An Assessment and Modeling of Copper Plumbing pipe Failures due to Pinhole Leaks

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ABSTRACT

Pinhole leaks in copper plumbing pipes are a big concern for the homeowners. The problem is spread across the nation and remains a threat to plumbing systems of all ages. Due to the absence of a single acceptable mechanistic theory no preventive measure is available to date. Most of the present mechanistic theories are based on analysis of failed pipe samples however an objective comparison with other pipes that did not fail is seldom made. The variability in hydraulic and water quality parameters has made the problem complex and unquantifiable in terms of plumbing susceptibility to pinhole leaks.

The present work determines the spatial and temporal spread of pinhole leaks across United States. The hotspot communities are identified based on repair histories and surveys. An assessment of variability in water quality is presented based on nationwide water quality data. A synthesis of causal factors is presented and a scoring system for copper pitting is developed using goal programming. A probabilistic model is presented to evaluate optimal replacement time for plumbing systems. Methodologies for mechanistic modeling based on corrosion thermodynamics and kinetics are presented.

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CHAPTER-1

SPATIAL AND TEMPORAL DISTRIBUTION OF PINHOLE LEAKS

Introduction

Pinhole leaks in copper plumbing pipes have been a concern for manufacturers, water utilities and the consumers for the past few decades. Figure 1, shows the spread of pinhole leaks on a nationwide scale. The figure is created based on number leak incidents reported to Copper Development Association (CDA) during 1998~2004 and the results of the Experts opinion survey (2004).

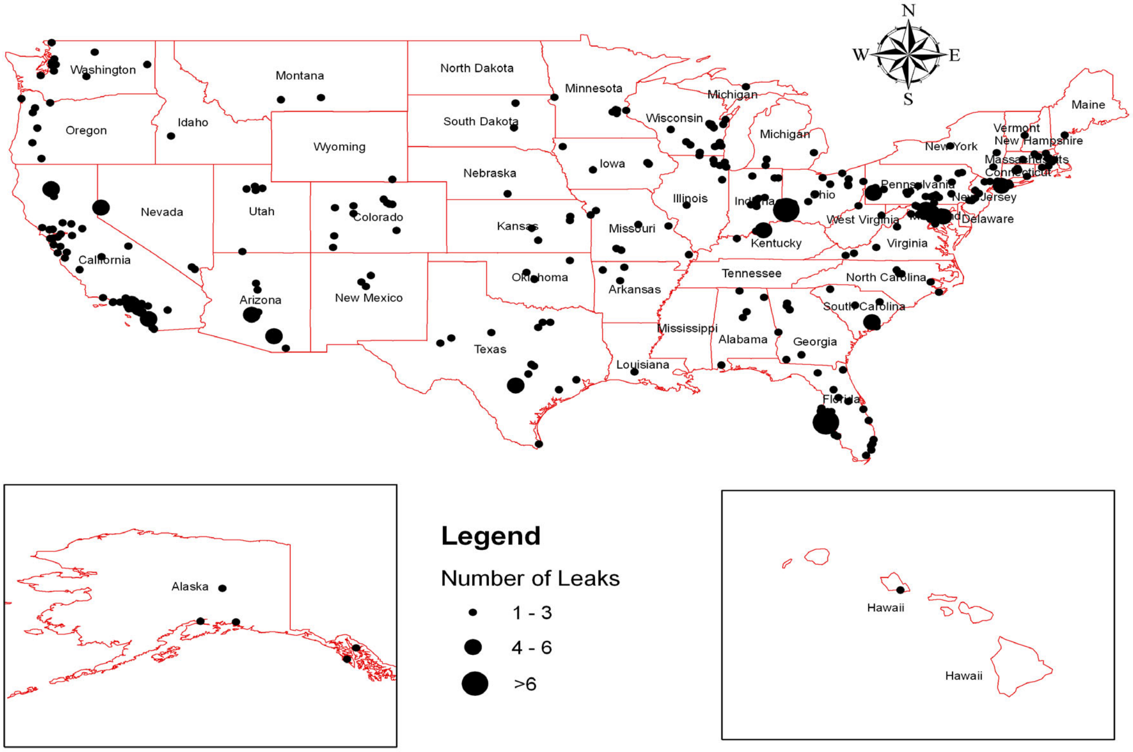


Figure 1 Nationwide pinhole leaks during 1998~2004 based on CDA failure reports and Experts' opinion survey

Figure 1 is created in GIS (Arc Map) using the number of leak incidents from CDA database and the Expert opinion survey. Each dot in Figure 1 corresponds to a location (city/ county) from where the leak is reported during 1998~2004 period. Larger dots indicate more leak incidents during the period. The smallest dot size represents locations with three or lesser leaks, the largest size represents locations with seven or more leaks, and the intermediate size represents locations that have reported four to six leaks. Certain areas of the country such as Washington Suburban Sanitary Commission (WSSC) area (Maryland), some parts of Ohio, Florida and California clearly show more pinhole leak incidents. Since, a large percentage of pinhole leaks may remain un-reported (Edwards et al. 2004), it can be inferred that the extent of the problem is much larger than what is reflected in Figure 1. The major concerns due to pinhole leaks include damages to houses, increased cost of home insurance, denial of insurance claims, undesirable growth of mold and mildew which sometimes decreases the resale value of the house, loss of water resources due to undetected leaks and mental stress. (http://www.toolbase.org/tertiaryT.asp?TrackID=&CategoryID=1495&DocumentID=4847)

Repair of the pinhole leaks is usually a lengthy process. Since the plumbing pipes are hidden behind dry walls, under the floor or above the ceiling, the leaks remain undetected until significant damage is caused to structural elements and other valuable assets. Even after the effects of the leaks are seen, it requires significant effort to trace the location of the leak. Typically an acoustic detector is used to locate the leak location. The homeowner may have to engage multiple contractors for leak detection, repair of plumbing, repair of structural members and finishing that increases the financial burden significantly.

Importantly, a repair does not ensure a cure for future leaks. The data seems to suggest that once pinhole leaks arrive, the home becomes susceptible to more leaks in future (WSSC data). The duration before the next leak occurs is random. To re-plumb a home with copper pipe is a major decision for a homeowner as it does not guarantee safeguard against future pinhole occurrences. If a homeowner does not choose copper, the choice of material becomes a crucial issue, as the options lead to plastics PVC/ CPVC and PEX or Stainless steel. The use of PEX is banned in some localities in California due to possible leaching of chemicals and its reaction with chlorine (http://www.plumbingsupply.com/pex.html). Other disadvantages of plastic pipes include microbial growth inside the pipes, weak fire resistance properties, cracking, and taste/odor issues. Stainless steel is costly and may not be readily available at all locations, as the use of stainless steel is mostly limited to industrial applications.

Copper is the most widely used plumbing material over the past few decades. Due to its little or no reactivity and affordability copper pipes are commonly used in commercial, institutional and residential establishments. Several other desirable properties of copper include durability, availability, affordability, little or no health hazards, better fire resistance, recyclability, and less maintenance cost. Copper pipes used for plumbing in United States conform to American Society of Testing and Materials (ASTM B 88) standards which ensure the composition of the pipes contains at least 99.9 % copper and pure silver combined. Three types of pipes K, L & M, are generally used for plumbing installations. The thickness of the pipe wall differs depending upon the diameter, and the type of pipe (K, L or M). For a given diameter of the pipe, K-type copper has the maximum wall thickness while M-type has the minimum wall thickness. For example, for a ½ inch nominal diameter, the thicknesses of K, L and M type pipes are 0.049 inches, 0.040 inches and 0.028 inches respectively, the thickness increases with increase in diameter. Types K and L are available as *hard* and *soft* seamless copper tubes, while Type M is available as *hard* piping only. The details about the pipe thickness, pipe characteristics, installation and soldering guidelines are provided in the handbook from Copper Development Association. The handbook can be accessed on http://copper.org/applications/plumbing/techref/cth/cth_main.htm.

Copper corrosion, in potable water pipes may initiate from its *external* or *internal* surfaces. *External* corrosion is common in underground pipe lines or service lines that are typically embedded in soil. The failure generally occurs due to the presence of corrosive environment which includes presence of moisture and oxygen. The external corrosion is excluded from the scope of this study. *Internal* corrosion of copper pipes may broadly be classified into *uniform* and *non- uniform corrosion*. The uniform corrosion involves corrosion attack on the total surface of the pipe wall almost uniformly. Such type of corrosion may not necessarily produce tube failures but it can cause high copper levels in tap water and is often referred to as *cuprosolvency*. The problem is also identified as *blue / green water,* and may cause other problems such as staining of plumbing fixtures and metallic taste in water. The rate of metal loss in uniform corrosion is high but the loss is spread uniformly over the entire surface causing thinning of pipe wall with age. The USEPA lead-copper rule (1991) restricts the levels of dissolved copper to 1.3 mg/L at the tap and therefore, curtailing uniform corrosion is crucial.

The *non uniform* corrosion is localized in nature, it does not involve considerable loss of metal but due to its localized nature it produces a localized incision in the pipe. This type of corrosion is also known as *pitting*. The rest of the surface is generally unaffected by corrosion. When pitting becomes severe, the incision can cause a perforation in the pipe wall producing a leak. Due to its small size, it is known as *pinhole leak*. The rate of the pitting is much faster as compared to uniform corrosion and is capable of creating a perforation in the pipe wall as fast as within few months of installation. However, anecdotal evidences suggest large variability in the time to leak hence, the pitting rate varies considerably. The variability in rate of pitting is dependant on several parameters that include water quality parameters, hydraulic parameters (pressure and velocity), age of plumbing, soldering and flux material, and to some extent the history of pinhole leaks of the home and neighboring community.

This study synthesizes various physical and chemical factors that can lead to pinhole leaks in copper home plumbing. The objectives of the study are:

i. Determine the current patterns of pinhole leaks both spatially and temporally based on repair histories.
ii. Assess trends in rate of occurrence and causality factors of pinhole leaks in terms of hydraulic, water quality and water treatment characteristics.
iii. Assess the factors that determine selection of copper for home and commercial plumbing.

Chapter-I presents the spatial and temporal distributions of pinhole leaks in United States. The analyses of failure reports from Copper Development Association (CDA) for 30 year period are presented. The temporal patterns for the failure causes are also given. A summary of the surveys, databases and other resources utilized in this study is presented. Chapter-II presents the synthesis of pinhole leaks with respect to physical and chemical parameters. The chapter presents a detailed literature review of the copper pitting and its causes that have been reported in the literature to date. The causal mechanisms in terms of the water quality and hydraulic parameters are identified and highlighted in terms of the likelihood of corrosion. Chapter-III presents a probabilistic methodology for determining the optimal replacement time for the home plumbing system. The leak patterns are obtained using the data from Copper Development Association (CDA) and the Homeowners' Survey. Chapter-IV presents details on the chemical nature of corrosion, a methodology for estimating time to failure is presented based on the mechanistic approach.

Databases and Surveys

Following databases and surveys are used in the present study to assess the spatial and temporal distribution of pinhole leaks.

AWWARF/ AWWA utility survey

The AWWARF/ AWWA utility survey is available in the form of a database "*WATER:\STATS*". It consists of survey information from AWWA member utilities. The last survey was conducted in the year 1996 with 898 utilities responding to the survey out of a total of 3200 AWWA member utilities. The database includes information on financial and revenue records, water treatment and disposal practices, finished water quality parameters at the plant, pipe material and water quality information in the distribution system. The data provides information only about the pipe material used in *service laterals* in the respondent utilities.

Therefore, the database could not be used for studying *spatial* and *temporal* patterns of pinhole leaks inside a house.

Copper Development Association (CDA) database

Copper Development Association (CDA) has shared its database consisting of 38 years (1966 ~ 2004) of failure reports. These failure reports are based on the analysis of failed pipe samples that are voluntarily sent to CDA. Typically, a failure report consists of location (state, city) of dwelling unit, description of, type of failure, size of pipe, source of water , and a set of findings based on the physical and chemical analyses conducted by the CDA or other laboratories using the failed specimen. Since, each CDA report typically provides information about the city and state from where the sample was collected, the CDA database is extensively used for determining spatial and temporal patterns of the pinhole leaks. The analyses followed by CDA are discussed in detail along with summaries of the findings that are presented in form of tables and charts in Appendixes A-1 and B-1.

Plumber Survey- I

The objective of the Plumber Survey-I, is to verify the results obtained from preliminary spatial analysis. An initial analysis based on 5 years (2000 ~ 2004) of the CDA reports and the results from the Expert Opinion Survey (explained later in the chapter) concluded the absence of pinhole leak incidents in five states namely Delaware, Louisiana, Mississippi, North Dakota and New Hampshire. Additionally, four of the five heavily populated cities, namely, Austin (TX), Columbus (OH), Detroit (MI) and Memphis (TN) did not surface in the preliminary spatial analysis that was based on the 5 years of CDA reports and the Expert Opinion Survey. Hence, a total of nine cities, namely New Orleans (LA), Wilmington (DE), Jackson (MS), Manchester (NH), Bismarck (ND), Austin (TX), Columbus (OH), Detroit (MI) and Memphis (TN) were considered for the survey. The survey was conducted through telephone by contacting plumbers in these cities. The results of the survey for 55 respondents out of 242 calls are summarized and discussed in detail later in the chapter.

Expert Opinion Survey

This survey was conducted electronically via email in October 2004. The survey was conducted by *social and economic* group working on this project. The group includes faculty and students from Agriculture and Economics department, Civil and Environmental Engineering department and Community Heath department at Virginia Tech, Blacksburg. The survey was targeted to gather expert opinion and study the spatial and causal factors of pinhole leaks. A total of twelve experts responded to the survey, the experts were from academia, government and industry. The experts identified 107 locations in 32 states (including Washington DC) that have been affected by pinhole leaks. The survey results are used later in the chapter for the spatial analysis.

Home Owner Survey

A telephone survey was conducted on a national scale by the Virginia Tech Survey Center in summer 2005. The center also has conducted a Phase II-Plumber survey in spring 2006. The objective of the homeowner survey is to assess the homeowner reaction to pinhole leaks. The survey had questions on the extent of the problem, the interaction of homeowners with other stakeholders like plumbers, contractors and insurance companies, frequency of leaks with the age of the plumbing, and costs. Three hot spot areas namely, selected communities in Ohio, Florida and some parts of California were the major thrust regions with 100 completions each, while 420 completions were spread randomly over the rest of the United States. Out of 720 completions 83 respondents reported to have experienced pinhole leak in their plumbing system. The data from the homeowner survey is utilized to simulate leak time distributions and subsequently in analysis of the optimal replacement criteria in Chapter-3.

Analysis of the CDA Database

The Copper Development Association (CDA) advises consumers to send failed pipes to them for a laboratory analysis. If there is a manufacturing defect a claim can be made (http://www.plumbingsupply.com/cuinfo.html). Typically failed pipes of a few inches in length are sent to a regional manager of the CDA who in turn sends the pipe specimen to their New York office for laboratory examination. Based on the test results, a failure report is generated. For this study, a total of 1313 reports from 1975 to 2004 have been analyzed. Each report typically contains the following information as the background:

1) Regional manager who sent in the sample
2) Establishment/home from which the specimen was obtained
3) Type K, L, and M of copper pipe
4) Diameter of pipe
5) Orientation of pipe (horizontal/vertical)
6) Type of system: Plumbing pipe for cold or hot water; service lateral; hydronic heating system; refrigeration; and heat pump

7) Year of installation of the system

8) Year in which failures started occurring

9) Name of utility supplying the water

10) Indication of surface or groundwater if that information is available

11) Note on availability of data on temperature for hot water, pressure, velocity if hot water is circulated and water quality.

The CDA reports contain pipe failures pertaining to pipe internal corrosion, soil corrosion, mechanical damage or external corrosion.

Protocol of Tests and Results as defined in CDA reports

Each specimen submitted to CDA is tested in accordance to the protocol defined in the subsequent paragraphs. The causes and the factors that led to the failure are ascertained by CDA based on the physical and chemical examination. While the CDA database contains useful information, there are some limitations that should be noted. First, each analysis was based upon the current level of understanding of mechanisms leading to of copper failures at that time. Recently, there have been profound advances in the science of copper pitting, but many unknowns still persist. There are undoubtedly some conclusions in the CDA databases that would be questionable, if not deemed incorrect. For example, many now consider there to be an over-characterization of fluxed induced failures in the database.

Secondly, addresses in the database can be used to construct a map of potential copper pipe failures. Locations of leaks are not uniformly represented for the following reasons. Many homeowners, who were unaware of this service, did not send their pipe specimens to CDA (under-representation). Certain regional managers were also more active in collecting pipes in their area (over-representation). The net result is that some locations may have a disproportionately high occurrence of leaks, while other areas will seem to be leak free.

In the following sections pertaining to the CDA databases, these authors are not confirming or validating their methodology or conclusion, but rather are only reporting and summarizing these databases. In addition, no experiments were conducted to validate the CDA findings. Even considering the potential limitations of the CDA, the information in these reports still has value and will be presented.

Physical Examination

Each pipe specimen is physically examined with a stereomicroscope for perforations on the pipe whether they are on the outside or from the inside. Subsequently, the specimens are sectioned lengthwise in order to examine the inside surfaces. Examination of the inside surfaces confirms whether the pinhole perforations through the tube walls occurred from the inside or not.

The inside pipe walls of the sections are examined for localized areas of corrosion attack and *erosion corrosion*. Narrow bands of pits running longitudinally along the pipe are typically attributed to soldering flux runs (typically termed as the "ghosts" of flux). U-shaped pits and undercutting wavelet formation is typically reported due to erosion-corrosion. Water pressure greater than 80 psi (gage) and velocities greater than 4 to 5 feet per second are reasoned to promote erosion corrosion. For hot water, a temperature in excess of 160 degrees Fahrenheit is very often attributed to cause erosion corrosion. In general, erosion corrosion has been attributed to waters that are soft with near zero hardness and especially containing dissolved oxygen or carbon dioxide.

The isolated perforation sites associated with *pinholes* are examined for characteristics of the tubercles. The diameter of the pit formation is examined at the surface and through the tube wall. Typically, it is reported that the size of the tubercle is proportional to the depth and extent of the underlying pit. The corrosion products are subject to chemical analysis.

In addition to ascertaining whether corrosion was from the inside or from the outside, physical examination includes identification of *longitudinal and circumferential cracks*. Most of the reports associate the cracks to stresses and fatigue. Cracks are also associated with local brittleness of the normally ductile copper pipe. For copper pipes the specific environment which is usually associated with stress corrosion cracking is the presence of ammonia containing species. In addition, presence of oxygen, moisture, and surface tensile stresses are very often reported as essential for cracking.

The inside pipe wall is also examined for possible *poor workmanship* based on the nature of the cuts joining the tubes. If the tube is not squarely cut and reamed properly prior to soldering, the resulting protrusions and irregularities are associated as the cause of the localized turbulence followed by erosion corrosion downstream.

Pointed-micrometer wall thickness measurements in the unpitted areas after removing the deposits from the water are taken to check against the American Society of Testing Materials

(ASTM) standard specification for seamless copper water tube of the appropriate type (K, L, M) and diameter. The conformance of the wall thickness to the ASTM standards is reported.

Chemical Examination

The chemical examination includes Energy dispersive spectroscopy (EDS) and microchemical analysis (MCA) to determine the chemical constituents present in the corrosion products. Constituents that are typically reported include major amounts of copper, oxygen, semi-major quantities of carbonate, minor amounts of aluminum, silicon, sulfur, and chloride, and semi-minor quantities of carbon. Often the tubercles are reported to consist of copper carbonate [malachite $CuCO_3.Cu(OH)_2$]. The unpitted areas are examined for cupric oxide (CuO, tenorite). All the constituents may not be reported in every failure report.

The specimen testing procedure is also accompanied by a request from the CDA to the concerned utility for the historical water quality data. Sometimes, the data pertaining to water quality is obtained through other sources like a private testing laboratory. Upon completion of the specimen testing, CDA ascertains the possible causes of the failure using the water quality parameters and the observations from the laboratory tests. Based on the findings, CDA provides a set of conclusions and recommendations.

The presence of *chloride* in the pits has been attributed to flux runs or oxidizing chemicals used for disinfection (typically chlorine, sodium hypochlorite, calcium hypochlorite and chlorinated cyanurates) resulting in *localized pits*. It is typically reported that the fluxes commonly contain activating chlorides such as ammonium chloride, zinc chloride, tin chloride, and hydrochloric acid. The unaffected areas (no localized pitting) are examined for protective tarnish film of reddish-brown cuprous oxide. The cuprous oxide is typically reported to overlay a thin, friable layer of deposits including greenish-colored products associated with pitting of copper upstream.

Certain major pitting activity is attributed to silicon containing material (*silica*) deposited on the copper surface which is reported to promote pitting with aluminum sulfate coagulant. The differential deposition of silica that forms highly localized anodic sites along with low dissolved oxygen content of the water is usually associated to promote pitting attack of *oxygen differential type- concentration cell corrosion*. Excessive heating of water containing aluminum (greater than 0.1 mg/l) is usually attributed to permit deposition of aluminum hydroxide on hot copper surface; if iron is present, hydrated hematite deposits are reported to promote microgalvanic corrosion.

Near *stagnant water* are associated with increased bacterial activity. The reports identify patches of bacterial colonies that result in *microbial corrosion* in the form of patches of corrosion pits.

The analysis results of the CDA database can be grouped into three categories, namely, the *causes identified by CDA* based on the forensic examination of the failed pipe samples, the *spatial patterns of pinhole leak*, and the *temporal patterns of pinhole leak*.

Table 1 provides a summary of various causes of failures and the associated characteristics as identified by CDA.

Table 1 Causes of copper pitting as determined by CDA based on their forensic examination of failed pipe samples

Causes enumerated in CDA reports [a]	**Physical characteristics as observed during examination of the samples**	**Characteristics of Water**	**Chemical characteristics of the corrosion products**
Chloride/ Chlorine induced pitting. (Possible source soldering flux or disinfectant)	Narrow bands of pits running longitudinally along the pipe. Pits are generally localized. Presence of greenish copper corrosion products that may have broken loose from larger tubercules.	If there is no soldering flux used for the installation, then the possible source of chloride/ chlorine may be strong oxidizing chemical which are used for disinfection (some of the chemicals include sodium hypochlorite, calcium hypochlorite and chlorinated cyanurates). If the corrosion is induced due to soldering flux then it may be due to ammonium chloride, zinc chloride, tin chloride and/ or hydrochloric acid that are typically present in the flux.	Presence of reddish brown copper oxide along with major amounts of copper, oxygen and chloride, minor quantities of silicon, aluminum and calcium and semi-minor amounts of iron, sulfur and potassium. Presence of chlorides in major quantities, typically the greenish colored products contain copper chloride which may coexist with porous cuprous oxide. The tubercules contain primarily basic copper carbonate ($CuCO_3.Cu(OH)_2$)
Pitting occurred by oxygen-differential -type, concentration-cell corrosion.	Deposition of silica in presence of aluminum, Iron or sulfate. Presence of tubercules of greenish color copper corrosion products.	Aluminum or Iron > 0.1 mg/L with appreciable amounts of silica and presence of dissolved oxygen.	Presence of major amounts of copper, iron, silica and oxygen along with lesser amounts of aluminum, semi major amount of calcium and semi minor amounts of phosphorous and sulfur. The tubercules primarily of basic copper carbonate ($CuCO_3.Cu(OH)_2$) or basic copper sulfate ($CuSO_4.3Cu(OH)_2$) or both. Significant amount of copper oxide (Cu_2O) with lesser quantities of chloride and phosphorus. Deposits may include hematite (Fe_2O_3), and silica dioxide (SiO_2).

Table 1 Causes of copper pitting as determined by CDA based on their forensic examination of failed pipe samples

Causes enumerated in CDA reports [a]	**Physical characteristics as observed during examination of the samples**	**Characteristics of Water**	**Chemical characteristics of the corrosion products**
Heating of water containing appreciable amount of iron, Aluminum or Silicon	Presence of Localized pitting with porous reddish brown cuprous oxide overlaid with greenish colored corrosion products.	Water with appreciable amount of iron or iron oxides OR Water with significant amount of silica (as SiO_2) OR Water with aluminum > 0.1 mg/L	Presence of major amounts of copper, oxygen and carbonates, minor amounts of sulfur (as sulfate), semi minor amounts of aluminum and silicon. The greenish colored products primarily consist of basic copper carbonate ($CuCO_3.Cu(OH)_2$) which may be admixed with some deposits of cuprous oxide. Presence of cupric oxide (CuO) is common where the temperature exceed 160 F
Failure initiated from outer side of the pipe (Possible reasons include soil corrosion, mechanical crack etc)	The deposits may have varied physical description depending on the soil composition. Presence of longitudinal or circumferential cracks in case of stress corrosion.	Generally the stress cracks are associated with high pressure 80 psi (gage)	Greenish colored products primarily consisting copper chloride. The corrosion products may include major amounts of copper, oxygen and chloride and lesser amount of Aluminum, silicon, phosphorous, potassium, carbon and iron depending upon the soil composition.
Erosion/ corrosion due to higher velocities or Localized turbulent flow	U-shaped pits and under cutting wavelet formation. Significant reduction in tube wall, absence of any corrosion products at the location of pinhole.	Soft water or water with zero hardness and especially containing dissolved oxygen or carbon dioxide. Or water greater than 80 psi (gage) and velocities greater than 4 to 5 feet per second. For hot water, a temperature greater than 160 F.	Cupric oxide (CuO) may be present in hot water pipes where temperature exceeds 160 F
No corrosion or no reason established.	One or more conditions from all the reasons cited above that may be simultaneously occurring together.		

Table 1 Causes of copper pitting as determined by CDA based on their forensic examination of failed pipe samples

Causes enumerated in CDA reports [a]	**Physical characteristics as observed during examination of the samples**	**Characteristics of Water**	**Chemical characteristics of the corrosion products**
Poor workmanship.	Joining tubes not squarely cut and reamed properly prior to soldering. Globule of solder may be present. Leak may initiate at joints or may be triggered just downstream of the solder joint that is improperly cut finished	NA	The loosely friable greenish material contains products having carbonate.
Sulfide induced pitting.	Presence of localized pits covered with relatively larger tubercules of friable copper corrosion products. The size of the tubercule proportional to the depth of the perforation.	Sulfide > 0.02 mg/L	Presence of major amounts of Copper and oxygen, semi major quantities of silicon and minor amounts of sulfur, carbonate and phosphorous. Presence of copper carbonate ($CuCO_3.Cu(OH)_2$) and copper sulfate, some of which in the form of brochantite ($CuSO_4.3Cu(OH)_2$).
Aggressive water	Presence of voluminous tubercules of green colored copper corrosion products. The corrosion induced pits under the tubercules contain reddish brown cuprous oxide (Cu_2O).	Carbon dioxide exceeding 25 mg/ L and appreciable suspended solids in form of silica.	Major amounts of copper, silicon and oxygen, with semi major amounts of carbonates and semi- minor to minor quantities of iron, magnesium, aluminum, manganese and calcium. The tubercules primarily contain basic copper carbonate ($CuCO_3.Cu(OH)_2$) that may be mixed with variety of products like hydrated hematite, silica and calcium carbonate.

Table 1 Causes of copper pitting as determined by CDA based on their forensic examination of failed pipe samples

Causes enumerated in CDA reports [a]	**Physical characteristics as observed during examination of the samples**	**Characteristics of Water**	**Chemical characteristics of the corrosion products**
Microbial Induced	Patches of corrosion induced pits (generally found in regions of stagnant water) with greenish colored copper corrosion products. The orientation of the patches is nearly parallel to the longitudinal axis.	Stagnant waters or waters with improper treatment.	Presence of major amounts of copper, semi major amount of carbonate, minor amount of sulfur (as sulfate), semi-minor quantities of calcium and silicon with traces of iron. The tubercules primarily contain basic copper carbonate ($CuCO_3.Cu(OH)_2$). Pits may contain copper chloride and copper sulfate with porous cuprous oxide.

[a] These causes are determined by CDA based on the forensic analysis of the failed samples. The causes may not necessarily express the opinion of the author. The causes enumerated by CDA do not provide any chemical reaction involved in the corrosion mechanism. A detailed review of the parameters that influence corrosion in presented in chapter-2.

Distribution of pinhole leak failures based on CDA reports (1975~ 2004)

Distribution of pinhole leak failures by various pipe functions

Most of the pipe failures were in cold water pipes with about forty-two percent, seventeen percent of the leaks were in hot water pipes, and sixteen percent failures were in hydronic system which circulates hotwater continuously. It is pointed out that this constant circulation results in turbulence and possible high velocities leading to erosion corrosion. The distribution of the failure reports based on the pipe category is presented in Figure 2. The details of the annual breakup for each category of pipe are presented in Table A-1.1 (Appendix A-1).

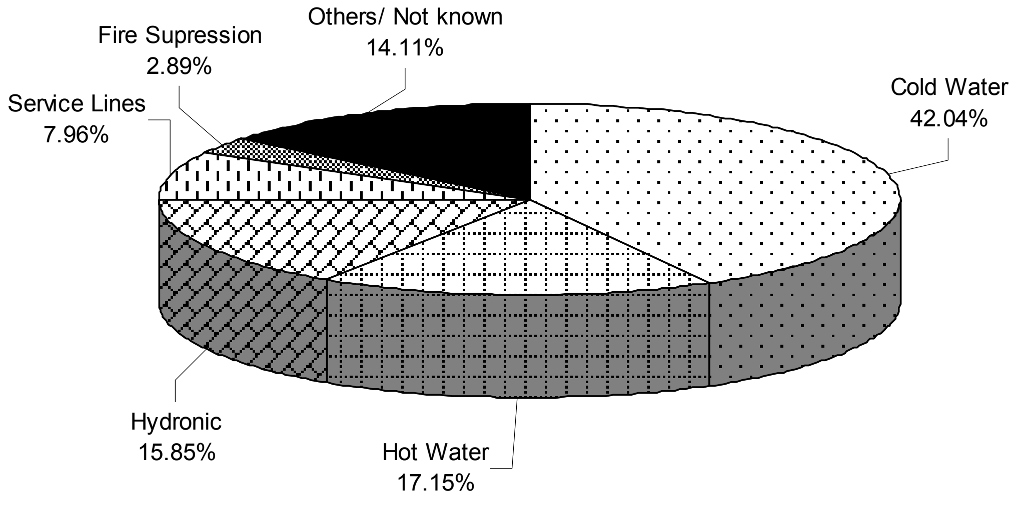


Figure 2 Average percent failures by pipe categories

Distribution of pinhole leak failures by various failure mechanisms

Figure 3 shows the averaged percent distribution of causes of failures. Chloride induced pitting constituted thirty percent of the leaks; seventeen percent erosion corrosion; thirteen percent due to external corrosion or mechanical damage; eleven percent due to oxygen-differential type - concentration cell corrosion; ten percent due to aggressive water; eight percent due to excessive heating of water that contains iron or salts of iron; and eleven percent due to poor workmanship, sulfide and microbial corrosion. In most cases where the chloride induced pitting has taken place, soldering flux or improper soldering are identified as the sources of chloride. Other identified sources of chloride include chlorine or other oxidizing agents used for disinfection these include sodium hypochlorite, calcium hypochlorite and chlorinated cyanurates.

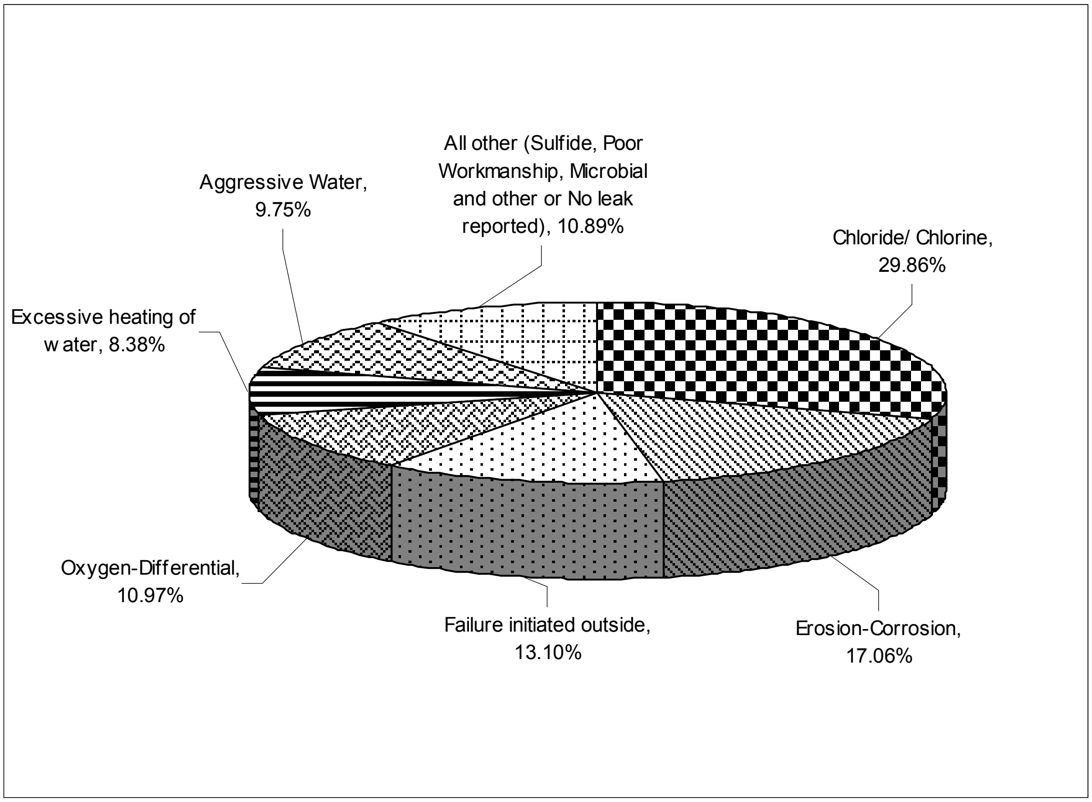


Figure 3 Average percent distribution causes of failures for all categories of pipe

The temporal patterns based on the failure causal mechanisms over a 30 year period (1975 ~ 2004) are presented in Figures A-1.1 through A-1.10 (*Appendix A-1*). Chloride induced pitting, Oxygen differential type pitting and pitting due to Excessive heating of water show an increasing trend, while failures due to Erosion corrosion and Aggressive water show a decreasing trend over a thirty year period. Other causes do not show either increasing or decreasing trend over the stated period. The annual break down for the failure causal mechanisms is presented in Table A-1.2 (*Appendix A-1*). The failure causes are further segregated based on the pipe category (cold water, hot water, and unknown). The *cold water category* consists of failure reports from cold water pipes, service laterals and fire suppression system. The *hot water category* consists of failure reports from hot water pipes and hot water recirculation system. The others/ unknown category consists of failure reports for which the pipe category is not defined in the CDA reports.

Cold water category

A total of 731 reports fall into this category. Figure 4 shows the averaged percent distribution of causes of failure. On an average, chloride/ chlorine induced pitting constituted forty-three percent of the failures; aggressive water fifteen percent; oxygen-differential twelve percent; external failures twelve percent; and eighteen percent due to erosion-corrosion, poor workmanship, sulfide, microbiological and no leak or no corrosion. The temporal patterns of failure mechanisms for cold water category are presented in Figure A-1.11 through A-1.15 (*Appendix A-1*). The annual breakup of the failure mechanisms for this category is presented in Table A-1.3 (*Appendix A-1*).

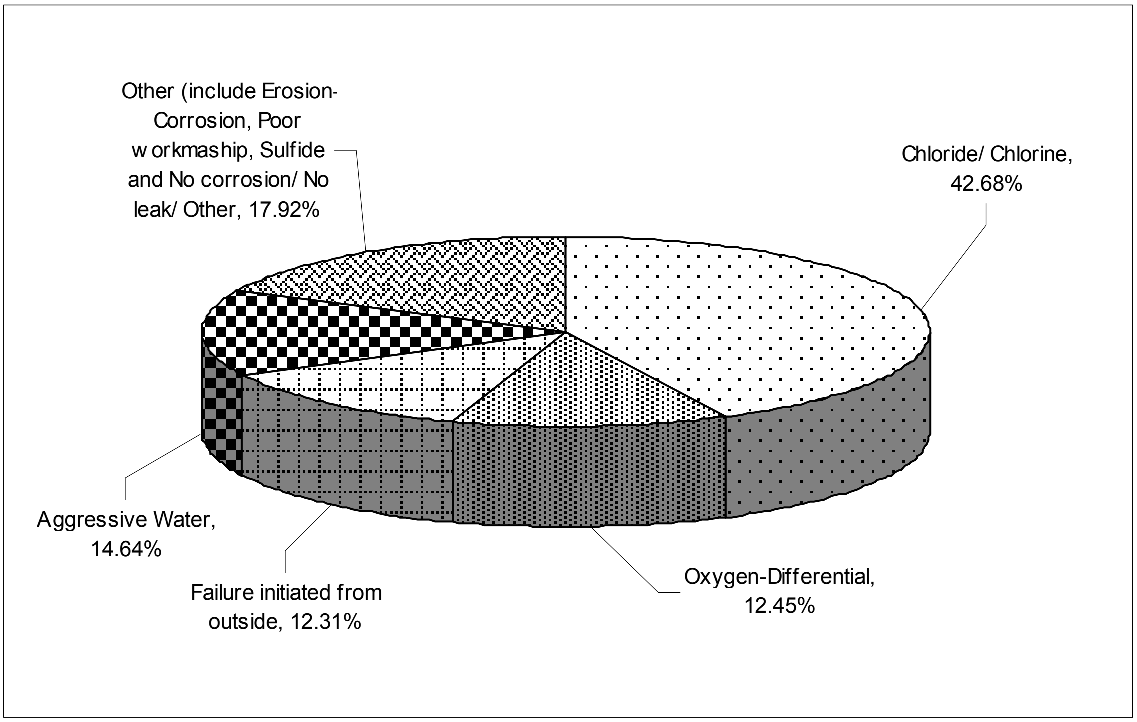


Figure 4 Average percent distribution causes of failures for cold water category

Hot water category

A total of 456 reports fall into this category. The averaged percent breakup of the failure causes for this category is shown in Figure 5. On an average, erosion-corrosion constitutes thirty-four percent of the failures; excessive heating of water twenty three percent; chloride eleven percent; external failures eleven percent; and twenty one percent constitutes oxygen differential type, aggressive water, poor workmanship, sulfide, microbiological and no corrosion/ no cause established. The temporal patterns of failure mechanisms for hot water category are presented in Figures A-1.16 through A-1.20 (*Appendix A-1*). The annual breakup of failure mechanism for this category is presented in Table A-1.4 (*Appendix A-1*).

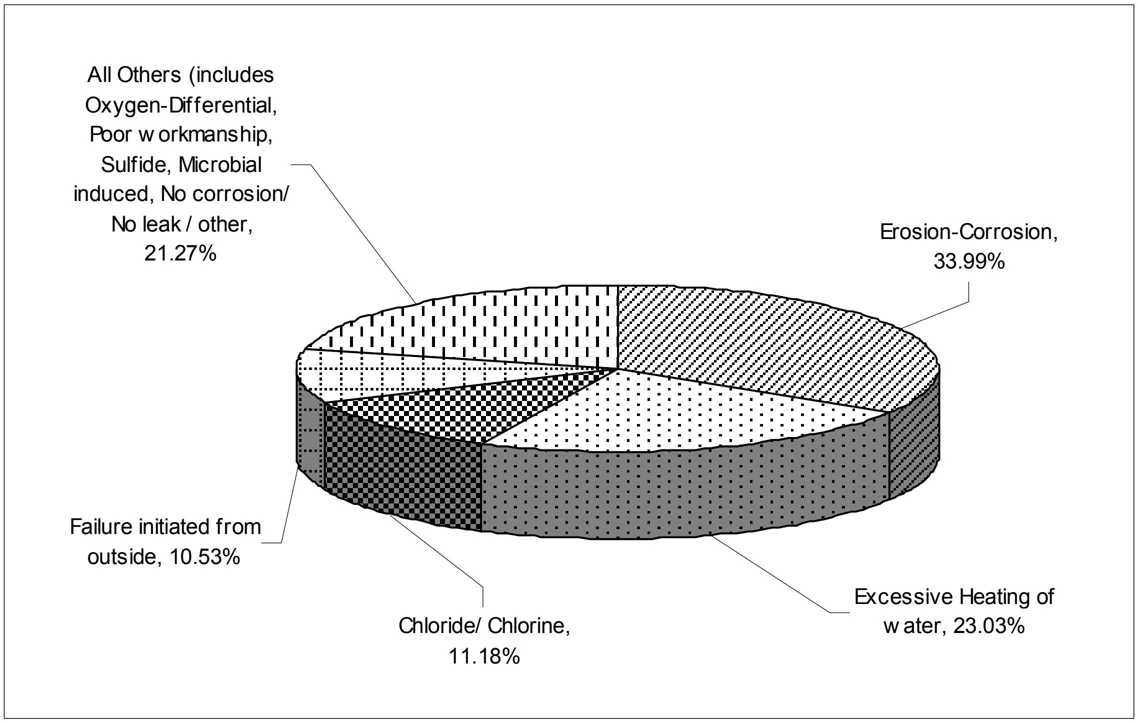


Figure 5 Average percent distribution causes of failures for hot water category

Other or unknown pipe category

A total of 195 reports fall into this category. The averaged percent breakup of the failure causes for this category is shown in Figure 6. On an average, externally initiated failure constitutes twenty percent of this category; chloride nineteen percent; no corrosion/ no cause established fifteen percent; erosion corrosion thirteen percent; and thirty one percent includes, oxygen-differential type, sulfide induced, aggressive water, poor workmanship and excessive heating of water. The annual breakup of failure mechanism for this category is presented in Table A-1.5 (*Appendix A-1*).

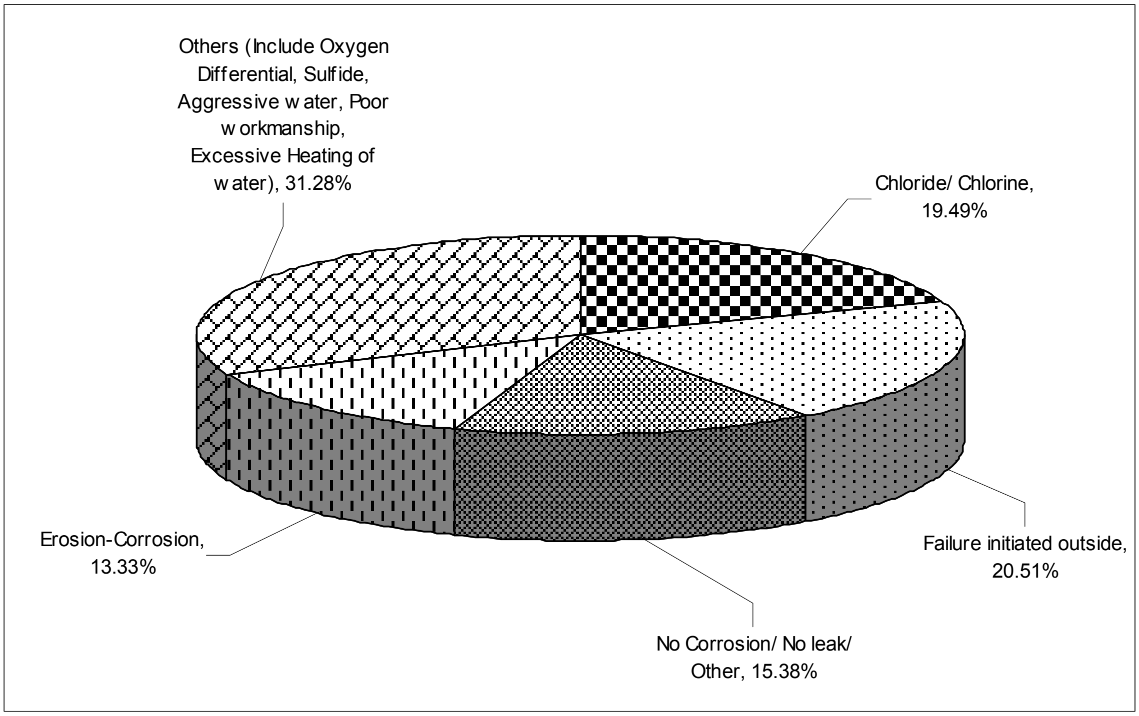


Figure 6 Average percent distribution causes of failures for other/ unknown category

Distribution of pinhole leak failures by pipe characteristics

The analysis results for 476 reports from 1998~ 2004, are presented in Tables B-1.1 through B-1.3 (*Appendix B-1*).

Leak types

On an average, seventy-one percent of the reports were for pinhole type pipe failures, twenty-nine percent reports contained information about other types of failures. The annual breakup for both these categories of failures is presented in Table B-1.1 (*Appendix B-1*).

Pipe type

Most of the leaks occurred in the M and L type of copper pipes with, forty-four percent for L-type, and forty-three percent for M-type, nine percent for K-type, and three percent were left unclassified. The lesser number of leak incidents in K type pipe is understood as K type pipes have more thickness as compared to M and L type pipes. The annual breakup for each category of pipes is presented in Table B-1.2 (*Appendix B-1*).

Pipe Orientation

Most of the reported failures were in the horizontal pipes, on an average, forty-four percent of the reported failures were in horizontal pipes, ten percent were in vertical pipes and forty six percent reports did not contain information about the leak location. The annual breakup for the leak location is included in Table B-1.2 (*Appendix B-1*).

Pipe size

Majority of failure reports were constituted by half inch (0.5 in) and three quarter inch (0.75 in) pipe sizes, with thirty-seven percent of the failure reports are for half an inch pipe, and thirty-nine percent for three quarter inch pipe, and ten percent for one inch pipe and fourteen percent are for non-plumbing systems including refrigerant systems, heat pumps, and service laterals. The annual breakup of failure reports for different pipe sizes in shown in Table B-1.3 (*Appendix B-1*).

Source of water

Most of the reported failures are from dwelling units that are having a well water supply with forty-six percent of failures, nineteen percent for Surface/ River/ Lake water supply and thirty-five percent with unknown supply source. The annual breakup of various sources of water supply is included in Table B-1.3 (*Appendix B-1*).

Comments on CDA analysis

To summarize the temporal trends of the failure mechanisms suggest a significant decrease in the failures due to *aggressive water*. Aggressive water is a generic term used by CDA, some of the definitions of aggressive water from CDA reports include, water with higher (> 25 mg/L) carbon dioxide concentration, and / or with high sulfate to bicarbonate ratio and / or high sulfate to chloride ratio. The role of carbon dioxide in copper corrosion is not clearly defined in literature. Some of the failure causes enumerated by CDA do not define a supporting mechanism based on water chemistry; hence a firm opinion on the exact cause of failure cannot be formed. Most often when chloride was cited as the cause of the failure, the source of chloride was identified as the soldering flux or disinfectants, although the CDA reports do not explain the possible reaction or kinetics that could have been involved in such a reaction. Importantly, the role of chloride ion is questionable with respect to the present understanding of copper pitting, on many instances chloride is identified as a species that initiates pitting (Warraky et al. 2004) while some scientists have reported that chloride inhibits pitting in long term (Edwards et al. 1994). The failure causes were identified based on the failed specimen; however the pipes that did not fail in the same home were not tested for an objective comparison. Hence, any firm conclusion on the causes of failure cannot be made based on the CDA findings. A detailed review of the physical and chemical parameters that influence pitting is provided in chapter-2.

Analysis of the CDA database suggests that majority of the failures are in horizontal cold water pipes that are ½” and ¾” type M or L copper tubes. The data shows majority of failures for homes that have ground water supply.

Spatial patterns of pinhole leaks

Methodology

The spatial distribution of the pinhole leaks is studied using the CDA data base and the Expert Opinion survey. The results of the analysis from the CDA data base and the Expert opinion survey were verified by the Plumber Survey-I. For the present analysis, spatial information about pinhole leak occurrence is obtained from *Expert Opinion Survey* and *CDA database*. Since, the analysis of CDA database was done progressively with time, five years (2000~ 2004) of CDA data is used for this analysis. The objectives behind studying the spatial patterns are to identify hotspots as well as areas that are relatively free of pinhole leak incidents. A weighted count system is used to obtain a preliminary classification on a city and state level. The preliminary classification is then tested for pinhole leak incidents for the areas that do not surface in the preliminary analysis.

The weighted count is assigned by assessing the information parameters provided by that particular database/ survey. Some of the crucial information parameter used for assigning the weighted count are, information related to the location (address), type of dwelling unit, water quality parameters, pipe size, hot or cold water pipe, horizontal or vertical pipe, type of copper pipe (K, L or M), time of installation and time of first leak, any hydraulic parameter (pressure and velocity). Each year of CDA database was treated as a single data set. Since, the CDA reports contain most of the information parameters that identifies each pinhole failure in spatial and temporal terms hence every failure report from CDA database was assigned a weight of “1”. For example year 1999 and year 2000 are treated as two different data sets. Also, if a city appears more than once in a particular year, it is counted that many times because each data point in CDA corresponds to a different dwelling unit. The *Expert Opinion Survey*, provided names of the affected communities and states where pinhole leak were reported at least once. Moreover, the survey does not provide specific information parameters that could identify every leak in terms of spatial and temporal coordinates. There was also a chance of multiple references could have been made for a single incident. Hence, a weight of "1" is assigned to any city or state irrespective of the number of times it appears in the survey results.

