0.66	0.04	0.08	0.01	0.01	0.02	0.01	$\sigma$
Pressure	1.19	0.50	0.23	0.16	0.15	0.51	0.02	$\mu$
Control	0.22	0.28	0.13	0.01	0.01	0.04	0.01	$\sigma$

D. FORTRAN PROGRAMS AND WEIGHT LOSS SUMMARY DATA

Copies of two of the data treatment programs are included here, followed by their relevant data files. The first example is program WTCALC.CU which calculates for copper plates the cumulative weight loss data. The program writes the results in a CUMUL.metal file. The following quantities are calculated:

RUST A: Corroded weight - Initial weight

RUST B: Corroded weight - Final clean weight

NET LOSS: Initial weight - Final clean weight

The second example is program SUMCALC.CU1 which calculates, for one set of experimental conditions (type of cell, type of metal and experiment number), the average specific weight losses and corrosion rates, as detailed in Appendix A. The program writes the results in a SUM.pH.metal file.

## Program WTCALC.CU

```

1 C234567890.....0.....0.....0.....
2 C THIS PROGRAM IS TO CALCULATE THE WEIGHT VARIATIONS FOR EACH PLAT
3 C GIVEN ITS NUMBER.
4 C THE PROGRAM WILL READ THE INITIAL WEIGHTS FROM A FILE IDENTIFIED
5 C BY THE LABEL 50, THE CORRODED WEIGHTS FROM THE FILE IDENTIFIED B
6 C THE LABEL 51, AND THE FINAL WEIGHTS FROM 52. THESE LABELS ARE
7 C GIVEN WITH THE $RUN INSTRUCTION FOR THE PROGRAM.
8 C
9 C THIS VERSION WORKS FOR FILES FORMATTED 1X,A5,2X,A9 ONLY.
10 C
11 C THE FIRST LINE OF THE INITIAL WEIGHT FILE MUST BE THE NUMBER OF
12 C ENTRIES IN TOTAL, FORMAT A5.
13 C
14 C DATA TYPES AND INITIAL VALUES
15 C
16 C REAL*8 DATA(150,7)/1050*0.0/,NO,WT
17 C
18 C READING THE NUMBER OF ENTRIES
19 C
20 C READ(50,10) N
21 C I=1
22 C
23 C READING A VALUE IN RUST.XX
24 C
25 C 300 READ(51,11,END=200) NO,WT
26 C
27 C READING A VALUE IN CLEAN.XX
28 C
29 C 200 READ(50,11,END=99)DATA(I,1),DATA(I,2)
30 C IF(NO.EQ.DATA(I,1)) GO TO 100
31 C I=I+1
32 C GO TO 200
33 C
34 C IF THE PLATES ARE THE SAME, WRITE THE DATA IN
35 C
36 C 100 DATA(I,3)=WT
37 C DATA(I,5)=DATA(I,3)-DATA(I,2)
38 C
39 C READING A VALUE IN FINAL.XX
40 C
41 C READ(52,11)NO,WT
42 C DATA(I,4)=WT
43 C
44 C CALCULATING THE COOROSION PRODUCT WT AND THE OVERAL
45 C WT LOSS
46 C
47 C DATA(I,6)=DATA(I,3)-DATA(I,4)
48 C DATA(I,7)=DATA(I,2)-DATA(I,4)
49 C I=I+1
50 C GO TO 300
51 C
52 C WRITING THE TITLES AND RESULTS
53 C
54 C 99 WRITE(6,12)
55 C DO 1 I=1,N
56 C WRITE(6,13)(DATA(I,J),J=1,7)
57 C 1 CONTINUE
58 C
59 C 10 FORMAT(I5)
60 C 11 FORMAT(1X,A5,2X,F9.4)
61 C 12 FORMAT(1X,'NO',2X,'INITIAL WT',1X,'CORRODED',1X,'FINAL WT',1X,
62 C +2X,'RUST B',2X,'NET LOSS',/)
63 C 13 FORMAT(A7,3(F9.4),3(F8.4))
64 C
65 C STOP
66 C END

```

## Cumulative weight loss data for cast iron coupons, first experiment.

Listing of CUMUL.FE1 at 14:50:54 on NOV 13, 1985 for CCid=LOMI Page 1

1	m-113	8.3447	8.3389	8.2876	-0.0058	0.0513	0.0571
2	m-114	8.8558	8.8488	8.7966	-0.0070	0.0522	0.0592
3	m-115	8.8100	8.8014	8.7515	-0.0086	0.0499	0.0585
4	m-116	8.7281	8.7260	8.6744	-0.0021	0.0516	0.0537
5	m-117	8.1601	8.1364	8.0619	-0.0237	0.0745	0.0982
6	1-1	11.4787	11.4663	11.4030	-0.0124	0.0633	0.0757
7	1-10	11.4780	11.4710	11.3890	-0.0070	0.0820	0.0890
8	1-11	10.9756	10.9618	10.9101	-0.0138	0.0517	0.0655
9	1-16	11.3888	11.3954	11.2757	0.0066	0.1197	0.1131
10	1-17	11.4872	11.4752	11.4308	-0.0080	0.0484	0.0564
11	1-18	10.8496	10.8085	10.7146	-0.0411	0.0939	0.1350
12	1-19	11.5272	11.6467	11.2000	0.1195	0.4467	0.3272
13	1-2	11.0650	11.0701	11.0209	0.0051	0.0492	0.0441
14	1-21	11.9900	11.9534	11.8650	-0.0366	0.0884	0.1250
15	1-22	11.4407	11.5389	11.1128	0.0982	0.4261	0.3279
16	1-23	11.2347	11.2142	11.1675	-0.0205	0.0467	0.0672
17	1-24	10.7122	10.6748	10.6206	-0.0374	0.0542	0.0916
18	1-26	11.7377	11.7304	11.6883	-0.0073	0.0421	0.0494
19	1-27	10.8109	10.8108	10.7498	-0.0001	0.0610	0.0611
20	1-28	11.5390	11.5134	11.4636	-0.0256	0.0498	0.0754
21	1-29	11.3768	11.3231	11.2317	-0.0537	0.0914	0.1451
22	1-30	11.1136	11.1114	11.0593	-0.0022	0.0521	0.0543
23	1-31	11.6043	11.6002	11.5511	-0.0041	0.0491	0.0532
24	1-32	10.5855	10.5726	10.5125	-0.0129	0.0601	0.0730
25	1-33	11.1463	11.1916	10.9442	0.0453	0.2474	0.2021
26	1-34	11.1406	11.1226	11.0121	-0.0180	0.1105	0.1285
27	1-35	11.4867	11.4971	11.3312	0.0104	0.1659	0.1555
28	1-36	11.1993	11.2088	11.0477	0.0095	0.1611	0.1516
29	1-37	11.1896	11.1874	11.1329	-0.0022	0.0545	0.0567
30	1-38	11.6455	11.7424	11.2869	0.0969	0.4555	0.3586
31	1-39	12.2229	12.1934	12.1186	-0.0295	0.0748	0.1043
32	1-40	11.3253	11.3105	11.2522	-0.0148	0.0583	0.0731
33	1-43	12.2757	12.2417	12.1743	-0.0340	0.0674	0.1014
34	1-44	12.2568	12.2400	12.1934	-0.0168	0.0466	0.0634
35	1-45	12.2023	12.2025	12.1398	0.0002	0.0627	0.0625
36	1-46	11.2106	11.2230	11.1014	0.0124	0.1216	0.1092
37	1-47	12.3759	12.3532	12.2735	-0.0227	0.0797	0.1024
38	1-48	11.4351	11.4488	11.2923	0.0137	0.1565	0.1428
39	1-49	12.4856	12.4788	12.4322	-0.0068	0.0466	0.0534
40	1-50	11.6270	11.6956	11.4110	0.0686	0.2846	0.2160
41	1-51	12.2553	12.3608	11.9289	0.1055	0.4319	0.3264
42	1-52	11.7634	11.7552	11.6944	-0.0082	0.0608	0.0690
43	1-54	11.3085	11.2653	11.1831	-0.0432	0.0822	0.1254
44	1-55	11.7428	11.7277	11.6307	-0.0151	0.0970	0.1121
45	1-56	12.3946	12.3774	12.3312	-0.0172	0.0462	0.0634
46	1-57	11.4148	11.4228	11.3281	0.0080	0.0947	0.0867
47	1-58	11.3468	11.3548	11.2565	0.0080	0.0983	0.0903
48	1-59	10.6307	10.6314	10.5698	0.0007	0.0616	0.0609
49	1-6	11.3951	11.3724	11.3212	-0.0227	0.0512	0.0739
50	1-60	11.5002	11.5147	11.4208	0.0145	0.0939	0.0794
51	1-62	11.3114	11.2891	11.2103	-0.0223	0.0788	0.1011
52	1-64	12.3272	12.3655	12.1459	0.0383	0.2196	0.1813
53	1-65	11.8317	11.8378	11.7656	0.0061	0.0722	0.0661
54	1-66	11.1520	11.1197	11.0508	-0.0323	0.0689	0.1012
55	1-67	11.6526	11.7532	11.3404	0.1006	0.4128	0.3122
56	1-68	11.2635	11.2316	11.1711	-0.0319	0.0605	0.0924
57	1-69	11.6117	11.6261	11.4760	0.0144	0.1501	0.1357
58	1-70	11.6364	11.8218	11.1831	0.1854	0.6387	0.4533
59	1-8	10.3093	10.2763	10.2073	-0.0330	0.0690	0.1020
60	1-9	11.7064	11.6901	11.5668	-0.0163	0.1233	0.1396