Results and Discussions

The weighted count analysis was performed for city and state, separately. The top five states with maximum number of counts are California, Maryland, Ohio, Florida and Pennsylvania. Interestingly, five states, namely, Delaware, Louisiana, Mississippi, North Dakota, and New Hampshire do not appear in the preliminary classification. Amongst, the top fifteen heavily populated cities, four cities are absent in the preliminary classification, these cities are Austin (TX), Columbus (OH), Detroit (MI) and Memphis (TN).

Plumber Survey-I

As a verification of the preliminary classification, a telephone survey was conducted by calling plumbers in the nine locations. The description of the Plumber Survey-I is presented in the following section. As mentioned earlier, five states were not referenced in the previous CDA reports namely or from any of the previous expert or initial surveys: Louisiana, Delaware, Mississippi, New Hampshire, and North Dakota. A survey was conducted to confirm whether copper pitting is occurring in these states. Plumbers in the major city of each state were interviewed via telephone. In addition, four of the top fifteen heavily populated cities namely, Austin (TX), Columbus (OH), Detroit (MI) and Memphis (TN) were also included in this survey.

Survey Method

The names, addresses and telephone numbers of the plumbers were selected, randomly from telephone directory yellow pages. The survey was conducted from July 7th 2005 through August 8th 2005. Due to difficulties in contacting plumbers on the phone, the survey was conducted at different times of the day. Despite spreading the call- schedule, the success rate for the survey was fairly low as shown in Table 2. Most calls ended up with no response. The successful calls, that did reach the plumbers, were rather short due to their busy schedules. Because of these reasons, all the questions listed in Table 3 could not be asked to a single plumber, instead the questions were asked in decreasing order of priority. First priority was given to the set of questions that relate to the extent of the pinhole leaks in that particular area. These included questions on the possible causes of the pinhole leaks. Second priority was given to the questions related to the cost of repair, cost of re- plumbing, and questions related to the process of repair and pipe materials.

Survey Results

A total of two hundred forty-two calls were attempted, and fifty-five calls were successful (22% success rate). Out of fifty-five plumbers surveyed, twenty-two responded with a definite yes about the existence of the pinhole leaks, twenty-five stated that it is not a common problem, and eight stated that the problem does not exist. The city-wise results from the survey about the extent of pinhole leaks are tabulated in Table 2. There were several factors enumerated by the plumbers that could lead to pinhole leaks (Table 4).

All of the plumbers stated that they do the repairs on an hourly basis, with the material cost added to the labor cost. They also stated that fixing the dry wall is not a part of the plumbing job and the homeowner has to engage a separate general contractor for drywall fixing and finishing. The labor rate for repair jobs varied from city to city, generally the labor rate for the repairs varies between \$ 45 and \$ 75 (Table 5). Data regarding the cost of a complete re-plumbing was obtained for only two of the cities. The cost of re-plumbing for a two bath, two story house in Austin (TX) varied between \$ 2500 ~ \$ 3500, while in Columbus (OH) the cost of re plumb varied between \$ 3000 ~ \$ 4000. Most of the plumbers in other cities either refused to give prices on phone or they expressed their inability to answer questions related to costs.

Comments on Plumber-I survey

Although, these cities/ states were not referenced by any of the sources used for preliminary spatial classification, but the survey results have verified the occurrence of pinhole leaks by at least one plumber in all these areas except Detroit. However, in an earlier survey of plumbers by Dr Marc Edwards, the plumbers in Detroit had reported pinhole leaks. Hence, the discrepancy in the present results may be due to small sample of plumbers considered during the survey. Among the causes enumerated by the plumbers, the most cited reasons include the age of the plumbing, intrusions in pipe, well water and soldering flux. Interestingly, the first three causes (namely, Age of the pipe, Intrusions or weak spots inside pipes and well water) have never been cited in the CDA database.

Based on the plumber survey, it is established that even the locations that are not cited by the Experts and the CDA database, have been confirmed for pinhole incident by at least one plumber. Interestingly, there is no leak incident reported from Delaware in the entire 38 years period (1966~ 2004), however, 7 out of 9 plumbers in Wilmington confirmed the pinhole leak incidents in the city. Hence, it is concluded that the pinhole leak is a wide spread problem and even with the best available resources the spread of pinhole leak could not be ascertained.

The spatial patterns based on the CDA reports are shown in Figure 1, in the beginning of the chapter. Additional data for 1998 and 1999 was added to create Figure 1. Certain hot spots emerge very clearly from Figure 1, these include communities in Ohio and Florida and certain parts of California. Although, the data used for the creation of Figure 1 is not complete representative of the spatial spread of pinhole leaks, but even with the limited data, the spread of the pinhole leak is evident on a nationwide scale.

Table 2 City wise results from Plumber's Survey about the extent of pinhole leaks

S.no	**City**	**State**	**Total # of calls made**	**Total # of successful calls**	**# of response on Pinhole Leaks**		
					Yes	**Not a common problem**	**No**
1	Austin	TX	30	4	1	3	0
2	Columbus	OH	23	6	2	4	0
3	Detroit	MI	25	6	0	1	5
4	Memphis	TN	35	4	1	2	1
5	New Orleans	LA	36	6	1	4	1
6	Wilmington	DE	24	9	7	2	0
7	Jackson	MS	33	5	1	4	0
8	Manchester	NH	17	7	6	1	0
9	Bismarck	ND	19	8	2	5	1

Table 3 List of questions for the Plumber Survey

Questions	**Remarks**
Do you have pinhole leaks in copper plumbing in your area?	Priority-1
How often do you get complaints of pinhole leaks? Is it a common problem?	Priority-1
By your experience what are the factors that cause pinhole leaks?	Priority-1
How much does it costs to repair a pinhole leak?	Priority-2
What is the cost of re plumbing a 2 BR, two storey house with 2 bathrooms?	Priority-2
Is the dry wall removal & fixing cost included in the above costs?	Priority-2
Do you remove the old pipes or leave them in place when you re plumb a house?	Priority-2
By your experience which pipe material works out best for the home plumbing system?	Priority-2

Table 4 Causes of pinhole leaks enumerated by plumbers

S no	**Causes as enumerated by the Plumbers**	**Number of plumbers that cited this reason.**	**Rank**
A	Age of the pipe [1]	9	1
B	Intrusion or weak spots inside copper pipe[2]	5	2
C	Well water (having more minerals like iron etc)	5	2
D	Flux in soldering that induces leak near joints	4	3
E	Hardness of water [3]	3	4
F	Acidic water (with low pH)	3	4
G	Water quality (did not specifically elaborate)	3	4
H	Poor workmanship at the time of installation	3	4
I	Poor quality pipes imported from various countries	2	5
J	Electrical earthing or grounding of electrical circuits	2	5
K	Lightning due to thunder storm or bad weather	2	5
L	Due to water treatment system that people use at home. (Reverse osmosis (RO) system takes out the minerals so water eats through copper)	2	5
M	New homes (within one or two years of installation)	2	5
N	Turbulence in flow	1	6
O	Any metal in contact with copper [4]	1	6
P	Vibrations due to improper clamping	1	6
Q	Thickness of pipe (thin pipes M-type copper are more prone to leaks)	1	6
R	Due to change in material properties due to bending of the pipes (elbows are more prone to leaks)	1	6
S	Erosion / corrosion in straight portion of pipes	1	6
T	Chemical reaction between copper and water	1	6
U	Electrolysis in water	1	6
V	Mechanical damage (probably this person never distinguished between a normal damage and a pinhole leak)	1	6
W	Joint failure due to seasonal changes in temperature	1	6

[1] 15 years or older

[2] manufacturing defects in the pipes

[3] use water softeners to eliminate this problem

[4] galvanic corrosion

Table 5 Details of the labor rates for repairing pinhole leaks

City	State	Labor rate for repair per hour
Austin	TX	$ 50 ~$ 60
Columbus	OH	$ 55 ~$ 60
Detroit	MI	$ 55 ~$ 60
Memphis	TN	~ $ 50
New Orleans	LA	na [1]
Wilmington	DE	$ 65 ~$ 75
Jackson	MS	$75
Manchester	NH	na [1]
Bismarck	ND	$ 45 ~$ 55

[1] inability to quote price on phone

Temporal Patterns of pinhole leaks

Methodology

The temporal patterns of pinhole leaks are studied by analysis of the decadal shifts in leak patterns over a thirty year period. The CDA data is used to classify the states based on the number of leak incidents in each decade that were reported to CDA. In order to account for the variability in the population density of different states, the classification is done based on number of housing units. The statewide information for number of housing units is obtained from US Census bureau http://www.census.gov/. Using the following information, a leak index is developed for each state. The leak index is used as the basis of classification.

Leak Index is defined as

I = Number of leaks per million housing units per 10 year period.

Results

For every decade, the Leak Index is calculated, based on the total leak incidences reported to CDA in that decade and the number of housing units corresponding to that decade.

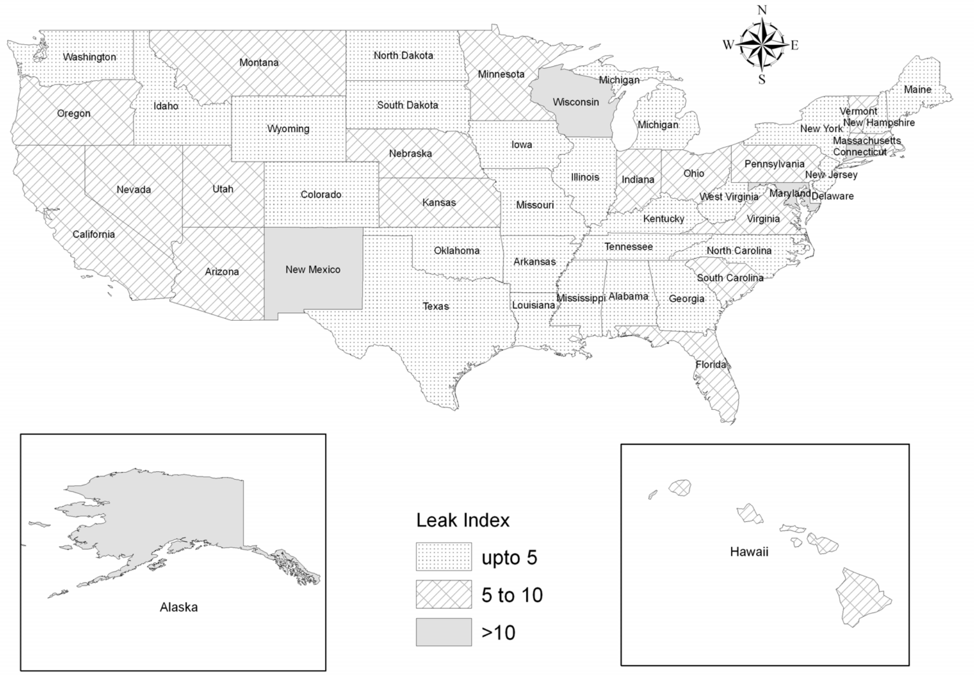
The decades are considered in reverse chronological order for the analysis. These are namely, first decade (1995~2004), second decade (1985~1994) and third decade (1975~1984). An increase or decrease in the "Leak Index" is considered as an indicator of the shift in trend of pinhole leaks in that state. The classification based on the leak index for the three decades is presented in Figure 7 through 9. The temporal shifts in leak patterns between the decades are presented in Figure 10 and 11. The results of the analysis are presented in Table 6.

Table 6 Analysis for decadal patterns of pinhole leaks, based on CDA data (1975~2004)

	Leak Index = Total Leaks per million housing units			Trend based on change in Leaks Index	
States	**Decade 1 (1995~2004)**	**Decade 2 (1985~1994)**	**Decade 3 (1975~1984)**	**Decade 1~2**	**Decade 1~3**
Alaska	15.07	12.90	6.14	Increase	Increase
Alabama	3.47	2.39	2.73	Increase	Increase
Arkansas	4.16	2.00	1.11	Increase	Increase
Arizona	7.30	13.26	16.22	Decrease	Decrease
California	7.68	5.81	6.47	Increase	Increase
Colorado	3.11	7.45	25.12	Decrease	Decrease
Connecticut	15.68	1.51	1.73	Increase	Increase
Delaware	0.00	0.00	0.00	No change	No change
Florida	5.12	6.72	5.02	Decrease	Increase
Georgia	2.01	1.14	3.94	Increase	Decrease
Hawaii	6.38	28.22	2.99	Decrease	Increase
Iowa	3.18	1.75	6.19	Increase	Decrease
Idaho	1.81	4.84	10.66	Decrease	Decrease
Illinois	2.01	2.88	1.62	Decrease	Increase
Indiana	9.18	2.23	0.96	Increase	Increase
Kansas	5.18	2.87	2.09	Increase	Increase
Kentucky	3.90	0.00	0.00	Increase	Increase
Louisiana	0.53	0.58	1.29	Decrease	Decrease
Massachusetts	6.79	5.26	4.08	Increase	Increase
Maryland	17.30	2.11	3.82	Increase	Increase
Maine	1.50	0.00	1.99	Increase	Decrease
Michigan	1.62	1.56	0.56	Increase	Increase
Minnesota	5.16	3.25	3.72	Increase	Increase
Missouri	3.60	0.91	1.01	Increase	Increase
Mississippi	0.00	0.00	0.00	No change	No change

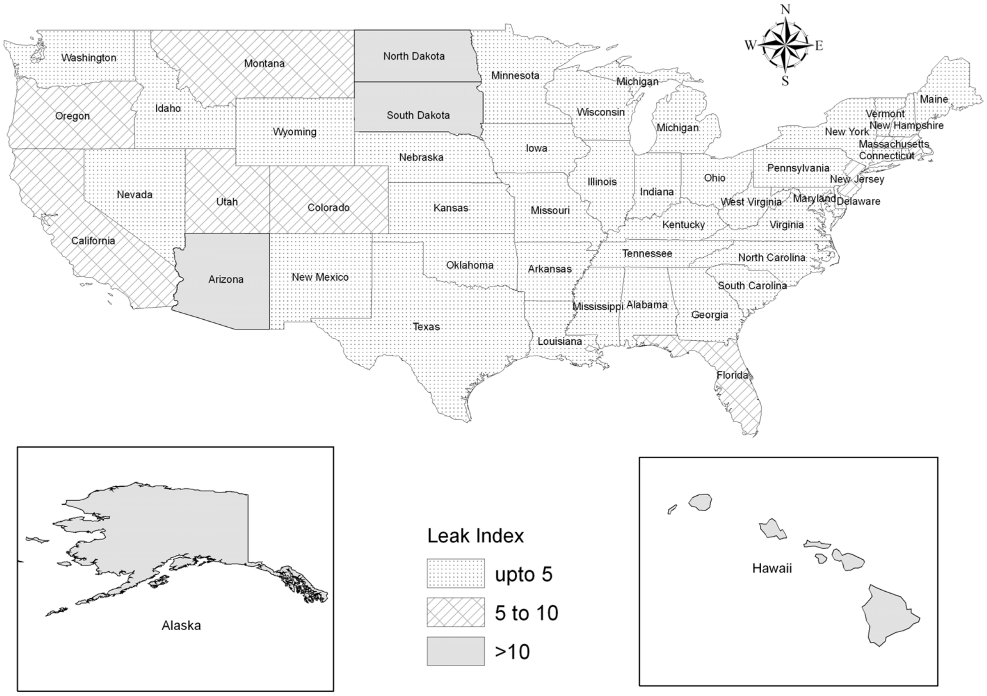
Table 6 Analysis for decadal patterns of pinhole leaks, based on CDA data (1975~2004)

	Leak Index = Total Leaks per million housing units			Trend based on change in Leaks Index	
States	**Decade 1 (1995~2004)**	**Decade 2 (1985~1994)**	**Decade 3 (1975~1984)**	**Decade 1~2**	**Decade 1~3**
Montana	7.19	5.54	18.27	Increase	Decrease
North Carolina	1.62	0.35	0.44	Increase	Increase
North Dakota	0.00	18.09	15.46	Decrease	Decrease
Nebraska	8.12	0.00	16.00	Increase	Decrease
New Hampshire	0.00	0.00	7.76	No change	Decrease
New Jersey	4.45	5.20	5.41	Decrease	Decrease
New Mexico	11.18	4.75	19.69	Increase	Decrease
Nevada	8.87	3.85	5.88	Increase	Increase
New York	2.84	3.18	1.75	Decrease	Increase
Ohio	7.79	1.60	3.89	Increase	Increase
Oklahoma	3.24	0.71	3.23	Increase	Increase
Oregon	6.02	5.86	0.00	Increase	Increase
Pennsylvania	8.82	2.03	1.96	Increase	Increase
Rhode Island	4.51	4.82	0.00	Decrease	Increase
South Carolina	5.48	0.00	0.87	Increase	Increase
South Dakota	3.01	13.68	3.61	Decrease	Decrease
Tennessee	0.40	1.48	1.72	Decrease	Decrease
Texas	2.47	1.43	3.97	Increase	Decrease
Utah	9.89	8.36	67.35	Increase	Decrease
Virginia	5.32	2.40	1.48	Increase	Increase
Vermont	6.68	0.00	0.00	Increase	Increase
Washington	3.56	0.98	0.59	Increase	Increase
Wisconsin	12.15	1.95	3.22	Increase	Increase
West Virginia	2.35	0.00	0.00	Increase	Increase
Wyoming	0.00	0.00	10.63	No change	Decrease
District of Columbia	7.34	3.59	10.82	Increase	Decrease
US (Total)	**5.15**	**3.28**	**4.12**	**Increase**	**Increase**



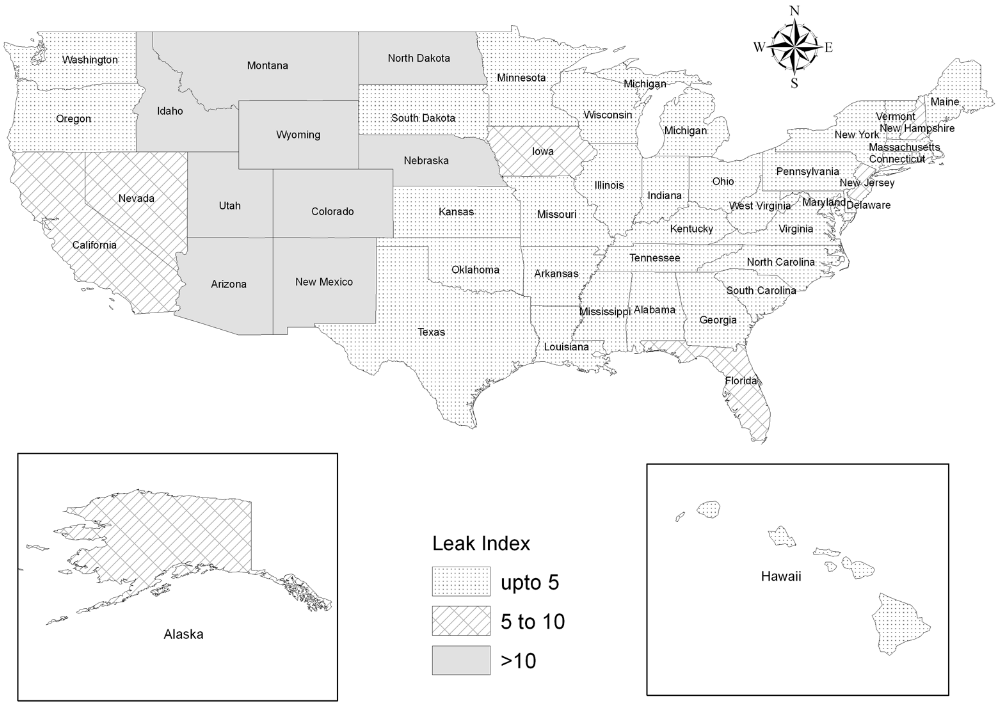
Based on number of pinhole leaks per million housing units

Figure 7 A three tier nationwide classification based on CDA reports (1995~2004)



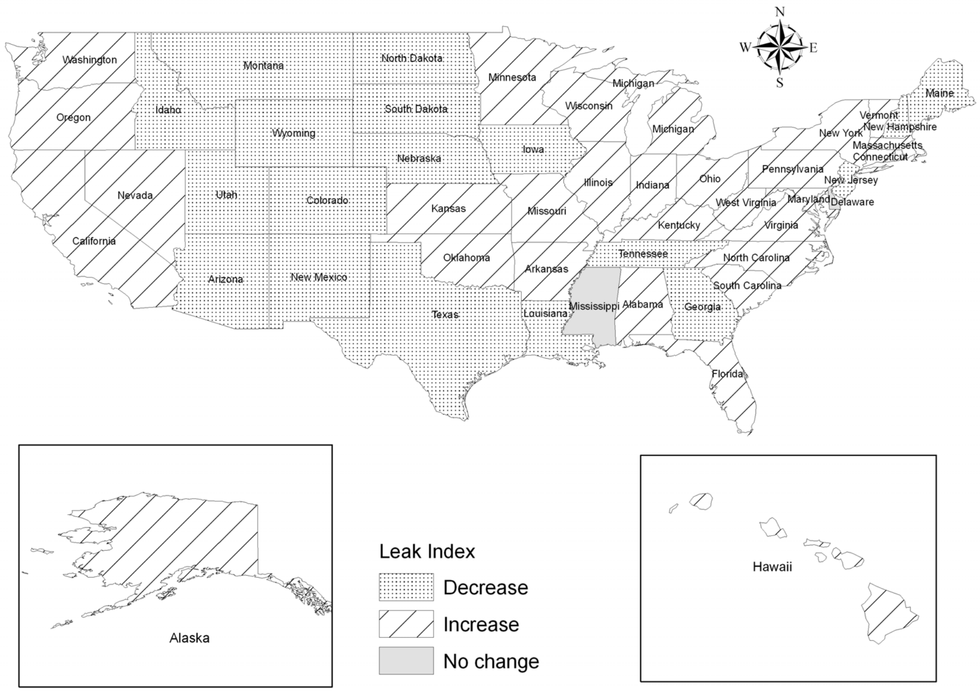
Based on number of pinhole leaks per million housing units

Figure 8 A three tier nationwide classification based on CDA reports (1985~1994)



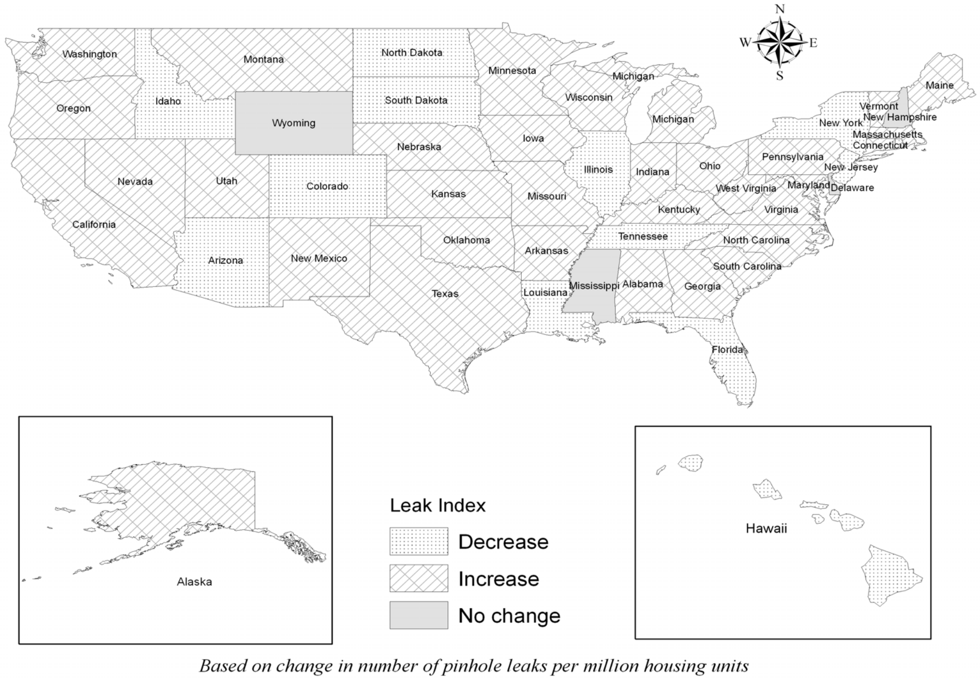
Based on number of pinhole leaks per million housing units

Figure 9 A three tier nationwide classification based on CDA reports (1975~1984)



Based on change in number of pinhole leaks per million housing units

Figure 10 Spatial shift of leak patterns between (1995~2004) and (1975~1984)



Based on change in number of pinhole leaks per million housing units

Figure 11 Spatial shift of leak patterns between (1995~2004) and (1985~1994)

Conclusions

Based on the leak index the states namely, Arizona, Colorado, Idaho, Louisiana, North Dakota, New Jersey, South Dakota and Tennessee show a decreasing trend between first and second decade and also between first and third decade. The states that do not show any change in the leak index in all the three decades are Delaware and Mississippi; it is because these states do not contain any report in the CDA database. Interestingly, the total US figures show an increasing trend over the three decades consistently.

Maryland, California and Ohio show increasing trend, which is in agreement with the present information on certain hotspots in these states. Interestingly, Florida shows a decreasing trend when compared with the previous decade (1985~1994), although there have been many leak incidents in one community in the present decade (1995~2004) and it has emerged as a hotspot for pinhole leaks. Overall, considering the 30 years span of failures, copper has been a relatively good plumbing material, except in a few hot spots that have experienced a high frequency of failures. It has been either determined or assumed that a particular mechanism has caused or is causing the premature copper failures. Factors that can lead to potentially aggressive copper corrosion are discussed in the next chapter.

The present analysis shows some states with no change in leak incidents, it is primarily due to absence of reported failures from these states. Because of this reason, the calculated *leak index* is zero (Table 6). Since, the CDA reports are based on voluntary submission of failed samples, the leak index based analysis remains inconclusive. The results should be treated as preliminary. The actual spatial shift in patterns with time cannot be established based on CDA database alone even though that is the well documented one.

Factors Determining Copper Pipe Selection

There are numerous factors that influence consumer’s decision in selection of a particular pipe material. These factors encompass a spectrum of issues including durability, affordability, resistance to corrosion, performance (taste, odor and color), safety against possible health hazards, fire resistance, serviceability during extreme weather conditions, cost, added value to house/ dwelling unit, willingness to pay, willingness to take risk, magnitude and type of risk, consumers’ perception, past experience, loss of revenue (for commercial) and to some extent the local regulations and neighborhood’s experience. For instance the use of PEX pipe is banned in certain areas of California, although its use is approved in all the other 49 states, like wise in some parts of Florida, the use of copper pipe is less preferred due to acuteness of pinhole leak problems.

From manufacturing perspective, the characteristics that are generally desirable in the raw materials are ductility and malleability. Since most of the metals and plastics (including modified polymers) are intrinsically ductile and malleable, plumbing pipes are generally manufactured out of metal, metal alloys and plastics. In general the options available to the consumer in terms of pipe materials include Galvanized iron, Copper, Plastics (CPVC, PVC, PEX, Polybutylene) and Stainless steel. Galvanized iron pipes are still used but their use is not very frequent especially in residential establishments (http://www.nsf.org/consumer/plumbing/index.asp). The major concern with galvanized iron includes build up of rust over a period of time. The rusting inside the galvanized iron pipe may cause loss of hydraulic conductivity and may leach rust particles in water causing *red water* problems.

PVC and CPVC are cost effective options however, PVC pipes tend to be more brittle and often crack when exposed to weather; due to this CPVC is often a chosen over PVC. CPVC pipes are corrosion resistant and can withstand high pressures, and due to their ease in installation they are often preferred by plumbers. The concerns with CPVC pipe include microbial growth, cracking in the event of an earthquake, plastic taste and melting in the event of fire. The solvents used for joining these pipes may leach volatile organic compounds (VOCs). Additional concerns with CPVC include leaching of vinyl chloride monomer (VCM), the extended exposure to VCM can lead to neurological and liver disorders as well as cancer. The health issues related to CPVC pipes are subjected to controversies (http://www.builderswebsource.com/techbriefs/cpvccopper.htm#Benefits%20CPVC). It is important to note that the magnitude of potential risk associated with the leaching of VCM (in CPVC pipes) is not known hence the issues related to health concerns remain questionable. Additionally, PVC and CPVC pipe are approved for use in United States, and these pipes comply with NSF/ ANSI health requirements. The plastic pipes for potable water supply, bear "NSF-PW" or "NS-61" mark, which shows that the product complies with the health requirements set by NSF/ ANSI. (http://www.nsf.org/consumer/plumbing/index.asp). The PVC and CPVC pipes are tested twice annually in accordance with NSF standards to ensure that the VCM level remains below the maximum allowable limits, also the products with "NSF-PW" mark are tested at regular interval to ensure compliance for all other properties including properties related to health. (http://www.builderswebsource.com/techbriefs/cpvccopper.htm#Introduction).

PEX (polyethylene cross linked) pipes are flexible pipes (like electrical cables), these pipes require different plumbing design altogether, instead of a branch and main arrangement, these pipes require individual pipe lengths for every fixture which is connected to a common manifold. This design increases the number of pipes and the total pipe length required for a house. But due to lower unit price the overall cost almost equals the cost of plumbing with any other plastic pipe. The main advantage is that each pipe is *free of joints* and therefore less prone to any kind of leak. PEX pipes are also available in form for a composite pipe material, where a layer of aluminum is sandwiched between two layers of PEX (polyethylene cross linked) material. The use of PEX is banned in some parts of California due to potential risk of leaching MTBE (methyl tertiary butyl ether) and benzene into drinking water, and due to its ability to spread fire rapidly.

(http://www.prnewswire.com/cgi-bin/stories.pl?ACCT=109&STORY=/www/story/11-18-2004/0002464315&EDATE=). However, its use is approved in all other 49 states, and importantly PEX pipes comply with the health requirement set by NSF/ ANSI. The plastic pipes for potable water supply, bear “NSF-PW” or “NS-61” mark, which shows that the product complies with the health requirements set by NSF/ ANSI. (http://www.nsf.org/consumer/plumbing/index.asp).

Polybutylene (PB) is flexible pipe which can be easily bent, cut and easily installed at a lower price. The material was introduced in 1970’s and has been used in about six million homes in United States. (http://accuspec.biz/PB Plumbing.htm). Due to leak problems associated with PB pipes, there have been several lawsuits against the PB manufacturers. The law suit settlement was administered by Consumer Plumbing Recovery Center (CPRC) and some of the consumers were offered a free replacement of the entire plumbing under this settlement. (http://www.pbpipe.com/index1.htm).

Stainless steel pipes are mainly used in industrial applications. Stainless steel provides excellent resistance to corrosion, due to presence of chromium that forms 17~20% of stainless steel. The stainless steel is expensive due to which its use is limited to specialized industries for conveying chemicals or other such applications. The concern with stainless steel pipes include leaching of chromium. However, the stainless steel pipe is approved for use in United States, and complies with NSF/ ANSI health requirements. (http://www.nsf.org/business/newsroom/press_release.asp?p_id=12241).

Copper is the most widely used material in residential and commercial plumbing. The advantages of using copper include affordability, fire resistance, little or no health hazards, and durability. However, due to pinhole leak incidents consumers often prefer plastic pipes over copper. If copper pipes are used in potable waters with lower pH (< 6.5), the problems of copper leaching may increase. The USEPA lead copper rule (1991) regulates the concentration of copper in drinking water to a maximum contaminant limit of 1.3 mg/ L. Additional concerns with copper pipes include metal taste especially with long stagnation periods and increased consumption of residual disinfectant by the pipe walls.

In summary the selection of pipe material is subjective to consumers' perception and choice. In general, for residential establishments, cost, performance (taste, color and odor), resistance to corrosion, affordability, durability, added value to house and health effects are expected to be more dominant among the various factors. For commercial establishments, the decision matrix is expected to be governed by cost and fire resistance as compared to other parameters. The issues related to health are expected to be of lesser importance in case of commercial establishments. Although, the selection of pipe material is highly subjective to ones' preferences and may change from one consumer to another, hence a generic statement for the selection criteria for either residential or commercial establishments cannot be made. Other secondary factors which may influence consumer's decision are consumer's access to information, attractive marketing strategies, special discount offers or purchase incentives and advise from others (plumbers, consultants, architects, neighbors etc). Thus the actual decision matrix of a consumer is complex however it is expected that the decision is likely to be influenced by many of the factors discussed above.

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7. Loganathan G.V., Lee Juneseok, Farooqi Owais, *Plumber Survey-I (2005).*

8. Virginia Tech Survey Research Center, *Plumber Survey-II (2006).*

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9. http://www.toolbase.org
10. http://www.plumbingsupply.com
11. http://copper.org
12. http://www.census.gov
13. http://www.nsf.org
14. http://www.builderswebsource.com
15. http://www.prnewswire.com
16. http://accuspec.biz
17. http://www.pbpipe.com

APPENDIX A-1

Temporal Patterns of Pinhole Leak due to various Corrosion Mechanisms

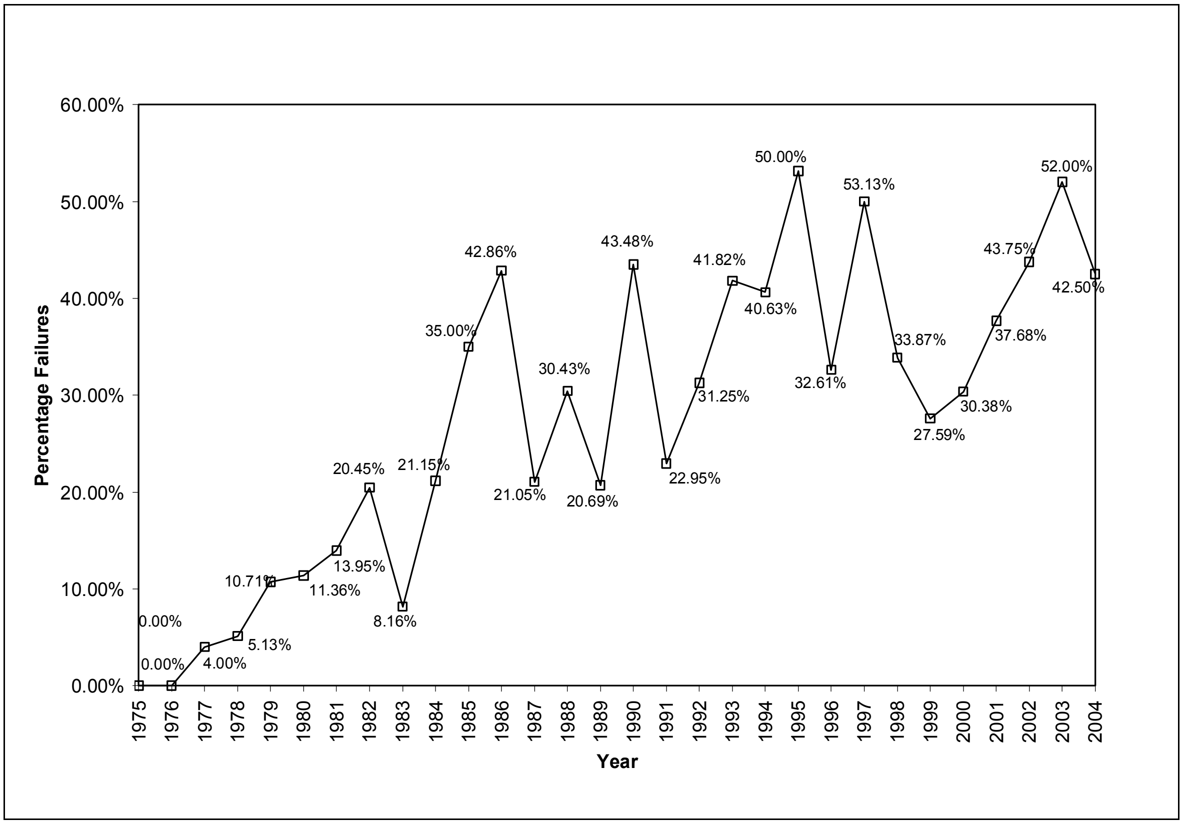

Figure A-1.1 Variation in annual percentage of failures due to Chloride over (1975~2004)

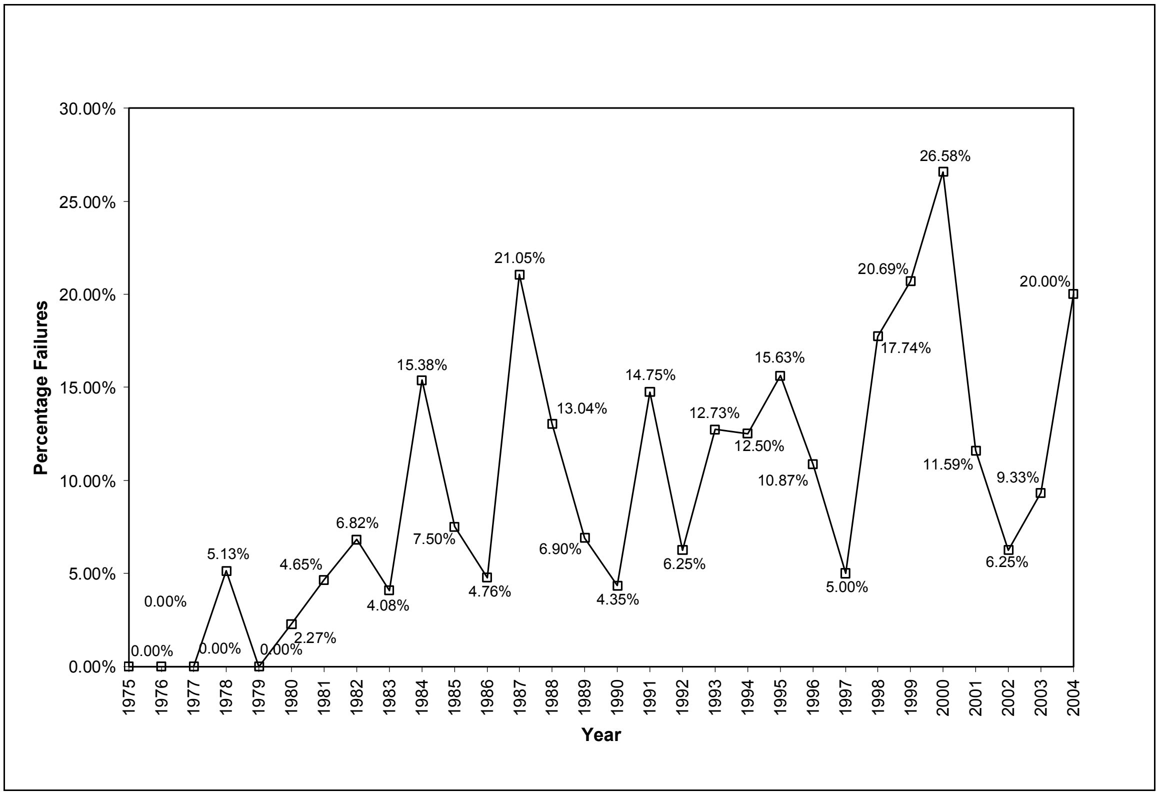

Figure A-1.2 Variation in annual percentage of failures due to Oxygen-Differential over (1975~2004)

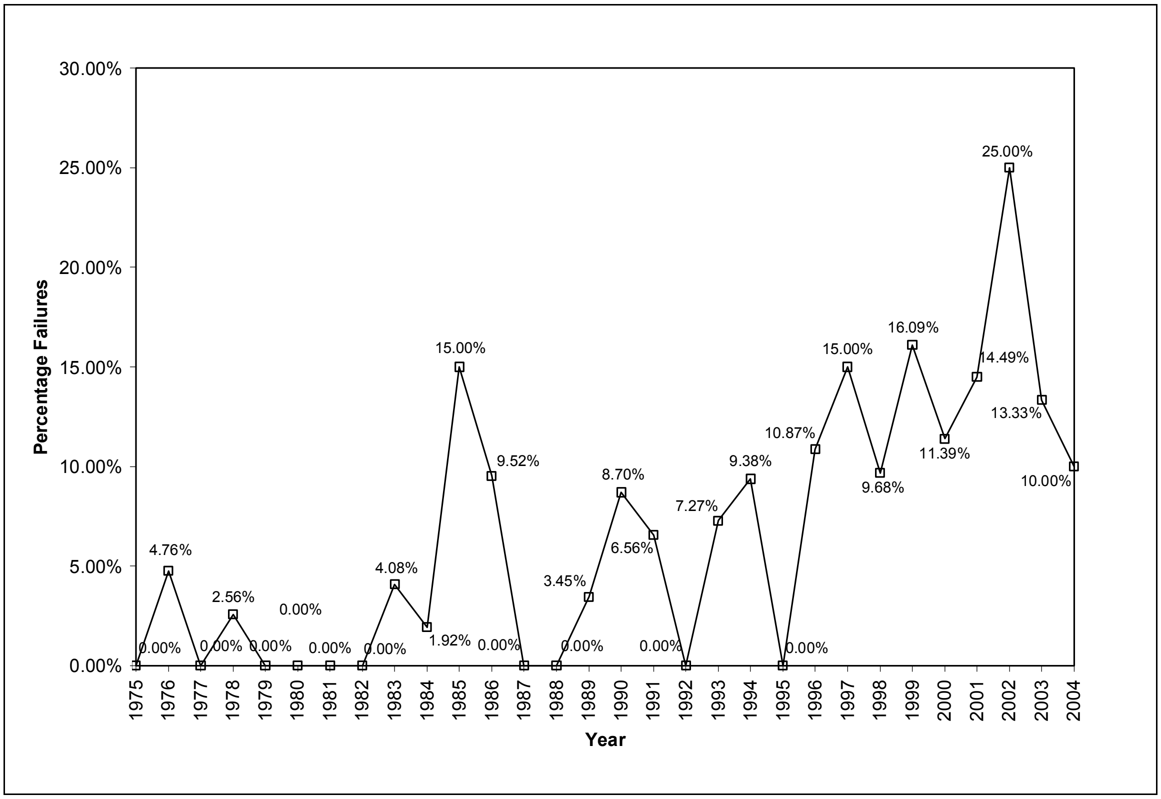

Figure A-1.3 Variation in annual percentage of failures due to *Excessive heating* over (1975~2004)

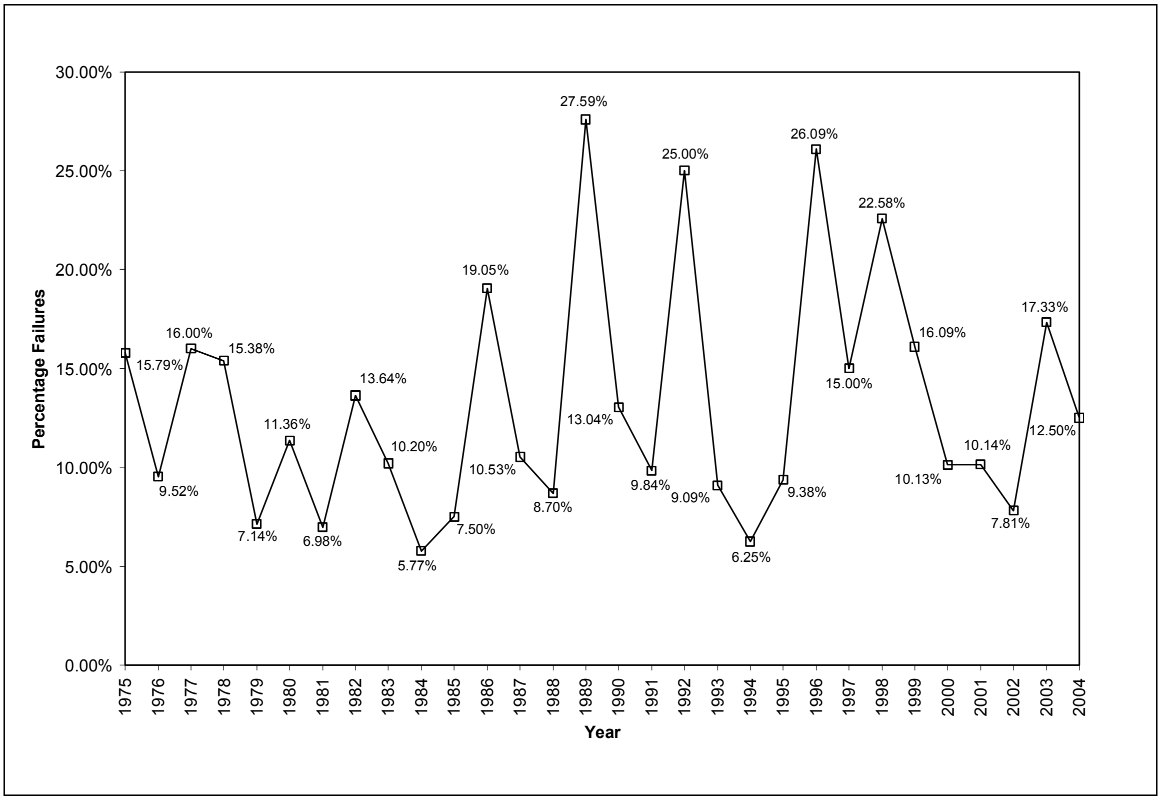

Figure A-1.4 Variation in annual percentage of failures due to External failures over (1975~2004)

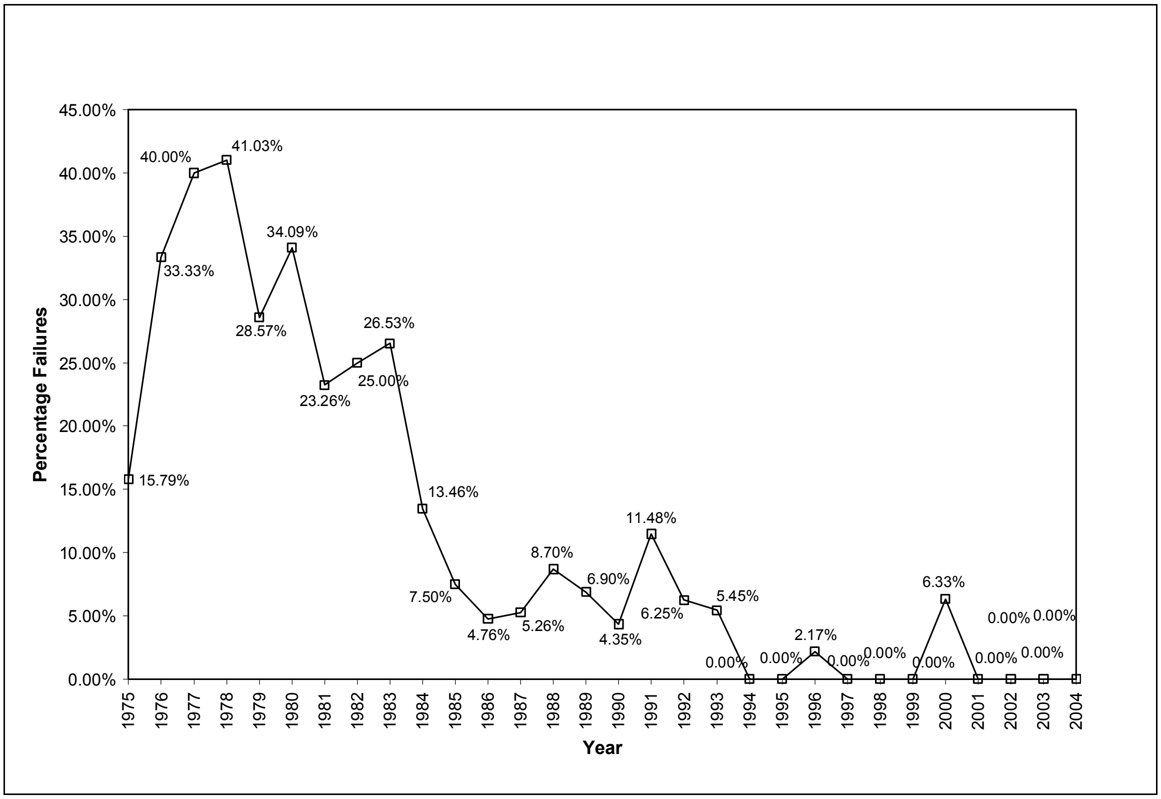

Figure A-1.5 Variation in annual percentage of failures due to *Aggressive water* over (1975~2004)