## Cumulative weight loss data for copper coupons, first experiment.

Listing of CUMUL.CUI at 14:50:54 on NOV 13, 1985 for CCid=L0M1 Page 1

1	1-101	11.0636	11.0667	11.0326	0.0031	0.0341	0.0310
2	1-102	11.3872	11.3838	11.3704	-0.0034	0.0134	0.0168
3	1-103	11.2423	11.2394	11.2307	-0.0029	0.0087	0.0116
4	1-105	11.0647	11.0616	11.0568	-0.0031	0.0048	0.0079
5	1-106	11.0597	11.0608	11.0444	0.0011	0.0164	0.0153
6	1-107	11.1257	11.1268	11.1142	0.0011	0.0126	0.0115
7	1-108	10.9527	10.9534	10.9484	0.0007	0.0050	0.0043
8	1-34	11.0667	11.0472	11.0564	-0.0195	-0.0092	0.0103
9	1-35	10.8826	10.8806	10.8733	-0.0020	0.0073	0.0093
10	1-36	11.4298	11.4314	11.4159	0.0016	0.0155	0.0139
11	1-37	11.0571	11.0550	11.0499	-0.0021	0.0051	0.0072
12	1-38	11.3395	11.3400	11.3329	0.0005	0.0071	0.0066
13	1-39	10.9262	10.9270	10.9202	0.0008	0.0068	0.0060
14	1-40	11.0124	11.0146	10.9802	0.0022	0.0344	0.0322
15	1-41	11.3057	11.3052	11.3007	-0.0005	0.0045	0.0050
16	1-45	11.2359	11.2383	11.2145	0.0024	0.0238	0.0214
17	1-46	11.2684	11.2701	11.2619	0.0017	0.0082	0.0065
18	1-47	11.0992	11.0951	11.0880	-0.0041	0.0071	0.0112
19	1-48	11.2463	11.2480	11.2138	0.0017	0.0342	0.0325
20	1-49	11.3548	11.3576	11.3313	0.0028	0.0263	0.0235
21	1-51	11.0644	11.0634	11.0554	-0.0010	0.0080	0.0090
22	1-52	10.9786	10.9767	10.9692	-0.0019	0.0075	0.0094
23	1-53	11.0294	11.0298	11.0204	0.0004	0.0094	0.0090
24	1-54	11.0923	11.0894	11.0807	-0.0029	0.0087	0.0116
25	1-55	11.0775	11.0784	11.0543	0.0009	0.0241	0.0232
26	1-56	11.3397	11.3419	11.3373	0.0022	0.0046	0.0024
27	1-60	11.3496	11.3501	11.3437	0.0005	0.0064	0.0059
28	1-61	10.9884	10.9912	10.9665	0.0028	0.0247	0.0219
29	1-62	11.0171	11.0188	10.9955	0.0017	0.0233	0.0216
30	1-63	11.2474	11.2481	11.2406	0.0007	0.0075	0.0068
31	1-64	11.2623	11.2647	11.2450	0.0024	0.0197	0.0173
32	1-65	11.1460	11.1484	11.1313	0.0024	0.0171	0.0147
33	1-66	11.0848	11.0786	11.0725	-0.0062	0.0061	0.0123
34	1-67	11.0611	11.0613	11.0555	0.0002	0.0058	0.0056
35	1-68	11.0927	11.0957	11.0619	0.0030	0.0338	0.0308
36	1-69	11.2535	11.2549	11.2430	0.0014	0.0119	0.0105
37	1-70	11.3081	11.3098	11.2896	0.0017	0.0202	0.0185
38	1-71	10.9095	10.9090	10.8956	-0.0005	0.0134	0.0139
39	1-73	11.1895	11.1900	11.1792	0.0005	0.0108	0.0103
40	1-75	11.0923	11.0926	11.0879	0.0003	0.0047	0.0044
41	1-76	11.0914	11.0881	11.0726	-0.0033	0.0155	0.0188
42	1-77	11.0302	11.0319	11.0173	0.0017	0.0146	0.0129
43	1-78	11.3706	11.3723	11.3539	0.0017	0.0184	0.0167
44	1-79	11.1933	11.1961	11.1667	0.0028	0.0294	0.0266
45	1-80	11.0633	11.0584	11.0441	-0.0049	0.0143	0.0192
46	1-81	11.0343	11.1060	11.0875	0.0717	0.0185	-0.0532
47	1-82	11.0085	11.0118	10.9813	0.0033	0.0305	0.0272
48	1-84	11.2856	11.2883	11.2585	0.0027	0.0298	0.0271
49	1-85	11.2563	11.2548	11.2476	-0.0015	0.0072	0.0087
50	1-87	11.2492	11.2515	11.2377	0.0023	0.0138	0.0115
51	1-88	11.0679	11.0691	11.0551	0.0012	0.0140	0.0128
52	1-89	11.2258	11.2270	11.2144	0.0012	0.0126	0.0114
53	1-91	11.2647	11.2638	11.2600	-0.0009	0.0038	0.0047
54	1-92	11.2801	11.2814	11.2661	0.0013	0.0153	0.0140
55	1-93	11.0055	11.0047	10.9970	-0.0008	0.0077	0.0085
56	1-95	11.2149	11.2136	11.2041	-0.0013	0.0095	0.0108
57	1-96	10.9334	10.9366	10.9122	0.0032	0.0244	0.0212
58	1-97	11.2462	11.2475	11.2349	0.0013	0.0126	0.0113
59	1-98	11.0417	11.0429	11.0127	0.0012	0.0302	0.0290
60	1-99	11.1653	11.1668	11.1561	0.0010	0.0107	0.0097

## Cumulative weight loss data for cast iron coupons, second experiment.

Listing of CUMUL.FE2 at 14:50:55 on NOV 13, 1985 for CCid=LOMI Page 1

1	010	11.3410	11.3363	11.2928	-0.0047	0.0435	0.0482
2	51	11.8866	11.8810	11.8006	-0.0056	0.0804	0.0860
3	50	12.2035	12.1972	12.1517	-0.0063	0.0455	0.0518
4	49	12.2108	12.2020	12.2732	-0.0088	-0.0712	-0.0624
5	48	12.3225	12.3144	12.0942	-0.0081	0.2202	0.2283
6	47	12.3005	12.2989	12.2067	-0.0020	0.0922	0.0942
7	46	12.4385	12.4406	12.3790	0.0021	0.0626	0.0605
8	45	12.1527	12.1468	12.1040	-0.0059	0.0428	0.0487
9	44	12.3000	12.2990	12.2467	-0.0010	0.0523	0.0533
10	43	12.3638	12.3645	12.3138	0.0007	0.0507	0.0500
11	42	12.3008	12.2920	12.2508	-0.0088	0.0412	0.0500
12	41	12.3123	12.3003	12.2215	-0.0120	0.0788	0.0908
13	40	12.4211	12.4240	12.3672	0.0029	0.0568	0.0539
14	39	11.0753	11.0723	11.0326	-0.0030	0.0397	0.0427
15	38	12.5429	12.5402	12.4894	-0.0027	0.0508	0.0535
16	37	12.2316	12.2175	12.1586	-0.0141	0.0589	0.0730
17	36	11.2978	11.2822	11.2111	-0.0156	0.0711	0.0867
18	35	12.4731	12.4572	12.4068	-0.0159	0.0504	0.0663
19	34	12.5195	12.5134	12.4684	-0.0061	0.0450	0.0511
20	33	12.3688	12.3618	12.2571	-0.0070	0.1047	0.1117
21	32	12.1200	12.1164	12.0763	-0.0036	0.0401	0.0437
22	31	11.8079	11.8202	11.7343	0.0123	0.0859	0.0736
23	30	12.1308	12.1312	12.0706	0.0004	0.0606	0.0602
24	29	12.0022	12.0014	11.9539	-0.0008	0.0475	0.0483
25	28	12.1879	12.1704	12.1217	-0.0175	0.0487	0.0662
26	27	12.6497	12.6454	12.5967	-0.0043	0.0487	0.0530
27	26	12.3190	12.2972	12.2468	-0.0218	0.0504	0.0722
28	25	12.3484	12.3332	12.1980	-0.0152	0.1352	0.1504
29	24	12.4859	12.5109	12.2579	0.0250	0.2530	0.2280
30	23	12.2479	12.2328	12.1369	-0.0151	0.0959	0.1110
31	22	12.4018	12.4016	12.2898	-0.0002	0.1118	0.1120
32	21	12.2005	0.0	0.0	0.0	0.0	0.0
33	20	12.5788	12.5760	12.4957	-0.0028	0.0803	0.0831
34	19	12.3601	12.3359	12.2466	-0.0242	0.0893	0.1135
35	18	12.3950	12.4102	12.2933	0.0152	0.1169	0.1017
36	17	12.6206	12.6341	12.4231	0.0135	0.2110	0.1975
37	16	12.4607	12.4564	12.4061	-0.0043	0.0503	0.0546
38	15	12.5165	12.5145	12.4590	-0.0020	0.0555	0.0575
39	14	12.5799	12.5708	12.5176	-0.0091	0.0532	0.0623
40	13	12.3130	12.3148	12.2527	0.0018	0.0621	0.0603
41	12	12.3145	12.2988	12.1868	-0.0157	0.1120	0.1277
42	11	12.3811	12.3672	12.2278	-0.0139	0.1394	0.1533
43	10	10.8455	10.8457	10.7646	0.0002	0.0811	0.0809
44	09	12.0936	12.0918	12.0121	-0.0018	0.0797	0.0815
45	08	12.5309	12.5268	12.4309	-0.0041	0.0959	0.1000
46	07	12.0172	12.0350	11.9169	0.0178	0.1181	0.1003
47	06	12.5054	12.4993	12.3701	-0.0061	0.1292	0.1353
48	05	12.2840	12.2861	12.2187	0.0021	0.0674	0.0653
49	04	11.7655	11.7673	11.6854	0.0018	0.0819	0.0801
50	03	10.9970	0.0	0.0	0.0	0.0	0.0
51	02	12.5413	12.5422	12.4564	0.0009	0.0858	0.0849
52	01	12.0858	12.0892	12.0227	0.0034	0.0665	0.0631
53	0	12.3599	12.3715	12.1543	0.0116	0.2172	0.2056
54	0A	12.0888	12.0749	11.7003	-0.0139	0.3746	0.3885
55	0AB	12.1134	12.0392	11.9078	-0.0742	0.1314	0.2056
56	0ABCD	11.8080	11.8634	11.5719	0.0554	0.2915	0.2361
57	0ABCDE	11.7739	11.7710	11.6102	-0.0029	0.1608	0.1637
58	0ABCDEF	11.3830	11.2776	11.1215	-0.1054	0.1561	0.2615
59	0ABCDEF	11.0041	10.9948	10.8912	-0.0093	0.1036	0.1129
60	0ABD	11.6995	11.6700	11.3728	-0.0295	0.2972	0.3267
61	0ABDE	11.4728	11.4316	11.3116	-0.0412	0.1200	0.1612
62	0ABDEF	11.6111	11.6429	11.3877	0.0318	0.2552	0.2234
63	0ABDF	11.9510	11.9268	11.7384	-0.0242	0.1884	0.2126