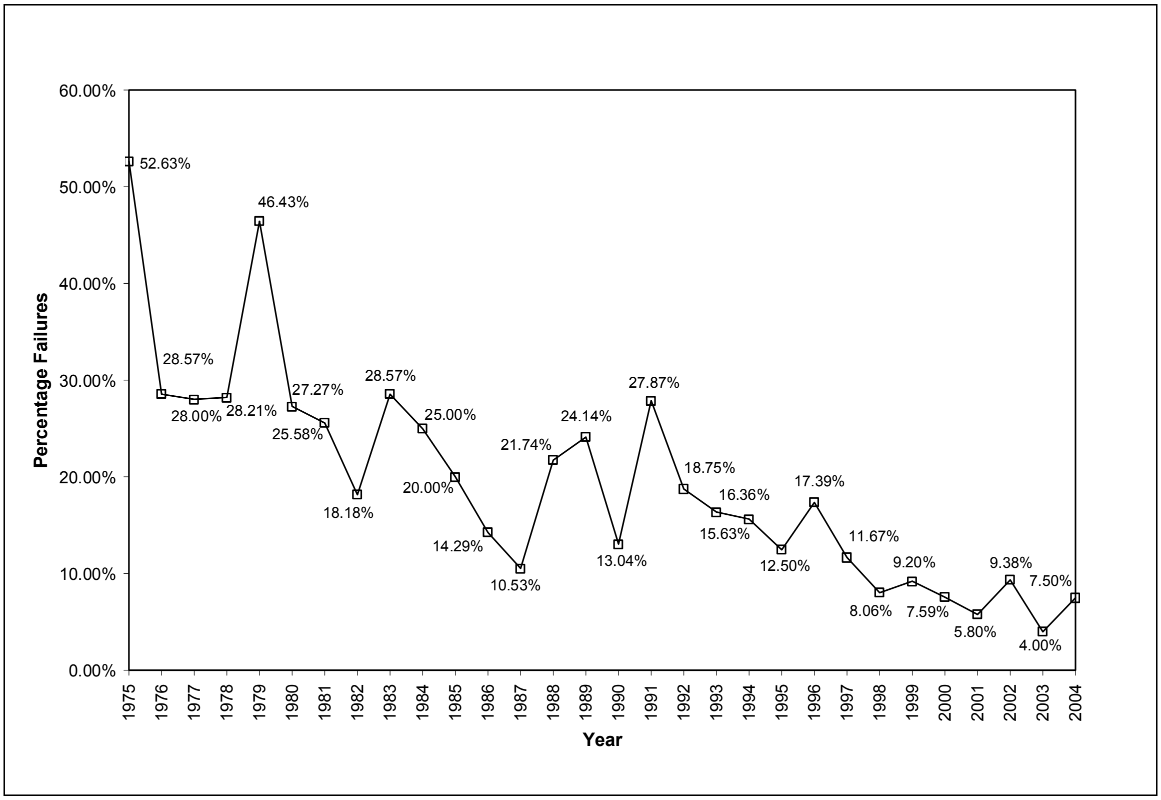

Figure A-1.6 Variation in annual percentage of failures due to Erosion Corrosion over (1975~2004)

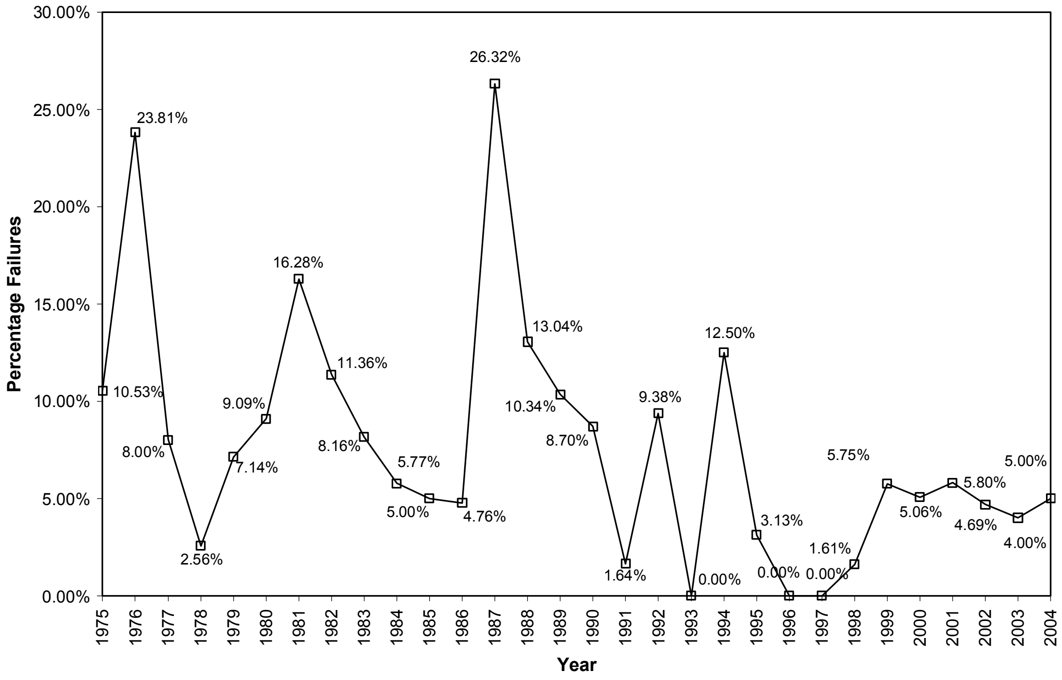

Figure A-1.7 Variation in annual percentage of failures due to No corrosion/ not known over (1975~2004)

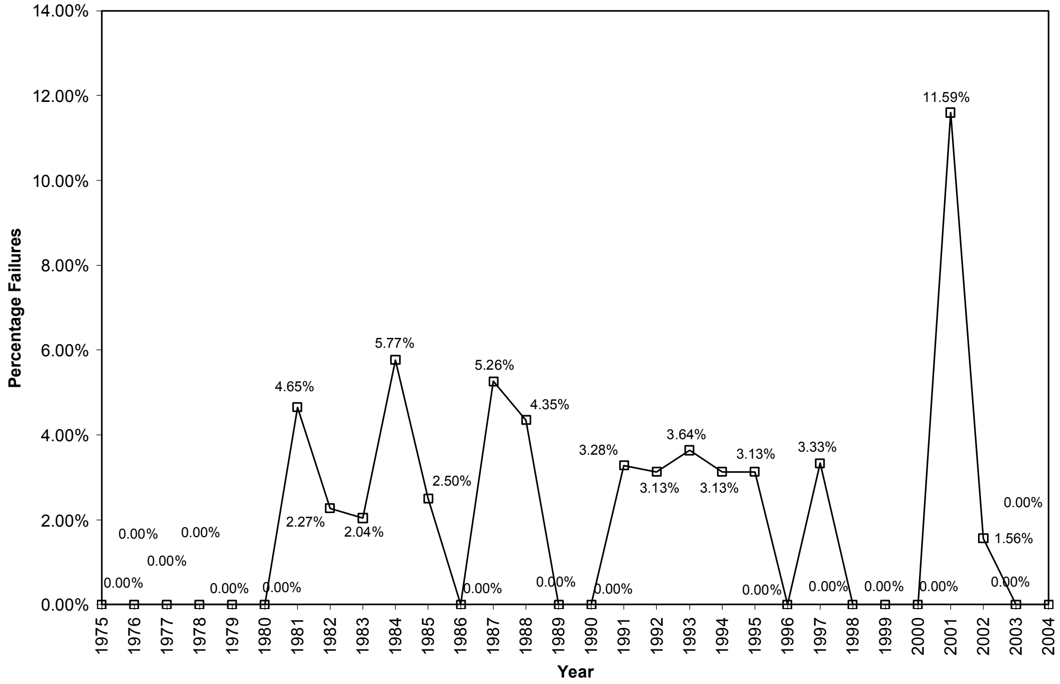

Figure A-1.8 Variation in annual percentage of failures due to Sulfide over (1975~2004)

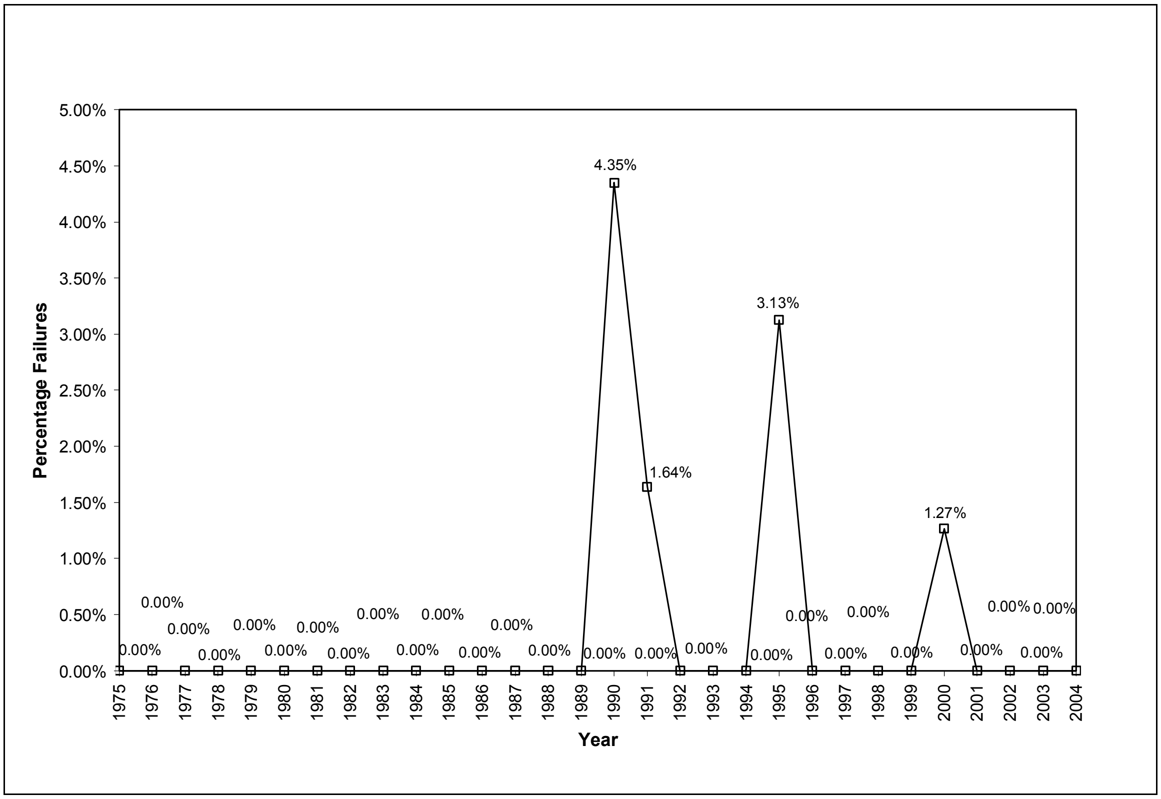

Figure A-1.9 Variation in annual percentage of failures due to *Microbiological* over (1975~2004)

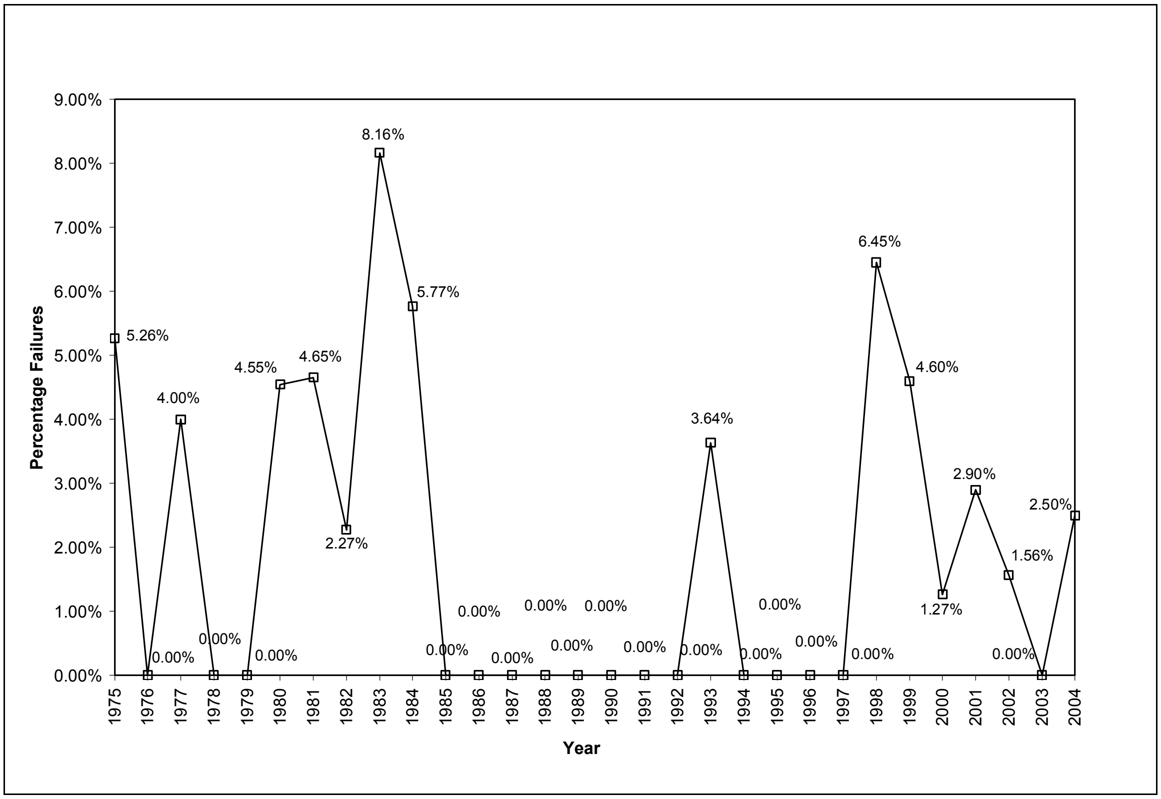

Figure A-1.10 Variation in annual percentage of failures due to Poor workmanship over (1975~2004)

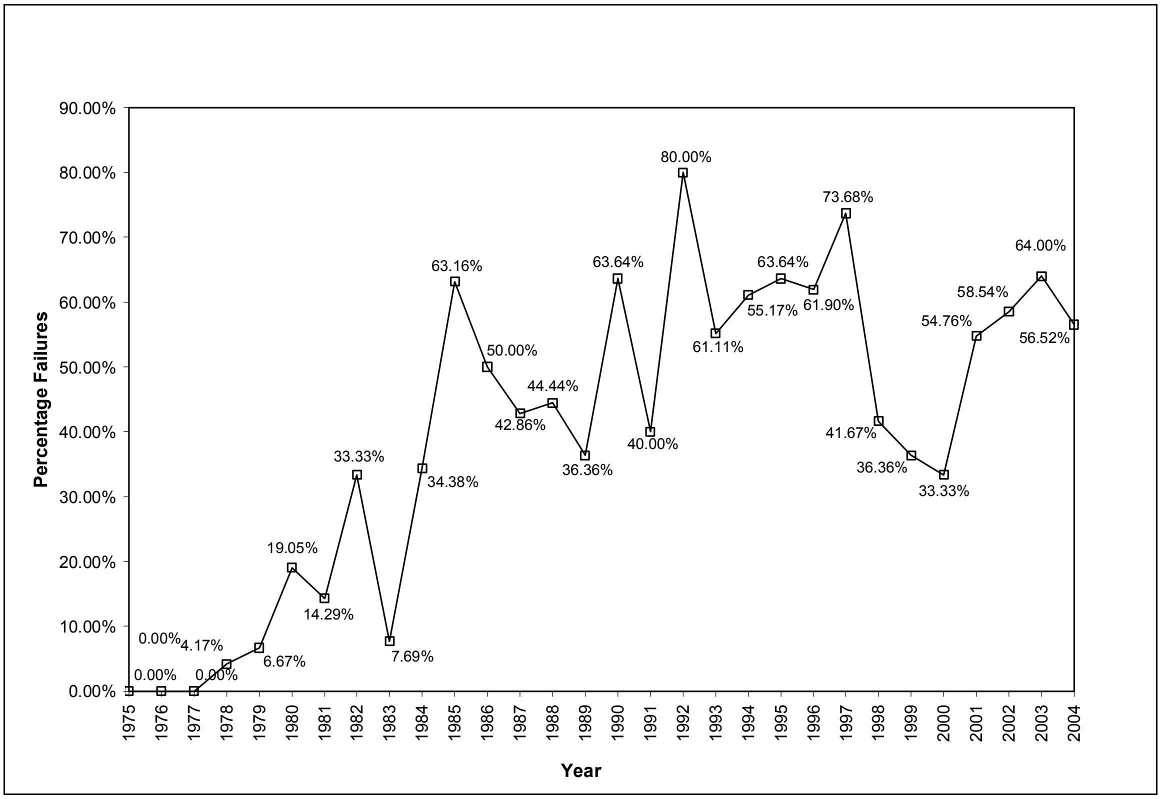

Figure A-1.11 Variation in annual percentage of failures for *cold water category* due to *chloride/ chlorine*

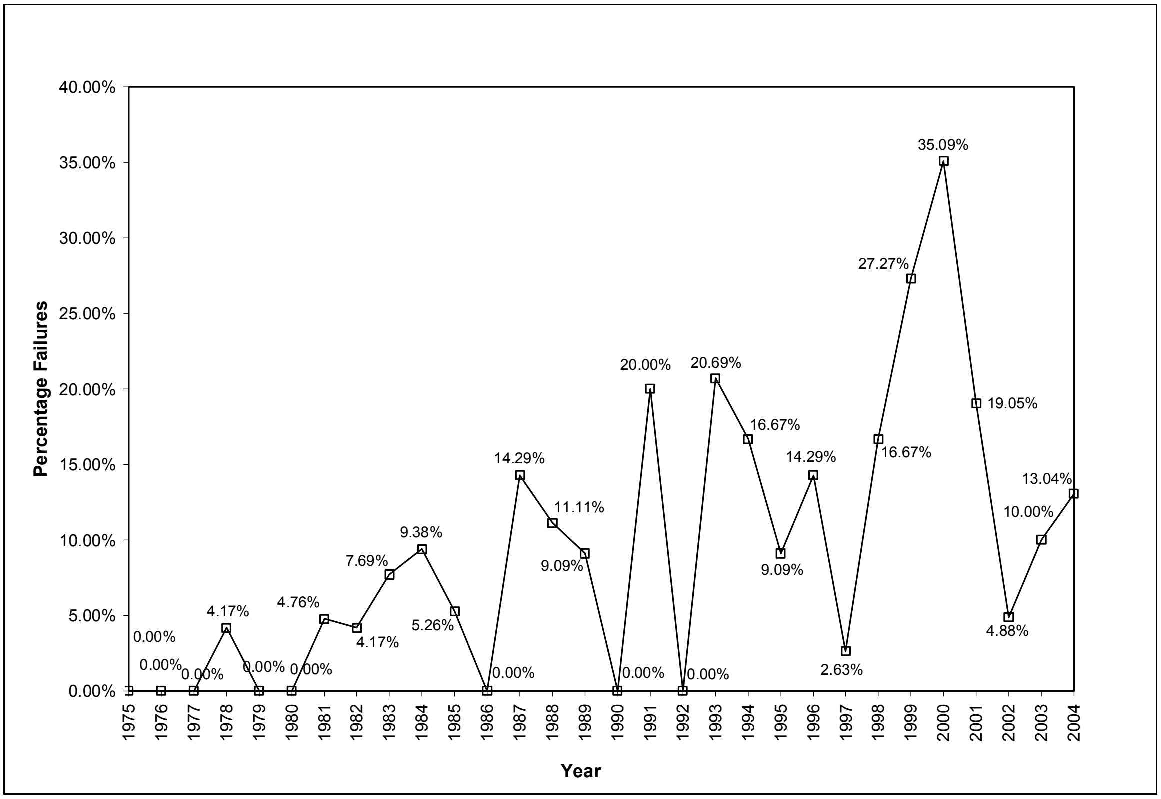

Figure A-1.12 Variation in annual percentage of failures for cold water category due to oxygen-differential

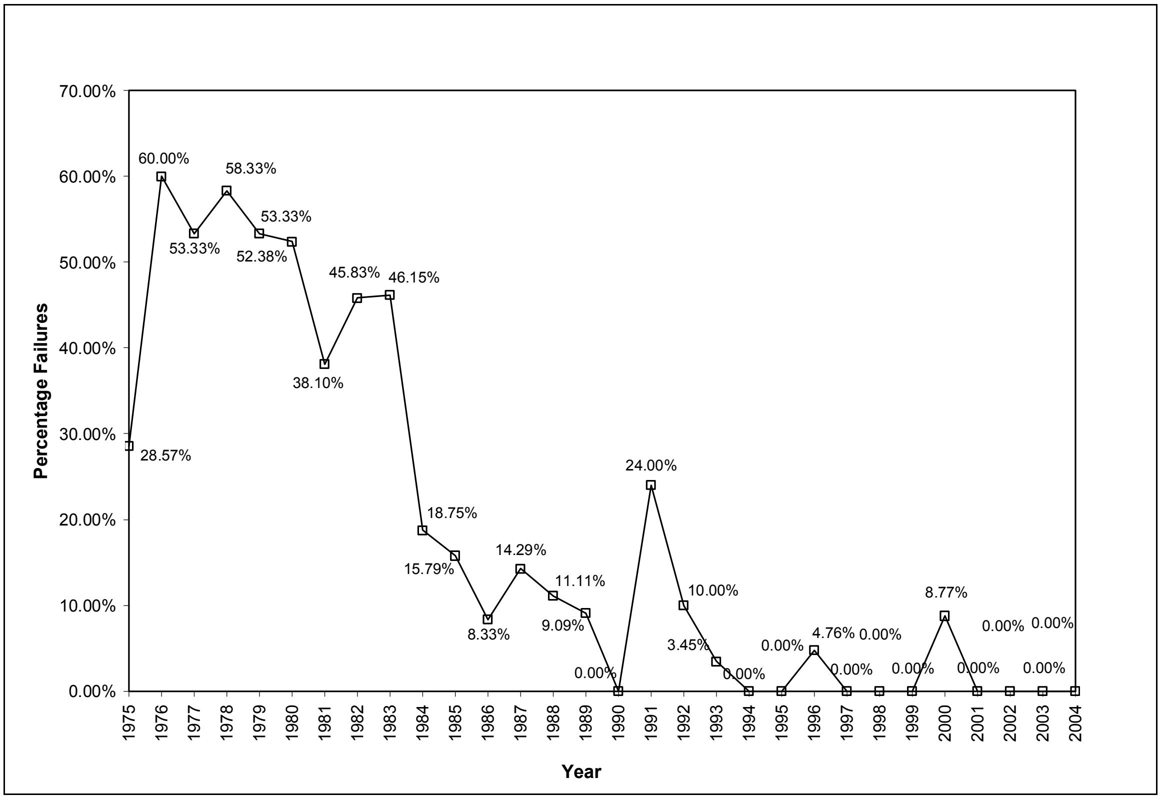

Figure A-1.13 Variation in annual percentage of failures for cold water category due to aggressive water

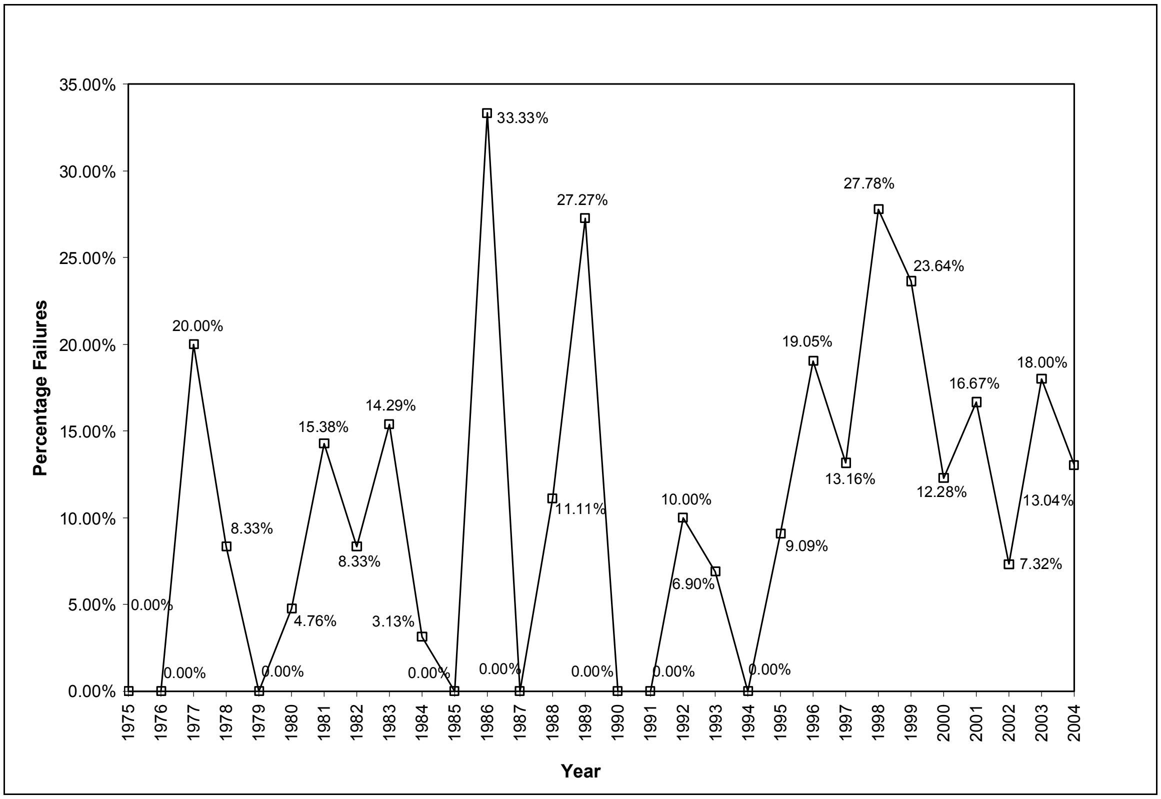

Figure A-1.14 Variation in annual percentage of failures for cold water category due to external failures

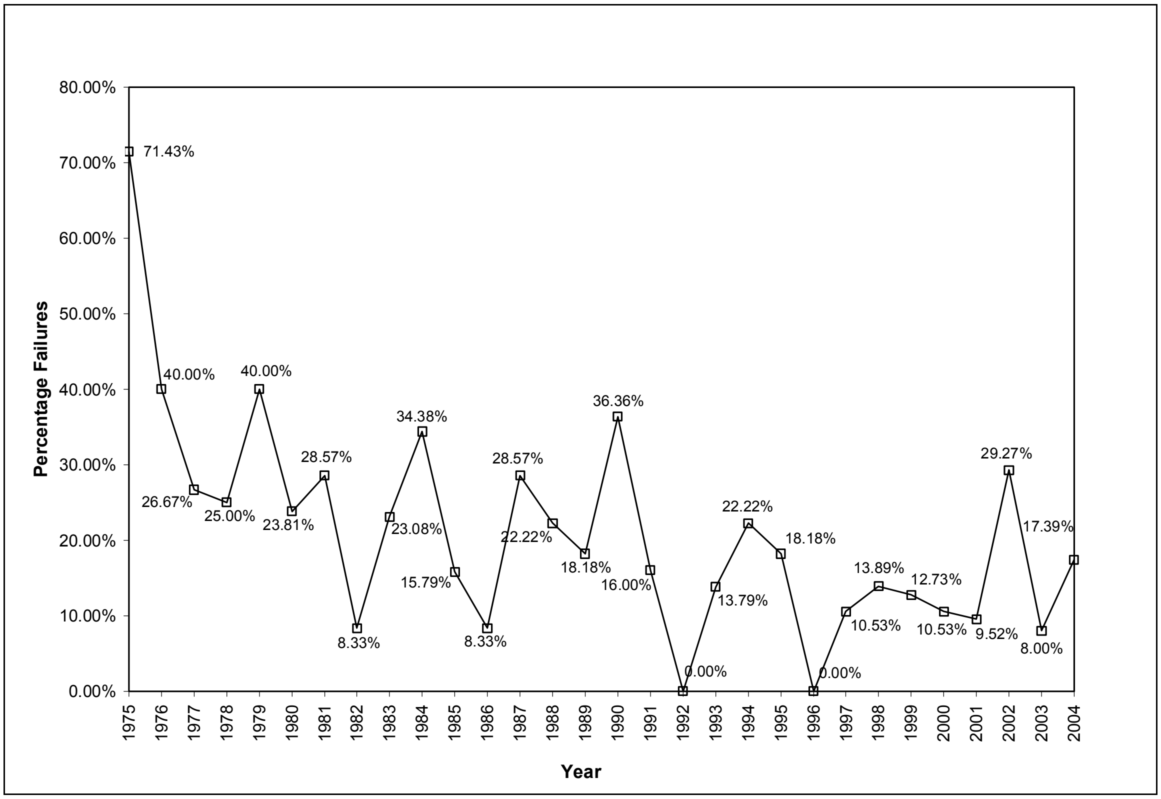

Figure A-1.15 Variation in annual percentage of failures for cold water category due to minor causes

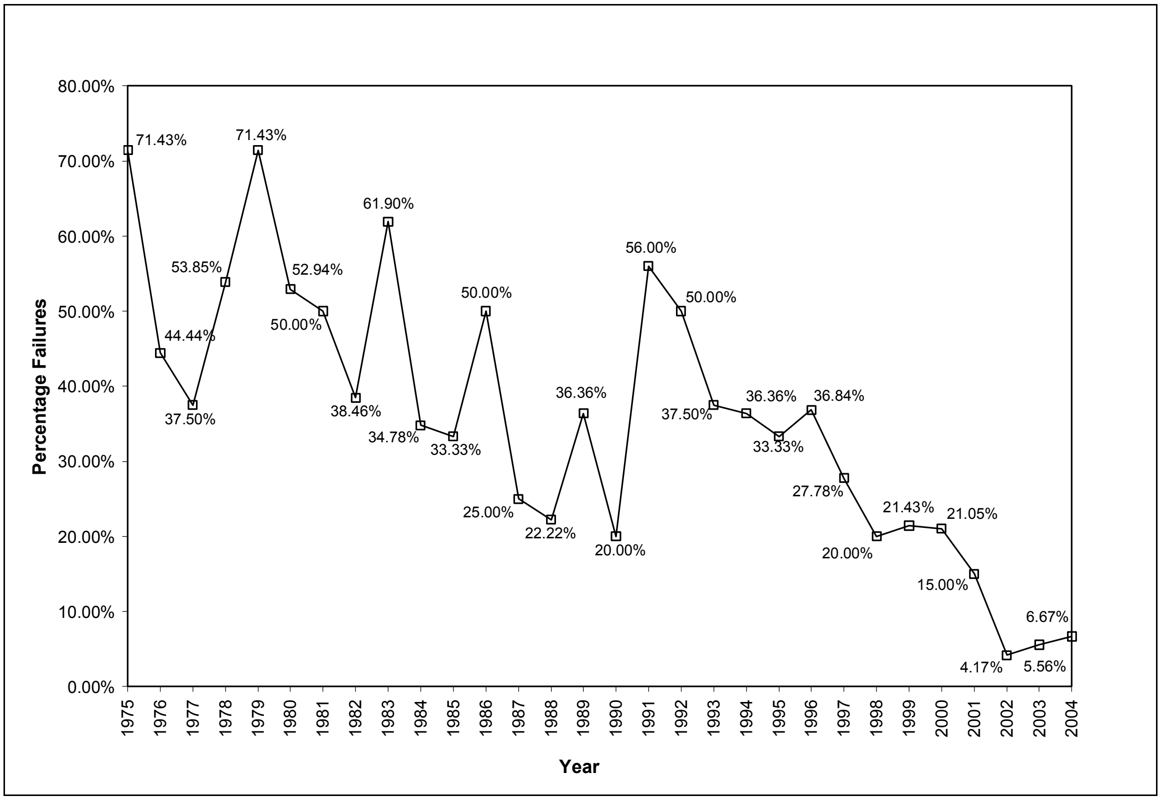

Figure A-1.16 Variation in annual percentage of failures for hot water category due to erosion corrosion

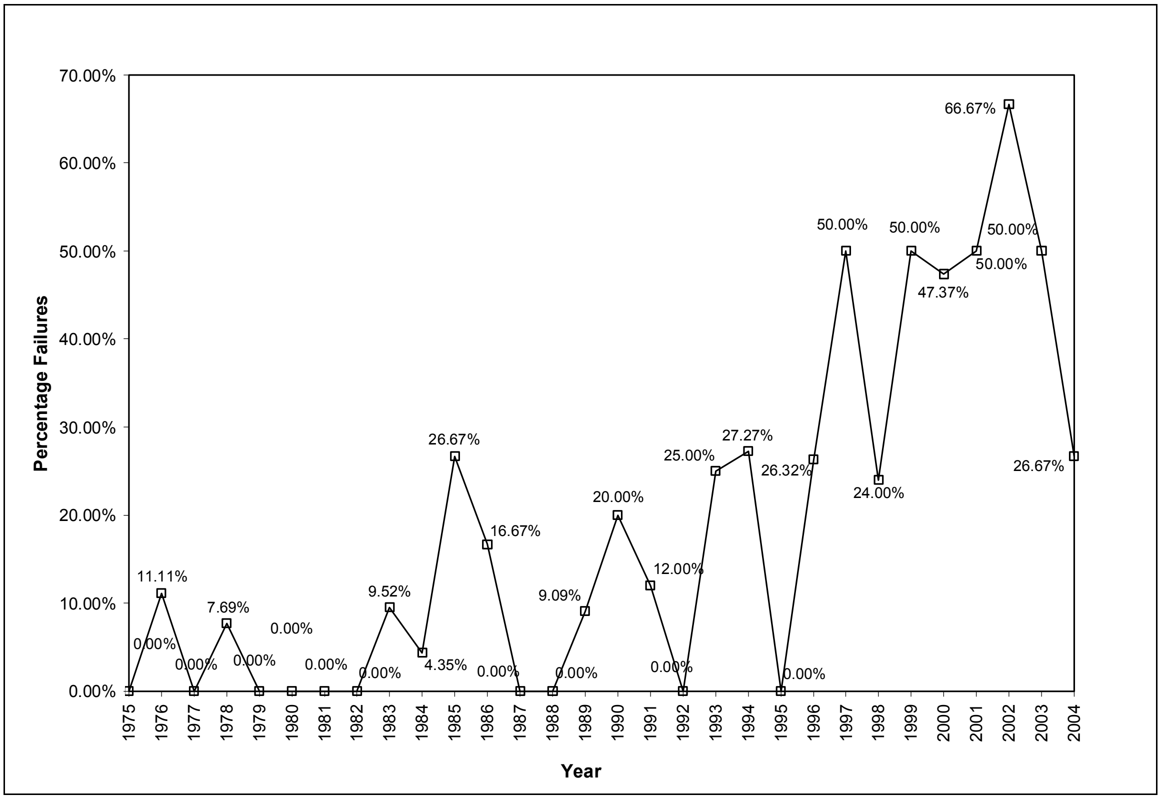

Figure A-1.17 Variation in annual percentage of failures for hot water category due to excessive heating

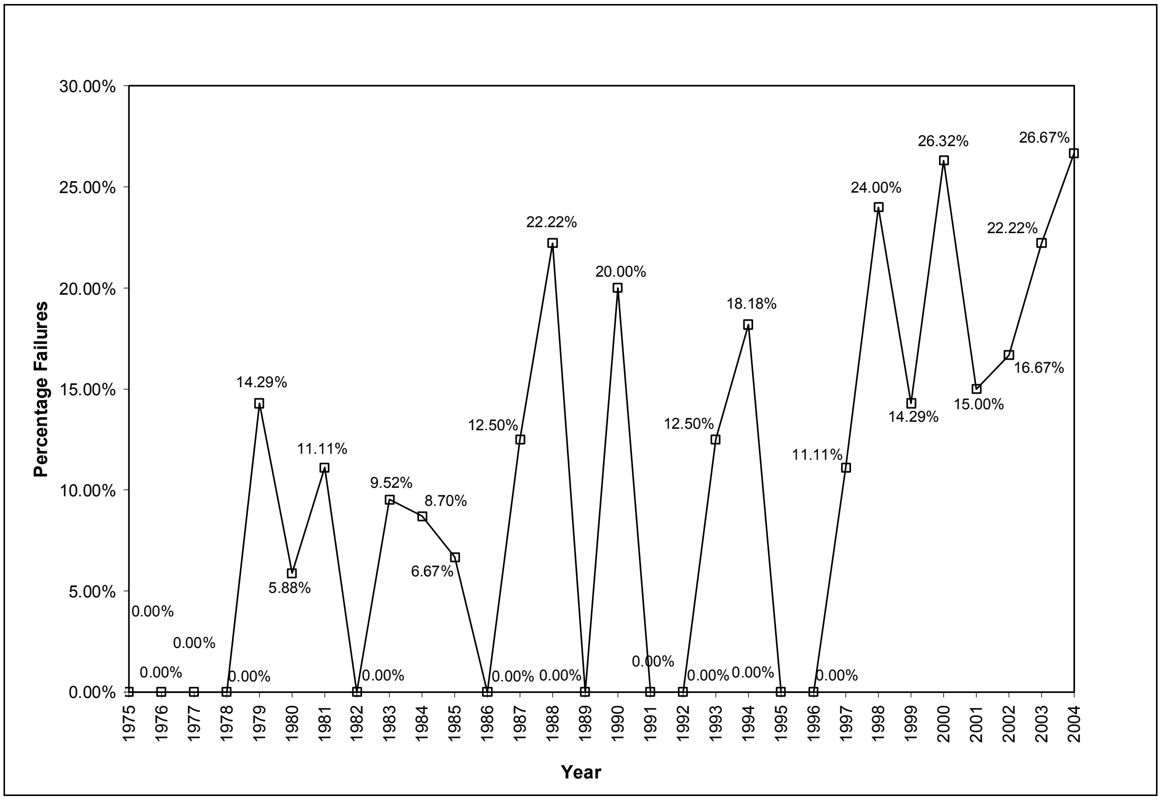

Figure A-1.18 Variation in annual percentage of failures for hot water category due to chlorine/ chloride

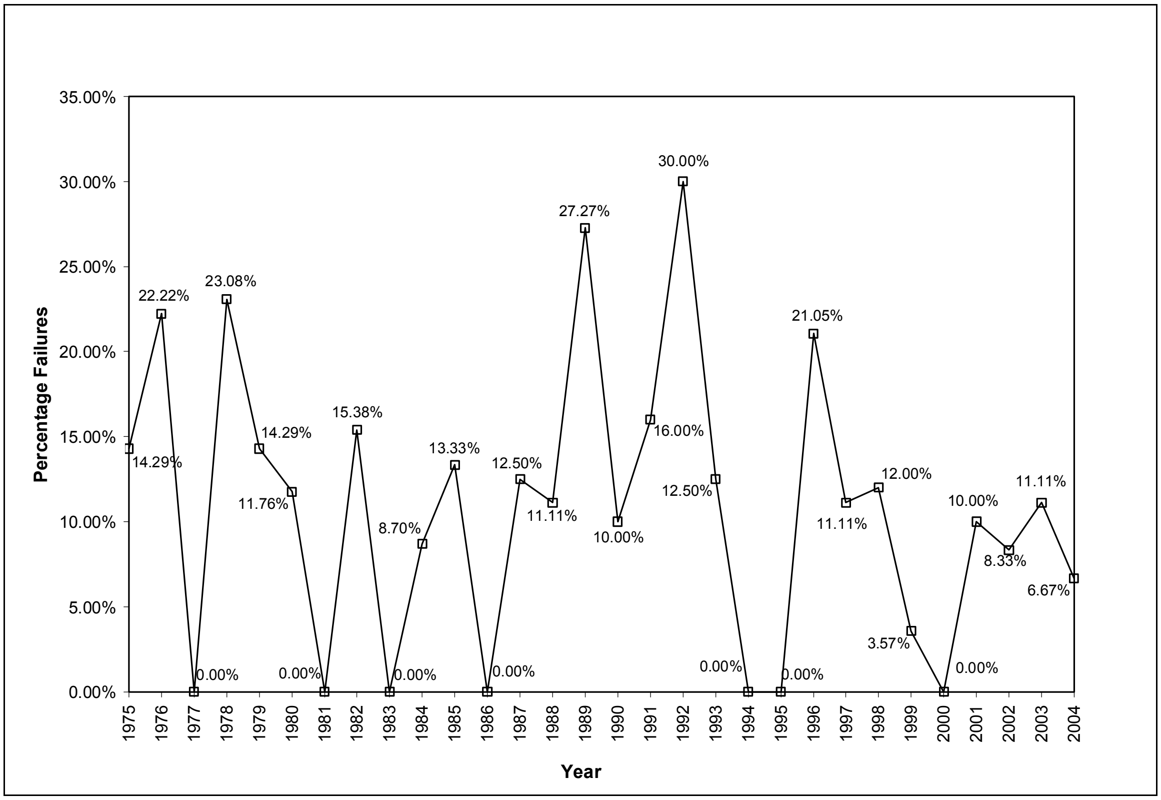

Figure A-1.19 Variation in annual percentage of failures for hot water category due to external failure

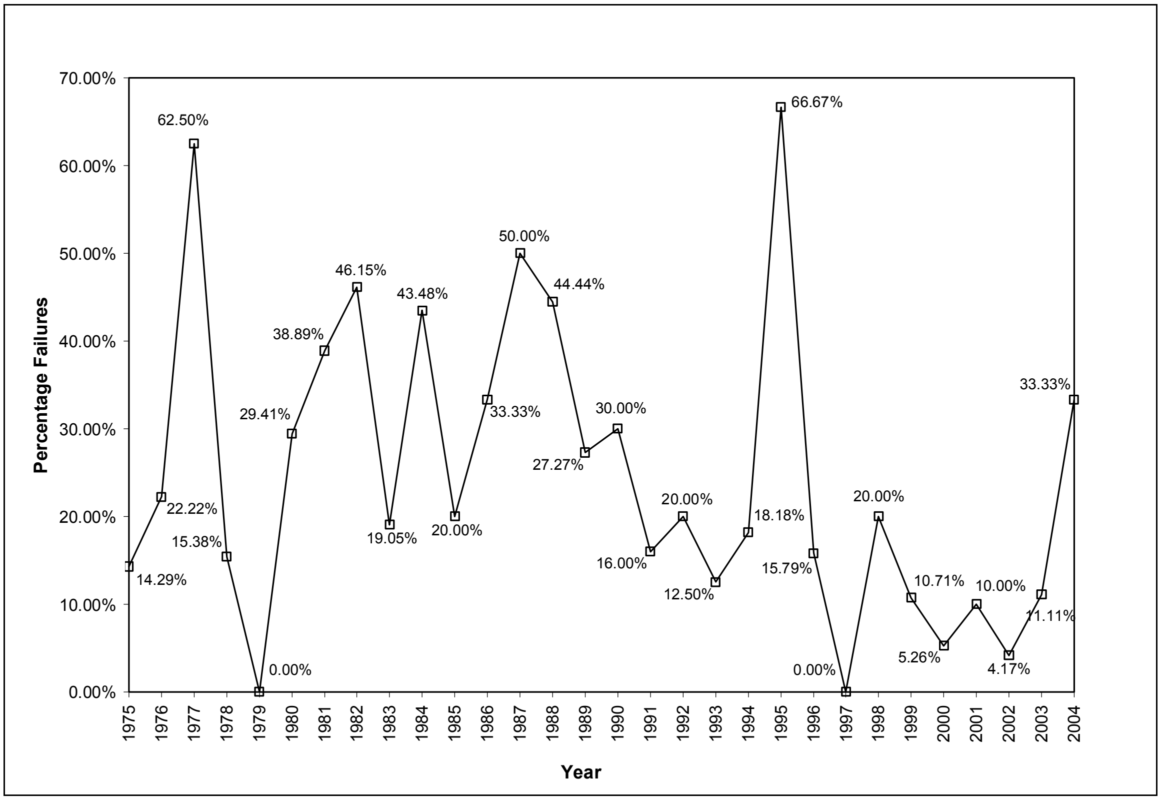

Figure A-1.20 Variation in annual percentage of failures for *hot water category* due to *minor causes*

Appendix A-1

Table A-1.1 Annual breakup of failures categorized by pipe types, CDA data (1975~2004)

		Pipe Type					
Year	**Number of reports**	**Cold Water**	**Hot Water**	**Hydronic**	**Service Lines**	**Fire Suppression**	**Others/ Not known** [a]
2004	40	19	13	2	4	0	3
		46.34	*31.71*	*4.88*	*9.76*	*0.00*	*7.32*
2003	75	43	13	5	7	0	8
		56.58	*17.11*	*6.58*	*9.21*	*0.00*	*10.53*
2002	64	31	19	5	8	2	4
		44.93	*27.54*	*7.25*	*11.59*	*2.90*	*5.80*
2001	69	35	16	4	6	1	14
		46.05	*21.05*	*5.26*	*7.89*	*1.32*	*18.42*
2000	79	50	15	4	6	1	7
		60.24	*18.07*	*4.82*	*7.23*	*1.20*	*8.43*
1999	87	48	19	9	5	2	5
		54.55	*21.59*	*10.23*	*5.68*	*2.27*	*5.68*
1998	62	22	19	6	13	1	4
		33.85	*29.23*	*9.23*	*20.00*	*1.54*	*6.15*
1997	60	32	3	15	4	2	5
		52.46	*4.92*	*24.59*	*6.56*	*3.28*	*8.20*
1996	46	17	7	12	2	2	7
		36.17	*14.89*	*25.53*	*4.26*	*4.26*	*14.89*
1995	32	18	3	3	2	2	5
		54.55	*9.09*	*9.09*	*6.06*	*6.06*	*15.15*
1994	32	13	5	6	2	3	3
		40.63	*15.63*	*18.75*	*6.25*	*9.38*	*9.38*
1993	55	21	6	10	2	6	11
		37.50	*10.71*	*17.86*	*3.57*	*10.71*	*19.64*
1992	32	5	4	6	4	1	12
		15.63	*12.50*	*18.75*	*12.50*	*3.13*	*37.50*
1991	61	20	13	12	2	3	15
		30.77	*20.00*	*18.46*	*3.08*	*4.62*	*23.08*
1990	23	10	5	5	1	0	5
		38.46	*19.23*	*19.23*	*3.85*	*0.00*	*19.23*
1989	29	6	6	5	3	2	8
		20.00	*20.00*	*16.67*	*10.00*	*6.67*	*26.67*
1988	23	6	3	6	1	2	6
		25.00	*12.50*	*25.00*	*4.17*	*8.33*	*25.00*

Table continues on the next page

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Table A-1.1 Annual breakup of failures categorized by pipe types, CDA data (1975~2004)

		Pipe Type					
Year	**Number of reports**	**Cold Water**	**Hot Water**	**Hydronic**	**Service Lines**	**Fire Suppression**	**Others/ Not known [a]**
1987	19	4	4	4	0	3	6
		19.05	*19.05*	*19.05*	*0.00*	*14.29*	*28.57*
1986	21	8	3	3	1	3	5
		34.78	*13.04*	*13.04*	*4.35*	*13.04*	*21.74*
1985	40	11	8	7	6	2	8
		26.19	*19.05*	*16.67*	*14.29*	*4.76*	*19.05*
1984	52	26	14	9	6	0	9
		40.63	*21.88*	*14.06*	*9.38*	*0.00*	*14.06*
1983	49	19	4	17	6	1	4
		37.25	*7.84*	*33.33*	*11.76*	*1.96*	*7.84*
1982	44	18	2	11	6	0	8
		40.00	*4.44*	*24.44*	*13.33*	*0.00*	*17.78*
1981	43	16	4	14	4	1	8
		34.04	*8.51*	*29.79*	*8.51*	*2.13*	*17.02*
1980	44	18	2	15	3	0	7
		40.00	*4.44*	*33.33*	*6.67*	*0.00*	*15.56*
1979	28	15	5	9	0	0	2
		48.39	*16.13*	*29.03*	*0.00*	*0.00*	*6.45*
1978	39	22	5	8	2	0	4
		53.66	*12.20*	*19.51*	*4.88*	*0.00*	*9.76*
1977	25	13	4	4	2	0	3
		50.00	*15.38*	*15.38*	*7.69*	*0.00*	*11.54*
1976	21	10	8	1	0	0	4
		43.48	*34.78*	*4.35*	*0.00*	*0.00*	*17.39*
1975	19	5	5	2	2	0	5
		26.32	*26.32*	*10.53*	*10.53*	*0.00*	*26.32*
Total	**1313 [b]**	**581**	**237**	**219**	**110**	**40**	**195**
Overall Average		***42.04***	***17.15***	***15.85***	***7.96***	***2.89***	***14.11***

The numbers in italics represent the percentage of the said attribute for that particular year.

[a] These include the reports that did not contain any information about the pipe type, also this attribute includes cases from refrigerant pipes, drain pipes, solar heating systems.