## Cumulative weight loss data for cast iron coupons, second experiment (cont'd).

Listing of CUMUL.FE2 at 14:50:55 on NOV 13, 1985 for CCid=L0MI Page 2

64	OABE	11.8932	11.8348	11.6415	-0.0584	0.1933	0.2517
65	OABEF	11.2628	11.2644	11.1633	0.0016	0.1011	0.0995
66	OABF	11.9820	11.9109	11.7807	-0.0711	0.1302	0.2013
67	OAC	12.1268	12.0479	11.9139	-0.0799	0.1340	0.2129
68	OACD	12.1794	12.1626	11.9710	-0.0168	0.1916	0.2084
69	OACDE	11.5554	11.5016	11.4154	-0.0538	0.0862	0.1400
70	OACDEF	11.3756	11.3517	11.1872	-0.0239	0.1645	0.1884
71	OACDF	11.9752	11.9580	11.8243	-0.0172	0.1337	0.1509
72	OACE	11.2231	11.2167	11.0624	-0.0064	0.1543	0.1607
73	OACEF	11.4536	11.4836	11.2200	0.0300	0.2636	0.2336
74	OACF	11.9800	11.9788	11.8326	-0.0012	0.1462	0.1474
75	OAD	12.2391	12.2297	12.0306	-0.0094	0.1991	0.2085
76	OADE	11.8691	11.8725	11.6650	0.0034	0.2075	0.2041
77	OADEF	11.8541	11.8665	11.6222	0.0124	0.2443	0.2319
78	OADF	11.9435	11.9230	11.7783	-0.0205	0.1447	0.1652
79	OAE	12.3593	12.3117	12.0935	-0.0476	0.2182	0.2658
80	OAEF	11.8458	11.7780	11.5921	-0.0678	0.1859	0.2537
81	OAF	11.8454	11.8236	11.7336	-0.0218	0.0900	0.1118
82	OC	12.0988	12.0780	11.9083	-0.0208	0.1697	0.1905
83	OCD	12.0112	11.9336	11.8007	-0.0776	0.1329	0.2105
84	OCDE	10.9220	10.9181	10.5052	-0.0039	0.4129	0.4168
85	OCDEF	10.9653	10.9845	10.7318	0.0192	0.2527	0.2335
86	OCDF	12.2906	12.2996	12.0997	0.0090	0.1999	0.1909
87	OCE	11.8083	11.7979	11.6116	-0.0104	0.1863	0.1967
88	OCEF	11.8286	11.7390	11.5736	-0.0896	0.1654	0.2550
89	OCF	12.0000	11.9814	11.8775	-0.0186	0.1039	0.1225
90	OE	12.1674	12.1894	12.0018	0.0220	0.1876	0.1656
91	OEF	11.2763	11.2586	11.1168	-0.0177	0.1418	0.1595
92	OF	11.2352	11.2272	10.9523	-0.0080	0.2749	0.2829
93	I	11.3555	11.3539	11.1000	-0.0016	0.2539	0.2555
94	IA	11.5151	11.5169	11.3719	0.0018	0.1450	0.1432
95	IAB	11.8507	11.7628	11.6026	-0.0879	0.1602	0.2481
96	IABCD	11.8236	11.8155	11.5654	-0.0081	0.2501	0.2582
97	IABCDE	11.3878	11.3886	11.2842	0.0008	0.1044	0.1036
98	IABCDEF	11.5603	11.5323	11.1085	-0.0280	0.4238	0.4518
99	IABCDF	11.4344	11.3736	11.2010	-0.0608	0.1726	0.2334
100	IABD	11.5511	11.5054	11.3476	-0.0457	0.1578	0.2035
101	IABDE	11.5060	11.4495	11.3275	-0.0565	0.1220	0.1785
102	IABDEF	11.2024	11.1909	11.0769	-0.0115	0.1140	0.1255
103	IABDF	11.8425	11.8694	11.7117	0.0269	0.1577	0.1308
104	IABE	11.7244	11.6066	11.5730	-0.1178	0.0336	0.1514
105	IABEF	11.2943	11.3160	11.0696	0.0217	0.2464	0.2247
106	IABF	11.7905	11.7551	11.5975	-0.0354	0.1576	0.1930
107	IAC	11.7495	11.7213	11.3994	-0.0282	0.3219	0.3501
108	IACD	11.9401	11.9646	11.7207	0.0245	0.2439	0.2194
109	IACDE	11.7679	11.7234	11.5793	-0.0445	0.1441	0.1886
110	IACDEF	11.2479	11.2478	10.9761	-0.0001	0.2717	0.2718
111	IACDF	11.4775	11.4755	11.2896	-0.0020	0.1859	0.1879
112	IACE	11.1157	11.0942	11.0119	-0.0215	0.0823	0.1038
113	IACEF	11.3725	11.4333	10.8877	0.0608	0.5456	0.4848
114	IACF	11.7776	11.8190	11.6412	0.0414	0.1778	0.1364
115	IAD	12.2049	12.2062	12.0304	0.0013	0.1758	0.1745
116	IADE	11.7978	11.7767	11.6463	-0.0211	0.1304	0.1515
117	IADef	10.9385	10.9584	10.5242	0.0199	0.4342	0.4143
118	IADF	11.8791	11.8471	11.7336	-0.0320	0.1135	0.1455
119	IAE	11.3564	11.3133	11.2243	-0.0431	0.0890	0.1321
120	IAEF	10.8933	10.9315	10.6534	0.0382	0.2781	0.2399
121	IAF	11.7190	11.7090	11.5370	-0.0100	0.1720	0.1820
122	IC	11.3527	11.2504	11.1794	-0.0023	0.1710	0.1733
123	ICD	11.7832	11.7451	11.4306	-0.0381	0.3145	0.3526
124	ICDE	11.7173	11.6575	11.5422	-0.0598	0.1153	0.1751
125	ICDEF	10.3096	10.2772	10.0953	-0.0324	0.1819	0.2143
126	ICDF	11.5854	11.5540	11.4270	-0.0314	0.1270	0.1584
127	ICE	12.0333	11.9907	11.8980	-0.0426	0.0927	0.1353
128	ICEF	12.0393	12.0322	11.7201	-0.0071	0.3121	0.3192
129	ICF	11.8384	11.8332	11.7428	-0.0052	0.0904	0.0956
130	IE	11.8672	11.9578	11.6893	-0.0094	0.1625	0.1779
131	IEF	11.8479	11.8618	11.6100	0.0139	0.2518	0.2379
132	IF	12.0823	12.0800	11.6563	-0.0023	0.4237	0.4260

## Cumulative weight loss data for copper coupons, second experiment.

Listing of CUMUL.CU2 at 14:50:54 on NOV 13, 1985 for CCid=L0MI Page 1

1	293	10.8707	10.8709	10.8631	0.0002	0.0078	0.0076
2	292	11.0798	11.0796	11.0610	-0.0002	0.0136	0.0188
3	291	11.1644	11.1609	11.1464	-0.0035	0.0145	0.0180
4	290	10.6083	10.6102	10.5886	0.0019	0.0216	0.0197
5	289	10.9701	10.9727	10.9421	0.0026	0.0306	0.0280
6	288	10.7796	10.7769	10.7628	-0.0027	0.0141	0.0168
7	287	11.1471	11.1476	11.1209	0.0005	0.0267	0.0262
8	286	11.1162	11.1161	11.1127	-0.0001	0.0034	0.0035
9	285	10.8355	10.8356	10.8206	0.0001	0.0150	0.0149
10	284	11.0274	0.0	0.0	0.0	0.0	0.0
11	283	11.0460	11.0468	11.0320	0.0008	0.0148	0.0140
12	282	11.3284	11.3332	11.2804	0.0048	0.0528	0.0480
13	281	11.0477	11.0477	11.0426	0.0	0.0051	0.0051
14	280	10.8388	10.8385	10.8350	-0.0003	0.0035	0.0038
15	279	11.1775	11.1770	11.1724	-0.0005	0.0046	0.0051
16	278	11.0767	11.0769	11.0650	0.0002	0.0119	0.0117
17	277	11.3095	11.3098	11.2841	0.0003	0.0257	0.0254
18	276	11.0420	11.0422	11.0232	0.0002	0.0190	0.0188
19	275	11.0983	11.0996	11.0861	0.0013	0.0135	0.0122
20	274	11.2288	11.2290	11.2200	0.0002	0.0090	0.0088
21	273	10.9282	10.9288	10.9127	0.0006	0.0161	0.0155
22	272	10.8880	0.0	0.0	0.0	0.0	0.0
23	271	10.9344	0.0	0.0	0.0	0.0	0.0
24	270	11.0889	11.0912	11.0744	0.0023	0.0168	0.0145
25	269	10.5676	10.5669	10.5496	-0.0007	0.0173	0.0180
26	268	11.2129	0.0	0.0	0.0	0.0	0.0
27	267	10.8254	10.8290	10.7709	0.0036	0.0581	0.0545
28	266	11.1488	11.1473	11.1314	-0.0015	0.0159	0.0174
29	265	10.7418	10.7420	10.7310	0.0002	0.0110	0.0108
30	264	11.0841	11.0829	11.0658	-0.0012	0.0171	0.0183
31	263	10.9875	0.0	0.0	0.0	0.0	0.0
32	262	10.6360	0.0	0.0	0.0	0.0	0.0
33	261	11.1154	11.1139	11.0963	-0.0015	0.0176	0.0191
34	260	10.8820	10.8727	10.8311	-0.0093	0.0416	0.0509
35	259	10.6156	10.6189	10.5646	0.0033	0.0543	0.0510
36	258	11.1687	11.1693	11.1430	0.0006	0.0263	0.0257
37	257	10.9976	10.9812	10.9502	-0.0164	0.0310	0.0474
38	256	11.5587	11.5402	11.5071	-0.0185	0.0331	0.0516
39	255	10.5815	10.5662	10.5276	-0.0153	0.0386	0.0539
40	254	10.9441	10.9517	10.8901	0.0076	0.0616	0.0540
41	253	10.8627	10.8649	10.8122	0.0022	0.0527	0.0505
42	252	10.9561	10.9586	10.9434	0.0025	0.0152	0.0127
43	251	11.0911	11.0752	11.0347	-0.0159	0.0405	0.0564
44	250	11.1347	11.1348	11.1250	0.0001	0.0098	0.0097
45	249	11.0610	11.0616	11.0468	0.0006	0.0148	0.0142
46	248	11.0089	11.0127	10.9941	0.0038	0.0186	0.0148
47	247	11.0453	11.0479	11.0311	0.0026	0.0168	0.0142
48	246	11.0877	11.0896	11.0670	0.0019	0.0226	0.0207
49	245	10.9875	10.9884	10.9695	0.0009	0.0189	0.0180
50	244	10.7235	0.0	0.0	0.0	0.0	0.0
51	243	10.7923	10.7953	10.7685	0.0030	0.0268	0.0238
52	242	11.0483	11.0494	11.0262	0.0011	0.0232	0.0221
53	241	10.8804	10.8815	10.8629	0.0011	0.0186	0.0175
54	240	11.1011	0.0	0.0	0.0	0.0	0.0
55	239	10.8855	10.8928	10.8574	0.0073	0.0354	0.0281
56	238	11.0660	11.0677	11.0420	0.0017	0.0257	0.0240
57	237	10.9487	10.9598	10.8980	0.0111	0.0618	0.0507
58	236	10.9749	10.9878	10.9333	0.0089	0.0545	0.0456
59	235	10.9843	10.9856	10.9612	0.0013	0.0244	0.0231
60	234	11.0203	11.0270	11.0030	0.0067	0.0240	0.0173
61	233	10.8298	10.8410	10.7996	0.0112	0.0414	0.0302
62	232	10.3697	10.3730	10.3540	0.0033	0.0190	0.0157
63	231	10.9244	10.9160	10.8657	-0.0084	0.0503	0.0587

## Cumulative weight loss data for copper coupons, second experiment (cont'd).

Listing of CUMUL.CU2 at 14:50:54 on NOV 13, 1985 for CCid=LOMI Page 2

64	230	11.0155	0.0	0.0	0.0	0.0	0.0
65	229	11.2324	11.2336	11.2103	0.0012	0.0233	0.0221
66	228	11.1082	11.1115	11.0840	0.0033	0.0275	0.0242
67	227	11.0452	11.0562	10.9921	0.0110	0.0631	0.0521
68	226	10.9852	10.9861	10.9660	0.0009	0.0201	0.0192
69	225	10.9254	10.9269	10.8981	0.0015	0.0288	0.0273
70	224	11.0994	11.1085	11.0523	0.0091	0.0562	0.0471
71	149	10.9246	10.9144	10.8728	-0.0102	0.0416	0.0518
72	148	10.9622	10.9663	10.9115	0.0041	0.0548	0.0507
73	147	11.5943	11.5966	11.5736	0.0023	0.0230	0.0207
74	146	10.9953	11.0066	10.9554	0.0113	0.0512	0.0399
75	145	10.6011	10.6017	10.5798	0.0006	0.0219	0.0213
76	144	11.1414	11.1427	11.1275	0.0013	0.0152	0.0139
77	143	11.1353	11.1351	11.1193	-0.0002	0.0158	0.0160
78	142	10.7869	10.7845	10.7341	-0.0024	0.0504	0.0528
79	141	10.9769	10.9770	10.9593	0.0001	0.0177	0.0176
80	140	11.0224	11.0071	10.9667	-0.0153	0.0364	0.0537
81	139	11.0175	11.0086	10.9494	-0.0089	0.0592	0.0681
82	138	11.1537	11.1597	11.1020	0.0060	0.0577	0.0517
83	137	10.8072	10.7975	10.7570	-0.0097	0.0405	0.0502
84	136	11.6529	11.6461	11.6033	-0.0068	0.0428	0.0496
85	135	11.0759	11.0758	11.0543	-0.0001	0.0215	0.0216
86	134	11.8720	11.8729	11.8503	0.0009	0.0226	0.0217
87	133	11.3731	11.3735	11.3551	0.0004	0.0184	0.0180
88	132	11.1675	0.0	0.0	0.0	0.0	0.0
89	131	10.8943	0.0	0.0	0.0	0.0	0.0
90	130	11.2568	11.2573	11.2438	0.0005	0.0135	0.0130
91	129	11.2363	11.2219	11.1817	-0.0144	0.0402	0.0546
92	128	11.2242	11.2301	11.1960	0.0059	0.0341	0.0282
93	127	11.3301	11.3315	11.3030	0.0014	0.0285	0.0271
94	126	11.2932	11.2989	11.2466	0.0057	0.0523	0.0466
95	125	11.1587	11.1506	11.1173	-0.0081	0.0333	0.0414
96	124	10.8643	10.8711	10.8303	0.0068	0.0403	0.0335
97	123	11.3407	11.3409	11.3321	0.0002	0.0088	0.0086
98	122	11.0635	11.0572	11.0316	-0.0063	0.0256	0.0319
99	121	11.3018	11.2969	11.2688	-0.0049	0.0281	0.0330
100	120	10.9872	10.9879	10.9830	0.0007	0.0049	0.0042
101	119	11.2718	11.2729	11.2666	0.0011	0.0063	0.0052
102	118	11.2237	11.2238	11.2161	0.0001	0.0077	0.0076
103	117	10.9333	10.9319	10.9284	-0.0014	0.0035	0.0049
104	116	11.3462	11.3466	11.3406	0.0004	0.0060	0.0056
105	115	10.9804	10.9802	10.9780	-0.0002	0.0022	0.0024
106	114	11.1308	11.1300	11.1140	-0.0008	0.0160	0.0168
107	113	11.2848	11.2841	11.2742	-0.0007	0.0099	0.0106
108	112	11.0503	11.0496	11.0354	-0.0007	0.0142	0.0149
109	111	11.3095	11.3081	11.3029	-0.0014	0.0052	0.0066
110	110	10.9132	10.9135	10.9071	0.0003	0.0064	0.0061
111	109	11.3967	11.3967	11.3927	0.0	0.0040	0.0040
112	108	11.5379	11.5436	11.4853	0.0057	0.0583	0.0526
113	107	11.0217	11.0211	11.0195	-0.0006	0.0016	0.0022
114	106	11.0520	11.0505	11.0477	-0.0015	0.0028	0.0043
115	105	11.3123	11.3123	11.3121	0.0	0.0002	0.0002
116	104	11.1913	11.1932	11.1769	0.0019	0.0163	0.0144
117	103	11.3029	11.3045	11.2883	0.0016	0.0162	0.0146
118	102	11.2747	11.2734	11.2617	-0.0013	0.0117	0.0130
119	101	10.9058	10.9059	10.9004	0.0001	0.0055	0.0054
120	100	11.0061	11.0105	10.9663	0.0044	0.0442	0.0398
121	099	10.9822	10.9823	10.9764	0.0001	0.0059	0.0058
122	098	11.0365	11.0366	11.0292	0.0001	0.0074	0.0073
123	097	10.6707	10.6710	10.6662	0.0003	0.0048	0.0045
124	096	10.9163	10.9142	10.9065	-0.0021	0.0077	0.0098
125	095	11.3471	11.3487	11.3329	0.0016	0.0158	0.0142
126	094	11.3624	11.3624	11.3580	0.0	0.0044	0.0044
127	093	11.2878	11.2831	11.2707	-0.0047	0.0124	0.0171
128	092	10.7580	0.0	0.0	0.0	0.0	0.0
129	091	10.8511	10.8515	10.8282	0.0004	0.0233	0.0229
130	090	11.2955	0.0	0.0	0.0	0.0	0.0
131	089	11.3523	11.3519	11.3467	-0.0004	0.0052	0.0056
132	088	11.1880	11.1888	11.1748	0.0008	0.0140	0.0132
133	087	10.3930	10.3924	10.3885	-0.0006	0.0039	0.0045
134	086	11.1209	11.1169	11.1017	-0.0040	0.0152	0.0192
135	085	11.0095	11.0091	10.9992	-0.0004	0.0099	0.0103
136	084	11.1491	11.1479	11.1430	-0.0012	0.0049	0.0061
137	083	11.1649	11.1637	11.1534	-0.0012	0.0103	0.0115
138	082	10.8300	0.0	0.0	0.0	0.0	0.0
139	081	10.8873	10.8874	10.8790	0.0001	0.0084	0.0083
140	080	10.9431	10.9475	10.9114	0.0044	0.0361	0.0317
141	079	11.0506	11.0507	11.0427	0.0001	0.0080	0.0079
142	078	11.1643	11.1648	11.1603	0.0005	0.0045	0.0040
143	077	10.9449	10.9486	10.9091	0.0037	0.0395	0.0358
144	076	10.8224	10.8231	10.8006	0.0007	0.0225	0.0218

## Program SUMCALC.CUI

Listing of SUMCALC.CUI at 14:45:32 on NOV 13, 1985 for CCid=LOMI Page 1

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1  C2345678901234567890.....
2  C THIS PROGRAM IS TO CALCULATE THE AVERAGE WEIGHT LOSSES OF
3  C THE PLATES BY EXPOSURE TIME. THE PROGRAM WILL READ THE
4  C REQUIRED TIMES IN A FILE TIME.ph.metal (DEVICE #50) AND
5  C SEARCH FOR THE CORRESPONDING WEIGHT LOSSES IN THE APPRO-
6  C PRIATE CUMUL.metal FILE (DEVICE #51).
7  C
8  C THE RESULTS WILL BE WRITTEN IN A SUM.ph.metal FILE (DEVICE #6)
9  C
10 REAL*8 SUM(30,13)/390*0.0/,NO,LOSS,INTER(13),TRISUM(30,13),
11 + CLEAN,AREA
12 N=0
13 C
14 C THROUGH AN ENTIRE TIME FILE
15 C
16 300 N=N+1
17 READ(50,10,END=400)SUM(N,2),SUM(N,1),SUM(N,4),SUM(N,6)
18 C
19 C LOOK FOR THE CORRESPONDING WEIGHT LOSSES
20 C
21 REWIND 51
22 100 READ(51,11,END=300)NO,CLEAN,LOSS
23 IF(NO.NE.SUM(N,2))GO TO 100
24 SUM(N,3)=LOSS
25 AREA=CLEAN/4742
26 SUM(N,9)=LOSS/AREA
27 C
28 C THE SECOND ONE
29 C
30 REWIND 51
31 200 READ(51,11,END=300)NO,CLEAN,LOSS
32 IF(NO.NE.SUM(N,4))GO TO 200
33 SUM(N,5)=LOSS
34 AREA=CLEAN/4742
35 SUM(N,10)=LOSS/AREA
36 C
37 C THE THIRD ONE
38 C
39 REWIND 51
40 201 READ(51,11,END=300)NO,CLEAN,LOSS
41 IF(NO.NE.SUM(N,6))GO TO 201
42 SUM(N,7)=LOSS
43 SUM(N,8)=(SUM(N,3)+SUM(N,5)+SUM(N,7))/3
44 AREA=CLEAN/4742
45 SUM(N,11)=LOSS/AREA
46 SUM(N,12)=(SUM(N,9)+SUM(N,10)+SUM(N,11))/3
47 SUM(N,13)=SUM(N,12)/(SUM(N,1)*7)
48 GO TO 300
49 C
50 C ORDER THE EXPOSURE TIMES
51 C
52 400 NUMBER=N-1
53 DO 1 J=1,NUMBER
54 DO 2 K=1,13
55 TRISUM(J,K)=SUM(J,K)
56 2 CONTINUE
57 DO 3 I=J,NUMBER
58 IF(TRISUM(J,1).LE.SUM(I,1))GO TO 3
59 DO 4 K=1,13
60 INTER(K)=TRISUM(J,K)
61 TRISUM(J,K)=SUM(I,K)
62 SUM(I,K)=INTER(K)
63 4 CONTINUE
64 3 CONTINUE
65 1 CONTINUE
66 C
67 C WRITE THE RESULTS, SORTED
68 C
69 WRITE(6,12)
70 DO 5 K=1,NUMBER
71 WRITE(6,13) TRISUM(K,1),TRISUM(K,2),TRISUM(K,3),TRISUM(K,8),
72 + TRISUM(K,9),TRISUM(K,12),TRISUM(K,13),TRISUM(K,4),
73 + TRISUM(K,5),TRISUM(K,10),TRISUM(K,6),TRISUM(K,7),
74 + TRISUM(K,11)
75 5 CONTINUE
76 C
77 10 FORMAT(A6,F4.1,/,A6,/,A6)
78 11 FORMAT(A7,F9.4,3X,F8.4)
79 12 FORMAT(1X,'TIME',2X,'NUMBERS',3X,'NET LOSS',2X,'AVERAGE',
80 + 2X,'PER AREA',2X,'AVERAGE',2X,'RATE',/)
81 13 FORMAT(1X,F4.1,2X,A7,1X,F9.4,F9.4,3(2X,F7.2),
82 + 2(/,7X,A7,1X,F9.4,11X,F7.2))
83 STOP
84 END