[b] The total number of reports is 1313, but the sum of the individual attributes will be more than this number as some reports contained failure reports for more than one type of pipes., such cases are counted twice (once for each attribute)

Table A-1.2 Annual break up for failure for All category pipes by failure causes, CDA data (1975~2004)

Year	**Chloride/ Chlorine**	**Erosion- Corrosion**	**Failure initiated outside**	**Oxygen- Differential**	**Aggressive Water**	**Excessive heating of water**	**No Corrosion/ No leak/ Other**	**Poor Workmanship**	**Sulfide**	**Microbial Induced**
2004	17 *42.50*	3 *7.50*	5 *12.50*	8 *20.00*	0 *0.00*	4 *10.00*	2 *5.00*	1 *2.50*	0 *0.00*	0 *0.00*
2003	39 *52.00*	3 *4.00*	13 *17.33*	7 *9.33*	0 *0.00*	10 *13.33*	3 *4.00*	0 *0.00*	0 *0.00*	0 *0.00*
2002	28 *43.75*	6 *9.38*	5 *7.81*	4 *6.25*	0 *0.00*	16 *25.00*	3 *4.69*	1 *1.56*	1 *1.56*	0 *0.00*
2001	26 *37.68*	4 *5.80*	7 *10.14*	8 *11.59*	0 *0.00*	10 *14.49*	4 *5.80*	2 *2.90*	8 *11.59*	0 *0.00*
2000	24 *30.38*	6 *7.59*	8 *10.13*	21 *26.58*	5 *6.33*	9 *11.39*	4 *5.06*	1 *1.27*	0 *0.00*	1 *1.27*
1999	24 *27.59*	8 *9.20*	14 *16.09*	18 *20.69*	0 *0.00*	14 *16.09*	5 *5.75*	4 *4.60*	0 *0.00*	0 *0.00*
1998	21 *33.87*	5 *8.06*	14 *22.58*	11 *17.74*	0 *0.00*	6 *9.68*	1 *1.61*	4 *6.45*	0 *0.00*	0 *0.00*
1997	30 *50.00*	7 *11.67*	9 *15.00*	3 *5.00*	0 *0.00*	9 *15.00*	0 *0.00*	0 *0.00*	2 *3.33*	0 *0.00*
1996	15 *32.61*	8 *17.39*	12 *26.09*	5 *10.87*	1 *2.17*	5 *10.87*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*
1995	17 *53.13*	4 *12.50*	3 *9.38*	5 *15.63*	0 *0.00*	0 *0.00*	1 *3.13*	0 *0.00*	1 *3.13*	1 *3.13*
1994	13 *40.63*	5 *15.63*	2 *6.25*	4 *12.50*	0 *0.00*	3 *9.38*	4 *12.50*	0 *0.00*	1 *3.13*	0 *0.00*
1993	23 *41.82*	9 *16.36*	5 *9.09*	7 *12.73*	3 *5.45*	4 *7.27*	0 *0.00*	2 *3.64*	2 *3.64*	0 *0.00*
1992	10 *31.25*	6 *18.75*	8 *25.00*	2 *6.25*	2 *6.25*	0 *0.00*	3 *9.38*	0 *0.00*	1 *3.13*	0 *0.00*
1991	14 *22.95*	17 *27.87*	6 *9.84*	9 *14.75*	7 *11.48*	4 *6.56*	1 *1.64*	0 *0.00*	2 *3.28*	1 *1.64*
1990	10 *43.48*	3 *13.04*	3 *13.04*	1 *4.35*	1 *4.35*	2 *8.70*	2 *8.70*	0 *0.00*	0 *0.00*	1 *4.35*
1989	6 *20.69*	7 *24.14*	8 *27.59*	2 *6.90*	2 *6.90*	1 *3.45*	3 *10.34*	0 *0.00*	0 *0.00*	0 *0.00*
1988	7 *30.43*	5 *21.74*	2 *8.70*	3 *13.04*	2 *8.70*	0 *0.00*	3 *13.04*	0 *0.00*	1 *4.35*	0 *0.00*

Table continues on the next page

Appendix A-1

Table A-1.2 Annual break up for failure for All category pipes by failure causes, CDA data (1975~2004)

Year	**Chloride/ Chlorine**	**Erosion-Corrosion**	**Failure initiated outside**	**Oxygen-Differential**	**Aggressive Water**	**Excessive heating of water**	**No Corrosion/ No leak/ Other**	**Poor Workmanship**	**Sulfide**	**Microbial Induced**
1987	4 *21.05*	2 *10.53*	2 *10.53*	4 *21.05*	1 *5.26*	0 *0.00*	5 *26.32*	0 *0.00*	1 *5.26*	0 *0.00*
1986	9 *42.86*	3 *14.29*	4 *19.05*	1 *4.76*	1 *4.76*	2 *9.52*	1 *4.76*	0 *0.00*	0 *0.00*	0 *0.00*
1985	14 *35.00*	8 *20.00*	3 *7.50*	3 *7.50*	3 *7.50*	6 *15.00*	2 *5.00*	0 *0.00*	1 *2.50*	0 *0.00*
1984	11 *21.15*	13 *25.00*	3 *5.77*	8 *15.38*	7 *13.46*	1 *1.92*	3 *5.77*	3 *5.77*	3 *5.77*	0 *0.00*
1983	4 *8.16*	14 *28.57*	5 *10.20*	2 *4.08*	13 *26.53*	2 *4.08*	4 *8.16*	4 *8.16*	1 *2.04*	0 *0.00*
1982	9 *20.45*	8 *18.18*	6 *13.64*	3 *6.82*	11 *25.00*	0 *0.00*	5 *11.36*	1 *2.27*	1 *2.27*	0 *0.00*
1981	6 *13.95*	11 *25.58*	3 *6.98*	2 *4.65*	10 *23.26*	0 *0.00*	7 *16.28*	2 *4.65*	2 *4.65*	0 *0.00*
1980	5 *11.36*	12 *27.27*	5 *11.36*	1 *2.27*	15 *34.09*	0 *0.00*	4 *9.09*	2 *4.55*	0 *0.00*	0 *0.00*
1979	3 *10.71*	13 *46.43*	2 *7.14*	0 *0.00*	8 *28.57*	0 *0.00*	2 *7.14*	0 *0.00*	0 *0.00*	0 *0.00*
1978	2 *5.13*	11 *28.21*	6 *15.38*	2 *5.13*	16 *41.03*	1 *2.56*	1 *2.56*	0 *0.00*	0 *0.00*	0 *0.00*
1977	1 *4.00*	7 *28.00*	4 *16.00*	0 *0.00*	10 *40.00*	0 *0.00*	2 *8.00*	1 *4.00*	0 *0.00*	0 *0.00*
1976	0 *0.00*	6 *28.57*	2 *9.52*	0 *0.00*	7 *33.33*	1 *4.76*	5 *23.81*	0 *0.00*	0 *0.00*	0 *0.00*
1975	0 *0.00*	10 *52.63*	3 *15.79*	0 *0.00*	3 *15.79*	0 *0.00*	2 *10.53*	1 *5.26*	0 *0.00*	0 *0.00*
Total = 1313 **Overall Average**	**392** ***29.86***	**224** ***17.06***	**172** ***13.10***	**144** ***10.97***	**128** ***9.75***	**110** ***8.38***	**82** [c] ***6.25***	**29** ***2.21***	**28** ***2.13***	**4** ***0.30***

The numbers in italics represent the percentage of the said attribute for that particular year.
The data presented contain the reports for all categories of pipe (hot water, hydronic, cold water, service lines, fire suppression and all pipes under unknown category). The segregation based on pipe categories is presented in subsequent tables.

[c] The number includes cases in which the failure cause was not established, or when the sample of pipe was drawn to study complaints about "Blue water" but there was no leak in the pipe.

The data is presented in figures 4 through 13.

Table A-1.3 Breakup of failures causes for Cold water category, CDA data (1975~2004)

Year	Chloride/ Chlorine	Aggressive Water	Oxygen-Differential	Failure initiated outside	Erosion-Corrosion	No Corrosion/ No leak/ Other	Poor Workmanship	Sulfide	Microbial Induced
2004	13	0	3	3	1	2	1	0	0
	56.52	*0.00*	*13.04*	*13.04*	*4.35*	*8.70*	*4.35*	*0.00*	*0.00*
2003	32	0	5	9	2	2	0	0	0
	64.00	*0.00*	*10.00*	*18.00*	*4.00*	*4.00*	*0.00*	*0.00*	*0.00*
2002	24	0	2	3	5	6	1	0	0
	58.54	*0.00*	*4.88*	*7.32*	*12.20*	*14.63*	*2.44*	*0.00*	*0.00*
2001	23	0	8	7	0	4	0	0	0
	54.76	*0.00*	*19.05*	*16.67*	*0.00*	*9.52*	*0.00*	*0.00*	*0.00*
2000	19	5	20	7	2	3	0	0	1
	33.33	*8.77*	*35.09*	*12.28*	*3.51*	*5.26*	*0.00*	*0.00*	*1.75*
1999	20	0	15	13	2	3	2	0	0
	36.36	*0.00*	*27.27*	*23.64*	*3.64*	*5.45*	*3.64*	*0.00*	*0.00*
1998	15	0	6	10	0	3	2	0	0
	41.67	*0.00*	*16.67*	*27.78*	*0.00*	*8.33*	*5.56*	*0.00*	*0.00*
1997	28	0	1	5	2	0	0	2	0
	73.68	*0.00*	*2.63*	*13.16*	*5.26*	*0.00*	*0.00*	*5.26*	*0.00*
1996	13	1	3	4	0	0	0	0	0
	61.90	*4.76*	*14.29*	*19.05*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*
1995	14	0	2	2	1	1	0	1	1
	63.64	*0.00*	*9.09*	*9.09*	*4.55*	*4.55*	*0.00*	*4.55*	*4.55*
1994	11	0	3	0	1	2	0	1	0
	61.11	*0.00*	*16.67*	*0.00*	*5.56*	*11.11*	*0.00*	*5.56*	*0.00*
1993	16	1	6	2	2	0	1	1	0
	55.17	*3.45*	*20.69*	*6.90*	*6.90*	*0.00*	*3.45*	*3.45*	*0.00*
1992	8	1	0	1	0	0	0	0	0
	80.00	*10.00*	*0.00*	*10.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*
1991	10	6	5		4	0	0	0	0
	40.00	*24.00*	*20.00*	*0.00*	*16.00*	*0.00*	*0.00*	*0.00*	*0.00*
1990	7	0	0	0	2	1	0	0	1
	63.64	*0.00*	*0.00*	*0.00*	*18.18*	*9.09*	*0.00*	*0.00*	*9.09*
1989	4	1	1	3	0	2	0	0	0
	36.36	*9.09*	*9.09*	*27.27*	*0.00*	*18.18*	*0.00*	*0.00*	*0.00*
1988	4	1	1	1	1	0	0	1	0
	44.44	*11.11*	*11.11*	*11.11*	*11.11*	*0.00*	*0.00*	*11.11*	*0.00*

Table continues on next page

Table A-1.3 Breakup of failures causes for Cold water category, CDA data (1975~2004)

Year	**Chloride/ Chlorine**	**Aggressive Water**	**Oxygen-Differential**	**Failure initiated outside**	**Erosion-Corrosion**	**No Corrosion/ No leak/ Other**	**Poor Workmanship**	**Sulfide**	**Microbial Induced**
1987	3	1	1	0	1	1	0	0	0
	42.86	*14.29*	*14.29*	*0.00*	*14.29*	*14.29*	*0.00*	*0.00*	*0.00*
1986	6	1	0	4	1	0	0	0	0
	50.00	*8.33*	*0.00*	*33.33*	*8.33*	*0.00*	*0.00*	*0.00*	*0.00*
1985	12	3	1	0	2	1	0	0	0
	63.16	*15.79*	*5.26*	*0.00*	*10.53*	*5.26*	*0.00*	*0.00*	*0.00*
1984	11	6	3	1	6	2	2	1	0
	34.38	*18.75*	*9.38*	*3.13*	*18.75*	*6.25*	*6.25*	*3.13*	*0.00*
1983	2	12	2	4	2	2	1	1	0
	7.69	*46.15*	*7.69*	*15.38*	*7.69*	*7.69*	*3.85*	*3.85*	*0.00*
1982	8	11	1	2	0	0	1	1	0
	33.33	*45.83*	*4.17*	*8.33*	*0.00*	*0.00*	*4.17*	*4.17*	*0.00*
1981	3	8	1	3	3	1	1	1	0
	14.29	*38.10*	*4.76*	*14.29*	*14.29*	*4.76*	*4.76*	*4.76*	*0.00*
1980	4	11		1	2	3	0	0	0
	19.05	*52.38*	*0.00*	*4.76*	*9.52*	*14.29*	*0.00*	*0.00*	*0.00*
1979	1	8	0	0	5	1	0	0	0
	6.67	*53.33*	*0.00*	*0.00*	*33.33*	*6.67*	*0.00*	*0.00*	*0.00*
1978	1	14	1	2	5	1	0	0	0
	4.17	*58.33*	*4.17*	*8.33*	*20.83*	*4.17*	*0.00*	*0.00*	*0.00*
1977	0	8	0	3	4	0	0	0	0
	0.00	*53.33*	*0.00*	*20.00*	*26.67*	*0.00*	*0.00*	*0.00*	*0.00*
1976	0	6	0	0	2	2	0	0	0
	0.00	*60.00*	*0.00*	*0.00*	*20.00*	*20.00*	*0.00*	*0.00*	*0.00*
1975	0	2	0	0	3	1	1	0	0
	0.00	*28.57*	*0.00*	*0.00*	*42.86*	*14.29*	*14.29*	*0.00*	*0.00*
Total =731	**312**	**107**	**91**	**90**	**61**[d]	**44**[d]	**13**[d]	**10**[d]	**3**[d]
Overall Average	***42.68***	***14.64***	***12.45***	***12.31***	***8.34***	***6.02***	***1.78***	***1.37***	***0.41***

The numbers in italics represent the percentage of the said attribute for that particular year.

[d] These attributes are categorized as minor causes and are shown together in figures.

The data is presented in figures

Table A-1.4 Breakup of failure causes for Hot water category, CDA data (1975~2004)

Year	**Erosion-Corrosion**	**Excessive heating of water**	**Chloride/ Chlorine**	**Failure initiated outside**	**Oxygen-Differential**	**No Corrosion/ No leak/ Other**	**Aggressive Water**	**Poor Workmanship**	**Sulfide**	**Microbial Induced**
2004	1	4	4	1	4	1	0	0	0	0
	6.67	*26.67*	*26.67*	*6.67*	*26.67*	*6.67*	*0.00*	*0.00*	*0.00*	*0.00*
2003	1	9	4	2	1	1	0	0	0	0
	5.56	*50.00*	*22.22*	*11.11*	*5.56*	*5.56*	*0.00*	*0.00*	*0.00*	*0.00*
2002	1	16	4	2	1	0	0	0	0	0
	4.17	*66.67*	*16.67*	*8.33*	*4.17*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*
2001	3	10	3	2	0	1	0	1	0	0
	15.00	*50.00*	*15.00*	*10.00*	*0.00*	*5.00*	*0.00*	*5.00*	*0.00*	*0.00*
2000	4	9	5	0	0	0	0	1	0	0
	21.05	*47.37*	*26.32*	*0.00*	*0.00*	*0.00*	*0.00*	*5.26*	*0.00*	*0.00*
1999	6	14	4	1	0	3	0	0	0	0
	21.43	*50.00*	*14.29*	*3.57*	*0.00*	*10.71*	*0.00*	*0.00*	*0.00*	*0.00*
1998	5	6	6	3	3	0	0	2	0	0
	20.00	*24.00*	*24.00*	*12.00*	*12.00*	*0.00*	*0.00*	*8.00*	*0.00*	*0.00*
1997	5	9	2	2	0	0	0	0	0	0
	27.78	*50.00*	*11.11*	*11.11*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*
1996	7	5	0	4	3	0	0	0	0	0
	36.84	*26.32*	*0.00*	*21.05*	*15.79*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*
1995	2	0	0	0	4	0	0	0	0	0
	33.33	*0.00*	*0.00*	*0.00*	*66.67*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*
1994	4	3	2	0	1	1	0	0	0	0
	36.36	*27.27*	*18.18*	*0.00*	*9.09*	*9.09*	*0.00*	*0.00*	*0.00*	*0.00*
1993	6	4	2	2	1	0	0	1	0	0
	37.50	*25.00*	*12.50*	*12.50*	*6.25*	*0.00*	*0.00*	*6.25*	*0.00*	*0.00*
1992	5		0	3	1	1	0	0	0	0
	50.00	*0.00*	*0.00*	*30.00*	*10.00*	*10.00*	*0.00*	*0.00*	*0.00*	*0.00*
1991	14	3	0	4	3	0	0	0	0	1
	56.00	*12.00*	*0.00*	*16.00*	*12.00*	*0.00*	*0.00*	*0.00*	*0.00*	*4.00*
1990	2	2	2	1	1	2	0	0	0	0
	20.00	*20.00*	*20.00*	*10.00*	*10.00*	*20.00*	*0.00*	*0.00*	*0.00*	*0.00*
1989	4	1	0	3	1	1	1	0	0	0
	36.36	*9.09*	*0.00*	*27.27*	*9.09*	*9.09*	*9.09*	*0.00*	*0.00*	*0.00*
1988	2	0	2	1	2	2	0	0	0	0
	22.22	*0.00*	*22.22*	*11.11*	*22.22*	*22.22*	*0.00*	*0.00*	*0.00*	*0.00*
Table continues on the next page										

Table A-1.4 Breakup of failure causes for Hot water category, CDA data (1975~2004)

Year	**Erosion-Corrosion**	**Excessive heating of water**	**Chloride/ Chlorine**	**Failure initiated outside**	**Oxygen-Differential**	**No Corrosion/ No leak/ Other**	**Aggressive Water**	**Poor Workmanship**	**Sulfide**	**Microbial Induced**
1987	2 *25.00*	0 *0.00*	1 *12.50*	1 *12.50*	2 *25.00*	0 *0.00*	1 *12.50*	0 *0.00*	1 *12.50*	0 *0.00*
1986	3 *50.00*	1 *16.67*	0 *0.00*	0 *0.00*	1 *16.67*	0 *0.00*	1 *16.67*	0 *0.00*	0 *0.00*	0 *0.00*
1985	5 *33.33*	4 *26.67*	1 *6.67*	2 *13.33*	2 *13.33*	0 *0.00*	1 *6.67*	0 *0.00*	0 *0.00*	0 *0.00*
1984	8 *34.78*	1 *4.35*	2 *8.70*	2 *8.70*	4 *17.39*	2 *8.70*	1 *4.35*	1 *4.35*	2 *8.70*	0 *0.00*
1983	13 *61.90*	2 *9.52*	2 *9.52*	0 *0.00*	0 *0.00*	2 *9.52*	1 *4.76*	1 *4.76*	0 *0.00*	0 *0.00*
1982	5 *38.46*	0 *0.00*	0 *0.00*	2 *15.38*	1 *7.69*	4 *30.77*	1 *7.69*	0 *0.00*	0 *0.00*	0 *0.00*
1981	9 *50.00*	0 *0.00*	2 *11.11*	0 *0.00*	1 *5.56*	5 *27.78*	1 *5.56*	0 *0.00*	0 *0.00*	0 *0.00*
1980	9 *52.94*	0 *0.00*	1 *5.88*	2 *11.76*	1 *5.88*	1 *5.88*	1 *5.88*	2 *11.76*	0 *0.00*	0 *0.00*
1979	10 *71.43*	0 *0.00*	2 *14.29*	2 *14.29*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*
1978	7 *53.85*	1 *7.69*	0 *0.00*	3 *23.08*	0 *0.00*	0 *0.00*	2 *15.38*	0 *0.00*	0 *0.00*	0 *0.00*
1977	3 *37.50*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*	2 *25.00*	2 *25.00*	1 *12.50*	0 *0.00*	0 *0.00*
1976	4 *44.44*	1 *11.11*	0 *0.00*	2 *22.22*	0 *0.00*	2 *22.22*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*
1975	5 *71.43*	0 *0.00*	0 *0.00*	1 *14.29*	0 *0.00*	0 *0.00*	1 *14.29*	0 *0.00*	0 *0.00*	0 *0.00*
Total = 456 **Overall Average**	**155** ***33.99***	**105** ***23.03***	**51** ***11.18***	**48** ***10.53***	**38**[e] ***8.33***	**31**[e] ***6.80***	**14**[e] ***3.07***	**10**[e] ***2.19***	**3**[e] ***0.66***	**1**[e] ***0.22***

The numbers in italics represent the percentage of the said attribute for that particular year.

[e] These attributes are categorized as minor causes and are shown together in figures.

Table A-1.5 Breakup of failure causes for others/ unknown category, CDA data (1975~2004)

Year	Failure initiated outside	Chloride/ Chlorine	No Corrosion/ No leak/ Other	Erosion-Corrosion	Oxygen-Differential	Sulfide	Aggressive Water	Poor Workmanship	Excessive heating of water
2004	1 *33.33*	0 *0.00*	0 *0.00*	1 *33.33*	1 *33.33*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*
2003	2 *25.00*	3 *37.50*	1 *12.50*	0 *0.00*	1 *12.50*	0 *0.00*	0 *0.00*	0 *0.00*	1 *12.50*
2002	0 *0.00*	0 *0.00*	2 *50.00*	0 *0.00*	1 *25.00*	1 *25.00*	0 *0.00*	0 *0.00*	0 *0.00*
2001	1 *7.14*	0 *0.00*	3 *21.43*	1 *7.14*	0 *0.00*	8 *57.14*	0 *0.00*	1 *7.14*	0 *0.00*
2000	3 *42.86*	0 *0.00*	3 *42.86*	0 *0.00*	1 *14.29*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*
1999	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*	3 *60.00*	0 *0.00*	0 *0.00*	2 *40.00*	0 *0.00*
1998	1 *25.00*	0 *0.00*	1 *25.00*	0 *0.00*	2 *50.00*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*
1997	2 *40.00*	1 *20.00*	0 *0.00*	0 *0.00*	2 *40.00*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*
1996	4 *57.14*	2 *28.57*	0 *0.00*	1 *14.29*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*
1995	1 *20.00*	3 *60.00*	0 *0.00*	1 *20.00*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*
1994	2 *66.67*	0 *0.00*	1 *33.33*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*
1993	1 *9.09*	6 *54.55*	0 *0.00*	1 *9.09*	0 *0.00*	1 *9.09*	2 *18.18*	0 *0.00*	0 *0.00*
1992	4 *33.33*	2 *16.67*	2 *16.67*	1 *8.33*	1 *8.33*	1 *8.33*	1 *8.33*	0 *0.00*	0 *0.00*
1991	2 *13.33*	4 *26.67*	1 *6.67*	2 *13.33*	2 *13.33*	2 *13.33*	1 *6.67*	0 *0.00*	1 *6.67*
1990	2 *40.00*	2 *40.00*	0 *0.00*	0 *0.00*	0 *0.00*	0 *0.00*	1 *20.00*	0 *0.00*	0 *0.00*
1989	2 *25.00*	2 *25.00*	0 *0.00*	3 *37.50*	0 *0.00*	0 *0.00*	1 *12.50*	0 *0.00*	0 *0.00*
1988	0 *0.00*	2 *33.33*	1 *16.67*	2 *33.33*	0 *0.00*	0 *0.00*	1 *16.67*	0 *0.00*	0 *0.00*

Table continues on next page

Table A-1.5 Breakup of failure causes for others/ unknown category, CDA data (1975~2004)

Year	**Failure initiated outside**	**Chloride/ Chlorine**	**No Corrosion/ No leak/ Other**	**Erosion-Corrosion**	**Oxygen-Differential**	**Sulfide**	**Aggressive Water**	**Poor Workmanship**	**Excessive heating of water**
1987	1	0	4	0	1	0	0	0	0
	16.67	*0.00*	*66.67*	*0.00*	*16.67*	*0.00*	*0.00*	*0.00*	*0.00*
1986	0	3	1	0	0	0	0	0	1
	0.00	*60.00*	*20.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*	*20.00*
1985	1	2	1	1	0	1	0	0	2
	12.50	*25.00*	*12.50*	*12.50*	*0.00*	*12.50*	*0.00*	*0.00*	*25.00*
1984	1	0	1	3	2	1	1	0	0
	11.11	*0.00*	*11.11*	*33.33*	*22.22*	*11.11*	*11.11*	*0.00*	*0.00*
1983	1	0	1	0	0	0	0	2	0
	25.00	*0.00*	*25.00*	*0.00*	*0.00*	*0.00*	*0.00*	*50.00*	*0.00*
1982	2	1	1	3	1	0	0	0	0
	25.00	*12.50*	*12.50*	*37.50*	*12.50*	*0.00*	*0.00*	*0.00*	*0.00*
1981	0	2	2	1	0	1	1	1	0
	0.00	*25.00*	*25.00*	*12.50*	*0.00*	*12.50*	*12.50*	*12.50*	*0.00*
1980	2	1	0	1	0	0	3	0	0
	28.57	*14.29*	*0.00*	*14.29*	*0.00*	*0.00*	*42.86*	*0.00*	*0.00*
1979	0	0	1	1	0	0	0	0	0
	0.00	*0.00*	*50.00*	*50.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*
1978	1	1	0	0	1	0	1	0	0
	25.00	*25.00*	*0.00*	*0.00*	*25.00*	*0.00*	*25.00*	*0.00*	*0.00*
1977	1	1	0	0	0	0	1	0	0
	33.33	*33.33*	*0.00*	*0.00*	*0.00*	*0.00*	*33.33*	*0.00*	*0.00*
1976	0	0	2	1	0	0	1	0	0
	0.00	*0.00*	*50.00*	*25.00*	*0.00*	*0.00*	*25.00*	*0.00*	*0.00*
1975	2	0	1	2	0	0	0	0	0
	40.00	*0.00*	*20.00*	*40.00*	*0.00*	*0.00*	*0.00*	*0.00*	*0.00*
Total= 195	**40**	**38**	**30**	**26**	**19**[f]	**16**[f]	**15**[f]	**6**[f]	**5**[f]
Overall Average	***20.51***	***19.49***	***15.38***	***13.33***	***9.74***	***8.21***	***7.69***	***3.08***	***2.56***

The numbers in italics represent the percentage of the said attribute for that particular year.

[f] These attributes are categorized as minor causes and are shown together in figures.

APPENDIX B-1

Temporal Patterns of Pinhole Leaks by Pipe Characteristics

Appendix B-1

Table B-1.1 Types of dwelling units and leaks, CDA (1998 ~ 2004)

Year		**Dwelling Unit Type**				**Leak Type**	
	Total reports	**Apartment**	**House**	**Commercial**	**Other [1] / not known**	**Pinhole**	**Other [2] / not known**
1998	62	4	42	11	5	34	28
		6.45	*67.74*	*17.74*	*8.06*	*54.84*	*45.16*
1999	87	7	63	9	8	53	34
		8.05	*72.41*	*10.34*	*9.20*	*60.92*	*39.08*
2000	79	3	61	9	6	64	15
		3.80	*77.22*	*11.39*	*7.59*	*81.01*	*18.99)*
2001	69	6	57	3	3	53	16
		8.70	*82.61*	*4.35*	*4.35*	*76.81*	*23.19*
2002	64	5	49	3	7	47	17
		7.81	*76.56*	*4.69*	*10.94*	*73.44*	*26.56*
2003	75	4	54	12	5	56	19
		5.33	*72.00*	*16.00*	*6.67*	*74.67*	*25.33*
2004	40	5	30	2	3	31	9
		12.50	*75.00*	*5.00*	*7.50*	*77.50*	*22.50*
Total	**476**	**34**	**356**	**49**	**37**	**338**	**138**
		7.14	***74.79***	***10.29***	***7.77***	***71.01***	***28.99***

[1] reports that do not contain information about the type of dwelling unit.

[2] reports do not contain information on the type of leak.

Italics are the percentage of the item pertaining to that particular year.

Table B-1.2 Types of pipes and pipe orientation, CDA (1998~2004)

Year	Pipe Type				Pipe Orientation		
	K-type	L-type	M-type	Other / not known [3]	Horizontal	Vertical	Not Known
1998	9 *14.06*	30 *46.88*	23 *35.94*	2 *3.13*	25 *39.68*	5 *7.94*	33 *52.38*
1999	7 *7.78*	41 *45.56*	39 *43.33*	3 *3.33*	46 *51.11*	12 *13.33*	32 *35.56*
2000	6 *7.14*	31 *36.90*	44 *52.38*	3 *3.57*	42 *50.60*	9 *10.84*	32 *38.55*
2001	6 *8.57*	30 *42.86*	31 *44.29*	3 *4.29*	22 *31.88*	5 *7.25*	42 *60.87*
2002	6 *9.23*	29 *44.62*	29 *44.62*	1 *1.54*	31 *48.44*	4 *6.25*	29 *45.31*
2003	6 *7.79*	37 *48.05*	31 *40.26*	3 *3.90*	30 *40.00*	8 *10.67*	37 *49.33*
2004	5 *12.20*	20 *48.78*	15 *36.59*	1 *2.44*	19 *46.34*	6 *14.63*	16 *39.02*
Total [4]	**45** ***9.16***	**218** ***44.40***	**212** ***43.18***	**16** ***3.26***	**215** ***44.33***	**49** ***10.10***	**221** ***45.57***

[3] pipe category other than plumbing pipe or not reported.

[4] total may vary from the total number of CDA reports due to multiple items reported in some reports. Some reports have both M and
L types of failure and such cases are counted twice.
Italics are the percentage of the item pertaining to that particular year.

Table B-1.3 Source of water and pipe sizes, CDA (1998~2004)

	Pipe Size (nominal diameter-inches)				**Source of Water**		
Year	**0.5**	**0.75**	**1**	**Other [5]**	**Ground water**	**Surface water**	**Other / not known**
1998	21	31	8	12	23	5	34
	29.17	*43.06*	*11.11*	*16.67*	*37.10*	*8.06*	*54.84*
1999	40	30	12	13	45	15	34
	42.11	*31.58*	*12.63*	*13.68*	*47.87*	*15.96*	*36.17*
2000	25	43	6	11	42	16	23
	29.41	*50.59*	*7.06*	*12.94*	*51.85*	*19.75*	*28.40*
2001	32	25	7	10	33	19	18
	43.24	*33.78*	*9.46*	*13.51*	*47.14*	*27.14*	*25.71*
2002	25	29	10	10	34	7	23
	33.78	*39.19*	*13.51*	*13.51*	*53.13*	*10.94*	*35.94*
2003	32	30	7	10	34	22	22
	40.51	*37.97*	*8.86*	*12.66*	*43.59*	*28.21*	*28.21*
2004	17	16	4	5	13	10	19
	40.48	*38.10*	*9.52*	*11.90*	*30.95*	*23.81*	*45.24*
Total [6]	**192**	**204**	**54**	**71**	**224**	**94**	**173**
	36.85	***39.16***	***10.36***	***13.63***	***45.62***	***19.14***	***35.23***

[5] other pipe sizes and pipes are from heating systems, refrigerant systems etc.

[6] total may vary from the total number of CDA reports due to multiple items reported. Some reports contain multiple sizes of failed pipes, such cases are counted twice.

Italics contain the percentage of the item pertaining to the particular year.

CHAPTER-2

CAUSAL ANALYSIS OF PINHOLE LEAKS

Introduction

Corrosion is an electrochemical process; by definition it requires the presence of four basic ingredients, an anode, a cathode, an electrolyte and a physical connection. All these four ingredients facilitate an electrochemical reaction in which the anode is consumed due to loss of metal whereas deposition occurs at cathode. By means of corrosion, the metals achieve higher oxidation states that are thermodynamically more stable. Copper metal is oxidized to the cuprous (+1) and cupric (+2) oxidation states in corrosion. A detailed overview of the thermodynamics and kinetics of the corrosion phenomenon is presented in Chapter 4. The nature and type of corrosion is highly dependant on the conditions of exposure and the environment. A summary of the different types of corrosion of copper is given in *Appendix A-2*.

In general, when metals are exposed to oxygen, they tend to form a protective oxide film. The film thus formed is usually thin and may not be visible to naked eye. The role of film is particularly important in corrosion mechanism as it virtually forms a physical barrier between the bare metal and the environment. However, the formation of the protective film does not guarantee protection against corrosion, but it at least slows down the corrosion mechanism. The extent to which the film may provide protection to the metal is highly dependent on its conditions of exposure, for instance, the protective film may become soluble under certain conditions thus leaving the metal unprotected.

In addition to the protective oxide film, other deposits may form on the surface of the metal. These deposits or scales are primarily metal salts, and are the direct result of the reaction of the metal with the constituents of its environment. The scales thus formed on the metal surface may be protective, non protective or even corrosive depending upon the morphology, anions in the solution and other environmental conditions including pH, temperature, alkalinity, velocity, pressure etc. The role of the scales is extremely important in understanding corrosion phenomenon; especially the scale seems to have a dominant role in copper pitting in home plumbing systems.

The chapter synthesizes various physical, chemical factors that can lead to pinhole leaks in copper home plumbing. The objectives of the chapter are:

i. Assess the variability in water quality based on nationwide water quality data from AWWARF/ AWWA utilities.
ii. Identify and summarize physical and chemical parameters that influence copper pitting in home plumbing systems.
iii. Identify the causal mechanisms in terms of the water quality and hydraulic parameters and quantify these parameters based on the likelihood of copper pitting.
iv. Develop a scoring system for water quality and hydraulic parameters that influence pinhole leak.

Overview of Water Quality

Almost all the home plumbing systems withdraw water from large municipal distribution systems. These large distributions systems are managed and operated by public or private utilities. The utilities withdraw water either from surface water bodies (i.e. lakes, springs and rivers) or from ground water aquifers or a combination of both. The water obtained from either surface or ground source is called *raw water,* it is then passed through a set of treatment stages at the treatment plant before it is sent into the distribution system. The treatment plants are generally located at or near the water source bodies and are typically far from residential establishments. The treated water or the *finished water* is then pumped into the bigger distribution system where it is conveyed through a system of pipe network. The branched network extends to street and service laterals that finally get connected to the home plumbing systems.

The quality of the raw water is dependant on the source from where it is withdrawn. In general, surface waters are more turbid as compared to ground waters (Tchobanoglous, 1985). Surface waters also have more organic contaminants and contain urban pollutants that reach the surface water bodies with surface runoff. Ground waters on the other hand, have higher TDS (total dissolved solids) because of mineral pickup from soil and rocks (Tchobanoglous, 1985). Ground waters may have dissolved gases like carbon dioxide [CO_2], ammonia [NH_3], hydrogen sulfide [H_2S] and sometimes iron and manganese.

In general, raw water contains impurities that are to be removed during the treatment process. These impurities may be classified into *organic* and *inorganic* impurities. *Organic* impurities include impurities due to the decay of natural vegetative and animal matter; these impurities are often found in surface water, where these are brought into with the surface runoff. The impurities include organic contaminant from urban and industrial establishments. The most common problems associated with the organic impurities include color formation, taste and odor issues, interference with water treatment process and formation of halogenated compounds during chlorination (Tchobanoglous, 1985). The amount of organic impurities present in most of the natural water is low (Tchobanoglous, 1985). The *inorganic* impurities can be classified into ionic and non ionic species. The principal ionic species typically found in waters are Calcium [Ca^{2+}], Magnesium [Mg^{2+}], Sodium [Na^{+}], Potassium [K^{+}] (as cations) and Bicarbonate [HCO_3^{-}], Sulfate [SO_4^{2-}], Chloride [Cl^{-}] and Nitrate [NO_3^{-}] (as anions). The most abundant compounds are Bicarbonate, Sulfate and Chlorides of Calcium, Magnesium and Sodium (Tchobanoglous, 1985). The non ionic inorganic impurity present in most of the water is Silica, which is usually present as Silicon Dioxide [SiO_2]. These organic and inorganic impurities need treatment prior to sending the water in distribution system. The USEPA has set *primary* and *secondary* standards for the finished water, to which the utilities should comply before supplying the water.

The national primary and secondary standards for drinking water are available on http://www.epa.gov/safewater/mcl.html. The national primary standards are *legally enforceable standards*, these consist of the list of contaminants that may have ill effects on public health, the standards define permissible limits for these contaminants in public water systems, and these limits are termed as *maximum contaminant level (MCL)*. The principal categories identified under primary standards include *microorganisms, disinfection byproducts, disinfectants, inorganic chemicals, organic chemicals and radionuclides*. Interestingly, the primary standards identify *residual disinfectants* as a contaminant that can affect public health. The standards set permissible limits for *maximum residual disinfectant level (MRDL)*, which is the highest level of residual disinfectant in water.

The secondary standards are *not legally enforceable standards*. These standards consist of the list of contaminants that may cause cosmetic hazards (skin or tooth discoloration), or may have aesthetics ill effects (taste, color and odor issues) in drinking water. These standards are recommendations by the USEPA, and are not enforced on public water systems. However, the states may choose to make these standards as legally enforceable. The secondary contaminant list with the possible ill effects is reproduced in Table 1.

In addition to primary and secondary standards, USEPA also identifies certain contaminants that are presently not subjected to any regulation but are anticipated to occur in public water systems and may require regulations under *safe drinking water act (SDWA)*. These contaminants are identified under *unregulated category* (*http://www.epa.gov/safewater/mcl.html*)

Table 1 Secondary maximum contaminant level (source USEPA)

Contaminant	**Secondary MCL**	**Noticeable Effects above the Secondary MCL**
Aluminum	0.05 to 0.2 mg/L*	colored water
Chloride	250 mg/L	salty taste
Color	15 color units	visible tint
Copper	1.0 mg/L	metallic taste; blue-green staining
Corrosivity	Non-corrosive	metallic taste; corroded pipes/ fixtures staining
Fluoride	2.0 mg/L	tooth discoloration
Foaming agents	0.5 mg/L	frothy, cloudy; bitter taste; odor
Iron	0.3 mg/L	rusty color; sediment; metallic taste; reddish or orange staining
Manganese	0.05 mg/L	black to brown color; black staining; bitter metallic taste
Odor	3 TON (threshold odor number)	"rotten-egg", musty or chemical smell
pH	6.5 - 8.5	*low pH:* bitter metallic taste; corrosion *high pH:* slippery feel; soda taste; deposits
Silver	0.1 mg/L	skin discoloration; graying of the white part of the eye
Sulfate	250 mg/L	salty taste
Total Dissolved Solids	500 mg/L	hardness; deposits; colored water; staining; salty taste
Zinc	5 mg/L	metallic taste
** mg/L is milligrams of substance per liter of water*		

Interestingly, some of the contaminants in the secondary list are often considered responsible for copper pitting, these include, Aluminum, Chloride, Sulfate, pH, Iron and Manganese. A detailed discussion about the effect of these parameters on copper pitting is presented later in the chapter. Since the secondary standards are not legally enforceable, it is expected that there should be considerable variability in these parameters across different utilities.

The *finished water* from the plant has to travel considerable distance through the distribution system before entering the home plumbing systems. The distribution system generally is comprised of pipes of various materials (e.g. Cast Iron, Reinforced Concrete, Plastics etc), these pipes can have several kinds of deposits on their inner surfaces. The deposits may be due to corrosion of these pipes, settling of silt or both. These deposits not only reduce the hydraulic efficiency of the distribution system but can also shield microorganisms from disinfectants. In order to check the unwanted growth of microorganism in the distribution system, certain utilities provide disinfectant booster doses at suitable locations *(booster stations)* in the bigger distribution system. Additionally, the pipes in distribution system can leach chemicals into water thus changing the water chemistry. For instance, leaching of Aluminum and Silica compounds from reinforced concrete pipes is a common concern. Considering the complexity and nature of the interaction of finished water within the distribution system it may be safer to assume that water entering the home plumbing system is different from the finished water.

Hence, the actual variability in the quality parameters of the water that reach the home plumbing system is expected to be much more than the variability in water quality of the finished water. A review of the water quality data for 898 AWWA utilities demonstrates considerable variability in water quality parameters for *finished water* on a nationwide scale. The summary of the analysis of water quality data from AWWARF/AWWA utility survey (*WATER:\STATS 1996 survey*) is presented.

AWWARF/AWWA Utility Survey

WATER:\STATS is a joint cooperative effort between American Water Works Association (AWWA) and American Water Works Association Research Foundation (AWWARF). It consists of survey information from AWWA member utilities. The last survey was conducted in the year 1996, 898 utilities responded to the survey out of a total of 3200 AWWA member utilities. The database includes information about financial and revenue records, water treatment and disposal practices, finished water quality parameters at the plant, and water quality information in the distribution system. The database is available on payment on http://www.awwa.org/Communications/h20stats/PriceTab.cfm.

Out of 898 water utilities that responded to the survey, (370) three hundred seventy are ground water utilities, (284) two hundred eighty four are surface water utilities, (140) one hundred forty are combined surface and ground water utilities, and (104) one hundred four are the utilities that responded to the survey but did not provide any information for either ground water or surface water. The database is segregated into six different spreadsheets; each spreadsheet consists of number of worksheets that typically contain information for the *respondent utilities* designated by an (R) in the title and *all utilities* designated by an (A) in the title. The *respondent utilities* are the ones that responded to each question of the survey, while *all utilities* contain all of the utilities that participated in the survey, even if they did not answer the corresponding question for that worksheet. Each utility is identified with a unique identification number in the database. Additionally, surface water utilities are also assigned a unique plant identification number for different treatment plants (if more than one) under the same utility identification number. For ground water utilities, the data is averaged across all the wells and hence, no separate plant identification number is assigned.

The first spreadsheet contains revenue information of the utilities. It includes information about the population served, service area, future water demand, ownership category (public/ private), ownership type (Municipal / investor/ State or Water District etc), present budgetary conditions (asset / liability), average day production, other services provided etc. The information is further segregated for ground and surface water utilities. The data in the spreadsheet is helpful for business planning and analysis purposes; hence it is not included in the present study.

The second spreadsheet contains data related to treatment practices, residuals and residual disposal for water utilities. The data includes information about the present and planned treatment practices for various treatment stages like raw storage, aeration, pre disinfection oxidation, coagulation & flocculation, filtration, disinfection, corrosion control, finished water storage etc for each utility. The data is segregated for ground and surface water utilities. The data may be of interest from water treatment and waste disposal perspective, hence it is not included in the present study.

The third spreadsheet contains data about the pipe materials for service lines and fire lines for the utilities. The pipe material data for the water mains and year wise number of breakages for the last five year is also provided. The database does not provide any information about the pipe materials in the home plumbing. Initially, it was perceived that the data could help in identifying hotspots for pinhole leaks based on the usage patterns of copper at various locations, but since the data does not have any information about the materials in home plumbing systems, any substantial conclusion could not be drawn from the analysis. For the present study the said data is thus excluded.

The spreadsheets four, five and six contain water quality data for finished ground water quality, finished surface water quality and distribution water quality, respectively. The data provides minimum, average and maximum values for each water quality parameter mentioned therein. A summary of the data from these spreadsheets is presented in Table 2, Table 3 and Table 4. Since, the available data is represented by three different values (minimum, maximum and average) for any parameter, the analysis for these values are done separately. The variation in minimum, maximum and average values is presented in Tables 2, Table 3 and Table 4 in three separate groups.

Table 2 Finished Ground Water Quality based on AWWA Utility Survey 1996

Parameter	**Average**					**Minimum**					**Maximum**				
	Min	Max	Mean	Mode	Median	Min	Max	Mean	Mode	Median	Min	Max	Mean	Mode	Median
Temperature C	4	28	16.42	13	16	1	25	14	14	14	6	38	19.49	22	19.49
pH	6.1	9.6	7.7	7.5	7.6	5.5	9.5	7.4	7	7.3	6.2	10	8.08	7.8	8
TDS (mg/L)	0	2000	309	350	270	12	1600	229	120	190	60	2000	421	450	360
Total Alkalinity (mg/L CaCO3)	0	420	137.5	50	128	0	392	106	40	95	0	510	163.5	220	154
Total Hardness (mg/L CaCO3)	0	685	167.6	50	137	0	650	124	110	100	2	1100	223.2	90	174
Nitrate (mg/L)	0	54	2.49	0	0.5	0	40	1.08	0	1.72	0	81	6.01	0	1.72
Iron (mg/L)	0	4	0.09	0	0.02	0	2.36	0.04	0	0	0	7	0.34	0	0.09
Manganese (mg/L)	0	19	0.099	0	0.001	0	4	0.03	0	0	0	9	0.108	0	0.02
True Color (units)	0	25	2.65	0	1	0	10	1.43	0	0	0	60	6.22	0	3
Turbidity (ntu)	0	26	0.492	0	0.18	0	20	0.22	0	0.07	0	57.1	1.63	0	0.4
Total particles (# ml)	0	122	20.9	0	12	0	25	8.57	4	4	2	256	91.3	NA	35
Total Coliform (monthly samples)	0	1040	49.81	10	25	0	900	54.6	4	28	0	1200	67.47	10	31
Total Coliform (monthly positive)	0	8	0.12	0	0	0	2	0.02	0	0	0	20	0.64	0	0
Total Organic Carbon (mg/l)	0	8	1.472	0	0.8	0	6	1.02	0	0.5	0	12	2.5	0	1.64
Free Chlorine (mg/L)	0	6.4	0.797	1	0.675	0	3.8	0.52	0.2	0.4	0	7	1.286	1	1.1
Combined Chlorine (mg/L)	0	6.6	1.38	0	1	0	4	1.02	0	0.75	0	7.4	1.93	0.2	1.7
Total THM	0	103	15.38	0	6	0	100	9.7	0	2	0	168	27.03	0	15.5

** Zero values include the cases where the said parameter was below detection level*

Table 3 Finished Surface Water Quality based on AWWA Utility Survey 1996

Parameter	**Average**					**Minimum**					**Maximum**				
	Min	Max	Mean	Mode	Median	Min	Max	Mean	Mode	Median	Min	Max	Mean	Mode	Median
Temperature C	3	29	14.9	13	15	0	23	5.9	1	5	8	37	24.4	27	25
pH	6.3	10	7.82	7.8	7.7	5.4	9.8	7.45	7	7.4	6.9	10.6	8.22	7.8	8.1
TDS (mg/L)	17	1564	229.6	160	186	1	1188	180	200	150	24	2645	322.4	180	258
Total Alkalinity (mg/L CaCO3)	2	700	73	20	60	0	184	53.6	20	41	8	350	94	40	89.5
Total Hardness (mg/L CaCO3)	2	596	114.9	140	108	0	460	89.2	130	79	6	867	149	150	142
Nitrate (mg/L)	0	11.5	0.85	0	0.3	0	8.6	0.42	0	0.12	0	25	1.88	0	0.77
Iron (mg/L)	0	1.8	0.03	0	0.01	0	0.32	0.01	0	0	0	6.8	0.103	0	0.03
Manganese (mg/L)	0	1.2	0.01	0	0	0	0.4	0.004	0	0	0	0.9	0.042	0	0.012
True Color (units)	0	35	1.8	0	1	0	10	0.8	0	0	0	110	4.91	0	3
Turbidity (ntu)	0	1.13	0.125	0.05	0.09	0	0.6	0.06	0.02	0.04	0.02	12	0.43	0.1	0.24
Total particles (# ml)	0	15000	383	0	24.5	0	4000	92.8	0	5	0	27000	947.5	0	90
Total Coliform (monthly samples)	0	679	67.96	30	31	0	576	67.7	28	30	0	731	80.64	31	40
Total Coliform (monthly positive)	0	5	0.051	0	0	0	1	0.01	0	0	0	16	0.47	0	0
Total Organic Carbon (mg/l)	0	16	2.49	3	2.19	0	12.6	1.76	0	1.56	0	29	3.84	5	3.18
Free Chlorine (mg/L)	0	6	1.21	1	1.1	0	4.8	0.87	1	0.8	0	7	1.68	1.5	1.5
Combined Chlorine (mg/L)	0	7	1.72	0.2	1.58	0	5.7	1.32	0	1.3	0	7.9	2.23	3	2.2
Total THM	0	100	40.03	50	40	0	70	23.5	0	22	0	198	67.04	100	61

** Zero values include the cases where the said parameter was below detection level*

Table 4 Distribution Water Quality based on AWWA Utility Survey 1996

Parameter	**Average**					**Minimum**					**Maximum**				
	Min	Max	Mean	Mode	Median	Min	Max	Mean	Mode	Median	Min	Max	Mean	Mode	Median
Temperature C	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
pH	6.5	9.9	7.77	7.8	7.7	5.4	9.8	7.4	7	7.3	6.7	10.5	8.21	8	8.1
TDS (mg/L)	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Total Alkalinity	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Total Hardness	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Nitrate (mg/L)	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Iron (mg/L)	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Manganese	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
True Color (units)	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Turbidity (ntu)	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Total particles	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Total Coliform (monthly samples)	0	1040	84.06	20	50	0	900	89.6	60	60	0	1200	110	20	66
Total Coliform (monthly positive)	0	10	0.15	0	0	0	3	0.02	0	0	0	50	1.16	0	0
Total Organic Carbon (mg/l)	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Free Chlorine (mg/L)	0	3.2	0.742	0.5	0.6	0	2.5	0.34	0.2	0.2	0	5	1.3	1	1.2
Combined Chlorine (mg/L)	0	87	1.51	1	1	0	60	0.86	0.1	0.4	0	100	2.2	2	1.75
Haloacetic Acids-HAA5	0	91	23.06	0	21	0	91	14.9	0	11	0	159	45.16	0	41
Total THM	0	121	33.8	0	32	0	85	19.9	0	17	0	216	59.4	0	59

** Zero values include the cases where the said parameter was below detection level*
** NR is not reported in the data set*

Table 2 and Table 3 present the summary of the *finished water quality* for ground water and surface water utilities respectively. Even if modal values are considered, the parameters in Table 2 and Table 3 show a fair degree of variability. The summary of the water quality parameters in distribution system is given in Table 4. The variability in values of pH, Chlorine, total hardness, total alkalinity, total dissolved solids and turbidity in Table 2 through 4 is of interest, as discussed later in the chapter these parameters have a dominant role in copper pitting.

Interestingly, the *maximum of the average values* for finished water for certain parameters in Table 2 and Table 3, exceed the maximum limit suggested by USEPA secondary standards. These parameters include pH, total dissolved solids, iron and manganese. Similarly, the *maximum of the average* concentrations for free chlorine and combined chlorine are about 6~7 mg/ L for finished water, which is above the maximum residual disinfectant level (*MRDL)* of 4.0 mg/ L as mandated by USEPA primary standards. The *maximum of the average* nitrate concentrations for both ground and surface water exceed the maximum contaminant limit (*MCL)* of 10 mg/L as mandated by USEPA primary standards. The reason for deviation from primary standards by these utilities is not explained in the data. A possible explanation may be because the data pertains to 1996 whereas the Disinfection / Disinfection byproduct rule-I was promulgated in 1998.

Some of the parameters like Sulfate, Carbon Dioxide, and Dissolved Oxygen are not reported in the database, it is very likely that these parameters were not measured.