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Average specific weight losses and corrosion rates, cast iron, first experiment  
Gravity control cell

	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
1							
2							
3	1.0	m-114	0.0592	0.0581	24.62	24.50	3.50
4		1-37	0.0567		24.42		
5		m-115	0.0585		24.46		
6	1.5	1-65	0.0661	0.0632	26.92	26.28	2.50
7		1-27	0.0611		27.24		
8		1-45	0.0625		24.68		
9	2.0	1-17	0.0564	0.0543	23.66	22.12	1.58
10		1-49	0.0534		20.61		
11		1-31	0.0532		22.09		
12	3.0	m-117	0.0982	0.0983	44.32	41.66	1.98
13		1-39	0.1043		41.12		
14		1-68	0.0924		39.53		
15	4.0	1-36	0.1516	0.1500	65.23	63.55	2.27
16		1-48	0.1428		60.18		
17		1-35	0.1553		65.24		

Goal pH 7 cell

	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
1							
2							
3	1.0	1-30	0.0543	0.0493	23.55	21.01	3.00
4		1-2	0.0441		19.21		
5		1-26	0.0494		20.28		
6	1.5	m-113	0.0571	0.0572	25.20	25.14	2.39
7		m-116	0.0537		22.60		
8		1-59	0.0609		27.61		
9	2.0	1-24	0.0916	0.0809	41.21	34.83	2.49
10		1-28	0.0754		31.49		
11		1-1	0.0757		31.78		
12	3.0	1-66	0.1012	0.1017	43.73	41.14	1.96
13		1-43	0.1014		39.81		
14		1-47	0.1024		39.87		
15	4.0	1-9	0.1395	0.1310	57.47	54.43	1.94
16		1-34	0.1285		55.58		
17		1-21	0.1250		50.24		

Goal pH 8 cell

	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
1							
2							
3	1.0	1-11	0.0655	0.0641	28.76	26.11	3.73
4		1-56	0.0634		24.65		
5		1-44	0.0634		24.93		
6	1.5	1-52	0.0690	0.0700	29.27	29.45	2.80
7		1-6	0.0739		31.25		
8		1-23	0.0672		28.82		
9	2.0	1-32	0.0730	0.0784	33.23	33.90	2.42
10		1-10	0.0890		37.37		
11		1-40	0.0731		31.10		
12	3.0	1-55	0.1121	0.1051	46.00	45.58	2.17
13		1-8	0.1020		47.68		
14		1-62	0.1011		43.07		
15	4.0	1-54	0.1254	0.1352	53.44	58.29	2.08
16		1-29	0.1451		61.46		
17		1-18	0.1350		59.96		

Pressure control cell

	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
1							
2							
3	1.0	1-58	0.0903	0.0855	38.35	36.07	5.15
4		1-57	0.0867		36.60		
5		1-60	0.0794		33.27		
6	1.5	1-69	0.1357	0.1193	56.32	50.37	4.80
7		1-46	0.1092		46.94		
8		1-16	0.1131		47.86		
9	2.0	1-50	0.2160	0.1998	89.52	82.59	5.90
10		1-33	0.2021		87.38		
11		1-64	0.1813		70.87		
12	3.0	1-51	0.3264	0.3219	128.35	131.42	6.26
13		1-19	0.3272		136.79		
14		1-67	0.3122		129.11		
15	4.0	1-70	0.4533	0.3799	187.73	158.08	5.65
16		1-22	0.3279		138.12		
17		1-38	0.3586		148.39		

Average specific weight losses and corrosion rates, copper, first experiment  
Gravity control cell

	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
1							
2							
3	1.0	1-81	-0.0532	0.0195	-22.96	8.29	1.18
4		1-64	0.0173		7.28		
5		1-62	0.0216		9.30		
6	1.5	1-96	0.0212	0.0222	9.19	9.49	0.90
7		1-49	0.0235		9.81		
8		1-61	0.0219		9.45		
9	2.0	1-79	0.0266	0.0279	11.27	11.46	0.82
10		1-82	0.0272		11.72		
11		1-84	0.0271		11.39		
12	3.0	1-68	0.0308	0.0283	13.17	12.13	0.58
13		1-55	0.0232		9.93		
14		1-101	0.0310		13.29		
15	4.0	1-98	0.0290	0.0312	12.45	13.34	0.48
16		1-40	0.0322		13.87		
17		1-48	0.0325		13.70		

Goal pH 7 cell

	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
1							
2							
3	1.0	1-63	0.0068	0.0065	2.87	2.74	0.39
4		1-38	0.0066		2.76		
5		1-39	0.0060		2.60		
6	1.5	1-67	0.0056	0.0060	2.40	2.53	0.24
7		1-60	0.0059		2.47		
8		1-46	0.0065		2.74		
9	2.0	1-89	0.0114	0.0121	4.82	5.16	0.37
10		1-34	0.0103		4.41		
11		1-65	0.0147		6.25		
12	3.0	1-87	0.0115	0.0135	4.85	5.69	0.27
13		1-66	0.0123		5.26		
14		1-78	0.0167		6.96		
15	4.0	1-70	0.0185	0.0184	7.76	7.78	0.28
16		1-106	0.0153		6.56		
17		1-45	0.0214		9.03		

Goal pH 8 cell

	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
1							
2							
3	1.0	1-91	0.0047	0.0062	1.98	2.65	0.38
4		1-41	0.0050		2.10		
5		1-53	0.0090		3.87		
6	1.5	1-75	0.0044	0.0037	1.88	1.58	0.15
7		1-56	0.0024		1.00		
8		1-108	0.0043		1.86		
9	2.0	1-99	0.0097	0.0116	4.12	4.88	0.35
10		1-97	0.0113		4.76		
11		1-36	0.0139		5.77		
12	3.0	1-73	0.0103	0.0108	4.37	4.56	0.22
13		1-69	0.0105		4.42		
14		1-107	0.0115		4.90		
15	4.0	1-77	0.0129	0.0132	5.55	5.64	0.20
16		1-88	0.0128		5.48		
17		1-92	0.0140		5.89		

Pressure control cell

	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
1							
2							
3	1.0	1-37	0.0072	0.0079	3.09	3.38	0.48
4		1-93	0.0085		3.66		
5		1-105	0.0079		3.39		
6	1.5	1-51	0.0090	0.0105	3.86	4.52	0.43
7		1-85	0.0087		3.67		
8		1-71	0.0139		6.04		
9	2.0	1-52	0.0094	0.0098	4.06	4.23	0.30
10		1-35	0.0093		4.05		
11		1-95	0.0108		4.57		
12	3.0	1-47	0.0112	0.0115	4.79	4.88	0.23
13		1-54	0.0116		4.96		
14		1-103	0.0116		4.89		
15	4.0	1-102	0.0168	0.0183	7.00	7.75	0.28
16		1-80	0.0192		8.23		
17		1-76	0.0188		8.04		

Average specific weight losses and corrosion rates, cast iron, second experiment  
Gravity control cell

Listing of SUM.G.FE2 at 14:51:25 on NOV 13, 1985 for CCid=LOMI Page 1

	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
1							
2							
3	1.0	010	0.0482	0.0510	22.08	22.31	3.19
4		40	0.0539		22.54		
5	1.5	46	0.0605	0.0603	25.27	25.52	2.43
6		30	0.0602		25.78		
7	2.0	13	0.0603	0.0613	25.44	25.58	1.83
8		14	0.0623		25.73		
9	3.0	01	0.0631	0.0642	27.12	27.37	1.30
10		05	0.0653		27.62		
11	4.0	02	0.0849	0.0840	35.17	34.74	1.24
12		20	0.0831		34.32		
13	6.0	1CF	0.0956	0.0975	41.95	43.92	1.05
14		0ABEF	0.0995		45.89		
15	6.0	0AF	0.1118	0.1078	49.03	48.77	1.16
16		1ACE	0.1038		48.51		
17	8.0	0ACDF	0.1509	0.1647	65.46	73.03	1.30
18		1ABDE	0.1785		80.59		
19	8.0	1A	0.1432	0.1453	64.60	64.26	1.15
20		0ACF	0.1474		63.92		
21	10.0	0CE	0.1967	0.1856	86.54	80.41	1.15
22		1AD	0.1745		74.28		
23	10.0	0C	0.1905	0.1819	81.80	80.55	1.15
24		1C	0.1733		79.30		
25	12.0	0ACDEF	0.1884	0.1852	86.04	83.36	0.99
26		1AF	0.1820		80.68		
27	12.0	1ABF	0.1930	0.1904	85.04	85.04	1.01
28		1ACDF	0.1879		85.05		

Goal pH 7 cell

	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
1							
2							
3	1.0	38	0.0535	0.0481	22.16	21.09	3.01
4		39	0.0427		20.03		
5	1.5	29	0.0483	0.0506	20.91	21.34	2.03
6		27	0.0530		21.77		
7	2.0	15	0.0575	0.0560	23.87	23.31	1.67
8		16	0.0546		22.76		
9	3.0	16	0.0867	0.0887	39.87	39.09	1.86
10		41	0.0908		38.31		
11	4.0	23	0.1110	0.1115	47.08	47.00	1.68
12		22	0.1120		46.92		
13	6.0	1CDF	0.1584	0.1520	71.03	67.33	1.60
14		1ADF	0.1455		63.63		
15	6.0	1CE	0.1353	0.1337	58.41	59.42	1.41
16		1AE	0.1321		60.43		
17	8.0	1ACDE	0.1886	0.1960	83.26	87.39	1.56
18		1ABD	0.2035		91.52		
19	8.0	0ABF	0.2013	0.1961	87.28	83.98	1.50
20		0CDF	0.1909		80.69		
21	10.0	0CEF	0.2550	0.2339	111.99	101.60	1.45
22		0AC	0.2129		91.20		
23	10.0	0CD	0.2105	0.2080	91.04	89.61	1.28
24		0AB	0.2056		88.17		
25	12.0	1ABCDF	0.2334	0.2238	106.04	107.01	1.27
26		1CDEF	0.2143		107.99		
27	12.0	0AEF	0.2537	0.2576	111.26	115.30	1.37
28		0ABCDE	0.2615		119.34		

Average specific weight losses and corrosion rates, cast iron, second experiment  
(cont'd)