These parameters have been very often identified as the principal causes for copper failures, although, their absence does not guarantee non occurrence of pitting. The database does not provide anionic breakdown for parameters like hardness, alkalinity, total dissolved solids, and turbidity, hence conclusions regarding pitting susceptibility of houses in specific utilities could not be made. Most of the parameters for distribution system water quality (Table 4) are either not measured or not reported in the database, thus the variability between the quality of finished water and quality of water in distribution system could not be assessed directly.

In summary the analysis suggests that the water quality parameters have fair degree of variability across different utilities and also within the distribution system. The variability in pH, chlorine, total hardness, total alkalinity, total dissolved solids and turbidity in finished water and in distribution system is of interest. Due to absence of complete anionic breakdown an objective comparison between the finished water quality and the distribution system water quality is difficult. Certain other parameters like, Dissolved Oxygen and Carbon Dioxide are not reported in the database. Based on the above data, the factors affecting the copper pitting are discussed with respect to the present literature.

Factors affecting copper pitting

The following text is based upon a review of a number of sources concerning copper corrosion. Since we did not conduct any experiments or studies, mechanisms or details as published by other sources are only reported and summarized herein, and these authors are not validating or confirming their conclusions. All attempts have been made to represent the current understanding of copper plumbing corrosion as accurately as possible. The factors that influence copper pitting may be broadly classified into two categories, namely physical and chemical parameters. Most of the corrosion problems are due to the complex synergy between these parameters (Schock, 1999). In general most of these parameters are dictated by the parameters of the major distribution system, where the variability in these parameters is much larger as compared to the variability of these parameters within the home plumbing system. A detailed discussion on the effect of these parameters is presented.

Physical parameters

The physical parameters include pressure, velocity, temperature and anthropogenic effects. While the pressure and velocity are proportional, certain devices such as valves, low flow faucets can affect the flow and hence the velocities. Temperature becomes a variable, when we consider cold water pipes, hot water pipes and hot water recirculation system. Many aspects of water chemistry like ionic dissociation and degasification of gases are related to temperature and pressure of water. Anthropogenic effects include poor workmanship, improper design, improper flushing after installation etc. The physical parameters and their effects are discussed in detail.

Pressure and Velocity

All home plumbing systems are pressurized systems. The pressure (p_i) and velocity (v_i) in any pipe in home plumbing system are highly dependent on the street level pressure (P_{street}). The street level pressure is the pressure measured in the street lateral that connects to the home plumbing system with a service line. Thus hydraulically, the street level pressure becomes a boundary condition for the home plumbing system. If the effects due to transience and compressibility are ignored, then the street level pressure (P_{street}) can be expressed in terms of pressure (p_i), velocity (v_i) and elevation (h_i) of any pipe using the energy equation.

$$\frac{p_i}{\gamma_{water}} + \frac{v_i^2}{2g} + h_i + H_{Losses} = \frac{P_{street}}{\gamma_{water}} \tag{1}$$

Where,

p_i is the pressure in any pipe (i) in home plumbing system

v_i is the velocity in pipe (i)

h_i is the difference in elevation between the street lateral and the point of measurement

g is the acceleration due gravity

γ_{water} is the unit weight of water (considering constant density)

H_{Losses} is the sum of minor and friction losses from the street lateral to the point of measurement

Hence, any change in the street level pressure (P_{street}) would affect the velocity and pressure in the home plumbing system. Thus the street level pressure (P_{street}) defines the boundary condition for any home plumbing system. Interestingly, the street level pressure is subjected to change with positioning of the house with respect to the pumping station. There may be high pressure and low pressure zones within the big distribution system, the behavior of a plumbing system in these zones would be markedly different from one another due to the change in the boundary condition. Additionally, the street level pressure may drop significantly during peak hours due to simultaneous withdrawal, causing much lower velocities (v_i) and pressure (p_i) as compared to the velocities and pressure in the non peak hours. The complexities and the variations of street level pressure itself is a subject of research.

The phenomenon of *erosion corrosion* is associated with higher flow rates. Due to impingement of water on the pipe wall the protective coating or the scale on the pipe wall gets damaged mechanically. This causes non uniform wearing of pipe wall locally, eventually causing a leak. A combination of high velocities, low pH and high DIC (dissolved inorganic copper) is extremely aggressive towards copper (Schock, 1999). Flow velocities (v_i) above 4~6 feet per second or pressure (p_i) above 80 psi are considered high (CDA reports). In general, the desirable velocity in plumbing system is between 4 and 6 feet per second (Woodson, 2002). Although, the threshold values of pressure (p_i) and velocity (v_i) which may cause pinhole formation are difficult to establish. In general, the threshold values will depend on several parameters including pipe diameter, water chemistry, flow constrictions, extent of faucet opening, presence of scale etc. Hence, the values ascertained by CDA reports can be considered as preliminary, the actual threshold values of pressure (p_i) and velocity (v_i) are not available in present literature.

On the other hand, higher velocities may increase the diffusion rates of protective species within the pipe, thereby helping in preventing corrosion (Schock, 1999). For instance, the formation of protective oxide film is dependant on the transport rate of dissolved oxygen, which is limited by the flow velocity. This can be mathematically modeled by assuming the pipe to behave like a plug flow reactor, and first order decay for oxygen in bulk solution,

$$\frac{\partial c(x,t)}{\partial t} + u(t)\frac{\partial c(x,t)}{\partial x} + kc(x.t) = 0 \qquad (2)$$

Where,

$c(x,t)$ is the concentration of any protecting species at a time t and distance x.

$u(t)$ is the flow velocity at time t.

k is the first order decay constant for the species in bulk solution.

However, in general the higher velocities are considered deleterious and should be kept within reasonable range. The cause of higher velocities may be high street level pressure or flow constrictions. The flow constrictions in the pipes may be due to sharp bends where the flow separates from the pipe boundary or may be due to presence of gaseous cavities at any cross section. These cavities are formed due to drop in pressure, which decreases the solubility of gases. The solubility of any gas in water is dependent on pressure and temperature hence the gases that are dissolved in water at higher pressure tend to strip out of water at lower pressure, if temperature is considered constant. The phenomenon can be explained considering water to be a homogenous two phased liquid.

The gases (oxygen, chlorine or other) are present in water in dissolved states. Considering water as a bubbly homogeneous mixture of these gases, and using Henry's law,

$$\frac{V_g}{V} \approx S \frac{p_s}{p_0} \tag{3}$$

Where,

S is the solubility coefficient.

V_g is the volume of dissolved gas.

V is the volume of water.

p_s is the saturation pressure of the dissolved gas (absolute).

p_0 is the standard pressure (absolute).

The left hand term of Eqn (3) is the void ratio of the gas and is pressure dependent. Hence, for any change in pressure the volume of dissolved gas should change for a given volume of water. This gives rise to the degasification of water at low pressures. It can be inferred that if the pressure is reduced to some other value p, then the volume of gas evolved per unit volume of liquid is given by $S(p_s - p)/p_0$. The values of S, are known for various gases at standard pressure conditions. If the release of gases or the degasification is assumed a one way phenomenon, then these gases once released should accumulate as isolated gaseous cavities at the highest elevation (being lighter than water). These isolated gaseous cavities may either combine to form bigger cavities and eventually reduce the net area of flow or these cavities may collapse at the pipe wall creating high pressure. In former case, the result is the higher flow velocities at the cross section which may cause erosion corrosion, while in later case, the effects may include damages due to gaseous impingement or vibrations or rattling of pipes. Both these effects may cause wear and tear at the pipe wall and in the protective scale. Velocity has been found to contribute to aluminum catalyzed pitting of copper at high pH and in the presence of chlorine. A recent masters' thesis (Nguyen, 2005) determined that this type of pitting did not occur if velocity was too low. Thus, there is a possibility that high velocities are a necessary precondition for certain types of pitting attack, even if excessive velocity alone is not the sole cause.

In summary, the effects of flow velocities and pressure are complex and may give rise to multiple phenomenons that could cause wear and tear in the pipe. Excessive velocities, high and low pressure should be checked to avoid problems related to gaseous cavitation and erosion corrosion.

Temperature

Temperature plays a significant role in copper corrosion. The effects of temperature are complex and are often misunderstood (Schock, 1999). The change in temperature can affect solubility of solids, influence formation of complex ions, influence diffusion rates of dissolved gases and solution species and influence formation of certain scales on the copper surface. Sometimes, the changes in temperature influence multiple phenomenons and hence make the situation complex (Schock, 1999). The solubility of gases is decreased markedly by increase in temperature. Hence, in hot water pipes and hot water recirculation systems, the degasification of the water can lead to formation of gaseous cavities and hence increased velocities at certain cross sections leading to erosion corrosion. This fact is supported by the anecdotal evidence in CDA reports, wherein majority of failures in hot water pipes and hot water circulation system are due to erosion corrosion. Due to entrapment of gases and continuous flow conditions, the erosion corrosion is likely to affect hot water recirculation systems more than hot water pipes. Due to increase in temperature, most of the gases are expected to be released in hot water pipes and hot water recirculation system, hence water in these pipes is likely to have lesser dissolved oxygen, therefore the mechanism like oxygen differential cell corrosion and gaseous cavitation are less likely in these pipes as compared to cold water pipes. However, the occasional occurrence of these mechanisms in hot water pipes and hot water recirculation system is not ruled out.

The solubility of certain chemical species in water is also highly dependent on temperature. The solubility of Calcium Carbonate [$CaCO_3$] is decreased with increase in temperature (Schock, 1999). Hence, at higher temperatures, Calcium Carbonate tends to come out of water and form a scale on the pipe wall. The Calcium Carbonate scale is a protective scale. Hence in hot water pipes and hot water recirculation systems temperature may have beneficial effects with respect to scale formation. However, excessive scale may sometime decrease the hydraulic conductivity of the water lines and in the worst case may cause clogging of hot water lines.

The effects of temperature are also important with respect to pH changes, these effects are illustrated further. The dissolved inorganic carbon (DIC) is defined as a function of Carbonate species [CO_3^{2-}], Bicarbonate species [HCO_3^-] and [H_2CO_3*] Carbon dioxide gas and Carbonic acid molecules (Schock, 1999).

$$DIC= [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \qquad (4)$$

Where,

[CO_3^{2-}] is the concentration of Carbonate species in mol/ L

[HCO_3^-] is the concentration of Bicarbonate species in mol/ L

[H_2CO_3*] is the sum of dissolved Carbon dioxide and Carbonic acid molecules.

The increase in temperature increases the dissociation constant for water, thereby producing more H^+ and OH^- ions, which tends to decrease the pH of water, however, this phenomenon is accompanied by increase in dissociation of Carbonic acid [H_2CO_3], which increases H^+ and HCO_3^- ions in water, the Bicarbonate ions [HCO_3^-] provide buffer against change in pH. However, due to deposition of Calcium Carbonate scale, the DIC is reduced, thereby reducing the buffering effect provided by the Bicarbonate ions. For waters with low alkalinity (< 50 mg/L of $CaCO_3$), the overall effect may be reduction of pH at higher temperatures (Schock, 1999). Thus high temperatures in water with low alkalinity may bring down the pH of water significantly.

The role of temperature is also important with respect to the type of scale that forms on the copper surface. Edwards et al. (1994) state that brochantite [$Cu_4(OH)_6(SO_4)$], a scale that supposedly catalyses pitting, is more stable at higher temperatures. Also, malachite [$Cu_2(OH)_2CO_3$], a protective scale is comparative less stable at these temperature ranges. The higher frequencies of failures in hot water pipes is due to the formation of brochantite [$Cu_4(OH)_6(SO_4)$] where temperatures are much higher and closer to 100^{o} C (Edwards et al. 1994).

Overall, the effects of temperature are complex and may be deleterious to copper in both cold and hot water pipes. However, these effects are highly subjective to water chemistry like pH, alkalinity and concentration of other anions. For instance, the brochantite scale may not form in hot water with higher pH, since the solubility of brochantite is increased at higher pH (> 7.4), also the increase in concentration of bicarbonate at a lower pH (<7.4) may result in formation of malachite scale. Hence, the effect of increase in temperature is highly subjective to water chemistry.

Anthropogenic effects

These effects include the factors that are introduced due to human errors in the process of commissioning or installation of the home plumbing systems. The effects also include poor practices during or after the installation that can induce copper pitting. Poor workmanship is perhaps the most important cause and can induce pitting failures in less than a year of installation. The CDA reports define poor workmanship as improper cutting of pipes (pipes that are not squarely cut and not reamed), excessive soldering flux and improper joining of pipes. Poor workmanship may be a result of accelerated construction period, human negligence or under qualified plumbing technicians deployed during the installation. This category of failures is categorized as *soldering flux induced* failures in CDA reports. Soldering flux induced failures may be avoided by ensuring that the plumbing technicians use the industry standard material and practices when installing copper tube systems (Myers and Cohen, 2005). The fluxes should comply with ASTM B813 and soldering connections should be made in accordance to ASTM B 828 (Myers and Cohen, 2005). Ellis II, (2000) elaborates that excessive soldering flux reacts with cupric oxide to produce hydrochloric acid, which increases the rate of pitting by supplying chloride ions. Flux induced leaks, once started are difficult to stop, typically it requires re plumb after four or five leaks (Myers and Cohen, 2005).

In addition to the poor installation practices, sometimes post construction activities can cause pitting in home plumbing systems. If the copper pipes are not flushed properly, the debris accumulated at the bottom of the horizontal pipes may induce pitting due to oxygen differential mechanism (Rossum 1985). Long stagnation periods between installation and usage, may cause complete decay of the residual disinfectant which may induce copper pitting due microbiological growth. The period between the installation (when the water enters the copper pipes) and usage should not exceed two months (Rossum 1985).

All the above cited reasons are more of practical nature and are directly related to the practices during and after installation. To certain extent the above reasons are of human control and are a matter of embracing certain practices that can save pitting problems due to the aforesaid reasons.

Chemical parameters

Most of the theory and practical experiences suggest that the causes of pitting revolve around water chemistry. The nature of certain anion species (Chloride and Sulfate) seems to show variable character in different water chemistries. Some researchers have identified the role of pH and dissolved carbon dioxide as the dominating factor in copper pitting. However, there is no direct correlation of carbon dioxide concentration and its role in any corrosion mechanism (Schock, 1999). The nature of interaction of any anionic species in water with the copper is highly subjective to pH and pressure conditions. The review of chemical parameters affecting copper pitting is presented with respect to copper chemistry.

Review of Copper Chemistry

Copper metal is oxidized to the cuprous (+1) and cupric (+2) oxidation states in corrosion. Under strong oxidizing conditions, higher oxidation states of (+3) and (+4) for copper are also known but those are not important in plumbing corrosion (AWWA 1996). When copper corrodes to (+1) or (+2) oxidation states, it may form insoluble precipitates or soluble complexes. The soluble complexes contribute to copper concentrations in drinking water. The precipitates may form passivating film, cuprite [Cu_2O] or cupric species [CuO] or may be present in water in form of blue or green turbid suspensions. The formation of such scale (cuprite or cupric) plays a key role in reducing the rate of the corrosion (Edwards et al. 1994). The type of scale that forms on the copper surface is highly dependant on water chemistry. The type of scale not only depends on the anions present in water, but it also depends on other conditions like their relative concentration, pH and temperature. The common anions that may form solid scales are chloride, sulfate, nitrate and bicarbonate (Edwards et al. 1994). The scale thus formed may be soluble or precipitate as solids depending upon the pH and temperature of the water. Based on the Pourbaix diagram of copper, it can be inferred that the cuprite [Cu_2O] is stable on a narrow range of pE values, and tenorite [CuO] is stable at alkaline pH values for water at equilibrium with atmospheric oxygen (AWWA 1996).

Thus, in drinking water pipes it is hypothesized that the copper oxidizes to cuprous (+1) state by losing an electron in the first step, this process is facilitated by the electron acceptor species; generally aqueous chlorine ,dissolve oxygen or hydrogen ion. The anodic reaction is given by,

$$Cu_{(metal)} \rightarrow Cu^{+} + e^{-} \tag{5}$$

$$2Cu^{+} + H_2O \rightarrow Cu_2O_{(solid)} + 2H^{+} \tag{6}$$

Cuprite [Cu_2O], often known as cuprous oxide is brownish red and is often found as thin and continuous film on the pipe wall. Cuprite, being stable in a narrow range of pE, may be further oxidized to tenorite [CuO] at alkaline pH values in the second step. The reactions require an electron acceptor, which is generally aqueous chlorine, dissolved oxygen or hydrogen ions. Tenorite [CuO] is black in color and is more stable in alkaline pH range. The anodic reaction is given by,

$$\frac{1}{2}Cu_2O_{(solid)} + \frac{1}{2}H_2O \rightarrow Cu^{2+} + OH^- + e^- \qquad (7)$$

$$Cu^{2+} + H_2O \rightarrow CuO_{(solid)} + 2H^+ \qquad (8)$$

The corresponding cathodic reaction for both the steps may occur in three possible ways. If the water contains aqueous chlorine, it shall dominantly participate in the cathodic reaction as compared to hydrogen ions or dissolved oxygen; this is because chlorine has high electron affinity. The reaction takes place in two steps; the first step involves dissolution of gaseous chlorine in water forming Hypochlorous acid [HOCl]. The Hypochlorous acid ionizes in the second step, yielding hydrogen ion [H^+] and hypochlorite ion [OCl^-] (Viessman, 1993). The equations are given by,

$$Cl_2 + H_2O \Leftrightarrow HOCl + H^+ + Cl^- \qquad (9)$$

$$HOCl \Leftrightarrow OCl^- + H^+ \qquad (10)$$

The dissociation of Hypochlorous acid [HOCl] to hypochlorite ion [OCl^-] is rapid, so that equilibrium is maintained even if the former is being continuously consumed. At pH around 7.5, both the species [HOCl] and [OCl^-] occur almost in equal concentration (Viessman, 1993). At higher pH values (> 7.5) the dissociation rate of Hypochlorous acid increases, due to which Hypochlorite ion exists in abundance as compared to

Hypochlorous acid. The phenomenon is completely reversed at lower pH values (< 7.5). Hence, at lower pH values (<7.5), Hypochlorous acid [HOCl] becomes the dominant species that accepts electrons and facilitates cathodic reaction and at higher pH values (> 7.5), Hypochlorite ions [OCl^-] facilitates the cathodic reaction. The corresponding equations are given by,

For *pH < 7.5*

$$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O \tag{11}$$

For *pH > 7.5*

$$OCl^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O \tag{12}$$

In case free chlorine is not present, the cathodic reaction is facilitated by reduction of dissolved oxygen, the reaction is given by

$$O_2 + 2H_2O + 4e^- \Leftrightarrow 4OH^- \tag{13}$$

If even dissolved oxygen is not present, the cathodic reaction is facilitated by reduction of hydrogen ion to hydrogen. The reaction is given by

$$2H^+ + 2e^- \Leftrightarrow H_2 \qquad (14)$$

Irrespective of which reaction takes place at cathode, there is an increase in pH either due to consumption of hydrogen ions or due to production of hydroxyl ions. This drop in pH is localized and is different than the pH in bulk solution (Schock, 1999).

Another form of copper scale commonly found is copper carbonate or malachite [$Cu_2(OH)_2CO_3$]. Edwards et al. (1994), state that over a pH range of 5.5~9.5, tenorite [CuO] and malachite [$Cu_2(OH)_2CO_3$] are predicted to be dominant cupric solids. The presence of either of these solids depends on the bicarbonate concentration and the pH of water. For pH below 7.7 and high bicarbonate concentrations, malachite [$Cu_2(OH)_2CO_3$] is favored, whereas for higher pH values and high bicarbonate concentrations tenorite [CuO] is favored. For low bicarbonate concentrations, tenorite [CuO] is favored at all pH values above 6.5. Edwards et al. (1994) illustrate that the solubility of the tenorite [CuO] is increased at higher bicarbonate concentrations, hence water with high pH and high bicarbonate concentration is not expected to form a malachite [$Cu_2(OH)_2CO_3$] scale, additionally it would increase the solubility of the protective tenorite [CuO] film.

Since, the solubility of other copper solids like copper hydroxide, copper chloride, cupric nitrate is more than malachite [$Cu_2(OH)_2CO_3$] and tenorite [CuO], their presence on the scale in plumbing systems is very unlikely (Edwards et al. 1994). The other copper salt that is commonly present on pipe surface is brochantite [$Cu_4(OH)_6(SO_4)$], due to better stability at higher temperature, it is commonly found in hot water pipes or hot water recirculation system (Edwards et al.1994). However, the formation of the brochantite is subjective to the concentration of bicarbonates and pH conditions. Hence, for waters with high sulfate to bicarbonate ratio, pitting is likely in hot waters due to the formation of brochantite. In cold water pipes, the formation of brochantite formation is favored at high sulfate to bicarbonate ratio and high sulfate to chloride ratio. Brochantite formation is like to increase pitting in the waters that have undergone softening (Edwards et al. 1994).

To summarize, the formation of scale on the pipe surface is highly dependent on water chemistry, relative concentration of anions, alkalinity, temperature, pH etc. The scale thus formed may be protective or non protective depending upon the water chemistry. The most common scales that can form in copper water pipes are malachite [$Cu_2(OH)_2CO_3$], tenorite [CuO] and brochantite [$Cu_4(OH)_6(SO_4)$], other copper solids formed are generally soluble at the pH range of interest.

The following section elaborates the role of water quality parameters that can influence copper pitting. The influence of all the known parameters is discussed in detail. The role of some of the chemical parameters like, pH, total alkalinity (TALK), dissolved inorganic carbon (DIC), hardness, total dissolved solids (TDS), dissolved oxygen and corrosion inhibitors is presented in the following section. The role of other parameters, namely, nitrate, chloride, chlorine, chloramines, hydrogen sulfide, sulfate, Iron, zinc, manganese, aluminum and natural organic matter (NOM) is described in *Appendix B-2*.

pH

pH is a measure of the activity of hydrogen ions, H^+, present in water (Schock, 1999). For pure water the pH value is 7, which is considered as a value for neutral solutions. For acidic conditions pH ranged between 1 and 7, while for basic solutions the pH ranges between 7 and 14. Due to the presence of other species in potable waters the pH is generally not neutral. During corrosion, the metal corrodes and losses electrons, in order to facilitate this reaction the H^+ ions accept electrons (Schock, 1999). For pitting corrosion, pH is an important parameter, in the absence of protecting film, pitting is likely to occur between pH 5 and 9 (Schock, 1999). If pH is too low, uniform corrosion is expected (Edwards et al.1994). Uniform corrosion rapidly increases with decrease in pH, it is significant in acidic waters ($pH < 6$), and may cause high soluble copper concentrations (> 1.3 mg/L) without the evidence of "green or blue" water (AWWA 1996). At higher pH (> 7), the rate of the uniform corrosion is very small, mostly at pH exceeding 7, the copper corrosion is considered to be non uniform (AWWA 1996).

pH is also important in formation of scales on pipe walls (Edwards et al.1994). As discussed earlier with respect to copper chemistry, the role of pH is crucial for tenorite [CuO] and malachite [$Cu_2(OH)_2CO_3$] formation, as these scales are considered protective to copper. For pH below 7.7 and high bicarbonate concentrations, malachite [$Cu_2(OH)_2CO_3$] is favored, whereas for higher pH values and high bicarbonate concentrations tenorite [CuO] is favored. For low bicarbonate concentrations, tenorite [CuO] is favored at all pH values above 6.5 (Edwards et al. 1994).

Edwards et al. (1994) illustrate that the solubility of the tenorite [CuO] is increased at higher bicarbonate concentrations, hence water with high pH is not expected to form a malachite [$Cu_2(OH)_2CO_3$] scale, additionally it would increase the solubility of the protective tenorite [CuO] film if it has higher bicarbonate concentrations. The role of pH also affects the behavior of Sulfate [SO_4^{2-}] and Chloride [Cl^-] ions, a detailed discussion on the role of pH for these anionic species is provided later when these species are discussed. The adjustment of pH is usually done at the treatment plant as a part of corrosion control measure (Schock, 1999). pH control is also used for balancing certain chemical reactions (Maryland Task Force, 2004). The optimal pH required to prevent corrosion depends on several factors including the pipe material in distribution system, however, corrosion inhibitors like Orthophosphates require a narrow pH range for maximum effectiveness (Schock, 1999). The pH is generally brought at or above neutral levels ($pH \geq 7$), by injecting chemicals such as Calcium Oxide or quick lime [CaO], Calcium Bicarbonate [$Ca\ (HCO_3)_2$], hydrated lime [$Ca\ (OH)_2$], or soda ash [Na_2CO_3] in finished water (Maryland Task Force, 2004).

Altogether, pH plays a dominant role not only in dictating the type of corrosion but also in formation or dissolution of certain scales that are important for copper pitting. The measures to adjust the pH in the treatment plants depends on various factors including the pipe material in the distribution system, nevertheless it is one of the reasons of large variability in pH across various utilities.

From AWWARF utility survey, presented earlier, it is evident that the finished water has considerable variation in pH values. The pH ranges between 5.5 to 10 for finished ground waters and 5.4 to 10.6 for finished surface waters. The pH in distribution system is also in similar range.

Alkalinity and DIC (dissolved Inorganic Carbon)

Alkalinity is a measure of the ability of water to neutralize acids and bases (Schock, 1999). The dissolved inorganic carbon (DIC) is defined as a function of Carbonate species $[CO_3^{2-}]$, Bicarbonate species $[HCO_3^-]$ and $[H_2CO_3^*]$ Carbon dioxide gas and Carbonic acid molecules (Schock, 1999). Hence, mathematically,

$$DIC= [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \qquad \text{(4-rewritten)}$$

$$TALK = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+] \qquad (15)$$

Where,

DIC is expressed in mg C/L

$[CO_3^{2-}]$ is the concentration of Carbonate species in mol/ L

$[HCO_3^-]$ is the concentration of Bicarbonate species in mol/ L

$[H_2CO_3^*]$ is the sum of dissolved Carbon dioxide and Carbonic acid molecules.

$[OH^-]$ is the concentration of hydroxyl ions in mol/ L.

$[H^+]$ is the concentration of hydrogen ions in mol/ L.

TALK is total alkalinity in equivalents/ L.

The dissolved inorganic carbon (DIC) has carbon dioxide as one of its component (Eqn 4). The role of carbon dioxide in copper corrosion is in “considerable disagreement” (AWWA, 1996). Although, some researchers have identified carbon dioxide as the major culprit that causes copper pitting in presence of dissolved oxygen. In many of the CDA reports, carbon dioxide concentrations exceeding 25 mg/ L in presence of dissolved oxygen is associated with copper failures. The higher the dissolved concentration of carbon dioxide, the greater the potential of pitting related to cold water (Myers and Cohen, 2005; Cohen and Myers, 1984). Myers and Cohen, (2005), illustrate that the concentration of the dissolved carbon dioxide can be lowered by increasing the pH, by the following relationship.

$$Log(0.88 \div KI) + Log(TALK) + 0.05 - pH = Log(CO_2) \tag{16}$$

Where

$Log(0.88 \div KI)$ is the temperature factor, which is 6.35 at 55F.

Sobue et al. (2003) presented a possible correlation between the carbon dioxide and copper pitting. The authors of the paper have themselves shown reservations towards the hypothesis, and have expressed the need of further investigation. The possible reactions presented by Sobue et al. (2003) are,

$$CO_{2(g)} \rightarrow CO_{2(aq)} \tag{17}$$

$$CO_{2(aq)} + H_2O \rightarrow H_2CO_3 \tag{18}$$

$$HCO_3 \rightarrow HCO_3^- + H^+ \tag{19}$$

The authors of the paper have further suggested that the last step (Eqn 19) may possibly facilitate reduction of oxygen at cathode by supplying the hydrogen ion.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{20}$$

Since, the reduction of oxygen, is coupled with oxidation of copper at anode, the reaction will precede causing corrosion of copper. Nevertheless, the role of carbon dioxide remains unclear.

From Eqns (4) and (15), it is clear that there is a strong relationship between DIC and TALK. The concentration of Bicarbonate and Carbonate ions is directly related to pH of water (Schock, 1999). For a given pH and temperature, total alkalinity and DIC follow a straight line relationship. The slope of the line increases with increase in pH. Hence, for a given pH and temperature, an increase in DIC will increase the total alkalinity, while for a given DIC concentration and temperature a reduction in pH will cause a reduction in total alkalinity (Schock, 1999). The total alkalinity is usually expressed in mg $CaCO_3$/ L, it is calculated by alkalinity titration as carbonic acid equivalence point. When bases other than CO_3^{2-}, HCO_3^- and OH^- are present in water, the definition of the total alkalinity should include the concentration of all proton consuming species, with proper corrections for their respective dissociations (Schock, 1999). Schock, (1999) defines a general equation for total alkalinity, in waters containing orthophosphate, hypochlorite, ammonia, silica, and some singly charged organic species as,

$$TALK = 2[CO_3^{2-}]+[HCO_3^-]+[OCl^-]+[HPO_4^{2-}] +[OA^-] +[NH3]+[H_3SiO_4^-]+[OH^-]-[H^+] \qquad (21)$$

Where,

$[OCL^-]$ is the concentration of hypochlorite in mol/ L.

$[HPO_4^{2-}]$ is the concentration of orthophosphate in mol/ L.

$[OA^-]$ is the concentration of singly charged organic species in mol/ L

$[NH3]$ is the concentration of ammonia in mol/ L

$[H_3SiO_4^-]$ is the concentration of silicate in mol/ L

The above equation is based on the assumption that the concentrations of species like PO_4^{3-} and $H_2SiO_4^{2-}$ will be low due to small dissociation constants in the normal potable waters. The dissociation constants for these species increase markedly with increase in pH, thereby supporting the notion that increase in pH leads to increase in total alkalinity. Some of these species (orthophosphate and silicates) are used as corrosion inhibitors it is possibly due to this reason that pH adjustment becomes almost a necessary measure at the treatment plant. The increase in pH not only increases the dissociation of these species but it also strips carbon dioxide from water. As stated earlier, while adjusting the pH in the treatment, the alkalinity of the water is increased by increasing the carbonate, bicarbonate and hydroxyl species.

As discussed in copper chemistry, the oxidation of copper is facilitated by electron accepting species at cathode. The cathodic reaction is facilitated by the reduction of either hypochlorite [OCl^-], hypochlorous acid [HOCL] or hydrogen ion [H^+]. {refer Eqn (11) ~(14)}. And, the reaction at cathode is followed by a localized reduction in pH, which is different than pH in bulk solution (Schock, 1999). The rate of the cathodic reaction may be affected if the water resists such a change in pH. The ability of the water to resist such a change in pH is defined as its buffer intensity. Importantly, the DIC (dissolved inorganic carbon) plays a key role in providing buffer against the pH changes. The buffer intensity of water against an increase or decrease in pH is a function of alkalinity, DIC concentration, and pH of water (Schock, 1999). An increase in DIC provides higher buffer intensity to water for all pH ranges. For a particular DIC concentration, the buffer intensity changes with pH, the behavior is almost sinusoidal. The buffer intensity is maximum at about pH~7, any increase in pH decreases the buffer intensity and brings it to a minimum at about pH~ 8, higher values of pH causes an increase in buffer intensity. Interestingly, by increasing the alkalinity, the behavior of the buffer intensity does not change, additions of corrosion inhibiting species like orthophosphate, silicate does not increase the buffering ability of water at pH values till ~ 9 (Schock, 1999). Thus the carbonate and the bicarbonate system are primarily responsible for providing buffer.

This concludes that addition of carbonates and bicarbonates may provide beneficial effects at certain pH ranges with respect to buffer intensity, while at pH closer to ~8, the buffering effect of the carbonates and the bicarbonates is minimal and hence adding these species to water may not yield any substantive gain in terms buffering effects at the said pH range. Also, the addition of bicarbonate is generally believed to have beneficial effects and an increase in bicarbonate concentration increases the likelihood of formation of passivating scales (Edwards et al. 1994).

The AWWARF/ AWWA utility survey data presented earlier provides the range for alkalinity values (Table 2 & 3) for finished ground and surface waters, respectively. The total alkalinity for finished ground waters ranges between 0 and 510 mg/ L of $CaCO_3$. The total alkalinity range for surface waters is 0 to 700 mg/ L of $CaCO_3$. The breakdown of the anionic species that constitutes the total alkalinity values is not provided, hence, any conclusions could not be made regarding the dissolved inorganic carbon (DIC) and the buffer intensities of these waters.

Hardness and TDS (total dissolved solids)

Hardness is defined as the sum of Calcium [Ca^{2+}] and Magnesium [Mg^{2+}] concentrations and is expressed in equivalents of $CaCO_3$ (Tchobanoglous, 1985). The hardness can be further classified into carbonate hardness and non carbonate hardness. The carbonate hardness is associated with bicarbonate [HCO_3^-] and carbonate [CO_3^{2-}] species of magnesium and calcium, while non carbonate hardness is associated with other anions, mainly, chloride [Cl^-] and sulfate [SO_4^{2-}]. The type of hardness is extremely important from the perspective of scale formation. The formation of scale is highly dependant on the concentration of calcium carbonate in bulk solution.

Hence, waters with high carbonate hardness (and low non carbonate hardness), will have more carbonates and bicarbonates in bulk solutions, and hence more likely to form carbonate scale. Since, the alkalinity of water is dependent on carbonate and bicarbonate concentrations, such waters will have more alkalinity. On the other hand, hard waters with more non carbonate hardness (and less carbonate hardness), will have more sulfate or chloride anions as compared to carbonate and bicarbonate ions in the bulk solution. These waters are therefore less likely to form carbonate scale. Since, these waters have less carbonate and bicarbonate in bulk solution; they are lower in alkalinity as compared to the former case.

Hard waters are in general are less corrosive than soft waters, if sufficient alkalinity is present (Schock, 1999). The stress on alkalinity necessarily illustrates the type of hardness (carbonate or non carbonate) as explained above. The effects of temperature are important with respect to alkalinity. For instance, at high temperatures (in hot water pipe or hot water recirculation systems), the calcium carbonate scale is formed due to decrease in solubility of calcium carbonate. The scale thus formed is protective and hence beneficial from pitting perspective. In coldwater pipes, in general, the calcium carbonate scale does not form, exceptions to this rule may be found in systems where water is softened with lime or soda lime by making the water super saturated with

Calcium carbonate (Schock, 1999). The above discussion has led us to the definition of Type-I pitting.

Type I pitting is likely to occur in hard, cold, well waters with high sulfate concentration relative to chloride and bicarbonate and with high carbon dioxide in between pH 7~ 7.8 (Edwards et al. 1994). The conditions defined for Type-I pitting may be explained with respect to the previous discussion. If water has high sulfates relative to bicarbonates and chlorides, it follows that it is low in alkalinity, also almost all the hardness present in the water is sulfate (non carbonate hardness), now since the water is cold, the calcium carbonate scale should not form (as water is low in carbonates), hence leaving the surface of pipe exposed to sulfate anions that cause corrosion. The role of carbon dioxide is not clearly explained in the publication. The most likely explanation can be attributed to the increase in conductivity of the solution due to dissociation of carbonic acid, as explained in Eqn (18). This type of pitting is generally associated with cold water pipes; however, their occasional occurrence in hot waters is also reported (Edwards et al. 1994).

The reason of the occurrence of Type-I pitting in hot waters is attributed to the lack of comprehensive theory with respect to water quality (Edwards et al. 1994). However, this can be explained on the lines of above discussion. With increase in temperature, the solubility of the calcium carbonate should decrease and it would be expected that the calcium carbonate scale will form, however, another phenomenon dominates. Since, the water is low in carbonates and bicarbonates, it necessarily has lower DIC (dissolved inorganic carbon) and low alkalinity, because of lower DIC the water has poor buffer intensity against pH changes. In hot water pipes or hot water recirculation systems, initially, the higher temperatures cause a decrease in solubility of calcium carbonate, however, the net effect due to higher temperatures and low alkalinity is the reduction in pH (Schock, 1999). The decrease in pH increases the solubility of calcium carbonate thus preventing the scale formation, and leaving the pipe surface exposed to sulfate ions. It follows from the above discussion that alkalinity plays a significant role in Type-I pitting.

Type-II pitting may occur in hot water pipes with low pH (< 7.2) and high sulfate concentration relative to bicarbonate, with occasion deposits of manganese (Edwards et al. 1994). The possible explanation to this type of pitting is as follows. Since, there is no mention about the amount of calcium carbonate in the water, two possibilities arise. One, water has significant calcium carbonate almost equal to or nearly saturation level. Two, the calcium carbonate content in water is significantly low. The explanation for both these cases is presented. Since the pH and the bicarbonate concentration are low, the alkalinity of the water is determined by the concentration of carbonates (present as calcium carbonate). If the concentration of calcium carbonate is significant, then water would be highly alkaline and moderate DIC level. In hot water pipes, the likelihood of calcium carbonate scale formation is fairly high, as the DIC provides a buffer against the change in pH and the rise in temperature decreases the solubility of calcium carbonate without affecting the pH. Under these conditions the pitting is not likely. However, if the calcium carbonate concentration is low, then due to lower DIC the said water has poor buffer intensity against the pH change. With increase in temperature, there will be a further drop in pH which further increases the solubility of calcium carbonate. The calcium carbonate scale will not form. Hence, pitting is very likely. Importantly, from the above explanation, this type of pitting can also occur in cold water pipes, since calcium carbonate scale formation is less likely (carbonate is present in low concentration). The role of manganese in Type-II pitting is not very clear. There have been instances when hot water pitting is observed without manganese deposits (Edwards et al. 1994).

Nevertheless, the type of hardness is important from copper pitting perspective, if the hardness is present as carbonate hardness, then it may have some beneficial effects with respect to alkalinity and DIC, however, if the hardness is non carbonate hardness then water will have lower DIC and less buffer. The role of sulfate and chloride will be explained later in the chapter.

Soft waters on the other hand, are more prone to corrosion (Schock, 1999). This is primarily due to the absence of protection that is usually obtained from bicarbonate and carbonate ions. Due to little or no bicarbonate and carbonate ions, the alkalinity of the water is fairly low. Additionally, due to low DIC, these waters have very little buffer intensity. Pipes in these waters have very little protection against anionic species that are aggressive to copper because of the poor ability to aid the formation of either malachite or calcium carbonate scale. These waters provide little protection to copper surface against impingement of water or gases on pipe wall. The erosion corrosion can be severe in these waters specially if accompanied by formation of gaseous cavities. These conditions can be easily met in hot water recirculation systems provided these waters are significantly saturated with dissolved gases like dissolved oxygen or carbon dioxide (Myers and Cohen, 2005).

Another type of pitting associated with soft waters is Type-III pitting. This may occur in soft waters with low conductivity, low alkalinity and high pH (~8.2) in cold water pipes (Edwards et al. 1994). This type of pit may not cause failure and is characterized by voluminous release of insoluble corrosion products (Edwards et al. 1994). Since, the mechanism seldom causes any failure in copper pipes, it is not considered in the scope of present study.

Total dissolved solid (TDS) is the measure of the dissolved organic and inorganic species in water. Inorganic dissolved substances may include minerals, metals and gases. Organic dissolved substances include decay products of vegetation, from organic compounds (Peavy, 1985). The TDS is usually measured as milligrams per liter on a dry mass basis. The dissolved inorganic species may further be classified as ionic and non ionic species. The ionic species are mainly important from corrosion perspective. USEPA enlists total dissolved solids in national secondary standards. TDS concentration exceeding 500 mg/ L may have cause hardness in water, deposition in pipes or fixtures, colored water, staining and impart salty taste to water.

The dissolved ionic species in water increases the conductivity of water, which increases the corrosion current (Schock, 1999). Since the rate of corrosion is directly proportional to the corrosion current, it follows that more ionic species in dissolved form facilitates corrosion process. The extent to which these ionic species would affect the corrosion is highly dependant of the plumbing material as well as the type of ions. If the high TDS is mainly due to the bicarbonate and hardness ions, it is highly corrosive towards copper (Schock, 1999).

Most of the ground waters have higher TDS concentrations as compared to the surface waters (Tchobanoglous, 1985). Ground water consists of ionic species often in the form of sulfates, nitrates, chlorides, bicarbonates and carbonates. These anions if not removed will be associated with higher conductivity of water. This may be one of the reasons why copper pitting is often associated with ground waters. However, in the absence of relevant water quality data, these conclusions are mere rule of the thumb.

The AWWARF/ AWWA utility survey data provides a range of hardness for finished ground and surface waters. The hardness for finished ground water varies between 0 and 1100 mg/ L of $CaCO_3$, the corresponding TDS ranges between 0 and 2000 mg/ L. The hardness for finished surface water ranges between 0 and 867 mg/L, the corresponding TDS ranges between 1 and 2645 mg/L. In the absence of ionic breakdown of species that constitute this hardness and TDS, any inference related to conductivity and carbonate or non carbonate component of hardness cannot be made.

Dissolved Oxygen (DO)

Oxygen is present in aqueous solution as dissolved oxygen. The role of dissolved oxygen is often misunderstood with respect to corrosion (Schock, 1999). Actually, the presence of oxygen in environment is detrimental for any metal. Dissolved oxygen reacts with copper to form cuprous [Cu^+] and cupric [Cu^{2+}] species, depending upon the amount of oxygen present in water (Schock, 1999). The detrimental effects of dissolved oxygen for copper are strongly supported by CDA forensic analysis, where the presence of dissolved oxygen has been identified as the cause for pit propagation. This is coherent with the current literature, wherein the propagation of pitting is associated with oxygen reduction at the site of pit formation (Edwards et al. 1994). The presence of cuprous and cupric oxide under laying the tubercules (CDA reports) proves the direct reaction of dissolved oxygen with copper metal.

In order to trace back the source of dissolved oxygen, it is necessary to analyze the source and treatment of raw water. The dissolved oxygen is present in all the surface waters. The presence of dissolved oxygen is essential for aquatic life and aesthetic quality of water (Tchobanoglous, 1985). The oxygen demand for the aquatic life and for the oxidation of organic matter present in these surface water bodies is continuously met by atmospheric oxygen through diffusion. If seasonal changes due to temperature effects are ignored, then it may be assumed that the dissolved oxygen content in these surface waters is well maintained around some average value. Hence, when surface water is the source of raw water, it follows that dissolved oxygen exists in the water by default. The concentration of the dissolved oxygen in finished water is dependant on the concentration of the dissolved oxygen in raw water.

On the other hand, ground waters have lesser dissolved oxygen and sometimes may not have dissolved oxygen. Additionally, these waters may contain undesirable gases like carbon dioxide and hydrogen sulfide. Carbon dioxide is the result of bacterial decomposition of organic matter in soil. Apart from the questionable role of carbon dioxide in copper corrosion, it can interfere in treatment processes (Tchobanoglous, 1985). Hydrogen sulfide is the by product of reduction of sulfur in mineral deposits. Hydrogen sulfide imparts bad taste and odor in drinking water. The solubility of these gases at atmospheric pressure is small, but these gases tend to be more soluble under high pressures that are commonly found in deep aquifers. Ground waters can often contain small quantities of iron or manganese that are soluble in the absence of oxidizing agents. The removal of carbon dioxide, hydrogen sulfide, iron and manganese is obtained through *aeration*. During aeration, the iron and manganese are oxidized to higher oxidized states due to formation of non ionic compounds that are not soluble in water (Tchobanoglous, 1985). The aeration also helps in removal of carbon dioxide and hydrogen sulfide by helping in release of these gases from water under atmospheric conditions. In context of the aforesaid discussion, aeration is the treatment step where dissolved oxygen gets added to water; hence finished ground waters are expected to have significant level of dissolved oxygen.

From the above discussion, it can be inferred that the presence of dissolved oxygen is almost certain in all the finished waters. When the water is sent into the distribution system, the concentration of dissolved oxygen can decrease due to the consumption of dissolved oxygen or remain the same depending on conditions and nature of interaction inside the distribution system. For instance, dissolved oxygen can help in speciation of new microorganisms that are present in the distribution system (Schock, 1999). These microorganisms may shield themselves underneath the deposits or corrosion products that are accumulated in the distribution system. The dissolved oxygen may also get consumed in the event of bacterial decomposition of organic matter inside the distribution system. However, the presence of microorganisms or organic matter inside the distribution system is not desirable, as it has its own disadvantages. The nature of interaction of dissolved oxygen with pipe surface in the distribution system, its consumption based on chemical or biological reactions and its effect on water quality inside the distribution system is quiet complex and may not be important from the perspective of the present study.

The AWWARF/ AWWA utility survey does not provide any data for the dissolved oxygen in finished water or in distribution system. Nevertheless, the presence of dissolved oxygen is certain in these waters. It would be interesting to study the possible relationship between high dissolved oxygen zones in the distribution system and regions of pinhole occurrence.

Corrosion Inhibitors (Phosphates, Orthophosphates and Silicates)

Inhibitors are the chemical substances that are added to water to prevent corrosion. The inhibitors in general may either form a protective film at the pipe surface or may change the nature of corrosion (Schock, 1999). Three principal types of corrosion inhibitors are silicates [$H_3SiO_4^-$], orthophosphates [HPO_4^{2-}] and polyphosphates. The selection of an inhibitor may depend on several parameters, including the water quality parameters (pH, alkalinity, DIC etc), the type of corrosion for which it is selected, the material to be protected etc. An overview of the corrosion inhibitors is provided.

Silicates [$H_3SiO_4^-$] form a protective film and thus form a physical barrier between the pipe wall and its environment. These are highly basic compounds, and their dissociation causes an increase in pH and subsequently the alkalinity of water (refer Eqn 20). The silicates react with corrosion by products on the pipe surface and form a more protective scale (Schock, 1999). The effect of silicate anion has not been studied in great detail with respect to copper corrosion. Studies have shown that it is effective in providing inhibition at higher pH (Schock, 1999).

The performance of *Orthophosphates* [HPO_4^{2-}] with respect to copper has been somewhat unsatisfactory. It inhibits copper corrosion at near neutral pH, but at higher pH seem to have counterproductive effects (Schock, 1999). This is because it seems to interfere with the formation of protective film at higher pH. Zhe and Pehkonen, (2004) have shown that orthophosphate can provide effective protection to copper against chloride attack by formation of cuprous or cupric oxide scale that becomes smooth after extended period of exposure. Interestingly, for *copper pitting* orthophosphates have seemingly performed well, the Washington Suburban Sanitary Commision (WSSC) found an appreciable decrease in pinhole incidences within one year of using orthophosphates (Maryland Task force, 2004).

Polyphosphates have been found effective for treating localized or pitting corrosion by changing it to more uniform corrosion. This may cause increase in copper levels and increased metal loss, however, the overall life cycle of the pipe is increased since the corrosion becomes more uniform (Schock, 1999). Additionaly, polyphosphates may interfere with the precipitation of calcium carbonate or other calcium species. This is primarily because of change in alkalinity due to their addition (refer Eqn 21). An increased alkalinity increases the solubility of calcium carbonate at same pH (Schock, 1999). However, under these conditions the Langlier Saturation Index (LSI) will yield erratic results. Polyphosphates are sometimes used with orthophosphates to yield optimal benefits.

The role of other parameters, namely, nitrate, chloride, chlorine, chloramines, hydrogen sulfide, sulfate, Iron, zinc, manganese, aluminum and natural organic matter (NOM) is described in *Appendix B-2.*

A summary of the physical and chemical parameters that influence copper pitting is presented in Table 5.

Table 5 Summary of physical and chemical parameters that influence copper pitting.

Parameter	**Source**	**Effects on copper pitting**	**Synergetic effects**	**Related Mechanisms**
Pressure	Intrinsic property of plumbing system. Street level pressure is the boundary condition. Pressure and velocity inside the plumbing system (in any pipe) are complimentary to each other and are dependent on street level pressure.	Low pressure inside plumbing system may cause degasification of water which may lead to gaseous impingement or cavity formation.	May produce adverse effects with other parameters like temperature, alkalinity, pH and dissolved inorganic carbon (DIC).	*Gaseous Cavitation*
Velocity	Intrinsic property of plumbing system. Street level pressure is the boundary condition. Pressure and velocity inside the plumbing system (in any pipe) are complimentary to each other and are dependent on street level pressure.	Excessive velocities may cause localized wearing of protective scale or pipe wall. Long stagnation periods may cause decay of residual disinfectant which may induce microbiological corrosion.	May produce adverse effects with other parameters like temperature, alkalinity, pH and dissolved inorganic carbon (DIC).	*Erosion-corrosion*
Temperature	Intrinsic property.	Governs the conditions for scale formation. May cause degasification of water, decrease in pH (in poorly buffered waters). Higher temperatures are usually deleterious for copper.	May facilitate multiple phenomenons, e.g. change in solubility, precipitation of calcium carbonate, malachite or brochantite. The effects coupled with pH, temperature and other anions may produce complex effects.	Higher temperatures can promote Type-II pitting in hard waters, can cause lowering of pH in poorly buffered waters, can dissolve malachite, and can cause degasification of water. Beneficial effects of higher temperatures include precipitation of carbonate scale in hot water pipes. Carbonate scale does not form in cold water copper pipes. [a]

Table 5 Summary of physical and chemical parameters that influence copper pitting.

Parameter	**Source**	**Effects on copper pitting**	**Synergetic effects**	**Related Mechanisms**
Anthropogenic effects	Poor workmanship, poor quality fluxes used in soldering and improper flushing of pipes after installation.	May cause failure in a short time period.	Improper flushing of pipes may result in deposition of debris that may induce pitting due to presence of dissolved oxygen.	*Soldering flux induced* & *Oxygen differential pitting.*
pH	Intrinsic property.	Dominates several parameters including, solubility of CO_2, formation of scale, dissociation of orthophosphates and solubility of various anionic species.	Dominates many mechanisms, especially the role of various anionic species (Sulfate and Chloride). Combined effects with pressure and temperature are complex.	Pitting usually occurs at pH > 6.5. Uniform corrosion at pH < 6.5. It controls the type of scale that forms on pipe surface. The stability of scales like malachite, tenorite and brochantite is highly dependent on pH and temperature. [a]
Total Alkalinity (TALK) and Dissolved inorganic Carbon (DIC)	Measure of carbonate, bicarbonate and hydroxyl ions. Bicarbonate and carbonate may be present as hardness. Carbonate may be added during softening or pH adjustment.	Carbonate and bicarbonate form protective scale. DIC provides buffer against pH changes. Low alkalinity and/ or low DIC deleterious for copper.	Alkalinity and DIC are affected by pH and temperature changes.	Lower alkalinity and poorly buffered waters are subjected to pH changes more easily. The type of anion contributing to alkalinity is important. [a]
Hardness and TDS	Measure of carbonate, bicarbonate, sulfate and chloride anions. Mostly present in well waters. Carbonate may be added during softening or pH adjustment.	The type of hardness (carbonate or non carbonate) is important. If non carbonate hardness (sulfate and chloride) is more then deleterious for copper. Higher TDS (ionic species) increase conductivity and hence corrosion.	Related to alkalinity and DIC. Soft waters more prone to changes in pH due to lack of buffer.	Type-I, Type-II and Type-III pitting.

Table 5 Summary of physical and chemical parameters that influence copper pitting.

Parameter	**Source**	**Effects on copper pitting**	**Synergetic effects**	**Related Mechanisms**
Dissolved Oxygen	Naturally present in surface waters. In ground waters oxygen gets added during aeration.	Helps in propagation of pit by facilitating the cathodic reaction. Generally, deleterious for copper, however, may hinder corrosion due to formation of tenorite scale.	Can help in speciation of new microorganism in distribution system. Helps the growth of nitrifying bacteria and hence microbiological corrosion. May cause concentration cell corrosion under debris accumulated at the pipe wall.	Mostly responsible for pit propagation by facilitating cathodic reaction. Presence of dissolved oxygen can cause speciation of new micro organisms. Absence of oxygen allows SRBs to thrive. [a]
Nitrate	Contaminant classified by USEPA primary standards (10 mg/ L). May be present in surface and well waters. The principal sources of nitrates include fertilizers used for horticulture/ agricultural purposes and animal waste.	Nitrate concentrations exceeding 40 mg/ L are expected to increase pitting frequency. However, these concentrations are far beyond EPA maximum contaminant limit (10 mg/ L).	Not known	Not known
Hydrogen Sulfide	Well waters may contain dissolved H_2S or sulfate reducing bacteria.	Very deleterious to copper. The pitting is almost certain and once started it is difficult to mitigate.		*Sulfide induced pitting*
Free Chlorine/ Chloride	Gets added during disinfection as gaseous chlorine or sodium / calcium hypochlorite. Additional source of chloride ion may be excessive soldering flux at joints in copper pipes.	Free chlorine with high pH may produce pitting. In presence of high pH, high chlorine and aluminum, pitting is certain. Chloride ion seems to have a dual effect. In long term chloride mitigates pitting.	Free chlorine with high pH and aluminum deposits is extremely lethal to copper. Pitting is certain if these conditions are met.	*High pH-High chlorine- Al.* & *High pH-High chlorine*

Table 5 Summary of physical and chemical parameters that influence copper pitting.

Parameter	Source	Effects on copper pitting	Synergetic effects	Related Mechanisms
Chloramines	Product of disinfectant chlorine and ammonia. Added in disinfection process.	Not known	Not known	Not known
Sulfate	May be present as hardness anion or may get added during coagulation in form of aluminum sulfate and ferrous sulfate.	Causes pitting due to formation of brochantite scale at pH < 7.8 (typically). At higher pH, brochantite is soluble, hence pitting may not occur.	Highly dependent on pH and temperature. Higher temperatures and lower pH ideal for brochantite stability. The formation of brochantite is dependant on sulfate to bicarbonate and sulfate to chloride ratio.	Type-I, Type-II And Type-III pitting.
Iron, Zinc and Manganese	Iron and manganese may be present in well waters. Zinc is not a natural constituent, may get added in raw water as urban pollutants. Iron may be added as ferrous containing coagulants in coagulation process. Zinc chloride or zinc phosphate may be added as inhibitor.	No deleterious effects reported or explained in literature. The presence of manganese in hot water pitting is often marked but its role is not explained in literature.	None / Not known	None/ Not known.
Aluminum	May get added in form of aluminum containing coagulants or may get added in distribution system due to leaching effects of cement pipes.	Aluminum itself not corrosive to copper.	In presence of high chlorine and high pH, aluminum synergizes the pitting mechanism.	High pH-High chlorine-Al.
NOM	Present as organic impurities in raw water.	Scientists believe the NOM have beneficial effects from pitting perspective. May help in maintaining pH conditions that	The exact mechanisms that may contribute in prevention of corrosion are not established.	Not known

Table 5 Summary of physical and chemical parameters that influence copper pitting.

Parameter	Source	Effects on copper pitting	Synergetic effects	Related Mechanisms
		prevent stripping of calcium carbonate. Other benefits include inhibition of cathodic and anodic reactions by sorption. The exact mechanism of passivation is not well established.	Other effects include formation of disinfection byproducts that have harmful effects on human health.	
Corrosion Inhibitors	Added at treatment plant to control corrosion in distribution and home plumbing systems. The common species used are silicates, phosphates, orthophosphates and polyphosphates.	Inhibit corrosion by formation of complexes with metal and thus forming a physical barrier.	The effectiveness of inhibitors is dependent on pH range. Orthophosphates are effective at a narrow pH range. Polyphosphate may be very effective in changing the nature of corrosion (from pitting to uniform)	NA

[a] A detailed review is available in Schock M.R. (1999), Internal Corrosion and Deposition Control (Water Quality and Treatment- AWWA (1999), Chapter-17 and Edwards et al.(1994), The Pitting Corrosion of Copper (Journal of AWWA, 74-90)

Mechanisms for copper pitting from literature

Extensive research has been done in the past few decades to study the causes of the copper pitting in home plumbing systems. A comprehensive unified theory that can explain all the mechanisms is still lacking. It may be attributed to the lack of simulation capabilities in the laboratories that can capture the long term variability in water quality and hydraulic parameters and their effects on copper pitting. Scientists have tried to explain the causes of failure for the failed pipe samples based on certain hypothesis, but their hypothesis do not answer the questions like why the other pipes did not fail under similar circumstances. This has left us with several discrete theories, each acknowledging only a part of the pitting phenomenon. Additionally, each of these theories leave behind a degree of uncertainty for the occurrence of pitting under the conditions defined in each of them, due to which, the pitting phenomenon, has been unquantifiable in terms of system parameters.

The following work is focused on developing a scoring system for copper pitting in home plumbing. All the mechanisms reported in the literature to date are compiled along with their reported recipes. Each recipe typically consists of a set of parameters that were reported to have caused failure. The parameters generally consist of water quality and hydraulic parameters within some range, or any other condition that is reported as *necessary* for the particular failure to occur. The scores for these parameters are obtained based on the uncertainty, which is expressed as scientific certainty, for the reported mechanisms.

The forthcoming sections are organized as follows. First, the mechanisms from various sources are identified and compiled. These mechanisms are then assigned *scientific certainties* based on likelihood of pitting. Second, a numerical scale for the assigned scientific certainties is developed, in terms of unknown variables for each scientific certainty. Third, a set of mathematical inequalities and constraints is formulated based on the score ranges and the scientific certainties from the preceding steps. The mathematical inequalities are solved simultaneously, to obtain the scores for individual attributes and unknown variables of the numerical scale.

<u>*Identifying mechanisms*</u>

The analysis protocol followed by Copper Development Association was presented earlier in the Chapter 1. The CDA reports identify several pitting mechanisms based on the results from the physical examination (by stereomicroscope) and chemical analysis (using Energy dispersive spectroscopy (EDS) and micro-chemical analysis (MCA)) of the failed pipe samples. Each mechanism identified in the reports, typically contain a set of constituents (water quality or hydraulic parameters) that should *co exist within a specified range* for pitting to occur. CDA reports (1975~2004) categorize the failures into nine different mechanisms, namely, *Chlorine/ chloride (or flux) induced*, *Oxygen differential, Excessive heating of water, Externally initiated failure, Erosion corrosion, Sulfide induced, Microbial, Aggressive water, Poor workmanship and Blue water or no failure.*

The *Aggressive water* is a generic term used by CDA; it covers waters with different chemistries. The handbook on copper by ASM international (2001), provides a set of conditions under which water may be termed as *aggressive* and may cause pitting in copper tubes. The original publication (Cohen and Lyman, 1972), where the table is originally published is not readily available for reference. The publication is a part of research publications from CDA. An abbreviated version of the paper, that could be obtained, explains that the table is based on independent analysis of 65 different waters from different communities throughout United States. Most of the mechanism identified by Cohen and Lyman, (1972) underline the role of non carbonate hardness in water as the major cause of copper pitting. Among the various recipes, lower bicarbonate to sulfate, lower chloride to sulfate and high concentrations of carbon dioxide are identified as the principal causes of copper pitting.

CDA, in its later publication (Cohen and Myers, 1984), refined the causes for the cold water pitting, and presented a different analysis that is based on time to leak (TTL). The analysis results in the paper are based on a computer program (Automatic Interaction Diagram-AID), and are based on 118 domestic cold water failures in United Kingdom. The paper identifies ten different mechanisms based on the analysis of water quality data. The analysis involved creating hierarchies among the water quality parameters. A bifurcation is made at each hierarchy based on characteristic of water. The time to leak (TTL) at each bifurcation is provided based on the statistical data. Necessarily, the bifurcation is based on the minimum common parameters identified in a group of failed pipes. The bifurcation suggests that at low pH (< 7.8) high carbon dioxide, high dissolved oxygen and high sulfate hardness is most deleterious to copper. The underlying mechanisms are not explained in the paper. For high pH (> 7.8), the time to failure is considerably high, which suggests that high pH conditions inhibit corrosion. The role of some species like potassium and silicon dioxide is not explained, although their presence is reported to influence the time to leak and hence the rate of corrosion.

Rossum, 1985, proposed that pitting in copper tube may initiate if the pipes are not flushed properly after the installation. He proposed that the lag time between the pipe installation and its usage should be minimized as a preventive measure. The causes identified by Rossum were mainly related to practices in the post installation phase, he further related these practices with possible pitting mechanisms. The causes of these mechanisms were deposits due to dirt, debris or flux residuals that are left in the pipes due to lack of proper flushing after the installation. Oxygen differential pitting is explained as the underlying mechanism due to accumulation of dirt and debris. The effect of this debris was reported to worsen if the stagnation period between installation and usage were long.

Edwards et al. (1994), provide a comprehensive review of the copper pitting and water chemistry, and broadly categorized copper pitting into Type-I, Type-II and Type-III. The Type-I and Type-II pitting are associated with sulfate hardness, especially if the bicarbonate hardness is relatively low. Although, Type-I and Type-II pitting are generally referred as cold water and hot water pitting, but occasional occurrence of either type in cold water and hot water pipes is reported. Edwards et al. (1994) provide a detailed review of anionic species that may cause pitting. Among the major anionic species identified in the paper, are namely, chloride, sulfate, bicarbonate and nitrate. The paper identified the role of these anionic species with respect to the scale formation. The deleterious role of brochantite [$Cu_4(OH)_6(SO_4)$] scale, its solubility and its relevance to hot water and soft water pipe failure is emphasized. The paper defines the pitting mechanism as a two step process, involving pit initiation and pit propagation. The dual nature of chloride anion and its long term passivating effect on copper pitting is emphasized.

Ellis II, (2000) criticizes the AID analysis from CDA (Cohen and Myers, 1984), and propose that the causes of copper pitting are not related to water chemistry but are rather of “anthropogenic” nature. *Ellis II, (2000)* suggests that the anthropogenic element in the pitting is mainly due to soldering flux that reacts in aqueous conditions to produce acidic environment. Ellis II, (2000) illustrates that these acidic conditions are mainly the cause of copper tube failures and supported this assumption with the location of the failure, which is very often near the pipe joint.

Myers and Cohen, (2005) identify seven sources of copper corrosion based on more than 1500 investigations conducted over 25 years. These causes are similar to the causes identified in CDA reports. Although carbon dioxide is among the major corrosive elements but its involvement in the mechanism is unexplained.

Based on personal communications with Dr Marc Edwards, a list of possible mechanisms for copper pitting is obtained. These causes are also listed in research proposal for the project funded by AWWARF. Among the various causes, a combination of high pH, high chlorine and aluminum deposits is considered most corrosive. The mechanism is similar to the one that was observed in WSSC area. Other causes include *sulfide/ sulfate reducing bacteria, gaseous cavitation, erosion-corrosion, concentration cell corrosion and microbial corrosion*. Dr Edwards identify scientific certainty of each of these mechanism based on the experimental studies and physical evidences.

A summary of the mechanisms identified from the literature is given in Table C-2.1 (*Appendix C-2*). Interestingly, none of the sources in the literature identified all the causes together at a single instance. Due to this reason the causes reported by different sources are included for analysis. All the mechanisms along with the reported recipes are combined to obtain a holistic view; these causes are presented in Table 6. The causes reported from more than one sources are combined / merged.

Table 6 Compiled causes of copper pitting in cold water, hot water pipes and hot water recirculation systems.

	Mechanisms	$j = 1$	$j = 2$	$j = 3$	$j = 4$	**Scientific Certainty**
$i = 1$	*Cl_2-Al-High pH* Ref [1]	pH $\geq$ 7.8	Cold Water	Chlorine $\geq$2.5 ppm	Aluminum deposits	*100%*
$i = 2$	*High Cl_2-High pH* Ref [1,2,3]	pH > 8.5	Cold Water	Chlorine $\geq$ 0.5 ppm		*Strongly Suspected*
$i = 3$	*Chloramine-AL* Ref [1]	pH $\geq$ 7.8	Hot water Re-circulating systems	Chloramine $\geq$2.5 ppm	Aluminum deposits	*Strongly Suspected* [a]
$i = 4$	*Chloramine-AL* Ref [1]	pH $\geq$ 7.8	Hot water	Chloramine $\geq$2.5 ppm	Aluminum deposits	*Suspected*
$i = 5$	*Chloramine-AL* Ref [1]	pH $\geq$ 7.8	Cold Water	Chloramine $\geq$2.5 ppm	Aluminum deposits	*Suspected*
$i = 6$	*Aggressive Water* Ref [2,4]	pH $\geq$ 7.8	Cold Water	Bicarbonate < 40 ppm		*Suspected* [b]
$i = 7$	*Aggressive Water* Ref [2,4]	pH $\geq$ 7.8	Cold Water	$CO_2 \geq 4.8$	Bicarbonate $\geq$ 54.6 ppm	*Below Suspected* [b]
$i = 8$	*Aggressive Water* Ref [2,4]	pH $\geq$ 7.8	Cold Water	$CO_2 < 4.8$ ppm	Bicarbonate $\geq$ 54.6 ppm	*Below Suspected* [b]

Table 6 Compiled causes of copper pitting in cold water, hot water pipes and hot water recirculation systems.

	Mechanisms	$j = 1$	$j = 2$	$j = 3$	$j = 4$	**Scientific Certainty**
$i = 9$	*Aggressive Water* Ref [2,4]	pH < 7.8	Cold Water	$CO_2 \geq 25$ ppm	DO $\geq$ 7.8 ppm	*Strongly Suspected* [b]
$i = 10$	*Aggressive Water* Ref [2,4]	pH < 7.8	Cold Water	$CO_2 \geq 25$ ppm	DO < 7.8 ppm	*Suspected* [b]
$i = 11$	*Sulfate / (Type-I)* Ref [2,4,5]	pH < 7.8	Cold Water	Sulfate $\geq$ 17 ppm and $CO_2 < 25$ ppm	Sulfate: Chloride $\geq$ 3.3 and High Sulfate: Bicarbonate ratio	*Strongly Suspected* [b]
$i = 12$	*Sulfate / (Type-I)* Ref [2,4,5]	pH < 7.8	Hot Water	Sulfate $\geq$ 17 ppm and $CO_2 < 25$ ppm	Sulfate: Chloride $\geq$ 3.3 and High Sulfate: Bicarbonate ratio	*Suspected* [b]
$i = 13$	*Sulfate* Ref [4]	pH < 7.8	Cold Water	Sulfate $\geq$ 17 ppm and $CO_2 < 25$ ppm	Sulfate: Chloride < 3.3 and Potassium $\geq$ 5 ppm	*Below Suspected* [b]
$i = 14$	*Sulfate* Ref [4]	pH < 7.8	Cold Water	Sulfate $\geq$ 17 ppm and $CO_2 < 25$ ppm	Sulfate: Chloride < 3.3, and Potassium < 4.2 ppm and Silica dioxide $\geq$ 26.2 ppm	*Strongly Suspected* [b]
$i = 15$	*Sulfate* Ref [4]	pH < 7.8	Cold Water	Sulfate $\geq$ 17 ppm and $CO_2 < 25$ ppm	Sulfate: Chloride < 3.3 and Potassium < 4.2 ppm and Silica dioxide < 26.2 ppm	*Suspected* [b]
$i = 16$	*Aggressive Water* Ref [2,4]	pH < 7.8	Cold Water	Sulfate < 17 ppm and $CO_2 < 25$ ppm		*Below Suspected* [b]

Table 6 Compiled causes of copper pitting in cold water, hot water pipes and hot water recirculation systems.

	Mechanisms	$j = 1$	$j = 2$	$j = 3$	$j = 4$	**Scientific Certainty**
$i = 17$	*Type-II* Ref [2,3,5]	pH < 7.2	Hot Water	High sulfate to bicarbonate	Presence of Aluminum/ Iron > 0.1 mg/L or Silica/ Manganese	*Suspected* [b]
$i = 18$	*Type-II* Ref [2,3,5]	pH < 7.2	Cold Water	High sulfate to bicarbonate	Presence of Aluminum/ Iron > 0.1 mg/L or Silica/ Manganese	*Suspected* [b]
$i = 19$	*Sulfide* Ref [1,2,3]	Sulfide ≥ 0.02 mg/L or water with SRB				*Almost 100%*
$i = 20$	*Microbial induced pitting* Ref [1,2]	Low alkalinity	Hot water Re-circulating systems	Lack of disinfectant	Stagnant waters	*Strongly Suspected*
$i = 21$	*Gaseous Cavitation* Ref [1,2]	Pressure drop below Vapor pressure	Cold Water	Water Saturated with DO or CO_2 or any other gas	Flow constrictions or sharp bends.	*Strongly Suspected*
$i = 22$	*Flux Induced* Ref [2,3,6]	Excessive Soldering Flux at joints	Cold Water	Improper (initial) flushing of pipes, after installation	Long Stagnation periods after installation (before the occupancy and usage)	*Suspected*
$i = 23$	*Oxygen Differential* Ref [1,2,3]	Deposits of Aluminum /iron/ Silica or other deposits other than copper	Cold Water	DO in appreciable amount		*Suspected*
$i = 24$	*Erosion Corrosion* Ref [1,2,3]	Pressure ≥ 80 psi and/ or velocities greater than 4~5 fps	Hot water Re-circulating systems	Soft water with high DO or Carbon dioxide		*Suspected*

Table 6 Compiled causes of copper pitting in cold water, hot water pipes and hot water recirculation systems.

	Mechanisms	$j = 1$	$j = 2$	$j = 3$	$j = 4$	**Scientific Certainty**
$i = 25$	*Erosion Corrosion* Ref [2,3]	Pressure $\geq$ 80 psi and/ or velocities greater than 4~5 fps	Hot water Re-circulating systems	Presence of Silica or any other abrasive material		*Suspected*

[a] The mechanism is rated as "strongly suspected" in hot water re-circulating systems, based "Characteristic pit / location" in Table C-2.1 (*Appendix C-2*)

[b] The scientific certainty assigned based on time to leak (Table C-2.1 (*Appendix C-2*))

Table 6 contains 25 mechanisms, these mechanisms and their attributes are presented in form of a matrix (i & j) values. Each mechanism is identified with a distinct i value that ranges from 1 through 25. The attributes for each mechanism are identified with j values in the corresponding row; the j values range between 1 and 4. The mechanisms presented in Table 6 are broadly grouped in three categories, namely, with pH $\geq$ 7.8 ($i = 1$ to 8), with pH < 7.8 ($i = 9$ to 18) and mechanisms not dependant on pH ($i = 19$ to 25). The mechanisms ($i = 19$ to 25) are either *totally independent* of pH or their correlation with pH has not been reported. From Table 6, it can be inferred that for each mechanism to occur, a set of constituents (corresponding $j = 1$ to 4) should *co exist*, in a certain range. Since, the threshold values are not available in the literature, the minimum value that is reported to have caused a failure is enlisted.

Hence, any $X_{i,j}$ or "attribute" (as used from now on) of the matrix in Table 6, would define a particular parameter with a specified range / value, that forms a part of recipe of the i^{th} mechanism. Also all the pitting mechanisms require the co existence of specific set of *attributes*. Hence, the "co existence" of a *specific set* of attributes becomes a necessary condition for a particular mechanism.

Allocating scientific certainty to mechanisms

Although, the *co-existence* of a specific set of attributes becomes a necessary condition for pitting to occur, but it is not essential that pitting would occur if this criteria is met. This is established by the fact that there are other pipes that did not fail under the same set of attributes. Hence, there exists a degree of uncertainty whether or not the pitting will occur, even if all the required set of *attribute* coexists. This is expressed as *scientific certainty* which is assigned on a linguistic scale in Table 6. The mechanisms in Table 6, have been accumulated from more than one source where such a classification may not have been made, hence following procedure was adopted to assign the scientific certainties:

- The mechanisms identified in Table C-2.1 (*Appendix C-2*) (Dr Edwards personal communication), already contain the scientific certainty assigned to each of them. However, a separate mechanism ($i = 3$ in Table 6) is formulated for hot water recirculation system with a scientific certainty “Strongly Suspected”, this was based on the comments enlisted in “characteristic pit location” in Table C-2.1 (*Appendix C-2*). These comments elaborate that the mechanism is more severe in hot water recirculation systems; hence a separate case with a stronger scientific certainty is formulated.

- The mechanisms from Cohen and Myers, (1984) have been assigned the scientific certainty based on the average time to leak (TTL) values. For all the mechanism having a TTL less than 5 years are assigned “Strongly Suspected” category, for mechanisms with TTL greater than 5 years and less than 20 years are assigned “Suspected” category, all the mechanisms with TTL greater than 20 years are assigned “Below Suspected” category.

- All the other mechanisms are assigned “Suspected” category.

An interpretation of these scientific certainties is explained as follows. The maximum scientific certainty that can be assigned to any mechanism is “100%”, which means that by following the recipe from Table 6, a pit can be artificially induced in the laboratory. There is only one mechanism ($i = 1$) with a “100%” scientific certainty.

An “almost 100%” scientific certainty indicates that pitting with this recipe is almost sure to occur, although none of the sources have reported to have verified the recipe in a laboratory test to an extent of inducing a pinhole leak. Although, all the sources have unanimously agreed that the recipe is extremely corrosive to copper. There is only one mechanism ($i = 19$) with a “almost 100%” scientific certainty

The other scientific certainties include “Strongly Suspected”, “Suspected” and “Below Suspected” categories, and these terms express likelihood of copper pitting on a linguistic scale. These are mainly assigned based on time to leak, as explained previously. The Scientific certainties of all the mechanisms are expressed in the last column of Table 6. These values or linguistic intensities will be utilized subsequently to obtain the scores for each attribute.

To summarize, every row of matrix in Table 6 defines a particular pitting mechanism, the attributes listed in the i^{th} row ($j = 1$ to 4) are the minimum number of attributes that should *co-exist* as a necessary condition for the pitting to occur. Even if, all the attributes of the i^{th} row co-exist, the chances of pitting to occur will be the *scientific certainty* expressed in last column of i^{th} row.

Need of a numerical scale

The scientific certainties expressed in Table 6, are based on a linguistic scale of verbal intensities. These certainties are linguistic hierarchies, which define the system susceptibility in terms of the attributes. These intensities are not only subjected to ones' interpretation but are also difficult to quantify in physical sense. It may be noted that the terms used (such as "Suspected") in a linguistic scale cover a range and are not mere points on the intensity line (Figure 1). Although, the extents of the terms used in linguistic scale (such as "Suspected" and "Strongly suspected") may have well demarcated boundaries in literal meaning but the boundaries for each term is not well defined and quantifiable on an intensity line for the end user. This leaves zones of overlap, where it becomes extremely difficult for the user to quantify the extent of the problem in physical sense.

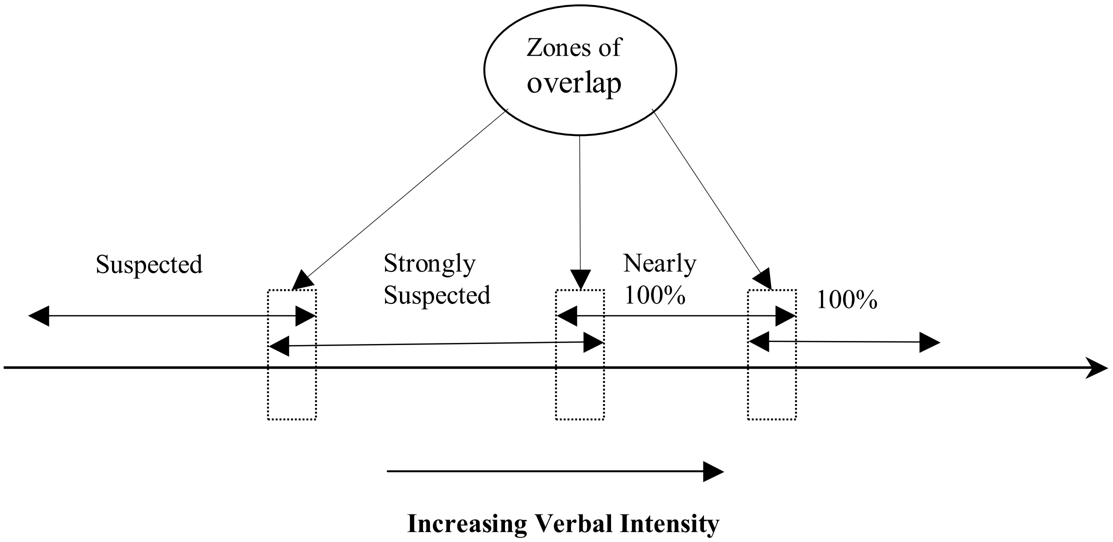

Figure 1   A schematic view of the linguistic scale, showing zones of verbal intensities.

In real time situations, one or more *attributes* of a particular recipe may not be present; the extent to which the system susceptibility to pitting would change becomes totally unquantifiable in such situations. Thus, it becomes imperative to correlate these pitting recipes and develop a *scoring system for attributes* that may be used with a *numerical scale* and can provide quantifiable results to the user.

The advantage with the *numerical scale* is that the zones of overlap are automatically eliminated. Although, to interpret results from a numerical scale, a linguistic scale is almost necessary. Hence, an ideal situation will be a scoring system that works on a numerical scale and that can yield quantifiable results which can ultimately be correlated with the linguistic scale.

The following section presents a methodology of developing a *scoring system for attributes* and a *numerical scale,* using the information from Table 6. The task to develop a scoring system that incorporates the relative intensities of the attributes and which is also consistent with the scientific certainties of each mechanism is divided into three steps. First, a numerical scale is developed by defining ranges for scientific certainties on a numerical scale with some unknown variables; these values are restricted by formulating a set of mathematical constraints. Second, by using the relative intensities of the attributes in Table 6, a set of mathematical constraints are formulated in terms of the score ranges of the numerical scale, developed in first step. In the third step, the mathematical constraints formed in the first and second step are solved simultaneously as a goal program to achieve the scale parameters and the scores of the attributes.

Developing numerical scale

The purpose of developing a numerical scale is to provide a quantifiable basis for scoring each attribute. As mentioned earlier, the numerical scale automatically eliminates the zones of overlap between the two consecutive terms of linguistic scale. An example of the numerical scale is shown in Figure 2.

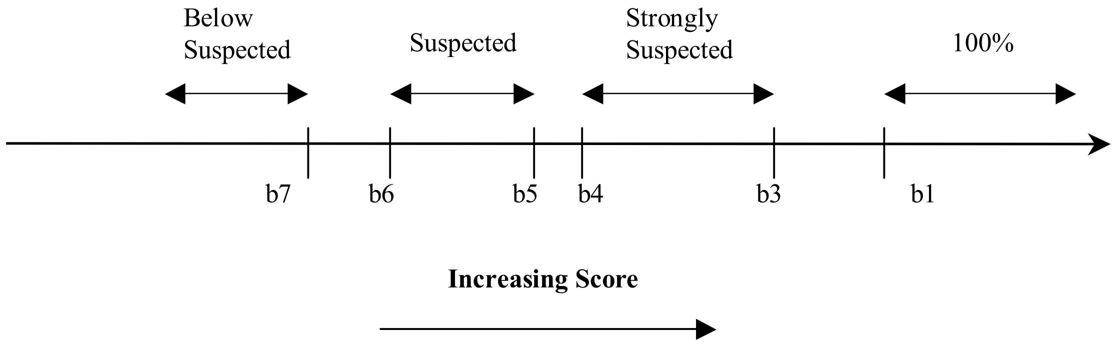

Figure 2 A schematic view of the numerical scale, used in the present study.

Figure 2, is based on the assumption that the attributes shall assume only integral scores. In order to avoid any overlap between the two consecutive terms on linguistic scale a difference of unity is maintained. This line of demarcation (by unity) between the two categories can only be maintained if all the attributes take integral values. If this assumption is not made, the decimal values of the attributes would be obtained. As the ultimate goal is to correlate the final scores of each mechanism with the linguistic scale, the decimal values may not add any significant benefit. On the other hand, integral values are easy to use; thus, the above assumption of integral values is adopted for developing the numerical scale.

Hence, if the score of the mechanism is greater than or equal to b_1, then the mechanism should have a "100%" scientific certainty. Similarly, the scores for mechanisms in "Suspected" category should be restricted between b_5 and b_6, and for "Strongly Suspected" category the score should be restricted between b_3 and b_4. Since, there is only one mechanism for "Almost 100%" category, the provision for this category in the scale is made by keeping the difference of at least 2 between b_1 and b_3. In order to create this demarcation and follow the other linguistic hierarchies, some mathematical constraints need to be formulated. These mathematical constraints are presented in the following section

$$b_1 - b_3 \geq 2 \tag{21}$$

$$b_3 - b_4 \geq 1 \tag{22}$$

$$b_4 - b_5 = 1 \tag{23}$$

$$b_5 - b_6 \geq 1 \tag{24}$$

$$b_6 - b_7 = 1 \tag{25}$$

These sets of constraints shall be used later to obtain the individual scores of the attributes. The approach is explained in the following section.

Obtaining individual scores for the attributes

For any scoring system to work, the sum of the scores of all attributes in a particular row should sum up to give a total score for that mechanism. Also, the score for each mechanism should correspond to the value range of its scientific certainty on the numerical scale. Hence, the total score obtained for any mechanism should be restricted to a value range according to its scientific certainty. From Table 6, each attribute can be identified by a set of i & j values. If the score corresponding to an attribute in i^{th} row and j^{th} column is designated by $X_{i,j}$, then the sum of the scores of the attribute in i^{th} row (designated by S_i) should be restricted to the value ranges in the numerical scale (Figure 2). This will lead to a system of inequalities that can be solved simultaneously to obtain individual $X_{i,j}$. These inequalities can be converted into equations using deviational variables, and can be solved simultaneously using goal programming techniques.

The formulation of these inequalities using the score ranges of the numerical scale is explained in *Appendix D-2*. Two formulations are shown below.

For $i = 1$ *(Cl_2-Al-High pH)*

The scientific certainty for the mechanism is "100 %", hence the score $S_1 \geq b_1$,

$$X_{1,1} + X_{1,2} + X_{1,3} + X_{1,4} \geq b_1 \tag{26}$$

Using deviational variable, the inequality is converted into an equation. If d_1 is a deviational variable, then it can be expressed as the difference of two positive numbers, hence

$$d_1 = d_1^+ - d_1^- \tag{27}$$

Using (27) and re writing (26) we get,

$$X_{1,1} + X_{1,2} + X_{1,3} + X_{1,4} - d_1^+ + d_1^- = b_1 \tag{28}$$

For $i = 2$ (*High Cl₂-High pH*)

The scientific certainty for the mechanism is "Strongly Suspected", hence the score $b_4 \leq S_2 \leq b_3$,

$$b_4 \leq X_{2,1} + X_{2,2} + X_{1,4} \leq b_3 \tag{29}$$

The inequalities for the upper and lower limit for the score are written separately, hence

$$X_{2,1} + X_{2,2} + X_{1,4} + d_2^+ - d_2^- = b_3 \quad \text{(For upper limit)} \tag{30}$$

And

$$X_{2,1} + X_{2,2} + X_{1,4} - d_3^+ + d_3^- = b_4 \quad \text{(For lower limit)} \tag{31}$$

Similarly, the inequalities for all the mechanisms are formulated. Based on the formulation (*Appendix D-2*), following goal program was obtained. The goal program was solved by minimizing the sum of the negative deviations.

$$Min\{Z\} = \sum_{n=1}^{45} d_n^-$$

Subjected to:

$$X_{1,1} + X_{1,2} + X_{1,3} + X_{1,4} - d_1^+ + d_1^- = b_1$$

$$X_{2,1} + X_{2,2} + X_{2,3} - d_2^+ + d_2^- = b_4$$

$$X_{2,1} + X_{2,2} + X_{2,3} + d_3^+ - d_3^- = b_3$$

$$X_{3,1} + X_{3,2} + X_{3,3} + X_{3,4} - d_4^+ + d_4^- = b_4$$

$$X_{3,1} + X_{3,2} + X_{3,3} + X_{3,4} + d_5^+ - d_5^- = b_3$$

$$X_{4,1} + X_{4,2} + X_{4,3} + X_{4,4} - d_6^+ + d_6^- = b_6$$

$$X_{4,1} + X_{4,2} + X_{4,3} + X_{4,4} + d_7^+ - d_7^- = b_5$$

$$X_{5,1} + X_{5,2} + X_{5,3} + X_{5,4} - d_8^+ + d_8^- = b_6$$

$$X_{5,1} + X_{5,2} + X_{5,3} + X_{5,4} + d_9^+ - d_9^- = b_5$$

$$X_{6,1} + X_{6,2} + X_{6,3} + d_{10}^+ - d_{10}^- = b_5$$

$$X_{6,1} + X_{6,2} + X_{6,3} - d_{11}^+ + d_{11}^- = b_6$$

$$X_{7,1} + X_{7,2} + X_{7,3} + X_{7,4} + d_{12}^+ - d_{12}^- = b_7$$

$$X_{8,1} + X_{8,2} + X_{8,3} + X_{8,4} + d_{13}^+ - d_{13}^- = b_7$$

$$X_{9,1} + X_{9,2} + X_{9,3} + X_{9,4} + d_{14}^+ - d_{14}^- = b_3$$

$$X_{9,1} + X_{9,2} + X_{9,3} + X_{9,4} - d_{15}^+ + d_{15}^- = b_4$$

$$X_{10,1} + X_{10,2} + X_{10,3} + X_{10,4} - d_{16}^+ + d_{16}^- = b_6$$

$$X_{10,1} + X_{10,2} + X_{10,3} + X_{10,4} + d_{17}^+ - d_{17}^- = b_5$$

$$X_{11,1} + X_{11,2} + X_{11,3} + X_{11,4} + d_{18}^+ - d_{18}^- = b_3$$

$$X_{11,1} + X_{11,2} + X_{11,3} + X_{11,4} - d_{19}^+ + d_{19}^- = b_4$$

$$X_{12,1} + X_{12,2} + X_{12,3} + X_{12,4} + d_{21}^+ - d_{21}^- = b_5$$

$$X_{12,1} + X_{12,2} + X_{12,3} + X_{12,4} - d_{21}^+ + d_{21}^- = b_6$$

$$X_{13,1} + X_{13,2} + X_{13,3} + X_{13,4} + d_{22}^+ - d_{22}^- = b_7$$

$$X_{14,1} + X_{14,2} + X_{14,3} + X_{14,4} + d_{23}^+ - d_{23}^- = b_3$$

$$X_{14,1} + X_{14,2} + X_{14,3} + X_{14,4} - d_{24}^+ + d_{24}^- = b_4$$

$$X_{15,1} + X_{15,2} + X_{15,3} + X_{15,4} + d_{25}^+ - d_{25}^- = b_5$$

$$X_{15,1} + X_{15,2} + X_{15,3} + X_{15,4} - d_{26}^+ + d_{26}^- = b_6$$

$$X_{16,1} + X_{16,2} + X_{16,3} + d_{27}^+ - d_{27}^- = b_7$$

$$X_{17,1} + X_{17,2} + X_{17,3} + X_{17,4} + d_{28}^+ - d_{28}^- = b_5$$

$$X_{17,1} + X_{17,2} + X_{17,3} + X_{17,4} - d_{29}^+ + d_{29}^- = b_6$$

$$X_{18,1} + X_{18,2} + X_{18,3} + X_{18,4} + d_{30}^+ - d_{30}^- = b_5$$

$$X_{18,1} + X_{18,2} + X_{18,3} + X_{18,4} - d_{31}^+ + d_{31}^- = b_6$$

$$X_{19,1} - d_{32}^+ + d_{32}^- = b_3 + 1$$

$$X_{19,1} + d_{33}^+ - d_{33}^- = b_1 - 1$$

$$X_{20,1} + X_{20,2} + X_{20,3} + X_{20,4} + d_{34}^{+} - d_{34}^{-} = b_3$$
$$X_{20,1} + X_{20,2} + X_{20,3} + X_{20,4} - d_{35}^{+} + d_{35}^{-} = b_4$$
$$X_{21,1} + X_{21,2} + X_{21,3} + X_{21,4} + d_{36}^{+} - d_{36}^{-} = b_3$$
$$X_{21,1} + X_{21,2} + X_{21,3} + X_{21,4} - d_{37}^{+} + d_{37}^{-} = b_4$$
$$X_{22,1} + X_{22,2} + X_{22,3} + X_{22,4} + d_{38}^{+} - d_{38}^{-} = b_5$$
$$X_{22,1} + X_{22,2} + X_{22,3} + X_{22,4} - d_{39}^{+} + d_{39}^{-} = b_6$$
$$X_{23,1} + X_{23,2} + X_{23,3} + d_{40}^{+} - d_{40}^{-} = b_5$$
$$X_{23,1} + X_{23,2} + X_{23,3} - d_{41}^{+} + d_{41}^{-} = b_6$$
$$X_{24,1} + X_{24,2} + X_{24,3} + d_{42}^{+} - d_{42}^{-} = b_5$$
$$X_{24,1} + X_{24,2} + X_{24,3} - d_{43}^{+} + d_{43}^{-} = b_6$$
$$X_{25,1} + X_{25,2} + X_{25,3} + d_{44}^{+} - d_{44}^{-} = b_5$$
$$X_{25,1} + X_{25,2} + X_{25,3} - d_{45}^{+} + d_{45}^{-} = b_6$$

$X_{1,1} = X_{3,1}$
$X_{3,1} = X_{4,1}$
$X_{4,1} = X_{5,1}$
$X_{5,1} = X_{6,1}$
$X_{6,1} = X_{7,1}$
$X_{7,1} = X_{8,1}$
$X_{9,1} = X_{10,1}$
$X_{9,1} = X_{10,1}$
$X_{10,1} = X_{11,1}$
$X_{11,1} = X_{12,1}$
$X_{12,1} = X_{13,1}$
$X_{13,1} = X_{14,1}$
$X_{14,1} = X_{15,1}$
$X_{15,1} = X_{16,1}$
$X_{17,1} = X_{18,1}$
$X_{24,1} = X_{25,1}$
$X_{1,2} = X_{2,2}$
$X_{2,2} = X_{5,2}$
$X_{5,2} = X_{6,2}$
$X_{6,2} = X_{7,2}$
$X_{7,2} = X_{8,2}$
$X_{8,2} = X_{9,2}$
$X_{10,2} = X_{11,2}$
$X_{11,2} = X_{13,2}$
$X_{13,2} = X_{14,2}$
$X_{14,2} = X_{15,2}$
$X_{15,2} = X_{16,2}$
$X_{16,2} = X_{18,2}$
$X_{18,2} = X_{21,2}$
$X_{21,2} = X_{22,2}$
$X_{22,2} = X_{23,2}$
$X_{3,2} = X_{20,2}$
$X_{20,2} = X_{24,2}$
$X_{24,2} = X_{25,2}$
$X_{4,2} = X_{12,2}$
$X_{12,2} = X_{17,2}$
$X_{3,3} = X_{4,3}$
$X_{4,3} = X_{5,3}$
$X_{9,3} = X_{10,3}$
$X_{11,3} = X_{12,3}$
$X_{12,3} = X_{13,3}$
$X_{13,3} = X_{14,3}$
$X_{14,3} = X_{15,3}$
$X_{17,3} = X_{18,3}$
$X_{1,4} = X_{3,4}$
$X_{3,4} = X_{4,4}$
$X_{4,4} = X_{5,4}$
$X_{7,4} = X_{8,4}$
$X_{11,4} = X_{12,4}$
$X_{17,4} = X_{18,4}$
$X_{i,j} \in I$

$X_{7,3} > X_{8,3}$
$X_{9,3} > X_{7,3}$
$X_{8,3} > X_{8,4}$
$X_{15,3} > X_{16,3}$
$X_{11,4} > X_{11,3}$
$X_{14,3} > X_{14,4}$
$X_{15,3} > X_{15,4}$
$X_{17,3} > X_{17,4}$
$X_{1,3} > X_{2,3}$
$X_{1,3} > X_{1,4}$
$X_{3,3} > X_{3,4}$
$X_{21,3} > X_{23,3}$
$X_{22,4} > X_{20,4}$
$X_{22,1} > X_{20,1}$
$X_{20,1} > X_{21,1}$
$X_{21,1} > X_{24,1}$
$X_{24,1} > X_{23,1}$
$X_{i,j} > 0$

$b_1 - b_3 \geq 2$ $\quad$ $b_4 - b_5 = 1$ $\quad$ $b_6 - b_7 = 1$

$b_3 - b_4 \geq 1$ $\quad$ $b_5 - b_6 \geq 1$ $\quad$ $b_i \in I$

$X_{1,3} + X_{1,4} > X_{2,3}$

$X_{2,3} > X_{3,3} + X_{3,4}$

$X_{3,3} + X_{3,4} > X_{6,3}$

$X_{6,3} > X_{7,3} + X_{7,4}$

$X_{7,3} + X_{7,4} > X_{8,3} + X_{8,4}$

$X_{11,3} + X_{11,4} > X_{9,3} + X_{9,4}$

$X_{9,3} + X_{9,4} > X_{14,3} + X_{14,4}$

$X_{14,3} + X_{14,4} > X_{10,3} + X_{10,4}$

$X_{10,3} + X_{10,4} > X_{15,3} + X_{15,4}$

$X_{15,3} + X_{15,4} > X_{17,3} + X_{17,4}$

$X_{17,3} + X_{17,4} > X_{13,3} + X_{13,4}$

$X_{13,3} + X_{13,4} > X_{16,3}$

The above goal program is solved using software "LP solve", the program is available for download on http://www.statslab.cam.ac.uk/~rrw1/opt/lp_solve/.

Results and Discussions

The summary of results is presented in Table 7 and Table 8. The values of the deviational variables are,

Deviational variables

$d_i^- = 0$, For all $i \in [1,45]$

$d_{44}^+ = d_{42}^+ = d_{40}^+ = d_{38}^+ = d_{31}^+ = d_{28}^+ = d_{27}^+ = d_{25}^+ = d_{21}^+ = d_{16}^+ = d_8^+ = d_7^+ = 3$,

$d_{36}^+ = d_{34}^+ = d_{23}^+ = d_{19}^+ = d_4^+ = d_2^+ = 2$,

$d_{15}^+ = d_{22}^+ = d_{14}^+ = d_{13}^+ = 1$

$d_{45}^+ = d_{43}^+ = d_{41}^+ = d_{39}^+ = d_{37}^+ = d_{35}^+ = d_{33}^+ = d_{32}^+ = d_{30}^+ = d_{29}^+ = d_{26}^+ = d_{24}^+ = 0$

$d_{20}^+ = d_{18}^+ = d_{17}^+ = d_{39}^+ = d_{12}^+ = d_{11}^+ = d_{10}^+ = d_6^+ = d_5^+ = d_3^+ = d_1^+ = 0$

Scale parameters

$b_1 = 24$, $b_3 = 22$, $b_4 = 20$, $b_5 = 19$, $b_6 = 16$, $b_7 = 15$

Table 7 Score ranges for scientific certainties.

Scoring Criteria	**Scientific Certainty**
$Sum \leq 15$	*Below Suspected*
$16 \leq Sum \leq 19$	*Suspected*
$20 \leq Sum \leq 22$	*Strongly Suspected*
$Sum = 23$	*Almost 100%*
$Sum \geq 24$	*100%*

Table 8 Attribute scores categorized by corrosiveness, based on the scores

Category	Attributes	Scores
pH	pH > 8.5	9
	pH ≥7.8	7
	pH < 7.2	5
	pH < 7.8	1
Temperature	Hot water Re-Circulation System	7
	Cold water	4
	Hot water	1
Most dominant chemical factors	Sulfide > 0.02 mg/ L or Water with SRB	23
	$CO_2 \geq 25$ ppm	13
	Chlorine ≥ 2.5 ppm	10
	Chlorine ≥ 0.5 ppm	9
	Sulfate: Chloride ≥ 3.3 AND High Sulfate: Bicarbonate ratio	9
	High Sulfate to Bicarbonate ratio	9
	Low alkalinity	8
	Water saturated with DO, CO_2 or any other gas	8
	$SO_4^{2-} \geq 17$ ppm AND $CO_2 < 25$ ppm	8
	DO in appreciable amount	7
Less dominant chemical factors	$SO_4^{2-} < 17$ ppm AND $CO_2 < 25$ ppm	7
	Sulfate: Chloride < 3.3, AND Potassium < 4.2 ppm AND Silica dioxide ≥ 26.2 ppm	7
	Chloramines ≥ 2.5 ppm	5
	$HCO_3^- < 40$ ppm	5
	Deposits of Aluminum/ Iron/ Silica or material other than copper	5
	Aluminum Deposits	3
	$CO_2 \geq 4.8$ ppm	3
	Sulfate: Chloride < 3.3, AND Potassium < 4.2 ppm AND Silica dioxide < 26.2 ppm	3
	$DO \geq 7.8$ ppm	3
	$CO_2 < 4.8$ ppm	2
	$HCO_3^- \geq 54.6$ ppm	1
	$DO < 7.8$ ppm	1
	Sulfate: Chloride < 3.3 AND Potassium ≥ 5 ppm	1
	Presence of Aluminum/ Iron > 0.1 mg/L or Silica/ Manganese	1
	Lack of Disinfectant	4
	Soft water with high DO or CO_2	3
Most dominant Physical factors	Excessive soldering flux at joints	9
	Pressure drop below vapor pressure	7
	Pressure > 80 psi and /or velocities greater than 4~5 fps	6
	Presence of Silica or any other abrasive material	3
Less dominant Physical factors	Long Stagnation periods after installation (before occupancy & usage)	2
	Improper (initial) flushing of pipes after installation	1
	Stagnant waters	1
	Flow constrictions or sharp bends.	1

Based on the scores, each attribute is classified into *most dominating* or *less dominating* category. Thus the scoring system helps in broader classification of the chemical and physical parameters. Although, certain lesser dominant factors can produce adverse affects in combination with pH, temperature or other attributes from most dominant category.

The interpretation of the scores should be done based on Table 6, 7 and 8. The present scoring system works on the minimum number of attributes. This is because each mechanism in Table 6 is defined based on minimum number of attributes that are required to produce a pinhole leak failure. Hence, the scores in Table 8 should be combined only for specific mechanisms that are defined in Table 6.

Formulations based on maximum number of attributes were attempted, but since some of the attribute change behavior with pH and temperature, such scoring system could not be formed. The inconsistency in the attempted formulation was mainly due to the behavior of sulfate and chlorine. Since, sulfate is dominant in pH < 7.8 range, and it does not contribute in pitting at pH≥ 7.8 range. This is primarily because increased solubility of brochantite scale at high pH values.

Similarly, chlorine is corrosive at high pH values (> 7.8) especially if aluminum deposits are present the synergy between aluminum and chlorine produces most corrosive combination. However at low pH (< 7.8) range none of the sources in the literature have reported any failure due to chlorine and aluminum. Most importantly, the role of sulfate is highly dependant on relative concentration between sulfate and chloride, the three zones of synergy were explained previously in the chapter. Hence, for a sulfate concentration of about 17 ppm, and sulfate the chloride ratio of about 3.3, the chloride concentration work out to be 5.65 ppm, which needs to be constrained as *not corrosive* under low pH concentration during the formulation. Due to this anomaly, the scoring system in the above problem is constrained and hence the use of Table 6 becomes necessary with Table 7 and Table 8.