Goal pH 7 cell

Listing of SUM.7.FE2 at 14:51:27 on NOV 13, 1985 for CCid=LOMI Page 1

1	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
2							
3	1.0	48	0.2283	0.2283	96.25	22.05	3.15
4		50	0.0518		22.05		
5	1.5	26	0.0722	0.0692	30.45	29.03	2.76
6		35	0.0663		27.61		
7	2.0	28	0.0662	0.0696	28.22	29.61	2.12
8		37	0.0730		31.00		
9	3.0	09	0.0815	0.0808	35.01	35.19	1.68
10		04	0.0801		35.37		
11	4.0	08	0.1000	0.1067	41.46	44.58	1.59
12		19	0.1135		47.70		
13	6.0	0EF	0.1595	0.1425	73.48	65.84	1.57
14		1ABDEF	0.1255		58.20		
15	6.0	0ACDE	0.1400	0.1218	62.94	55.10	1.31
16		1ABCDE	0.1036		47.26		
17	8.0	1CDE	0.1751	0.1681	77.63	75.31	1.34
18		0ABDE	0.1612		72.99		
19	8.0	0ADF	0.1652	0.1583	71.86	69.28	1.24
20		1ADE	0.1515		66.71		
21	10.0	1ABCD	0.2582	0.2308	113.45	102.48	1.46
22		1ABD	0.2035		91.52		
23	10.0	0ADE	0.2041	0.2063	89.33	89.11	1.27
24		0ACD	0.2084		88.89		
25	12.0	0ABDEF	0.2234	0.2285	99.95	102.95	1.23
26		0ACEF	0.2336		105.95		
27	12.0	0ADEF	0.2319	0.2283	101.63	102.49	1.22
28		1ABEF	0.2247		103.35		

Goal pH 8 cell

Listing of SUM.8.FE2 at 14:51:28 on NOV 13, 1985 for CCid=LOMI Page 1

1	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
2							
3	1.0	32	0.0437	0.0468	18.73	19.92	2.85
4		42	0.0500		21.12		
5	1.5	45	0.0467	0.0499	20.82	21.01	2.00
6		34	0.0511		21.20		
7	2.0	44	0.0533	0.0516	22.51	21.76	1.55
8		43	0.0500		21.01		
9	3.0	31	0.0736	0.0772	32.38	35.57	1.69
10		10	0.0809		38.75		
11	4.0	18	0.1017	0.1010	42.62	42.99	1.54
12		07	0.1003		43.36		
13	6.0	1ABDF	0.1308	0.1336	57.38	58.77	1.40
14		1ACF	0.1364		60.16		
15	6.0	0CF	0.1225	0.1177	53.03	53.17	1.27
16		0ABCDF	0.1129		53.30		
17	8.0	0ABCDE	0.1637	0.1708	72.23	75.05	1.34
18		1E	0.1779		77.88		
19	8.0	0E	0.1656	0.1631	70.70	72.55	1.30
20		0ACE	0.1607		74.39		
21	10.0	0AD	0.2085	0.2139	88.50	91.98	1.31
22		1ACD	0.2194		95.46		
23	10.0	1	0.2555	0.2305	116.89	101.65	1.45
24		0	0.2056		86.42		
25	12.0	0CDEF	0.2335	0.2348	110.62	107.25	1.28
26		0ABCD	0.2361		103.87		
27	12.0	1AEF	0.2399	0.2389	114.41	109.36	1.30
28		1EF	0.2379		104.31		

Average specific weight losses and corrosion rates, cast iron, second experiment  
(cont'd)

Pressure cell

Listing of SUM.P.FE2 at 14:51:26 on NOV 13, 1985 for CCid=L0MI Page 1

1	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
2							
3	1.0	47	0.0942	0.0901	39.78	38.68	5.53
4		51	0.0860		37.59		
5	1.5	33	0.1117	0.0246	46.91	46.91	4.47
6		49	-0.0624		-26.55		
7	2.0	12	0.1277	0.1315	53.87	55.04	3.93
8		06	0.1353		56.21		
9	3.0	11	0.1533	0.1513	64.32	63.30	3.04
10		25	0.1504		63.27		
11	4.0	24	0.2280	0.2127	94.86	88.08	3.15
12		17	0.1975		81.30		
13	6.0	1ACDEF	0.2718	0.2955	125.53	131.64	3.13
14		1CEF	0.3192		137.74		
15	6.0	0ABDF	0.2126	0.2477	92.42	111.61	2.66
16		0F	0.2829		130.81		
17	8.0	0AE	0.2658	0.2587	111.72	110.83	1.98
18		0ABE	0.2517		109.94		
19	8.0	0CDE	0.4168	0.3324	198.25	153.50	2.74
20		1AB	0.2481		108.76		
21	10.0	0ABD	0.3267	0.3396	145.07	150.26	2.15
22		1CD	0.3526		155.45		
23	10.0	1AC	0.3501	0.3693	154.80	160.87	2.30
24		0A	0.3885		166.95		
25	12.0	1F	0.4260	0.4389	183.17	193.10	2.30
26		1ABCDE	0.4518		203.03		
27	12.0	1ADEF	0.4143	0.4495	196.76	209.11	2.49
28		1ACEF	0.4848		221.46		

Average specific weight losses and corrosion rates, copper, second experiment  
Gravity control cell

Listing of SUM.G.CU2 at 14:51:25 on NOV 13, 1985 for CCid=L0MI Page 1

1	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
2							
3	1.0	085	0.0103	0.0112	4.33	4.70	0.67
4		275	0.0122		5.08		
5	1.5	103	0.0146	0.0145	5.97	5.96	0.57
6		104	0.0144		5.95		
7	2.0	095	0.0142	0.0137	5.79	5.62	0.40
8		088	0.0132		5.45		
9	3.0	290	0.0197	0.0238	8.59	10.19	0.49
10		289	0.0280		11.79		
11	4.0	077	0.0358	0.0337	15.12	14.25	0.51
12		080	0.0317		13.39		
13	6.0	108	0.0526	0.0462	21.08	18.90	0.45
14		100	0.0398		16.72		
15	6.0	233	0.0302	0.0291	12.90	12.41	0.30
16		239	0.0281		11.93		
17	8.0	237	0.0507	0.0481	21.41	20.31	0.36
18		236	0.0456		19.20		
19	8.0	227	0.0521	0.0496	21.80	20.71	0.37
20		224	0.0471		19.62		
21	10.0	148	0.0507	0.0493	21.37	20.48	0.29
22		282	0.0480		19.59		
23	10.0	126	0.0466	0.0491	19.07	20.25	0.29
24		138	0.0517		21.42		
25	12.0	267	0.0545	0.0525	23.27	22.38	0.27
26		253	0.0505		21.48		
27	12.0	259	0.0510	0.0525	22.21	22.51	0.27
28		254	0.0540		22.80		

Average specific weight losses and corrosion rates, copper, second experiment  
(cont'd)

Goal pH 6 basin

Listing of SUM.6.CU2 at 14:51:26 on NOV 13, 1985 for CCid=LOMI Page 1

	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
1							
2							
3	1.0	280	0.0038	0.0036	1.62	1.54	0.22
4		286	0.0035		1.46		
5	1.5	101	0.0054	0.0055	2.29	2.29	0.22
6		116	0.0056		2.28		
7	2.0	078	0.0040	0.0056	1.66	2.36	0.17
8		098	0.0073		3.06		
9	3.0	274	0.0088	0.0082	3.62	3.43	0.16
10		293	0.0076		3.23		
11	4.0	079	0.0079	0.0070	3.30	2.94	0.11
12		110	0.0061		2.58		
13	6.0	114	0.0168	0.0158	6.97	6.60	0.16
14		112	0.0149		6.23		
15	6.0	234	0.0173	0.0205	7.25	8.72	0.21
16		243	0.0238		10.19		
17	8.0	225	0.0273	0.0232	11.55	9.81	0.18
18		226	0.0192		8.08		
19	8.0	238	0.0240	0.0207	10.03	8.73	0.16
20		241	0.0175		7.43		
21	10.0	127	0.0271	0.0303	11.05	12.65	0.18
22		124	0.0335		14.25		
23	10.0	287	0.0262	0.0330	10.87	13.82	0.20
24		146	0.0399		16.77		
25	12.0	264	0.0183	0.0178	7.63	7.42	0.09
26		266	0.0174		7.22		
27	12.0	269	0.0180	0.0185	7.88	7.91	0.09
28		261	0.0191		7.94		

Goal pH 7 cell

Listing of SUM.7.CU2 at 14:51:27 on NOV 13, 1985 for CCid=LOMI Page 1

	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
1							
2							
3	1.0	120	0.0042	0.0047	1.77	1.95	0.28
4		119	0.0052		2.13		
5	1.5	117	0.0049	0.0046	2.07	1.93	0.18
6		106	0.0043		1.80		
7	2.0	094	0.0044	0.0051	1.79	2.11	0.15
8		099	0.0058		2.44		
9	3.0	278	0.0117	0.0133	4.88	5.62	0.27
10		285	0.0149		6.36		
11	4.0	118	0.0076	0.0081	3.13	3.32	0.12
12		123	0.0086		3.50		
13	6.0	265	0.0108	0.0182	4.65	7.64	0.18
14		258	0.0257		10.64		
15	6.0	242	0.0221	0.0200	9.25	8.41	0.20
16		245	0.0180		7.57		
17	8.0	229	0.0221	0.0214	9.09	8.86	0.16
18		246	0.0207		8.63		
19	8.0	228	0.0242	0.0236	10.07	9.90	0.18
20		235	0.0231		9.72		
21	10.0	145	0.0213	0.0176	9.28	7.52	0.11
22		144	0.0139		5.76		
23	10.0	147	0.0207	0.0173	8.25	7.06	0.10
24		283	0.0140		5.86		
25	12.0	130	0.0130	0.0179	5.34	7.54	0.09
26		091	0.0229		9.75		
27	12.0	076	0.0218	0.0186	9.31	7.93	0.09
28		273	0.0155		6.56		

Average specific weight losses and corrosion rates, copper, second experiment  
(cont'd)