Conclusions

The study concludes in identifying the chemical and physical parameters that are mainly responsible for causing copper failures in home plumbing. The role of water chemistry seems dominant in copper pitting but there are other hydraulic and physical parameters that can act in synergy to produce adverse effects. The exact causal mechanism of the copper pitting is not clear; this is due to lack of a unified theory. In the absence of such a mechanistic theory, the parameters that are responsible for copper pitting may be classified into dominant and lesser dominant categories based on the scoring system.

Due to variability in water chemistry the system susceptibility should be gauged based on the water quality at the tap. The scoring system can be used to gauge the system susceptibility. The system susceptibility should be gauged based on the mechanism that provides the maximum score for a particular plumbing system. For the homes where the pinhole leak has not occurred in past, the scoring system should be used only for advisory purposes. However, for the homes that have a previous history of pinhole leaks, the scoring system can provide good quantifiable results. The scoring system can identify the most critical mechanism for a particular plumbing system, and hence can be used to device suitable preventive action against future pinhole leaks. The combination of the scores should be done based on Table 6; other combinations should not be used for evaluation.

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APPENDIX A-2

Types of corrosion of copper

Types of corrosion

The handbook on copper metal published by ASM International (2001) contains comprehensive details about metallurgical properties of copper and its uses in various applications. It identifies nine types of corrosive attacks that can cause corrosion in copper. An overview of these types of corrosive attacks is presented.

General corrosion

This type of attack occurs over the entire surface at almost a uniform rate, hence it is often known as *uniform corrosion*. It results due to prolonged contact of the metal surface with its environment. The associated rate of corrosion is generally low and hence, this type of corrosion is considered least damaging to copper. In drinking water pipes, this type of corrosion seldom causes any failure, however, if severe, it may lead to high levels of leaching of copper, typically causing “Blue-water” or “Green-water” problems. Uniform corrosion rapidly increases with decrease in pH, it is significant in acidic waters (pH< 6), and may cause high soluble copper concentrations (> 1.3 mg/L) without the evidence of “green or blue” water (AWWA 1996). At higher pH (> 7), the rate of the uniform corrosion is very small, mostly at pH exceeding 7, the copper corrosion is considered to be non uniform (AWWA 1996). Soft waters in pH range 6 to 7 may cause uniform corrosion, often the phenomenon is associated to the high concentration of carbon dioxide in the said pH range, however, there is “considerable disagreement” on the role of carbon dioxide in copper corrosion (AWWA 1996). The present work is related to the non uniform corrosion of copper; hence *uniform corrosion* will not be discussed henceforth.

Galvanic Corrosion

This type of corrosion occurs when two dissimilar metals are connected and immersed in a conductive solution. This is due to the formation of an electrochemical cell because of the differences in electrode potential. The metal that is nobler becomes the cathode and the less noble metal becomes the anode and gets consumed in the electrochemical reaction. The surface area ratio of the anode and the cathode is important (Roberge 2000), if the surface area ratio of anode to cathode is small, he corrosion current may be concentrated over a small anodic area, hence may cause dissolution from that small area. The galvanic series of the metals from *National Aeronautics and Space Administration* (NASA) is available on http://corrosion.ksc.nasa.gov/galcorr.htm . The series id presented in Table A-2.1.

Copper in general is noble (cathodic) to most of the other metals used in the water distribution system and hence less likely to corrode. However, in certain specific conditions the metals like stainless steel exhibit variable behavior, that is, it may be anodic or cathodic to copper, depending upon the conditions of its exposure (ASM Handbook 2001). Hence, under these circumstances copper may become anodic to stainless steel and thus undergo corrosion. In general, galvanic corrosion is not very common in copper pipes that are used in home plumbing; however, it is generally recommended that the contact between the copper pipe and the other metal should be avoided.

Appendix A-2

Table A-2.1 Galvanic series of metals and alloys (*source NASA*)

Platinum	
Gold	**Non-corroded end (cathodic, or most noble)**
Graphite	
Silver	
18-8-3 Stainless steel, type 316 (passive)	
18-8 Stainless steel, type 304 (passive)	
Titanium	
13 percent chromium stainless steel, type 410 (passive)	
7NI-33Cu alloy	
75NI-16Cr-7Fe alloy (passive)	
Nickel (passive)	
Silver solder	
M-Bronze	↑
G-Bronze	
70-30 cupro-nickel	
Silicon bronze	
Copper	
Red brass	
Aluminum bronze	
Admiralty brass	
Yellow brass	
76NI-16Cr-7Fe alloy (active)	
Nickel (active)	
Naval brass	
Manganese bronze	
Muntz metal	
Tin	
Lead	
18-8-3 Stainless steel, type 316 (active)	↓
18-8 Stainless steel, type 304 (active)	
13 percent chromium stainless steel, type 410 (active)	
Cast iron	
Mild steel	
Aluminum 2024	
Cadmium	
Alclad	
Aluminum 6053	
Galvanized steel	
Zinc	
Magnesium alloys	**Corroded end (anodic or least noble)**
Magnesium	

Appendix A-2

Pitting Corrosion

Like other metals, copper undergoes pitting when exposed to certain conditions. The pitting corrosion may be localized or may be spread over the entire area. When spread over a large area, it roughens the surface and makes it irregular; in addition it may cause significant weight loss of the metal from the surface. However, localized pitting is considered to be the most dangerous form of corrosion, it is generally confined to a smaller area with pits of various shape and sizes. The weight loss due to localized pitting may not be significant but it may cause failures in a shorter time frame. Copper metal is susceptible to pitting mainly due to surface non-uniformity (metallurgical reasons) and due to environmental factors.

The pitting corrosion of copper is not completely understood with respect to environmental conditions. Even today, the pitting is considered somewhat random in terms of its occurrence and location. Copper pitting is a major concern in home plumbing systems. It has been reported in United States, Canada, Germany and other European countries. Despite of significant research, copper pitting is not completely understood. A detailed overview of the causes of the pitting that are reported in the literature is presented later in the section.

Crevice Corrosion is another form of localized corrosion which occurs near the crevice formed by two metals (copper and any other) or between the crevice formed by copper and any non metal. The attack is similar to pitting attack in terms of its unpredictable nature with respect to the location of its occurrence. Crevice corrosion may also result due to accumulation of foreign objects (dirt, vegetation or debris) on the surface of the metal. In home plumbing systems, it is often termed or *water line attack* or *oxygen differential cell corrosion*. In copper water lines, the attack generally occurs below the silica, aluminum or deposits of foreign material (other than copper) due to the differential in the oxygen concentration. The layer below the debris or the deposits is oxygen deficient with respect to the surface of the debris on the water side. This results in different electrochemical potential on two sides of the debris (AWWA 1996), the corrosion occurs to equalize the two potentials. The part of metal with high oxygen concentration acts as cathode, while the metal in contact with lower oxygen concentration becomes the anode (AWWA 1996). Since, the oxygen is not produced at either anode of cathode, the corrosion proceeds in such a way that the higher oxygen concentration is reduced (Uhlig 1938), if the pH is same on both the sides. Due to the resistance in diffusion of oxygen because of the debris or distance of transport, the differential in oxygen between the two layers is maintained; this continues the corrosion attack at low oxygen sites, leading to deepening of crevice in form of pitting (AWWA 1996).

Impingement

This type of attack occurs when the liquid, vapors or gases impinge the copper surface with high velocities. This attack is related to the flow conditions (velocity, pressure and temperature) of water. It is also dependant on the flow geometry (constrictions in flow, sharp bends in flows etc). It may be sub classified into Gaseous Cavitation and Erosion Corrosion. *Gaseous Cavitation* occurs due to impingement of bubbles (gases) on the inner pipe wall. Water may be assumed to be a two phase liquid, the gases (chlorine, oxygen etc) are dissolved in water and remain in equilibrium based on Henry's Law. The equilibrium concentrations of these dissolved gases are dependant on the pressure and temperature of the water. Due to increase in flow velocities (or drop in pressure) these gases may leave the liquid phase which results in degasification of water. The gases escape in form of bubbles that subsequently collapse after hitting the pipe walls. The pressure developed under the conditions of bubble collapse is extremely high and destroys the protective film of copper. The phenomenon is more prominent near sharp bends and flow constrictions. At higher temperatures, the capacity of the water to retain these gases decreases substantially.

Erosion Corrosion occurs when the flow velocities are higher than 4~5 fps, typically these conditions can occur under high street level pressures (greater than 80 psi), sharp irregularities at joints (due to poor workmanship or unreamed edges) or at flow constrictions, where the liquid jet constantly hits the pipe wall and damages the protective layer of copper. The phenomenon may be aggravated due to presence of dissolved oxygen and carbon dioxide due to the removal of protecting film and formation of concentration cells that subsequently form anodic sites, locally. *Impingement* is a common cause of copper tube failures in hot water recirculation systems; however incidences in cold water pipes are also reported in the literature.

Fretting

This form of attack appears in the form of pits or grooves marked by presence of corrosion products. This attack is associated with the surfaces that are subjected to repetitive (sliding) motion with other surface and the interface is subjected to some external load in presence of oxygen and moisture. All the three conditions, that is, relative motion between surfaces, external load, moisture and oxygen are necessary conditions for fretting corrosion to occur. Fretting is not a common type of corrosion in copper and copper alloys. In copper home plumbing systems, it is not of significance due to the absence of at least one of the necessary conditions.

Inter-granular Corrosion

This type of corrosion is associated with the metals that are subjected to exposure to high pressure steam. The corrosion occurs such that it penetrates the metal surface often to the depth of metal grains. This attack is associated with the chemical segregation effects (impurities present in the metal surface) (Roberge 2000). The form of corrosion is not relevant to home plumbing systems, hence it will be kept out of the scope of the present study.

De-alloying Corrosion

It is the process of removal of more active metal selectively from an alloy. This leaves behind a weak deposit of the more noble metal. It is generally observed in alloys like brass (dezincification of brass), aluminum and nickel. In general, the attack is more common in alloys having a significant proportion of more active (cathodic) metal. Since, the copper tubes used in home plumbing have more than 99.9% copper, these tubes are not susceptible to de-alloying attack.

Corrosion Fatigue

The combined action of corrosion (usually pitting) and cyclic stress may cause corrosion fatigue. This results in cracking of the metal, usually at right angles to the applied tensile stress. This type of failure usually involves more than one parallel cracks resulting into a failure of the metal. These cracks generally, originate from corrosion pits and may be finer and invisible to naked eye. These cracks are distinctly different from the cracks originated solely due to stress or cyclic stress cracks, as the latter generally does not involve more than one crack. Copper and copper alloys are fairly resistant to corrosion fatigue, and hence this type of failure is not considered in detail in the present study.

Stress-Corrosion Cracking

This type of corrosion occurs when the metal is subjected to combined effects of sustained stress and certain chemical substances. These chemical substances include ammonia, in presence of oxygen or carbon dioxide and moisture. These conditions are often met by underground copper service lines that corrode due to presence of the said chemicals and moisture in the soil. Since, the nature of these failures related to home plumbing is limited to failures that initiate from the outer side of the pipes; these failures are not considered in detail in the present work.

Another class of corrosion that is not defined in ASM handbook is *microbiologically induced corrosion*. An overview of microbiologically induced carrion is presented.

Appendix A-2

Microbiologically induced corrosion

This is a general class of corrosion, due to the result of bacterial and microbial interaction of the pipe wall. Microbiological induced corrosion (MIC) may cause degradation of pipe wall and problems like taste and odor issues. The growth (algae or fungi) may cause corrosion by influencing several parameters like pH, dissolved oxygen (Schock, 1999). The areas in the vicinity of pipe wall may contain different families of bacteria or microorganism species that are often shielded by the deposits or tubercules of corrosion products and find protection against the disinfectants or dissolved oxygen. The stagnant waters, dead ends in pipes and lower level of disinfectant residuals sometimes provide ideal breading ground for these species. The nature of the attack due to these bacteria and microbial activities sometimes necessitates mechanical cleaning before substantial control can be achieved through residual disinfectant (Schock, 1999). There are number of ways in which the bacteria can cause corrosion. The nitrifying bacteria can consume dissolved oxygen, cause oxygen concentration cells that produce lower pH and eventually causing localized or pitting corrosion (Schock, 1999).

APPENDIX B-2

Chemical parameters affecting copper pitting (Contd. from Chapter-2)

Chemical parameters affecting copper pitting

The following discussion is a continuation of the chemical parameters discussed in Chapter-2.

Nitrate

Nitrate ion [NO_3^-] is generally not aggressive to copper (Edwards et al. 1994). Importantly, nitrate is a contaminant and is regulated by USEPA national primary drinking water standards. The maximum contaminant level (*MCL*) for nitrate set by USEPA is 10 mg/ L. The consumption of nitrate above the MCL can pose serious health hazards to infants below the age of six months, the illness may be fatal if not treated (USEPA).The symptoms include shortness of breath and blue-baby syndrome.

From copper corrosion perspective, low levels of nitrates decrease the pitting frequency, while higher levels (> 40 mg/ L) of nitrate may increase the pitting frequency (Edwards et. al 1994). Since, such higher levels (> 40 mg/ L) are well beyond the maximum contaminant limit (< 10 mg/ L), these concentrations are not expected in finished drinking water. Pitting failures due to nitrates are rarely known, the CDA reports have never identified nitrates as the cause of the failure.

The AWWARF/ AWWA utility survey provides a range for nitrate concentration for finished ground and surface waters. The nitrate concentration for finished grond water varies 0 and 81 mg/L. The nitrate concentration for finished surface water varies between 0 and 25 mg/L. The range exceeds the maximum contaminant limit of 10 mg/L, enforced by USEPA primary standards. The cause of such higher concentrations of nitrates is not explained in the data.

Hydrogen Sulfide

Hydrogen sulfide is one of the most severe corrosive agents for copper. Sulfide is a natural constituent in well waters, resulting from the bacterial decomposition of sulfur in soil or in bed rocks. The process of reduction is facilitated by a class of bacteria known as *sulfate reducing bacteria* (SRB). The sulfate reducing bacteria grow by using large quantities of sulfur, sulfates and / or other forms of oxidized sulfur to generate hydrogen sulfide gas (AWWA, 2003). The presence of hydrogen sulfide or SRB in waters is often marked by bad odor "rotten eggs"; however, this smell is not typical as this smell is often associated with other bacteria, including many coliforms (AWWA, 2003). These bacteria, generally grow in anaerobic conditions, and vent hydrogen sulfide in water in the absence of dissolved oxygen (AWWA, 2003). A possible remedy to remove hydrogen sulfide and / or SRB is to increase dissolved oxygen (AWWA, 2003).

It can thus be inferred that the presence of hydrogen sulfide and/ or sulfate reducing bacteria can be very lethal from pitting perspective. This could lead to sulfide attack that could suddenly become severe (Schock, 1999). Copper failures in some parts of Florida are mainly due to the presence of sulfide in ground water. As the water in these utilities is withdrawn from deep aquifers, it is understandable that it provides ideal anaerobic conditions for SRB to flourish.

The attack by hydrogen sulfide is complex, very often the attack is not apparent for months and then it suddenly becomes severe (Schock, 1999). Interestingly, all the sources in the literature as well as the CDA reports have unanimously identified sulfide as the species that can cause copper failures almost single handedly. The sulfide attack is generally multi pronged, the presence of sulfide catalyzes the rate of corrosion in copper by about 1 ~2 orders at wide pH ranges (6.5 and 9.2) (Jacobs and Edwards, 2000), additionally, it prevents the formation of protective scale on copper surface. In presence of sulfide, the scale formed is thick, black and poorly adheres to copper surface (Jacobs and Edwards, 2000). The scale may contain cuprous sulfide [Cu_2S] or cupric sulfide [CuS] or other non stoichiometric species of copper sulfide (McNeil et al. (1993) and (1991)).

It is due to these factors that sulfide poses the greatest threat to copper as compared to other water quality parameters like chlorine, alkalinity, pH (Jacobs and Edwards, 2000). The threshold concentrations that can cause copper failure are not known but concentrations as low as 0.02 mg/ L are found to induce a leak in copper tubes (Myers and Cohen, 2005). The copper sulfide attack is often accompanied by "black water" problems; it is mainly due to the loosely attached sulfide scale on the copper surface.

The AWWARF/ AWWA utility survey does not provide any data for sulfide in finished ground or surface waters.

Chloride, Chlorine and Chloramines

Chlorine is a strong oxidizing agent; it is widely used for disinfection in utilities irrespective of the source of water. During the disinfection process, chlorine is either added in gaseous form or it is added as solids i.e. sodium or calcium hypochlorite (Peavy, 1985).The following equations described the formation of hypochlorous acid and hypochlorite ion,

$$Cl_2 + H_2O \Leftrightarrow HOCl + H^+ + Cl^- \tag{B1}$$

$$HOCl \Leftrightarrow OCl^- + H^+ \tag{B2}$$

If chlorination involves addition of solid sodium or calcium hypochlorite, then the equations are,

$$NaOCl \rightarrow Na^+ + OCl^- \tag{B3}$$

$$Ca(OCl)_2 \rightarrow Ca^{2+} + 2OCl^- \tag{B4}$$

$$OCl^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O \tag{B5}$$

The relative amount of chlorine present in chlorine gas or hypochlorite (of calcium or sodium) is expressed in terms of *available chlorine* (Haas, 1999). The concentration of hypochlorite may be determined by calculating electrochemical equivalent amount of Cl_2 to that compound. For example,

$$Cl_2 + 2e^- \Leftrightarrow 2Cl^- \tag{B6}$$

From Eqn (B6), one mole of elemental chlorine reacts with two electrons to form chloride, Eqn (B5) shows that one mole of hypochlorite will react with two electrons to form chloride ion, hence, one mole of hypochlorite is electrochemically equivalent to one mole of elemental chlorine and it can be said to have 70.91 g of available chlorine (Haas, 1999). Hence, calcium hypochlorite contains two moles of elemental chlorine, i.e. 141.8 g of available chlorine. If the available chlorine is divided by the molecular weights of calcium hypochlorite (143 g/ mol) and sodium hypochlorite (74.5 g/ mol), it shall yield the percentage of free chlorine in the compound. Hence, available chlorine for calcium hypochlorite is 99.2 percent and for sodium hypochlorite available chlorine is 95.8 percent by weight.

The dissociation of hypochlorous acid (Eqn B2) is primarily dependent on pH and temperature. The formation of hypochlorous brings down the pH of the solution, which restricts the formation of hypochlorite ion after one point (Peavy, 1985). When chlorine is added in solid form, the dissociation of hypochlorite ion (Eqn B5) causes rise in pH (Peavy, 1985). However, the change in pH in both these conditions is highly dependant on the buffer intensity and pH of the water. If water has sufficient dissolved inorganic carbon (DIC), it is like to provide a buffer against change in pH, with exceptions to pH near 8, where the buffer intensity is the minimum.

The sum of the hypochlorous acid and the hypochlorite ion is called *free chlorine residual*. And the sum of molecular chlorine (Cl_2), hypochlorous acid and hypochlorite ion is generally called *free available chlorine*. The *combined available chlorine residual* is the residual existing in chemical combination with ammonia or organic nitrogen compounds (Viessman, 1993).

USEPA regulates the maximum disinfectant residual levels to 4.0 mg/ L (measured as Cl_2), the item is in the national primary standards and hence legally enforceable. Increase chlorine residuals in water may pose health hazards that include eye/ nose irritation and stomach discomfort (USEPA). Chlorine gas is highly toxic to humans, since it is heavier than air it spreads slowly at ground level. Due to this reason, sometimes use of hypochlorites is mandated, especially if the treatment plant is located nearly populated areas (Peavy, 1985). Chlorine is a strong oxidizing agent, during the process of disinfection sometimes it reacts with natural organic matter to produce certain products that are not desirable and are carcinogenic to humans. These products are called *disinfection byproducts* (DBP). The main DBPs are Trihalomethanes (measured as total trihalomethane) TTHM and Haloacetic acid five (HAA5). USEPA, enforced the *disinfection byproduct rules (stage-I)* in the year 1998, the rule required the reduction of specific percentage of organic matter from finished water, in addition the rule enforced new limits on total trihalomethans and haloacetic acid.

Due to the enforcement of the D/ DBP rule, many utilities changed the disinfectant from chlorine to chloramines. Chloramines are the product of hypochlorous acids and ammonia. Chloramines primarily consist of three forms, monochloramine

[NH_2Cl], dichloramine [$NHCl_2$] and nitrogen tetrachloride or trichloramine [NCl_3]. The equations leading to formation of chloramines are,

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \tag{B7}$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \tag{B8}$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \tag{B9}$$

The chloramines residual is an identified contaminant in drinking water and is regulated in national primary standard. In most of the drinking water, the primary chloramines species is monochloramine (Cohn, 1999). The adverse health effects due to the consumption of chloramines have been limited to hemodialysis patient (Cohn, 1999).

In the background of the disinfection process, the role of chloride, chlorine and chloramines is examined with respect to copper pitting. The formation of chloride [Cl^-] is the direct result of addition of either gaseous or solid chlorine in water. Other than the disinfection process, the possible source of chloride could be dissolved inorganic ionic compounds of [Cl^-] anion. These solids may ionize in aqueous solution providing chloride ions. USEPA has enlisted chloride in the national secondary standards. Chloride concentration exceeding 250 mg/ L is likely to cause salty taste in drinking water. Researchers have repeatedly identified chloride as the major culprit leading to copper pitting; this hypothesis is overwhelmingly supported by the CDA reports where *chloride induced pitting* emerged as the largest cause of failure in cold water pipes. The sources of chloride identified by CDA are primarily the soldering flux and/ or the strong oxidizing agents used in disinfection, namely, gaseous chlorine, sodium hypochlorite, calcium hypochlorite and chlorinated cyanurates. The CDA reports identify chloride as the cause for pit initiation, while the propagation of pitting is attributed to the dissolved oxygen present in water. This hypothesis is supported by the pitting theory presented by Edwards et al. (1994).

Edwards et al. (1994), present a detailed overview of copper pitting, the mechanism leading to pitting is defined as a two step process, namely *pit initiation* and *pit propagation*. The *pit initiation* is followed by the formation of cuprous chloride film as soon as the copper comes in contact with aqueous solution containing chloride ion. The cuprous chloride is normally removed from the surface by number of possible reactions that include hydrolysis to cuprite [Cu_2O], dissolution into bulk solution and / or oxidation and formation of cupric salts. The above reactions lead to formation of passavating scale on the copper surface. Under certain conditions not clearly understood according to this theory, the rate of formation of cuprous chloride exceeds the rate of its loss, due to which the pitting initiates. The *pit propagation* is explained based on the Lucey's pitting theory, the theory states that the propagation of the pit is followed by the reduction of oxygen on the scale just above the pit, thus suggesting oxidation and reduction on the opposite side of the cuprite scale.

In summary the pitting of copper is described as a two step process, chloride [Cl^-] helps in pit initiation and dissolved oxygen is responsible for pit propagation. It follows from the above discussion that pit initiation and pit propagation are two different stages of copper pitting, the pits that are initiated by chloride [Cl^-] due to formation of cuprous chloride [CuCl], are highly subjective to propagation, a step governed by the reduction of oxygen. Further, the formation of cuprous oxide layer is essential for initiation and propagation of pitting. The hypothesis in the CDA reports is coherent with findings of Myers and Cohen, (2005). Warraky et al.(2004), have verified the role of chloride in pit initiation by laboratory tests. Warraky et al.(2004), tested that oxygen does not play a significant role in pit initiation and is rather responsible for propagation of pits.

However, there are contradictory opinions that suggest that chloride actually provides passivity to copper pitting in long term (Edwards et al. 1994). The authors of the paper, have supported this argument with long term laboratory tests over wide pH range, the results of the test demonstrate the dual nature of chloride in long and short term. The contradiction has not only questioned the present theory of copper pitting, but it has left the role of chloride in ambiguity.

The most viable explanation to the above anomaly could be explained based on the fact that the test carried by Edwards et al. (1994) were conducted in the absence of other anionic or cationic species and using de-ionized water. Thus, it may have not simulated the actual complexities that would have occurred due to mutual interaction of anion. However, by enlarge if both the opinions are put together, the role of chloride in copper pitting becomes hazy.

Rushing and Edwards, (2004) have established that high *free chlorine* in combination with high pH could enhance pitting rates, interestingly, when high free chlorine is present with aluminum and high pH, the rates of the corrosion are increased further. There seems to be a synergetic effect between free chlorine and aluminum solids that increases non uniform corrosion of copper (Rushing and Edwards, 2004; Maryland Task force, 2004).

Not much literature is available on the role of chloramines in copper pitting. The chloramines primarily contain nitrogen atom which is considered as a nutrient. There have been concerns that the presence of nitrogen could cause bacterial growth within the distribution system, since bacteria thrive in the presence of nutrient. There are increasing concerns amongst the scientist that the possible bacterial growth can create taste and odor issues in drinking water. However, since the transition to chloramines is recent, adequate data is not available to validate the aforesaid concerns.

The increase in bacterial growth in the distribution system may possibly increase the chances of microbial induced pitting. The problem is more likely to hit the hot water recirculation system, since anaerobic conditions in these systems coupled with higher temperatures may provide an ideal incubation ground for bacteria. The CDA reports do not contain any failure due to chloramines.

The AWWARF/ AWWA utility survey provides a range of values for free chlorine and combined chlorine. In finished ground water, the free chlorine concentration ranges between 0 and 7 mg/L, the corresponding combined chlorine ranges between 0 and 7.4 mg/L. In finished surface water, the free chlorine concentration ranges between 0 and 7 mg/L, the corresponding combined chlorine ranges between 0 and 7.9 mg/L. In distribution system, free chlorine concentration ranges between 0 and 5 mg/L, the corresponding combined chlorine ranges between 0 and 100 mg/L.

The high values for free chlorine and combined chlorine in distribution system are due to the data of one particular utility in California. The utility is a ground water utility, interestingly, the pH reported by the utility for the finished water quality also varies significantly with the one reported for the distribution system, the causes for these high deviations between the finished water quality and the distribution water quality are not reported in the database.

Sulfate

Sulfate is considered to be one of the most aggressive anionic species that could lead to copper pitting. The possible sources of sulfate in finished water are the sulfate coagulants (e.g. alum) and coagulant aids used during coagulation and/ or dissolved inorganic ionic compounds containing sulfate anion in raw waters. The coagulation is adopted typically for the treatment of surface waters, hence for well waters; the primary source of sulfate would be the hardness ions typically Magnesium sulfate and Calcium sulfate. Sulfate is a contaminant enlisted in national secondary standards by USEPA. Sulfate concentration exceeding 250 mg/ L can add salty taste to water (USEPA).

A detailed overview of Type-I, Type-II and Type-III pitting was provided with respect to alkalinity, hardness, DIC, pH and temperature, previously in the chapter.

Sulfate is the anionic species responsible for Type-I and Type-II pitting. The following section illustrates the role of sulfate in copper pitting.

The manner in which the sulfate causes corrosion in copper is markedly different than that of other anionic species. Sulfate cause copper pitting due to the formation of brochantite scale [$Cu_4(OH)_6(SO_4)$]. The formation of the scale causes the corrosion of copper (Edwards et al. 1994). Importantly, the interaction of sulfate with copper is controlled by its relative concentration to chloride and bicarbonate. The background of this important conclusion was probably, the notion that the waters that support pitting have more concentration of sulfates than chlorides (Cohen and Lyman, 1972). In the same paper, a sulfate to bicarbonate ratio > 1 is identified as the mechanism copper pitting.

Cohen and Myers, (1984) supports this fact with time to leak analysis of the failed pipes samples, the paper shows that the time to leak for high sulfate to chloride ratio (>3.3) was smaller than time to leak for samples with lower sulfate to chloride ratio. This was later supported by Edwards et al. (1994), while describing Type-I and Type-II pitting. Hence, the role of relative concentration of sulfate with chloride and bicarbonates is identified by several sources. These hypotheses are validated experimentally by Mankowski et al. (1997) and Duthil et al. (1996).

Mankowski et al. (1997), experimentally identify three regions that define the synergy between the sulfate and chloride ions. Based on the pit morphology and the corrosion rates Mankowski et al. (1997) conclude that at lower sulfate to chloride ratio, chloride is the dominant species, at higher sulfate to chloride ratio, sulfate is the dominant species while at intermediate sulfate to chloride ratio, the interaction is very complex. In similar work, Duthil et al. (1996), determine that the sulfate is more aggressive to copper than chloride.

Hence, it may be concluded that sulfate is more aggressive than chloride; further the relative concentration of sulfate and chloride determines the dominant anionic species. If sulfate dominates, then it would lead to formation of brochantite scale, which will eventually cause pitting. Edwards et al. (1994) provided a comprehensive review of the role of brochantite scale [$Cu_4(OH)_6(SO_4)$] with respect to pH and temperature. A discussion about the influence of pH and temperature on the formation of bronchatite is provided. The solubility of the brochantite is highly dependent on pH of water. The solubility increases with increase in pH (>7.4). Hence, the presence of brochantite is not expected at higher pH values (Edwards et al. 1994). From pitting perspective, since brochantite scale is essential, it follows that water with high pH should not pit even if sulfate is the dominant anionic species. This is in agreement with the work of Cohen and Myers, (1984), that identified sulfate as the dominating species only at lower pH (<7.8). However, the corrosion of copper may still occur, but the form of the corrosion will be different than pitting. Interestingly, at lower pH the malachite formation is also favored, however, malachite formation is limited by the availability of bicarbonate ions in the solution. Hence, if water has higher sulfate relative to bicarbonate, it should favor brochantite formation at lower pH, and water with high bicarbonate relative to sulfate should favor malachite formation at lower pH. The effect of temperature is important for stability of malachite and brochantite.

The stability of brochantite increases with increase in temperature, at higher temperatures brochantite is more stable than malachite (Edwards et al. 1994). Hence, in hot water pipes and hot water recirculation system, the presence of brochantite is very likely, as malachite is not stable at higher temperatures. However, as discussed previously, at higher temperatures there is an increased likelihood of formation of calcium carbonate scale at higher temperatures, due to decrease in solubility of calcium carbonate and especially if water has sufficient buffer intensity. A discussion about the implications of DIC, alkalinity and pH was provided previously.

The AWWARF/ AWWA utility survey does not distinctly provide the concentration of sulfates in finished water quality data.

Iron, Zinc, Manganese

The metals iron, zinc and manganese are anodic to copper, hence the chances of galvanic corrosion are ruled out. Iron and manganese are the natural constituents of raw waters. The iron and manganese are often present in well waters. Zinc is not a natural constituent of raw water it may be added to raw water sources (ground and surface) due to human intervention that includes urban or industrial pollutants. Occasionally, iron and zinc compounds are added during the treatment of water. Ferrous compounds including ferrous sulfate and ferric chloride are often used as coagulant in treatment of surface water (Viessman, 1993). Zinc chloride and zinc phosphate are sometimes used to reduce corrosion, these compounds react in water to form hard coatings of zinc carbonate or zinc sulfate (Schock, 1999).

All these metals are not desirable in drinking water and may have bad cosmetic and aesthetic effects (Table 1). USEPA has enlisted these metals in the national secondary standards. Iron concentration exceeding 0.3 mg/ L can affect the aesthetic quality of water by imparting rusty color, increased sediment, imparting metallic taste and reddish or orange staining in water. Zinc concentration exceeding 5 mg/ L may impart metallic taste to water. Manganese concentration exceeding 0.05 mg/ L may impart black to brown color, can cause black staining and add bitter metallic taste to water (USEPA).

The literature does not provide any evidence that any of these metals could cause copper pitting. Although, the presence of some of these metals has been occasionally reported in pits of the failed pipe samples, there is no evidence to correlate the direct effect of these metals on the corrosion of copper. The CDA reports have identified the presence of hydrated hematite [Fe_2O_3] and/ or manganese dioxide [MnO_2] with other corrosion products on many occasions; however, their presence was never identified as the cause of failure. The presence of iron or manganese exceeding 0.1 mg/L accompanied by higher temperatures could lead to initiation of pitting in copper hot water pipes (CDA reports). The same is in agreement with (Myers and Cohen, 2005). However, the mechanism leading to pitting is not explained in any of the above sources.

It may be of interest to mention that the deposits like hydrated hematite, manganese dioxide along with silicon dioxide [SiO_2] may form a layer of debris on the pipe surface. This debris may typically accumulate at the bottom of the horizontal pipes, in varied thicknesses. Under this debris, the concentration of oxygen is low as relative to the bulk solution. Also, thicker layers are relatively more devoid of oxygen than the thinner layers. This develops a difference in potential between the layers having different concentration of dissolved oxygen, eventually leading to pitting. The mechanism is usually described as concentration cell corrosion or oxygen differential corrosion. The phenomenon may be more expected in cold water pipes, since the dissolved oxygen content in hot water pipes and hot water recirculation system will be low and may not favor the phenomenon. The CDA reports have identified pitting failures due to the above phenomenon on many instances.

In summary, the effect of these metals may be categorized as suspicious if not neutral with respect to copper pitting. Although, some of the sources in the literature have reported their presence in failed pipes but the underlying mechanisms of pitting is not substantiated with any viable chemical reaction.

The AWWARF/ AWWA utility survey provides data for iron and manganese in finished ground and surface waters. In finished ground water, the concentration of Iron ranges between 0 to 7 mg/L, the corresponding concentration of manganese ranges between 0 to 19 mg/ L. In finished surface water, the concentration of Iron ranges between 0 to 6.8 mg/L, the corresponding concentration of manganese ranges between 0 to 1.2 mg/ L.

Aluminum

Aluminum is more anodic to copper and by itself not corrosive to copper. In raw waters aluminum is typically not present; however, sometimes small quantities of aluminum may be present in the form ionic compounds in that are dissolved in water. Aluminum may get added to water either during the treatment or distribution of water. For surface waters undergoing coagulation, the possible source of aluminum could be aluminum coagulants (e.g. alum) and/ or coagulant aids.

Other than the treatment, there is a high possibility of aluminum getting added in the distribution system, it is due to the leaching of aluminum from cement pipes. The Portland cement that constitutes the pipes contains aluminum in the forms of tricalcium aluminate (i.e., $3Ca \bullet Al_2O_3$) and tetra calcium aluminoferrite (i.e., $4CaO \bullet Al_2O_3 \bullet Fe_2O_3$) (CDA reports). Leaching can occur both in surface and ground waters, although the pH adjustments measures are taken at the treatment plant to keep it to a minimum level. USEPA enlists aluminum in national secondary standards. Aluminum concentrations exceeding 0.2 mg/L could have problems like colored water (USEPA).

Aluminum deposits are often found on copper pipe surfaces, even at low concentrations of aluminum in influent waters (Schock, 1999). The CDA reports have identified the presence of aluminum, at many instances in minor and major quantities based on results of *Energy dispersive spectroscopy* (EDS) of failed pipe samples. The presence of aluminum exceeding 0.1 mg/L accompanied by higher temperatures could lead to initiation of pitting in copper hot water pipes (CDA reports). The same is in agreement with (Myers and Cohen, 2005). Although, the sources do not explain any mechanism that aluminum could have caused.

Interestingly, aluminum has a synergetic effect when it is present with high chlorine at higher pH (Rushing and Edwards, 2004). This effect was due to the present of aluminum deposits. Although, the conclusions of the paper could not identify a possible mechanism for the synergetic effect of aluminum and chlorine, but it may be due to catalyses of the cathodic reaction between copper and chlorine (Maryland task force, 2004).

To summarize, aluminum by itself is not corrosive to copper, however, in the presence of certain conditions it can have a synergetic effect with other species to enhance the corrosion rates. More investigations are needed to establish the relationship of this synergy with variations of other parameters like pH (Rushing and Edwards, 2004).

The AWWARF/ AWWA utility survey does not provide any data for aluminum in finished water or in distribution system.

Natural organic matter (NOM)

NOM contains a large group of molecules with different molecular properties. The humic substances are the major component of the NOM. The humic substances are generally produced by different chemical and biological process such as decay of vegetation (Letterman, 1999). The humic substances can be divided into more soluble group (fulvic acid) and the less soluble group (humic acids) (Letterman, 1999). In broader terms, NOM consists of humic and fulvic acids, compounds with high molecular weights that contain negative charge, oxygenation functional groups (like carboxyl and carbonyls), hydroxyl, aromatic, carbohydrate and aliphatic derived groups (Edwards et al. 1994).

The NOM in drinking water is either produced within the water bodies through biological and chemical processes or it is derived into these water bodies through soil (Letterman, 1999). In general, the source of NOM is raw water; it can be surface water or ground waters that are under the influence of surface waters. It is measured as *total organic carbon* (TOC) in mg/ L. NOM reacts with the disinfectants in the drinking water forming disinfection byproducts (DBP), these DBP may have severe effect on human health and some of them are carcinogenic to humans (USEPA).

USEPA regulated the permissible limit of NOM in drinking water system, it also restricted the maximum disinfection residuals in the distribution system by the Disinfectants and Disinfection byproduct rule (D/ DBP), (Stage-I). The rule was promulgated by USEPA in 1998 and all the utilities that withdraw water either from surface water sources or from ground water sources (under the influence of surface water) are suppose to comply with the rule. The D/ DBP rule lowered the permissible concentrations of total trihalomethanes (TTM) and haloacetic acid five (HAA5) and imposed a new limit of maximum disinfectant residual (MDRL). The consumption of haloacetic acids 5 (HAA5) and trihalomethanes (THM) may be carcinogenic to humans, while trihalomethanes (THM) may additional cause liver, kidney and nervous system disorders.

Implications of these rules include enhanced coagulation or enhanced softening unless a system meets an alternative criterion (Maryland Task force, 2004). For relatively large water suppliers these changes were minor, while small suppliers may have ended up increasing the coagulant dose, hence increasing aluminum (Maryland Task force, 2004). In the background of these proceedings the role of NOM is discussed with respect to copper pitting. The behavior of NOM is complex with respect to copper pitting.

The NOM inhibitor seems to control corrosion by controlling the scale formation. In addition, humic and fulvic acids are thought to have indirect beneficial effects with respect to copper corrosion as these species maintained higher pH in some waters that prevented calcium carbonate precipitation (Edwards et al. 1994). Several other beneficial effects of NOM with respect to copper pitting includes, inhibition of cathodic or anodic reaction by sorbtion of organic molecules and altering the nature and structure of solids there by providing passivity to the copper (Edwards et al. 1994).

In addition to the above benefits, the NOM may create environments that are deleterious to copper metal. The NOM may serve as food for organisms in the distribution system. Since these organisms often shield themselves behind or underneath the corrosion products or other deposits, they often survive the disinfectant doses present in the distribution system. This microorganism when attack the surface of copper pipe may induce microbial induced pitting.

Although the groups that help in formation of the compounds or complexes are not known, but in general, the role of NOM is complex and may have a set of beneficial and deleterious effects on copper corrosion. Since, the above situations are beyond control to certain extent hence use of NOM for corrosion control is not recommended (Schock, 1999). Some of the scientists believe that the increase in incidents of pinhole leaks was synchronous with the decrease in the NOM in the distribution system; however, no direct correlation has been made in literature, possibly the effects of NOM reduction would take sometime to surface to be noticed amongst literal circles.

The AWWARF/ AWWA utility survey provides the total organic content for finished ground water and surface water utilities. The TOC for finished ground water ranges between 0 and 12 mg/L. The TOC for finished surface water ranges between 0 and 29 mg/L.

APPENDIX C-2

Summary of various Corrosion Mechanisms from literature

Appendix C-2

Table C-2.1 Summary of mechanisms of copper pitting from the literature

Mechanism	**Constituents (water quality or hydraulic parameters)**	**Characteristic pit / location**	**Scientific certainty/ Time to leak (years)**	**Source**
Chloride/ Chlorine	Soldering flux, or strong oxidizing chemical used for disinfection (some of the chemicals include sodium hypochlorite, calcium hypochlorite and chlorinated cyanurates).	Very often near the vicinity of joints.	6.38 years / 260 *	CDA reports (1975~2004)
Oxygen-differential type	Deposits of silicon dioxide, iron, aluminum or any other deposits other than copper. Presence of dissolved oxygen.	Horizontal pipes (typically)	13.95 years/ 67 *	CDA reports (1975~2004)
Excessive heating of water	Water with appreciable amount of iron or iron oxides OR Water with significant amount of silica (as SiO_2) OR Water with aluminum > 0.1 mg/L. Temperature exceeding 160 F.		13.18 years/ 64 *	CDA reports (1975~2004)
Externally initiated failures	Presence of moisture, ammonia or other corrosive species in soil.	Pipes buried under the soil (typically service lines)	5.6 years/ 107 *	CDA reports (1975~2004)
Erosion corrosion	Soft water or water with zero hardness and especially containing dissolved oxygen or carbon dioxide. Or water greater than 80 psi (gage) and velocities greater than 4 to 5 feet per second. For hot water, a temperature greater than 160 F.		6.78 years/ 127 *	CDA reports (1975~2004)
Poor workmanship	Joining tubes not squarely cut and reamed properly prior to soldering. Globule of solder may be present. Leak may initiate at joints or may be triggered just downstream of the solder joint that is improperly cut finished			CDA reports (1975~2004)

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Table C-2.1 Summary of mechanisms of copper pitting from the literature

Mechanism	**Constituents (water quality or hydraulic parameters)**	**Characteristic pit / location**	**Scientific certainty/ Time to leak (years)**	**Source**
Sulfide	Sulfide > 0.02 mg/L		8.94 years/ 17 *	CDA reports (1975~2004)
Aggressive water	Carbon dioxide exceeding 25 mg/ L and appreciable suspended solids in form of silica. High sulfate to bicarbonate, high sulfate to chloride (in general more sulfate hardness)		4.7 years/ 79 *	CDA reports (1975~2004)
Microbiological or Microbial	Stagnant waters or waters with improper treatment.		14 years/ 5*	CDA reports (1975~2004)
No corrosion/ Blue water/ more than one reasons			7.83 years/ 24 *	CDA reports (1975~2004)
Aggressive Water	Bicarbonate: Sulfate < 1			Cohen and Lyman (1972)
Aggressive Water	Well water at pH 7.5 + CO_2> 25 ppm + O_2 and intermittent use			Cohen and Lyman (1972)
Aggressive Water	pH < 7.8 + CO_2> 25 ppm + Sulfate > 17 ppm + Sulfate: Chloride > 3			Cohen and Lyman (1972)
Aggressive Water	7.1< pH < 7.8 + Magnesium Sulfate > 100 ppm			Cohen and Lyman (1972)
Aggressive Water	7.1< pH < 7.8 + Magnesium Sulfate > 100 ppm + Potassium < 4.2 ppm			Cohen and Lyman (1972)
Aggressive Water	7.1< pH < 7.8 + Magnesium Sulfate > 100 ppm + Silicate > 25 ppm			Cohen and Lyman (1972)
Aggressive Water	7.1< pH < 7.8 + Magnesium Sulfate > 100 ppm + Nitrate < 25 ppm			Cohen and Lyman (1972)

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Table C-2.1 Summary of mechanisms of copper pitting from the literature

Mechanism	**Constituents (water quality or hydraulic parameters)**	**Characteristic pit / location**	**Scientific certainty/ Time to leak (years)**	**Source**
Aggressive Water	Soft water with pH < 6.5 + 10 ppm < CO_2 < 50 ppm + Low in chloride, sulfate, nitrate ions + hot water system			Cohen and Lyman (1972)
Aggressive Water	pH > 7.8 + cold water + bicarbonate < 40 ppm		19.3 years/ 6 **	Cohen and Myers (1984)
Aggressive Water	pH > 7.8 + cold water + bicarbonate > 54.6 ppm + CO_2 > 4.8 ppm		37.7 years/ 9 **	Cohen and Myers (1984)
Aggressive Water	pH > 7.8 + cold water + bicarbonate > 54.6 ppm + CO_2< 4.8 ppm		50 years/ 11 **	Cohen and Myers (1984)
Aggressive Water	pH < 7.8 + cold water + + CO_2 > 25 ppm + Dissolved oxygen > 7.8 ppm		2.6 years/ 34 **	Cohen and Myers (1984)
Aggressive Water	pH < 7.8 + cold water + + CO_2 > 25 ppm + Dissolved oxygen < 7.8 ppm		9.4 years/ 18 **	Cohen and Myers (1984)
Aggressive Water	pH < 7.8 + cold water + + CO_2 < 25 ppm + Sulfate > 17 ppm + Sulfate : Chloride > 3:3		2.4 years/ 8 **	Cohen and Myers (1984)
Aggressive Water	pH < 7.8 + cold water + + CO_2 < 25 ppm + Sulfate > 17 ppm + Sulfate : Chloride < 3:3 + Potassium > 5 ppm		32.8 years/ 8 **	Cohen and Myers (1984)
Aggressive Water	pH < 7.8 + cold water + + CO_2 < 25 ppm + Sulfate > 17 ppm + Sulfate : Chloride < 3:3 + Potassium < 4.2 ppm + Silicon dioxide > 26.2 ppm		3.6 years/ 8 **	Cohen and Myers (1984)

Appendix C-2

Table C-2.1 Summary of mechanisms of copper pitting from the literature

Mechanism	**Constituents (water quality or hydraulic parameters)**	**Characteristic pit / location**	**Scientific certainty/ Time to leak (years)**	**Source**
Aggressive Water	pH < 7.8 + cold water + + $CO_2 < 25$ ppm + Sulfate > 17 ppm + Sulfate : Chloride $< 3:3$ + Potassium < 4.2 ppm + Silicon dioxide < 26.2 ppm		15.1 years/ 10 **	Cohen and Myers (1984)
Aggressive Water	pH < 7.8 + cold water + + $CO_2 < 25$ ppm + Sulfate < 17 ppm		34.3 years/ 6 **	Cohen and Myers (1984)
Oxygen differential	Long stagnation period between installation and usage. Improper flushing of pipes after installation. Presence of debris, dirt and flux residuals at pipe bottom.	Horizontal pipes		Rossum (1985)
Type-I	Hard, cold, well water + $7 <$ pH < 7.8 + high sulfate : chloride + high sulfate : bicarbonate + high CO_2. Stagnant water, debris in pipe, high chlorine residuals, water softeners and alum coagulation			Edwards et al. (1994)
Type-II	Hot water + pH < 7.2 + High sulfate : bicarbonate + Manganese (occasional). High temperature, high chlorine residual, alum coagulation.			Edwards et al. (1994)
Type-III	No failure but voluminous release of copper. Soft water + pH > 8.0. Stagnant water, alum coagulation and low chlorine residuals			Edwards et al. (1994)
Anthropogenic	Excessive soldering flux.	Near joints.		Ellis II (2000)

Appendix C-2

Table C-2.1 Summary of mechanisms of copper pitting from the literature

Mechanism	**Constituents (water quality or hydraulic parameters)**	**Characteristic pit / location**	**Scientific certainty/ Time to leak (years)**	**Source**
Soldering flux	Improper or excessive use of soldering flux, poor workmanship or Fluxes not conforming to ASTM B813 standards.			Myers and Cohen (2005)
Hydrogen Sulfide	Sulfide > 0.02 mg/L, or well waters with Sulfate reducing bacteria.			Myers and Cohen (2005)
Erosion corrosion	Velocities exceeding 4~5 fps or pressure exceeding 80 psi, shoddy workmanship, Soft water with nearly zero hardness and water containing appreciable amounts of dissolved oxygen and carbon dioxide. (hot water recirculation systems worst impacted)			Myers and Cohen (2005)
Cuprosolvency	Soft water with near zero hardness, pH less than 7 and low alkalinity. In general due to presence of CO_2.			
Concentration cell Corrosion	Deposits of iron oxides and/ Silica/ sand, presence of dissolved oxygen in water.			
Chemistry related to Cold-water pitting	Low pH, high alkalinity, well water or a combination of well and surface water. Corrosive agent is CO_2.			
Chemistry related to Hot-water pitting	Presence of iron, manganese, and/ or aluminum and often silica containing constituent. The concentrations require to initiate pitting be around 0.1 mg/L. Hot water temperatures above 160F.			
Sulfide attack	Raw water with sulfides or SRB	Near colonies of SRB	Nearly 100%	Dr Marc Edwards (Personal communications)
Cl_2-Al-high pH	$pH > 7.8$ $Cl_2 > 2.5$ ppm	Pipes in frequent flow and at locations	100%	Dr Marc Edwards (Personal communications)

Table C-2.1 Summary of mechanisms of copper pitting from the literature

Mechanism	**Constituents (water quality or hydraulic parameters)**	**Characteristic pit / location**	**Scientific certainty/ Time to leak (years)**	**Source**
	Cold water	with highest residual		
Chloramine-Al	Same as above, but seems to be hot water	Both hot and cold, but hot water recirculation lines worst impacted	Suspected	Dr Marc Edwards (Personal communications)
High Cl_2-High pH	pH > 8.5, Chlorine > 0.5 ppm Cold water	Pipes with frequent flow and closed to treatment plant.	Strongly Suspected	Dr Marc Edwards (Personal communications)
Gaseous Cavitation	Dissolved gas super saturation, hot and cold	Near bends and flow constrictions	Strongly Suspected	Dr Marc Edwards (Personal communications)
Particle/ Water Erosion Corrosion	Both hot and cold, although hot water more susceptible	Near bends	Suspected	Dr Marc Edwards (Personal communications)
Deposition Corrosion	Lines or mounds of deposits other than copper	Deposits often preferentially found on pipe bottom or outside bends	Suspected	Dr Marc Edwards (Personal communications)
Other Microbial	Low alkalinity and poor buffered water, lack of disinfectants	Farthest reaches of treatment plant.	Strongly Suspected	Dr Marc Edwards (Personal communications)

* The denominator implies number of failure reports used for calculating time to leak. A total of 763 reports (out of 1313 reports) from CDA provide time to leak information.