Goal pH 8 cell

Listing of SUM.8.CU2 at 14:51:28 on NOV 13, 1985 for CCid=LOMI Page 1

1	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
2							
3	1.0	109	0.0040	0.0032	1.62	1.32	0.19
4		115	0.0024		1.01		
5	1.5	105	0.0002	0.0042	0.08	1.80	0.17
6		081	0.0083		3.52		
7	2.0	097	0.0045	0.0045	1.95	1.97	0.14
8		087	0.0045		2.00		
9	3.0	281	0.0051	0.0051	2.13	2.12	0.10
10		279	0.0051		2.11		
11	4.0	111	0.0066	0.0044	2.70	1.81	0.06
12		107	0.0022		0.92		
13	6.0	252	0.0127	0.0112	5.36	4.69	0.11
14		250	0.0097		4.03		
15	6.0	248	0.0148	0.0152	6.22	6.61	0.16
16		232	0.0157		7.00		
17	8.0	128	0.0282	0.0249	11.61	10.03	0.18
18		134	0.0217		8.45		
19	8.0	247	0.0142	0.0142	5.94	5.94	0.11
20		249	0.0142		5.93		
21	10.0	135	0.0216	0.0198	9.01	8.16	0.12
22		133	0.0180		7.31		
23	10.0	143	0.0160	0.0168	6.64	7.03	0.10
24		141	0.0176		7.41		
25	12.0	270	0.0145	0.0199	6.05	8.22	0.10
26		277	0.0254		10.38		
27	12.0	292	0.0188	0.0188	7.85	7.86	0.09
28		276	0.0188		7.87		

Pressure control cell

Listing of SUM.P.CU2 at 14:51:25 on NOV 13, 1985 for CCid=LOMI Page 1

1	TIME	NUMBERS	NET LOSS	AVERAGE	PER AREA	AVERAGE	RATE
2							
3	1.0	089	0.0056	0.0059	2.28	2.40	0.34
4		084	0.0061		2.53		
5	1.5	113	0.0106	0.0118	4.34	4.84	0.46
6		102	0.0130		5.33		
7	2.0	083	0.0115	0.0106	4.76	4.46	0.32
8		096	0.0098		4.15		
9	3.0	288	0.0168	0.0174	7.21	7.33	0.35
10		291	0.0180		7.45		
11	4.0	086	0.0192	0.0181	7.98	7.49	0.27
12		093	0.0171		7.00		
13	6.0	122	0.0319	0.0324	13.33	13.41	0.32
14		121	0.0330		13.49		
15	6.0	260	0.0509	0.0518	21.61	22.12	0.53
16		142	0.0528		22.63		
17	8.0	231	0.0587	0.0500	24.83	20.99	0.37
18		125	0.0414		17.15		
19	8.0	137	0.0502	0.0499	21.47	20.57	0.37
20		136	0.0496		19.67		
21	10.0	140	0.0537	0.0609	22.51	25.54	0.36
22		139	0.0681		28.58		
23	10.0	129	0.0546	0.0532	22.46	22.19	0.32
24		149	0.0518		21.92		
25	12.0	251	0.0564	0.0551	23.50	23.52	0.28
26		255	0.0539		23.54		
27	12.0	257	0.0474	0.0495	19.93	20.28	0.24
28		256	0.0516		20.64		

E. AVERAGE METAL CONCENTRATION IN PRIVATE HOUSES

In all the following Tables, an asterisk indicates the values higher than the maximum acceptable levels set by the British Columbian or Canadian governments.

TABLE E.1 Metal Concentrations in mg/L - HOUSE A

Sample	Ca ±0.03	Cu ±0.01	Fe ±0.02	Mg ±0.01	K ±0.02	Na ±0.03	Zn ±0.01	Value
F.Flush	1.37	0.85	0.17	0.23	0.16	0.48	0.44	μ
Hot	0.09	0.26	0.03	0.05	0.01	0.02	0.38	σ
F.Flush	1.34	1.07*	0.19	0.23	0.15	0.46	0.20	μ
Cold	0.09	0.26	0.03	0.02	0.01	0.03	0.13	σ
Running	1.23	0.69	0.22	0.29	0.15	0.48	0.02	μ
Hot	0.07	0.10	0.04	0.03	0.01	0.03	0.004	σ
Running	1.40	0.86	0.18	0.20	0.15	0.46	0.02	μ
Cold	0.11	0.45	0.03	0.01	0.01	0.02	0.01	σ

TABLE E.2 Metal Concentrations in mg/L - HOUSE B

Sample	Ca ±0.03	Cu ±0.01	Fe ±0.02	Mg ±0.01	K ±0.02	Na ±0.03	Zn ±0.01	Value
F. Flush	1.35	0.61	0.23	0.78	0.14	0.43	0.16	μ
Hot	0.05	0.17	0.05	0.07	0.01	0.01	0.19	σ
F. Flush	1.43	1.60*	0.26	0.17	0.14	0.43	0.07	μ
Cold	0.05	0.74	0.07	0.04	0.01	0.01	0.03	σ
Running	1.35	0.38	0.24	0.76	0.14	0.43	0.03	μ
Hot	0.02	0.03	0.06	0.08	0.01	0.01	0.01	σ
Running	1.39	0.39	0.29	0.12	0.14	0.44	0.02	μ
Cold	0.05	0.12	0.06	0.01	0.01	0.02	0.01	σ

TABLE E.3 Metal Concentrations in mg/L - HIGH-RISE A

Sample	Ca ± 0.03	Cu ± 0.01	Fe ± 0.02	Mg ± 0.01	K ± 0.02	Na ± 0.03	Zn ± 0.01	Value
F.Flush Hot	1.26 0.13	1.23* 0.37	0.27 0.12	0.19 0.03	0.14 0.01	0.44 0.04	0.22 0.16	$\mu$ $\sigma$
F.Flush Cold	1.30 0.11	1.90* 0.34	0.23 0.04	0.18 0.01	0.14 0.01	0.43 0.03	0.07 0.04	$\mu$ $\sigma$
Running Hot	1.24 0.12	0.57 0.06	0.26 0.04	0.17 0.01	0.14 0.01	0.43 0.03	0.04 0.01	$\mu$ $\sigma$
Running Cold	1.21 0.12	0.76 0.57	0.26 0.06	0.17 0.01	0.14 0.01	0.43 0.03	0.01 0.02	$\mu$ $\sigma$

TABLE E.4 Metal Concentrations in mg/L - HIGH-RISE B

Sample	Ca ± 0.03	Cu ± 0.01	Fe ± 0.02	Mg ± 0.01	K ± 0.02	Na ± 0.03	Zn ± 0.01	Value
F.Flush Hot	1.01 0.06	0.59 0.12	0.27 0.08	0.19 0.02	0.14 0.01	0.45 0.01	0.20 0.21	$\mu$ $\sigma$
F.Flush Cold	1.07 0.08	0.46 0.25	0.24 0.04	0.16 0.01	0.14 0	0.45 0.01	0.05 0.02	$\mu$ $\sigma$
Running Hot	1.05 0.06	0.40 0.04	0.22 0.04	0.19 0.02	0.14 0.004	0.45 0.01	0.06 0.02	$\mu$ $\sigma$
Running Cold	1.08 0.07	0.35 0.15	0.22 0.05	0.16 0.01	0.14 0	0.45 0.01	0.02 0.01	$\mu$ $\sigma$

TABLE E.5 Metal Concentrations in mg/L - LOW-RISE A

Sample	Ca ±0.03	Cu ±0.01	Fe ±0.02	Mg ±0.01	K ±0.02	Na ±0.03	Zn ±0.01	Value
F.Flush Hot	1.05 0.13	0.29 0.02	0.59* 0.27	0.14 0.02	0.13 0.01	0.42 0.02	0.18 0.07	$\mu$ $\sigma$
F.Flush Cold	1.24 0.18	0.09 0.05	1.09* 0.39	0.14 0.01	0.14 0.01	0.41 0.02	2.18 0.36	$\mu$ $\sigma$
Running Hot	1.23 0.08	0.30 0.03	0.37* 0.35	0.14 0.01	0.14 0.01	0.44 0.01	0.40 0.01	$\mu$ $\sigma$
Running Cold	1.21 0.07	0.04 0.02	0.40* 0.36	0.14 0.01	0.14 0.004	0.43 0.02	0.10 0.01	$\mu$ $\sigma$

TABLE E.6 Metal Concentrations in mg/L - LOW-RISE B

Sample	Ca ±0.03	Cu ±0.01	Fe ±0.02	Mg ±0.01	K ±0.02	Na ±0.03	Zn ±0.01	Value
F.Flush Hot	1.03 0.04	0.88 0.10	0.21 0.03	0.20 0.02	0.14 0.01	0.46 0.02	0.11 0.04	$\mu$ $\sigma$
F.Flush Cold	1.06 0.04	2.05* 0.18	0.19 0.03	0.18 0.01	0.14 0.01	0.46 0.02	0.18 0.06	$\mu$ $\sigma$
Running Hot	0.94 0.02	0.21 0.01	0.22 0.04	0.18 0.01	0.14 0.01	0.46 0.02	0.03 0.01	$\mu$ $\sigma$
Running Cold	0.97 0.05	0.31 0.22	0.21 0.03	0.17 0.02	0.14 0.01	0.46 0.02	<0.01	$\mu$ $\sigma$

E. MAGNESIUM. POTASSIUM. SODIUM AND ZINC LABORATORY WATER  
CONCENTRATIONS VERSUS TIME

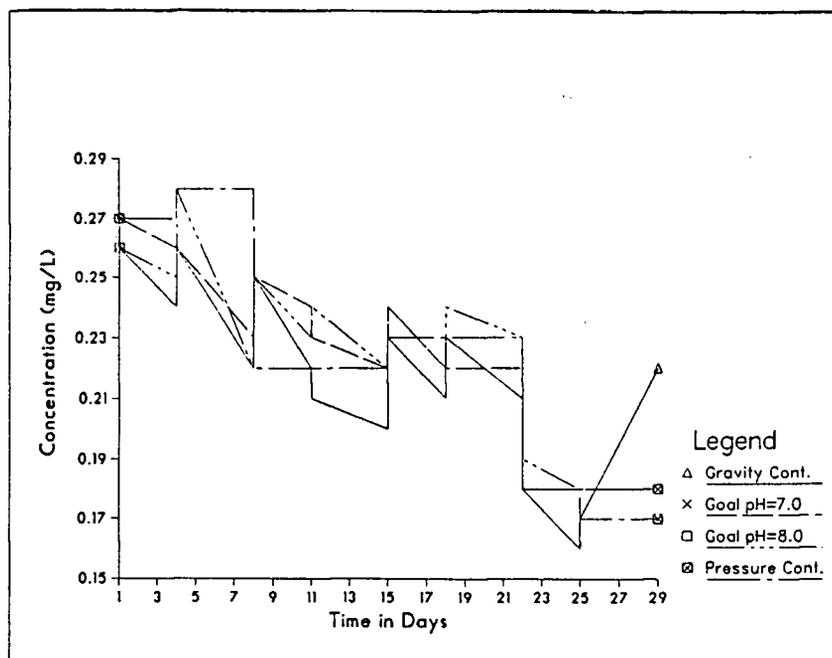


FIGURE F.1a) Magnesium Concentration vs Time - First Experiment

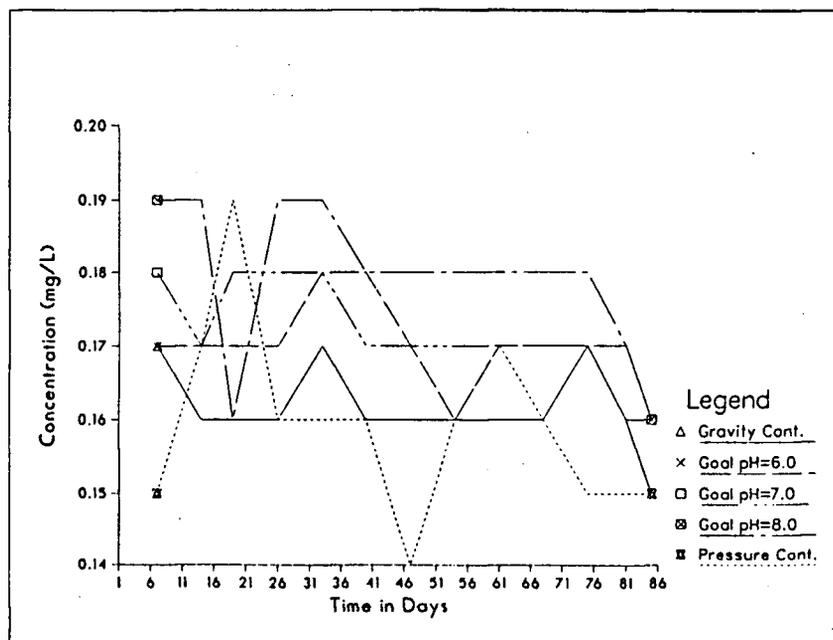


FIGURE F.1b) Magnesium Concentration vs Time - Second Experiment

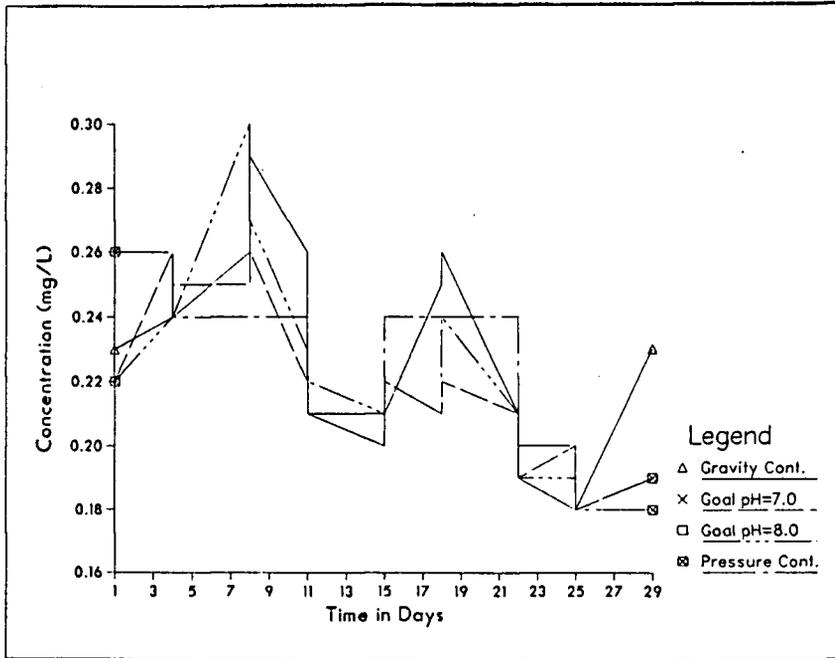


FIGURE F.2a) Potassium Concentration vs Time - First Experiment

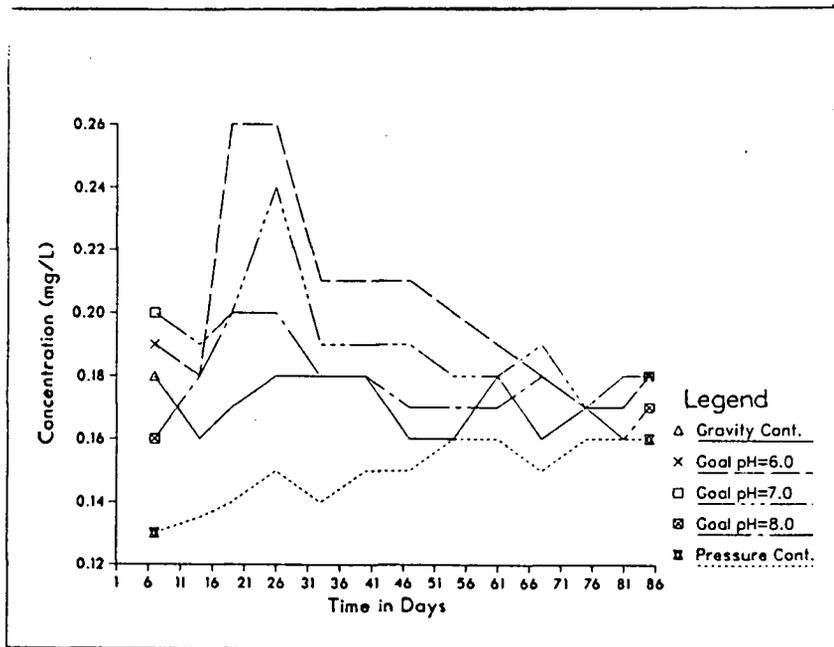


FIGURE F.2b) Potassium Concentration vs Time - Second Experiment

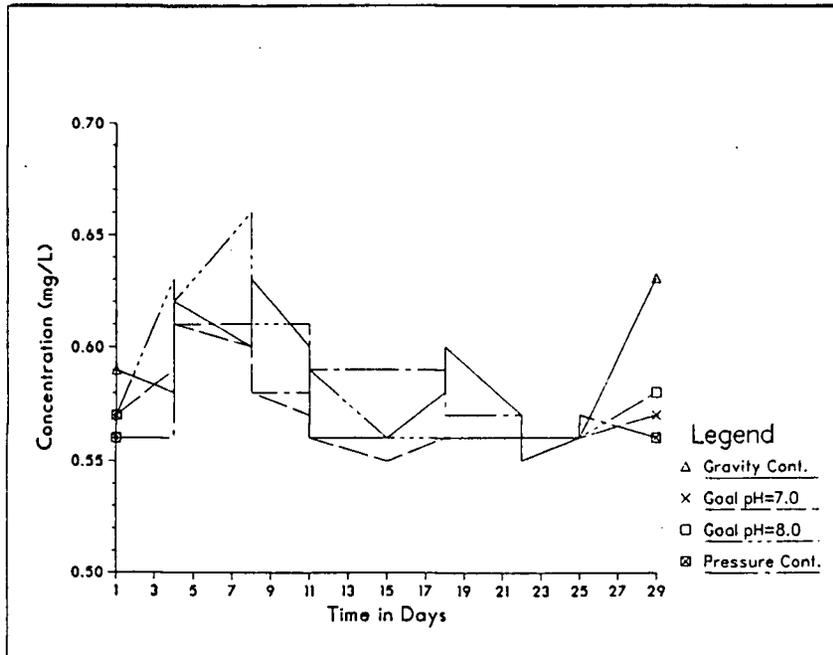


FIGURE F.3a) Sodium Concentration vs Time - First Experiment

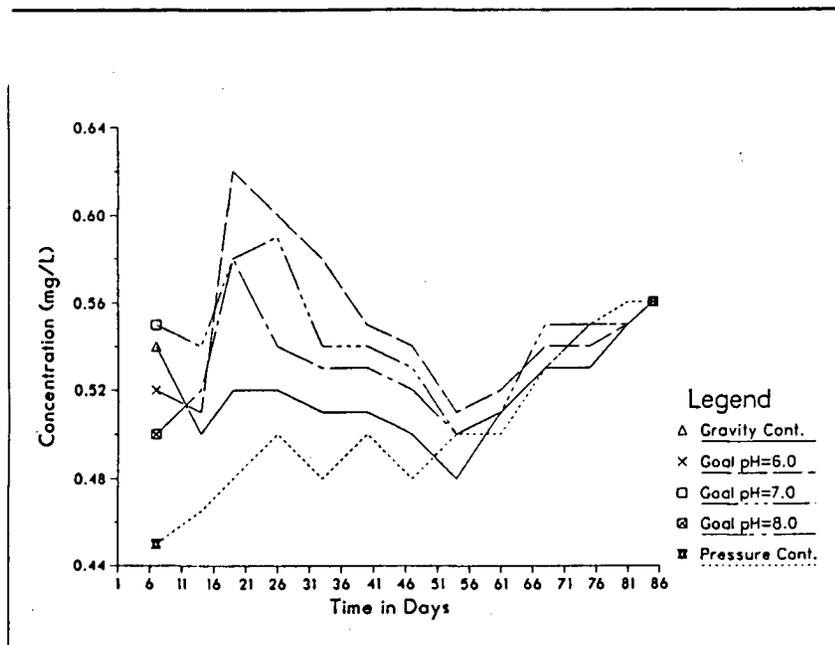


FIGURE F.3b) Sodium Concentration vs Time - Second Experiment

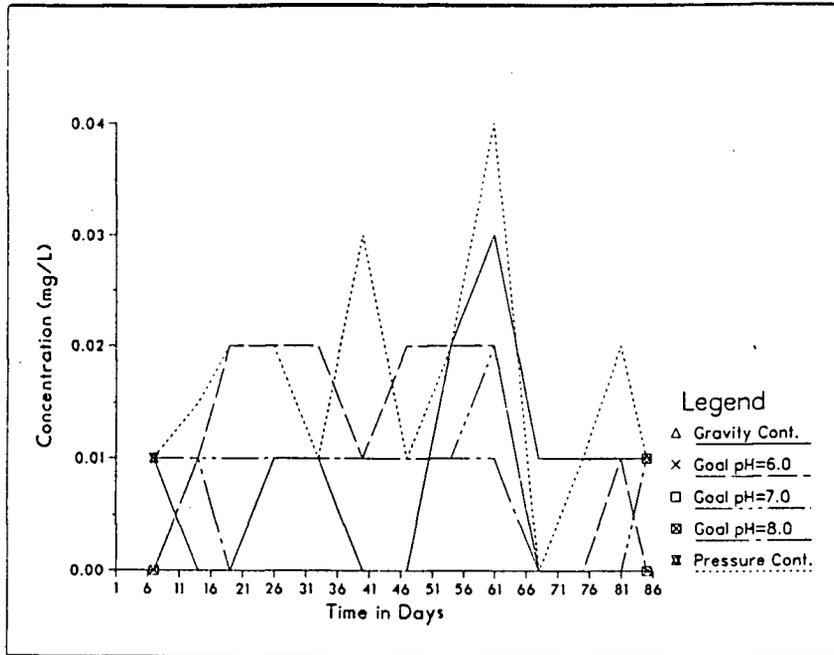


FIGURE F.4 Zinc Concentration vs Time - Second Experiment