** The denominator implies the number of reports used for calculating time to leak (Cohen and Myers, 1984)

APPENDIX D-2

Formulation of Goal Program

Formulation

The formulation of linear program is presented in the following section, based on the mechanism enlisted in Table 6.

For $i = 1$

The mechanism has "100 %" scientific certainty, hence $S_1 \geq b_1$

$$X_{1,1} + X_{1,2} + X_{1,3} + X_{1,4} \geq b_1$$

$$X_{1,1} + X_{1,2} + X_{1,3} + X_{1,4} - d_1^+ + d_1^- = b_1 \qquad \text{(D1)}$$

For $i = 2$

The mechanism has "Strongly Suspected" scientific certainty, hence $b_4 \leq S_2 \leq b_3$

$$b_4 \leq X_{2,1} + X_{2,2} + X_{2,3} \leq b_3 \qquad \text{(D2)}$$

$$X_{2,1} + X_{2,2} + X_{2,3} - d_2^+ + d_2^- = b_4 \qquad \text{(D3)}$$

$$X_{2,1} + X_{2,2} + X_{2,3} + d_3^+ - d_3^- = b_3 \qquad \text{(D4)}$$

For $i = 3$

The mechanism is classified as "Strongly Suspected", hence $b_4 \leq S_3 \leq b_3$

$$b_4 \leq X_{3,1} + X_{3,2} + X_{3,3} + X_{3,4} \leq b_3 \qquad \text{(D5)}$$

$$X_{3,1} + X_{3,2} + X_{3,3} + X_{3,4} - d_4^+ + d_4^- = b_4 \tag{D6}$$

$$X_{3,1} + X_{3,2} + X_{3,3} + X_{3,4} + d_5^+ - d_5^- = b_3 \tag{D7}$$

<u>For $i = 4$</u>

The mechanism is classified as "Suspected", hence $b_6 \le S_4 \le b_5$

$$b_6 \le X_{4,1} + X_{4,2} + X_{4,3} + X_{4,4} \le b_5 \tag{D8}$$

$$X_{4,1} + X_{4,2} + X_{4,3} + X_{4,4} - d_6^+ + d_6^- = b_6 \tag{D9}$$

$$X_{4,1} + X_{4,2} + X_{4,3} + X_{4,4} + d_7^+ - d_7^- = b_5 \tag{D10}$$

<u>For $i = 5$</u>

The mechanism is classified as "Suspected", hence $b_6 \le S_5 \le b_5$

$$b_6 \le X_{5,1} + X_{5,2} + X_{5,3} + X_{5,4} \le b_5 \tag{D11}$$

$$X_{5,1} + X_{5,2} + X_{5,3} + X_{5,4} - d_8^+ + d_8^- = b_6 \tag{D12}$$

$$X_{5,1} + X_{5,2} + X_{5,3} + X_{5,4} + d_9^+ - d_9^- = b_5 \tag{D13}$$

<u>For $i = 6$</u>

The mechanism is classified as "Suspected", hence $b_6 \le S_6 \le b_5$

$$b_6 \le X_{6,1} + X_{6,2} + X_{6,3} \le b_5 \tag{D14}$$

$$X_{6,1} + X_{6,2} + X_{6,3} + d_{10}^{+} - d_{10}^{-} = b_5 \tag{D15}$$

$$X_{6,1} + X_{6,2} + X_{6,3} - d_{11}^{+} + d_{11}^{-} = b_6 \tag{D16}$$

<u>For $i = 7$</u>

The mechanism is classified as “Below Suspected”, hence $S_7 \leq b_7$

$$X_{7,1} + X_{7,2} + X_{7,3} + X_{7,4} \leq b_7 \tag{D17}$$

$$X_{7,1} + X_{7,2} + X_{7,3} + X_{7,4} + d_{12}^{+} - d_{12}^{-} = b_7 \tag{D18}$$

<u>For $i = 8$</u>

The mechanism is classified as “Below Suspected”, hence $S_8 \leq b_7$

$$X_{8,1} + X_{8,2} + X_{8,3} + X_{8,4} \leq b_7 \tag{D19}$$

$$X_{8,1} + X_{8,2} + X_{8,3} + X_{8,4} + d_{13}^{+} - d_{13}^{-} = b_7 \tag{D20}$$

<u>For $i = 9$</u>

The mechanism has “Strongly Suspected” scientific certainty, hence $b_4 \leq S_9 \leq b_3$

$$b_4 \leq X_{9,1} + X_{9,2} + X_{9,3} + X_{9,4} \leq b_3 \tag{D21}$$

$$X_{9,1} + X_{9,2} + X_{9,3} + X_{9,4} + d_{14}^{+} - d_{14}^{-} = b_3 \tag{D22}$$

$$X_{9,1} + X_{9,2} + X_{9,3} + X_{9,4} - d_{15}^{+} + d_{15}^{-} = b_4 \tag{D23}$$

For $i = 10$

The mechanism is classified as "Suspected", hence $b_6 \leq S_{10} \leq b_5$

$$b_6 \leq X_{10,1} + X_{10,2} + X_{10,3} + X_{10,4} \leq b_5 \tag{D24}$$

$$X_{10,1} + X_{10,2} + X_{10,3} + X_{10,4} - d_{16}^{+} + d_{16}^{-} = b_6 \tag{D25}$$

$$X_{10,1} + X_{10,2} + X_{10,3} + X_{10,4} + d_{17}^{+} - d_{17}^{-} = b_5 \tag{D26}$$

For $i = 11$

The mechanism has "Strongly Suspected" scientific certainty, hence $b_4 \leq S_{11} \leq b_3$

$$b_4 \leq X_{11,1} + X_{11,2} + X_{11,3} + X_{11,4} \leq b_3 \tag{D27}$$

$$X_{11,1} + X_{11,2} + X_{11,3} + X_{11,4} + d_{18}^{+} - d_{18}^{-} = b_3 \tag{D28}$$

$$X_{11,1} + X_{11,2} + X_{11,3} + X_{11,4} - d_{19}^{+} + d_{19}^{-} = b_4 \tag{D29}$$

For $i = 12$

The mechanism is classified as "Suspected", hence $b_6 \leq S_{12} \leq b_5$

$$b_6 \leq X_{12,1} + X_{12,2} + X_{12,3} + X_{12,4} \leq b_5 \tag{D30}$$

$$X_{12,1} + X_{12,2} + X_{12,3} + X_{12,4} + d_{21}^{+} - d_{21}^{-} = b_5 \tag{D31}$$

$$X_{12,1} + X_{12,2} + X_{12,3} + X_{12,4} - d_{21}^{+} + d_{21}^{-} = b_6 \tag{D32}$$

For $i = 13$

The mechanism is classified as “Below Suspected”, hence $S_{13} \le b_7$

$$X_{13,1} + X_{13,2} + X_{13,3} + X_{13,4} \le b_7 \tag{D33}$$

$$X_{13,1} + X_{13,2} + X_{13,3} + X_{13,4} + d_{22}^{+} - d_{22}^{-} = b_7 \tag{D34}$$

For $i = 14$

The mechanism has “Strongly Suspected” scientific certainty, hence $b_4 \le S_{14} \le b_3$

$$b_4 \le X_{14,1} + X_{14,2} + X_{14,3} + X_{14,4} \le b_3 \tag{D35}$$

$$X_{14,1} + X_{14,2} + X_{14,3} + X_{14,4} + d_{23}^{+} - d_{23}^{-} = b_3 \tag{D36}$$

$$X_{14,1} + X_{14,2} + X_{14,3} + X_{14,4} - d_{24}^{+} + d_{24}^{-} = b_4 \tag{D37}$$

For $i = 15$

The mechanism is classified as “Suspected”, hence $b_6 \le S_{15} \le b_5$

$$b_6 \le X_{15,1} + X_{15,2} + X_{15,3} + X_{15,4} \le b_5 \tag{D38}$$

$$X_{15,1} + X_{15,2} + X_{15,3} + X_{15,4} + d_{25}^{+} - d_{25}^{-} = b_5 \tag{D39}$$

$$X_{15,1} + X_{15,2} + X_{15,3} + X_{15,4} - d_{26}^{+} + d_{26}^{-} = b_6 \tag{D40}$$

For $i = 16$

The mechanism is classified as “Below Suspected”, hence $S_{16} \leq b_7$

$$X_{16,1} + X_{16,2} + X_{16,3} \leq b_7 \tag{D41}$$

$$X_{16,1} + X_{16,2} + X_{16,3} + d_{27}^{+} - d_{27}^{-} = b_7 \tag{D42}$$

For $i = 17$

The mechanism is classified as “Suspected”, hence $b_6 \leq S_{17} \leq b_5$

$$b_6 \leq X_{17,1} + X_{17,2} + X_{17,3} + X_{17,4} \leq b_5 \tag{D43}$$

$$X_{17,1} + X_{17,2} + X_{17,3} + X_{17,4} + d_{28}^{+} - d_{28}^{-} = b_5 \tag{D44}$$

$$X_{17,1} + X_{17,2} + X_{17,3} + X_{17,4} - d_{29}^{+} + d_{29}^{-} = b_6 \tag{D45}$$

For $i = 18$

The mechanism is classified as “Suspected”, hence $b_6 \leq S_{18} \leq b_5$

$$b_6 \leq X_{18,1} + X_{18,2} + X_{18,3} + X_{18,4} \leq b_5 \tag{D46}$$

$$X_{18,1} + X_{18,2} + X_{18,3} + X_{18,4} + d_{30}^{+} - d_{30}^{-} = b_5 \tag{D47}$$

$$X_{18,1} + X_{18,2} + X_{18,3} + X_{18,4} - d_{31}^{+} + d_{31}^{-} = b_6 \tag{D48}$$

For $i = 19$

The mechanism is classified as “Almost 100%”, hence $b_3 + 1 \leq S_{19} \leq b_1 - 1$

$$b_3 + 1 \leq X_{19,1} \leq b_1 - 1 \tag{D49}$$

$$X_{19,1} - d_{32}^{+} + d_{32}^{-} = b_3 + 1 \tag{D50}$$

$$X_{19,1} + d_{33}^{+} - d_{33}^{-} = b_1 - 1 \tag{D51}$$

For $i = 20$

The mechanism has “Strongly Suspected” scientific certainty, hence $b_4 \leq S_{20} \leq b_3$

$$b_4 \leq X_{20,1} + X_{20,2} + X_{20,3} + X_{20,4} \leq b_3 \tag{D52}$$

$$X_{20,1} + X_{20,2} + X_{20,3} + X_{20,4} + d_{34}^{+} - d_{34}^{-} = b_3 \tag{D53}$$

$$X_{20,1} + X_{20,2} + X_{20,3} + X_{20,4} - d_{35}^{+} + d_{35}^{-} = b_4 \tag{D54}$$

For $i = 21$

The mechanism is classified as “Strongly Suspected”, hence $b_4 \leq S_{21} \leq b_3$

$$b_4 \leq X_{21,1} + X_{21,2} + X_{21,3} + X_{21,4} \leq b_3 \tag{D55}$$

$$X_{21,1} + X_{21,2} + X_{21,3} + X_{21,4} + d_{36}^{+} - d_{36}^{-} = b_3 \tag{D56}$$

$$X_{21,1} + X_{21,2} + X_{21,3} + X_{21,4} - d_{37}^{+} + d_{37}^{-} = b_4 \tag{D57}$$

For $i = 22$

The mechanism is classified as “Suspected”, hence $b_6 \le S_{22} \le b_5$

$$b_6 \le X_{22,1} + X_{22,2} + X_{22,3} + X_{22,4} \le b_5 \tag{D58}$$

$$X_{22,1} + X_{22,2} + X_{22,3} + X_{22,4} + d_{38}^{+} - d_{38}^{-} = b_5 \tag{D59}$$

$$X_{22,1} + X_{22,2} + X_{22,3} + X_{22,4} - d_{39}^{+} + d_{39}^{-} = b_6 \tag{D60}$$

For $i = 23$

The mechanism is classified as “Suspected”, hence $b_6 \le S_{23} \le b_5$

$$b_6 \le X_{23,1} + X_{23,2} + X_{23,3} \le b_5 \tag{D61}$$

$$X_{23,1} + X_{23,2} + X_{23,3} + d_{40}^{+} - d_{40}^{-} = b_5 \tag{D62}$$

$$X_{23,1} + X_{23,2} + X_{23,3} - d_{41}^{+} + d_{41}^{-} = b_6 \tag{D63}$$

For $i = 24$

The mechanism is classified as “Suspected”, hence $b_6 \le S_{24} \le b_5$

$$b_6 \le X_{24,1} + X_{24,2} + X_{24,3} \le b_5 \tag{D64}$$

$$X_{24,1} + X_{24,2} + X_{24,3} + d_{42}^{+} - d_{42}^{-} = b_5 \tag{D65}$$

$$X_{24,1} + X_{24,2} + X_{24,3} - d_{43}^{+} + d_{43}^{-} = b_6 \tag{D66}$$

For $i = 25$

The mechanism is classified as "Suspected", hence $b_6 \le S_{25} \le b_5$

$$b_6 \le X_{25,1} + X_{25,2} + X_{25,3} \le b_5 \tag{D67}$$

$$X_{25,1} + X_{25,2} + X_{25,3} + d_{44}^{+} - d_{44}^{-} = b_5 \tag{D68}$$

$$X_{25,1} + X_{25,2} + X_{25,3} - d_{45}^{+} + d_{45}^{-} = b_6 \tag{D69}$$

Constraints

From Table 6, for all the repeated attributes, we have

$$X_{1,1} = X_{3,1} \tag{D70}$$

$$X_{3,1} = X_{4,1} \tag{D71}$$

$$X_{4,1} = X_{5,1} \tag{D72}$$

$$X_{5,1} = X_{6,1} \tag{D73}$$

$$X_{6,1} = X_{7,1} \tag{D74}$$

$$X_{7,1} = X_{8,1} \tag{D75}$$

$$X_{9,1} = X_{10,1} \tag{D76}$$

$$X_{9,1} = X_{10,1} \tag{D77}$$

$$X_{10,1} = X_{11,1} \tag{D78}$$

$$X_{11,1} = X_{12,1} \tag{D79}$$

$$X_{12,1} = X_{13,1} \tag{D80}$$

$$X_{13,1} = X_{14,1} \tag{D81}$$

$$X_{14,1} = X_{15,1} \tag{D82}$$

$$X_{15,1} = X_{16,1} \tag{D83}$$

$$X_{17,1} = X_{18,1} \tag{D84}$$

$$X_{24,1} = X_{25,1} \tag{D85}$$

$$X_{1,2} = X_{2,2} \tag{D86}$$

$$X_{2,2} = X_{5,2} \tag{D87}$$

$$X_{5,2} = X_{6,2} \tag{D88}$$

$$X_{6,2} = X_{7,2} \tag{D89}$$

$$X_{7,2} = X_{8,2} \tag{D90}$$

$$X_{8,2} = X_{9,2} \tag{D91}$$

$$X_{9,2} = X_{10,2} \tag{D92}$$

$$X_{10,2} = X_{11,2} \tag{D93}$$

$$X_{11,2} = X_{13,2} \tag{D94}$$

$$X_{13,2} = X_{14,2} \tag{D95}$$

$$X_{14,2} = X_{15,2} \tag{D96}$$

$$X_{15,2} = X_{16,2} \tag{D97}$$

$$X_{16,2} = X_{18,2} \tag{D98}$$

$$X_{18,2} = X_{21,2} \tag{D99}$$

$$X_{21,2} = X_{22,2} \tag{D100}$$

$$X_{22,2} = X_{23,2} \tag{D101}$$

$$X_{3,2} = X_{20,2} \tag{D102}$$

$$X_{20,2} = X_{24,2} \tag{D103}$$

$$X_{24,2} = X_{25,2} \tag{D104}$$

$$X_{4,2} = X_{12,2} \tag{D105}$$

$$X_{12,2} = X_{17,2} \tag{D106}$$

$$X_{3,3} = X_{4,3} \tag{D107}$$

$$X_{4,3} = X_{5,3} \tag{D108}$$

$$X_{9,3} = X_{10,3} \tag{D109}$$

$$X_{11,3} = X_{12,3} \tag{D110}$$

$$X_{12,3} = X_{13,3} \tag{D111}$$

$$X_{13,3} = X_{14,3} \tag{D112}$$

$$X_{14,3} = X_{15,3} \quad \text{(D113)}$$

$$X_{17,3} = X_{18,3} \quad \text{(D114)}$$

$$X_{1,4} = X_{3,4} \quad \text{(D115)}$$

$$X_{3,4} = X_{4,4} \quad \text{(D116)}$$

$$X_{4,4} = X_{5,4} \quad \text{(D117)}$$

$$X_{7,4} = X_{8,4} \quad \text{(D118)}$$

$$X_{11,4} = X_{12,4} \quad \text{(D119)}$$

$$X_{17,4} = X_{18,4} \quad \text{(D120)}$$

Additional Constraints

$$X_{i,j} \in I \quad \text{(D121)}$$

$$b_1 - b_3 \geq 2 \quad \text{(D122)}$$

$$b_3 - b_4 \geq 1 \quad \text{(D123)}$$

$$b_4 - b_5 = 1 \quad \text{(D124)}$$

$$b_5 - b_6 \geq 1 \quad \text{(D125)}$$

$$b_6 - b_7 = 1 \quad \text{(D126)}$$

$$b_i \in I \quad \text{(D127)}$$

Appendix D-2

Constraints created from grouping

From assessment of $i = 1 \sim 3$, we get

$$X_{1,3} + X_{1,4} > X_{2,3} \tag{D128}$$

$$X_{2,3} > X_{3,3} + X_{3,4} \tag{D129}$$

Also, from the theory discussed earlier,

$$X_{3,3} + X_{3,4} > X_{6,3} \tag{D130}$$

And based on time to leak (TTL) from Figure 1, we get

$$X_{6,3} > X_{7,3} + X_{7,4} \tag{D131}$$

$$X_{7,3} + X_{7,4} > X_{8,3} + X_{8,4} \tag{D132}$$

$$X_{11,3} + X_{11,4} > X_{9,3} + X_{9,4} \tag{D133}$$

$$X_{9,3} + X_{9,4} > X_{14,3} + X_{14,4} \tag{D134}$$

$$X_{14,3} + X_{14,4} > X_{10,3} + X_{10,4} \tag{D135}$$

$$X_{10,3} + X_{10,4} > X_{15,3} + X_{15,4} \tag{D136}$$

$$X_{15,3} + X_{15,4} > X_{17,3} + X_{17,4} \tag{D137}$$

$$X_{17,3} + X_{17,4} > X_{13,3} + X_{13,4} \tag{D138}$$

$$X_{13,3} + X_{13,4} > X_{16,3} \tag{D139}$$

Constraint due to Carbon dioxide concentration

There has been considerable disagreement on the role of carbon dioxide in copper corrosion, but it has been generally agreed that a lower concentration of carbon dioxide is beneficial. Hence, a higher concentration of carbon dioxide should get a higher score as compared to a lower carbon dioxide concentration. Hence, we have

$$X_{7,3} > X_{8,3} \tag{D140}$$

$$X_{9,3} > X_{7,3} \tag{D141}$$

$$X_{8,3} > X_{8,4} \tag{D142}$$

Constraint due to Sulfate concentration

A higher sulfate concentration is considered more lethal for copper corrosion as compared to the lower sulfate concentration. Hence, we have

$$X_{15,3} > X_{16,3} \tag{D143}$$

Sulfate to bi carbonate & high Sulfate to Chloride

A high sulfate to chloride and high sulfate to chloride is the recipe for Type-I pitting, hence it should be more corrosive than only a higher Sulfate concentration exceeding 17 ppm, hence

$$X_{11,4} > X_{11,3} \tag{D144}$$

$$X_{14,3} > X_{14,4} \tag{D145}$$

$$X_{15,3} > X_{15,4} \tag{D146}$$

$$X_{17,3} > X_{17,4} \tag{D147}$$

Constraint due to Chlorine concentration

Higher chlorine should be more corrosive, hence

$$X_{1,3} > X_{2,3} \tag{D148}$$

Also the Aluminum is suppose to act in synergy with chlorine and chloramines, and by itself Aluminum does not have any deleterious effects. Hence,

$$X_{1,3} > X_{1,4} \tag{D149}$$

$$X_{3,3} > X_{3,4} \tag{D150}$$

Constraint due to DO concentration

Dissolved oxygen plays an important role in pitting initiation and propagation. A higher DO concentration should get a higher score than a lower DO concentration. Hence, we have

$$X_{21,3} > X_{23,3} \tag{D151}$$

Constraint due to Stagnation of water

Stagnation of water causes many problems including microbial growth, cuprosolvency etc, however, the initial period of stagnation (between installation and usage) is considered as more crucial with respect to corrosion (Rossum, 1985). Hence, we get

$$X_{22,4} > X_{20,4} \tag{D152}$$

Other Constraints (hierarchy in attributes not pH dependant)

Excessive Soldering Flux > Low alkalinity > Pressure drop below V.P. >

> Pressure above 80 psi > Deposits of aluminum / iron

Hence

$$X_{22,1} > X_{20,1} \tag{D153}$$

$$X_{20,1} > X_{21,1} \tag{D154}$$

$$X_{21,1} > X_{24,1} \tag{D155}$$

$$X_{24,1} > X_{23,1} \tag{D156}$$

$$X_{i,j} > 0 \tag{D157}$$

CHAPTER-3

PROBABILISTIC MODEL FOR REPLACEMENT OF PLUMBING PIPES

As discussed in the previous chapter, the occurrence of pinhole leaks in the home plumbing systems is dependent on synergy between physical, chemical, biological and anthropogenic parameters. The synergy between these parameters is not completely understood due to absence of a unified mechanistic theory, and hence to date any preventive measure for pitting corrosion could not be ascertained. It is perceived that once pinhole leaks arrive in a particular plumbing system, the system becomes prone to more leaks in future (WSSC data). The decision of the homeowner to repair or replace is dependent on leak frequency, cost, previous experience, personal perception of leak pattern willingness to pay, willingness to take risk and personal comfort.

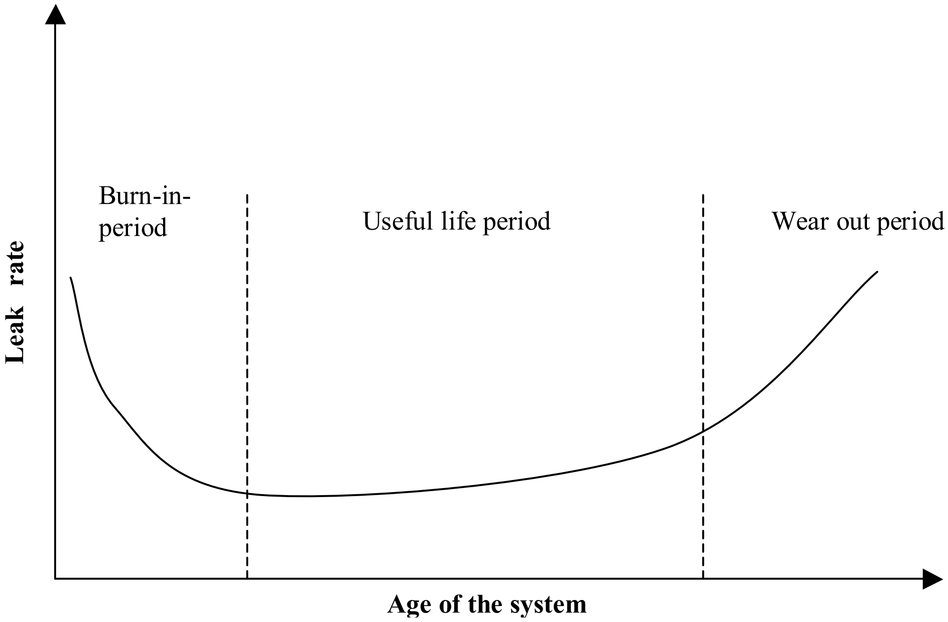

Figure 1 Variation of failure rate with age- a typical bath tub curve

The home plumbing systems are repairable systems; hence the variation in the failure rate with age of these systems can be approximated using a *bath tub curve,* shown in Figure 1. The life span of a typical home plumbing system can be divided into three phases based on the bath tub curve. The three phases are distinguished based on the *rate of occurrence of failure* (ROCOF), which is same as the leak rate or the failure rate.

The leak rate in the first phase or the *burn in phase* decreases from a higher value, the higher value in the initial stages of the life span can be due to the poor workmanship or small manufacturing defects in the pipes. Once these defects are rectified the leak rates in the system should stabilize to a lower value. The second phase or the *useful life period* is marked by a slow increase in the leak rates. In the event of pinhole leaks, it is perceived that the system deviates from the normal behavior and hence the useful life period is shortened considerably. The third phase or the *wear out period* is marked by a sudden increase in the leak rates, which keeps increasing with time; this is due to the wear and tear in the system because of its aging. Since the rate of failure is large in the third phase, it is generally beneficial to opt for a replacement during this phase. However, the point of optimal replacement should be based on some threshold value of the rate of failure or the leak rate.

The leak rate is a function of the inter event time and the number of leaks over a given period of time. If consecutive leaks are considered then the leak rate shall only be a function of the inter event time. Hence, from a home owners perspective the replacement of the system should be dependent on the inter event time of the consecutive leaks. This is a valid assumption, as in the event of a decreased inter event time or frequent leaks the homeowner would necessarily opt for an early replacement, similarly if the inter event time is large, the decision of the homeowner would be more inclined towards a repair rather than replacing the whole plumbing system. Hence, the threshold value of the inter event time is essential for a homeowner to decide the course of action in the event of a leak.

Interestingly, the information about the threshold leak rates is necessary but not a sufficient condition from decision making perspective. For instance, in the event of a n^{th} leak, the homeowner would know the inter event time between the n^{th} and $(n-1)^{th}$ leak, however this inter event time when compared to the threshold inter event time, will only validate the homeowner's decision that was taken at the time of $(n-1)^{th}$ leak, thus making the decision a post facto event. Hence, it is imperative that the inter event time between the n^{th} and the $(n+1)^{th}$ leak should be known ahead of time, specifically at the time of n^{th} failure or before. This necessitates the need of the probabilistic model that can pinpoint the n^{th} leak after which the system should be replaced.

It follows from the above discussion that from decision making perspective, the two essential parameters are the threshold value of the inter event time and the point on the time line at which this threshold value is reached. In order to account for the above requirements, the model should capture the variability of the leak rate with time. Assuming, the bath tub curve to be valid, the leak rates in the plumbing systems are expected to increase with age of the plumbing system. Thus the *leak rate curve* (as called from now on) becomes the essence of the probabilistic model.

The sections are organized as follows. First the available databases are discussed. Second the model building approach is discussed along with the assumptions, methodology and simulations. Third the simulation results are used to obtain optimal replacement criterion for plumbing systems.

Available Data

The databases that provide information about the temporal distribution of leaks are discussed. The data obtained from these sources is presented and the strength and the weaknesses of each database are discussed.

CDA database

The description and analysis protocol followed by Copper Development Association (CDA) was presented in chapter-1. The CDA failure reports typically provide information about the installation year of the plumbing system from which the failure specimen was withdrawn. Many of the CDA reports also furnish information about the year and month of the first leak.

A total of 763 CDA reports analyzed for this study contain the information about the installation year and the year of the first leak. The database does not provide any specific information about the inter event time of the subsequent leaks. The information provided in the CDA database is used to obtain the *time to first leak* distribution. Any other inference related to the leak rate curve could not be obtained from the database.

The time to first leak data for cold and hot water pipes is presented in the following section. The time to first leak was calculated by taking the difference between the first leak year and the installation year. The distribution of time to first leak for cold water and hot pipes are shown in Figure 2. The descriptive statistics are presented in Table 1. On an average, the cold water pipes have a smaller time to first leak as compared to hot water pipes, this is supported by the fact that hot water pipes are protected by formation of calcium carbonate scale, which does not form in cold water pipes unless the water is lime softened and saturated with carbonate ions.

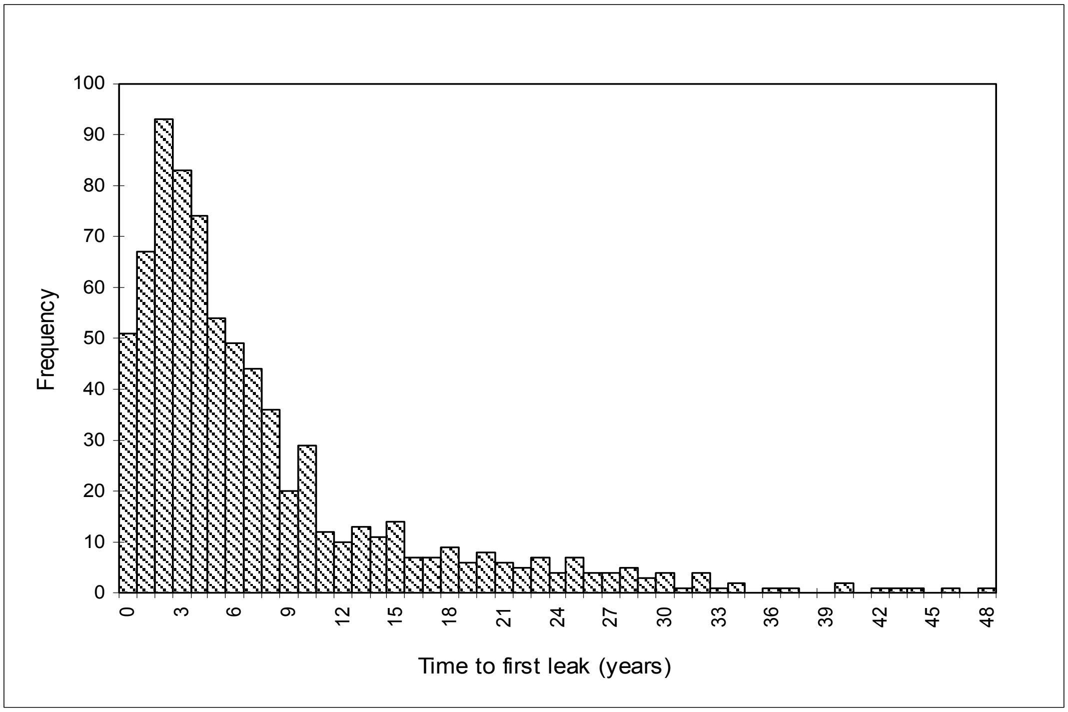

Figure 2 Frequency distribution for time to first leak in hot water and cold water pipes from CDA data

Table 1 Descriptive Statistics of time to first leak (years) distribution from CDA reports

	Count	**Minimum**	**Maximum**	**Mean**	**Median**	**Mode**	**Standard Error**	**Standard Deviation**	**Sample Variance**	**Skew ness**	**Range**
Cold water	512	0	40	6.73	4	2	0.325	7.36	54.171	1.992	40
Hot water	251	0	48	9.14	6	4	0.571	9.05	81.891	1.822	48
All Pipes (average)	***763*** [a]	***0***	***48***	***7.52***	***5***	***2***	***0.291***	***8.03***	***64.477***	***1.966***	***48***

[a] The data includes failure reports from both "inside out" and "externally initiated" failures.
All values reported are in years.

The descriptive statistics for cold and hot water pipes segregated by causes are presented in Table A-3.1 and Table A-3.2 (*Appendix A-3*). Separate frequency distributions for time to first leak in cold water pipes and hot water pipes are given in Figure A-3.1 and A-3.2 (*Appendix A-3*).

The data in Table 1, includes the failure reports that had reported externally initiated failures, all such data points may not be relevant from modeling pinhole leak where the failure is inside out. Also, the failure in first two years of installation is assumed to be analogous to *burn in* period of the bath tub curve. Hence, from modeling perspective, the data points for the external failures and the failures in first two years are pruned out. After pruning a total of 561 data points remained. An exponential distribution is fitted with a $R^2 = 0.96496$, the distribution is shown in Figure 3.

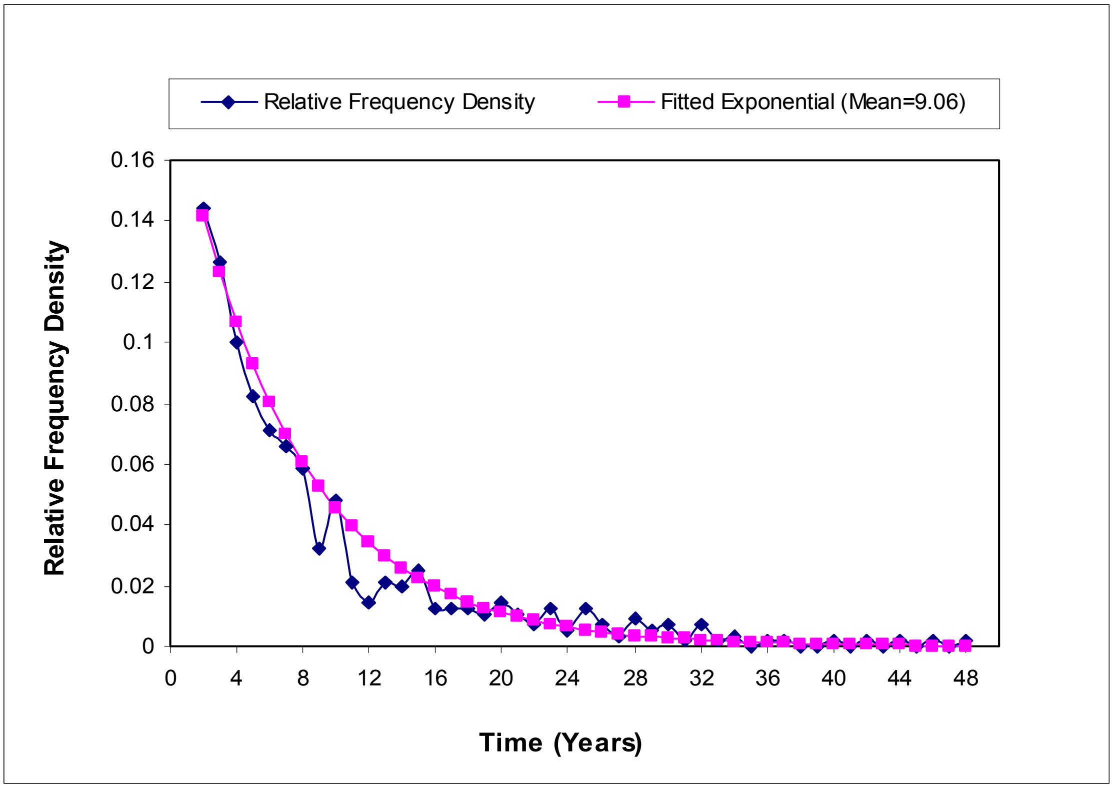

Figure 3 Fitted Exponential distribution for time to first leak.

The exponential distribution is not a strong fit, but due to significant noise in the middle portion of the data, the fit did not improve with truncation of data or even with other distributions. Due to this reason, the standard deviation of the fitted exponential distribution ($\sigma_{fit} = 7.06$) does not match very well with the standard deviation of the data set ($\sigma_{data} = 8.16$). The descriptive statistics of the data after pruning is given in Table A-3.3. The curve fitting calculations are shown in Table A-3.4.

Since the data is based on failures that were reported from different parts across the nation it closely represents the pattern of first leak time throughout the nation. The data is not location specific; hence the variability of the leak patterns due to change in climatic conditions, water quality, usage patterns, and other demographic aspects is well knitted within the data. The

CDA database does not provide any information about the subsequent leaks or their temporal distribution; hence from model building perspective the information is incomplete.

WSSC database

The Washington Suburban Sanitary Commission (WSSC) advises its costumers to report the pinhole incidents on http://www.wssc.dst.md.us/copperpipe/pipeleakhomepage.cfm . The homeowners are required to answer a questionnaire for reporting pinhole leaks. This web based data accumulation technique keeps the data continuously updated in a dynamic fashion. For the present study the data obtained in the year 2003 is discussed. The data is based on the pinhole failures in about 4500 homes in the area serviced by WSSC. The data provides information about the year of installation, year and month of first leak, total number of leaks and the year of last leak reported for these 4500 homes. There were some errors in the original data set; the errors included the inconsistency in reporting the years of installation and first leak in proper chronology, missing digits of year of installation etc. After omitting these errors and inconsistencies a total of 3786 data points remained for analysis.

The time of first leak was obtained by taking the difference between the year of first leak and the year of installation. The distribution for time to first leak from WSSC data is presented in Figure 4.

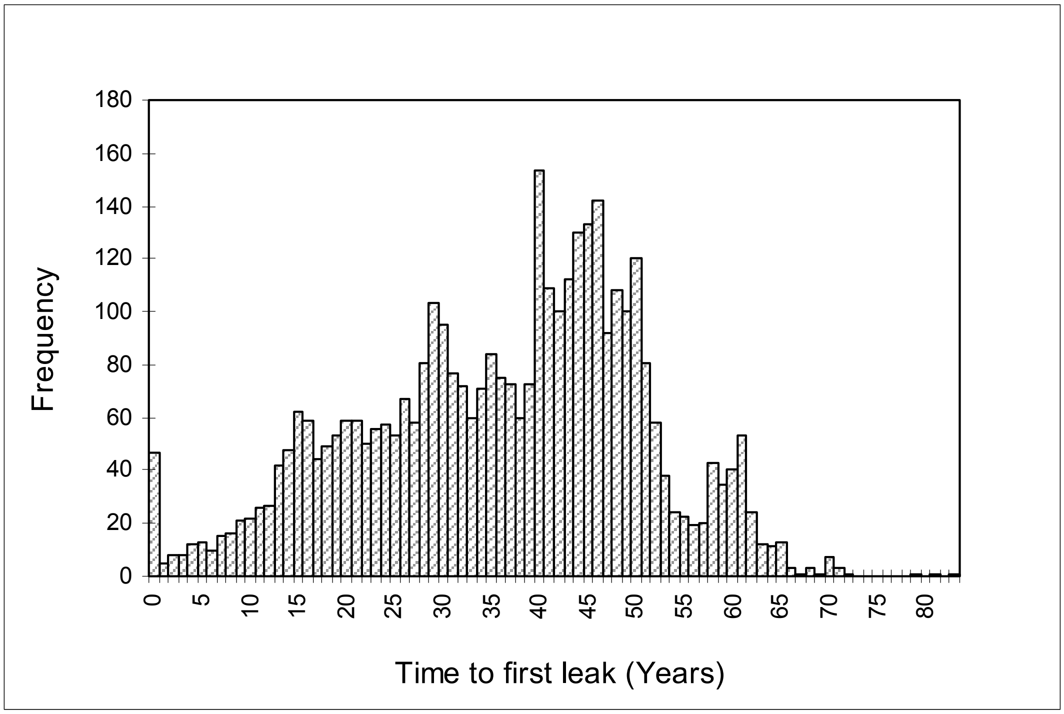

Figure 4 Frequency distribution for time to first leak in cold and hot water pipes from WSSC data

Interestingly, the first leak distribution from WSSC data is very different from the one obtained from CDA database. Figure 4 suggests that in most of the cases the pinhole leaks arrived in the homes that were fairly old. This is supported by the fact that the problem of pinhole leaks in WSSC area is believed to have started around 1994. A total of 3520 (~93 %) out of a total of 3786 homes reported leaks in or after 1994. The average age of the homes as in the year 2002 was 39.68 years. The descriptive statistics of the age of the homes and the first leak time are presented in Table 2. The distribution of the age of the homes in WSSC area is shown in Figure 5.

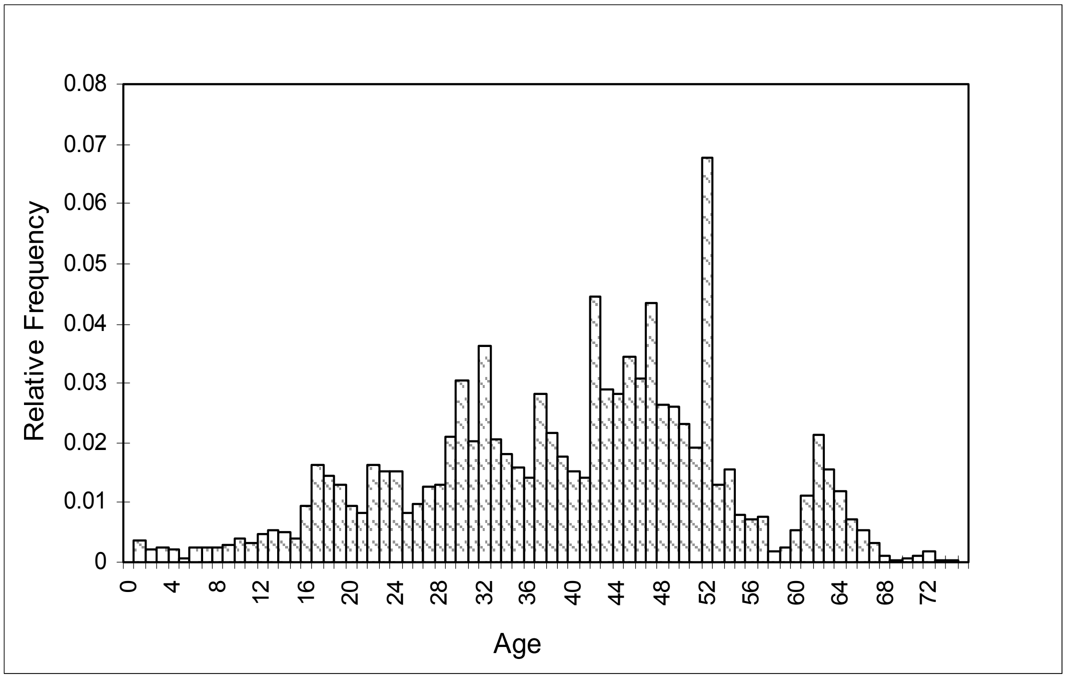

Figure 5 Relative Frequency distribution for the age of homes in WSSC area.

Table 2 Descriptive Statistics of the time to first leak and age of homes distribution from WSSC data

	Count	**Minimum**	**Maximum**	**Mean**	**Median**	**Mode**	**Standard Error**	**Standard Deviation**	**Sample Variance**	**Skew ness**	**Range**
Age of homes	3786	1	97	39.68	42	52	0.231	14.18	201.2	-0.26	96
Time to first leak	3786	0	95	36.05	38	40	0.236	14.57	212.2	-0.28	95
All values reported are in years.											

From the analysis of the age of the homes in WSSC area, it becomes clear that around 1994 there was a sudden increase in the pinhole leak incidents in the WSSC area, due to which the first leak arrived in majority of older homes that were leak free before that period. Due to this reason the first leak distribution is skewed to the left (Figure 4). The WSSC data captures the period of maximum intensity of pinhole leaks for a specific location or region, and hence a comparison with CDA data is not very justified.

The WSSC data also provides information about total number of leaks in the homes and the date of the occurrence of the last leak. Based on this information, the average leak rate was calculated. Following expression was used for the average leak rate calculation

Average leak rate

$$= \text{Total number of leaks} \div \{\text{Last leak year} - \text{First leak year} + 1\} \tag{1}$$

The homes were grouped by age in a ten year interval and the averaged value for each group was calculated. The variation of leak rates with age of the homes is shown in Figure 6.

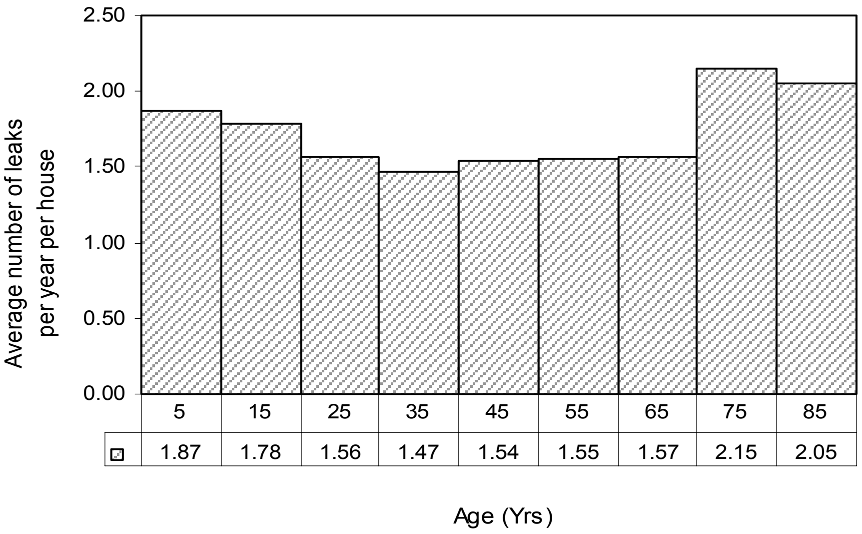

Figure 6 Average leak rates distribution with age of homes in WSSC area.

It may be concluded that the pinhole incidents struck the WSSC area when the houses in the region were fairly old. It is possible that most of these houses would have already entered in the *wear out period*, considering the bath tub curve. Hence, the leak incidents became severe within a small time period. Due to this reason, the first leak time and the leak rates obtained are much higher. Hence, the data from WSSC area represents the failures that would occur under the most severe combination. Additionally, the WSSC data is not a true representative of the nation wide pinhole leak occurrence, as it pertains to a specific location in comparison to CDA data. From model building perspective, the data may not be used directly and may require additional pruning or alterations in leak rates. Any model based on the WSSC data may not be very useful for other areas, as the leak rates obtained from WSSC data are high.

Homeowner Survey

The homeowner survey, conducted by Virgina Tech Survey Research Center, consists of leak time information from 83 respondents, who reported to have experienced pinhole leaks in their homes. However, out of 83 respondents, 45 reported to have copper pipes in their home plumbing. There is a slight discrepancy in the survey data, as some of the respondents who reported to have pipes other than copper in their plumbing, later reported copper as the material in which the failure occurred, while some of the respondents who chose copper as the material in their plumbing later chose other material in which the failure occurred. For the purpose of this study, only the 45 respondents that reported copper as their plumbing material were considered. Out of 45 data points available from the survey, 6 respondents did not provide the year of installation or the year or first leak or both. Hence, a total of 39 data points remained for analysis.

Out of these 39 respondents, 10 were from an unnamed community in Florida, 6 from an unnamed community in Ohio, 5 from California and 18 were from rest of United States. The two unnamed communities in Florida and Ohio were previously identified as hotspots. The time to first leak distribution from the homeowner survey data is presented in Figure 7.

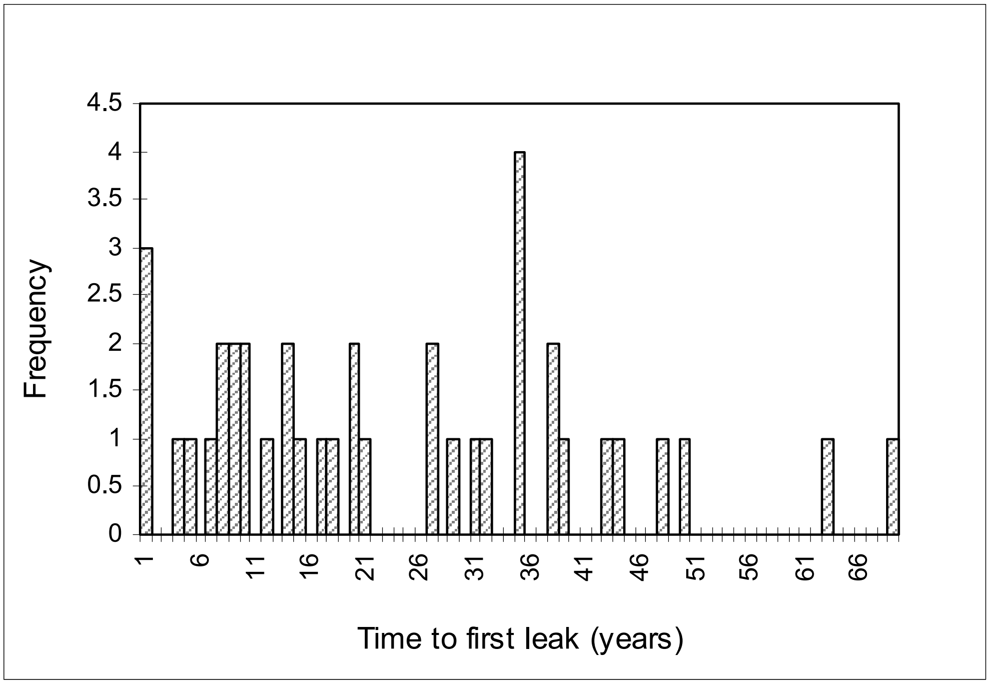

Figure 7 Frequency distribution for time to first leak from homeowner survey data

As such the time to first leak from the survey does not show any specific pattern and is sparse. This may be because of lack of sufficient data points for the analysis. Hence, no conclusion about the pattern of the first leak time could be made from the survey results.

Based on the information about the subsequent leaks, the leak rates were calculated from the survey by grouping houses in different age groups. A 10 year time interval was adopted for grouping the houses, the leak rates calculated were averaged for each group. The variation of leak rates with the age is presented in Figure 8.

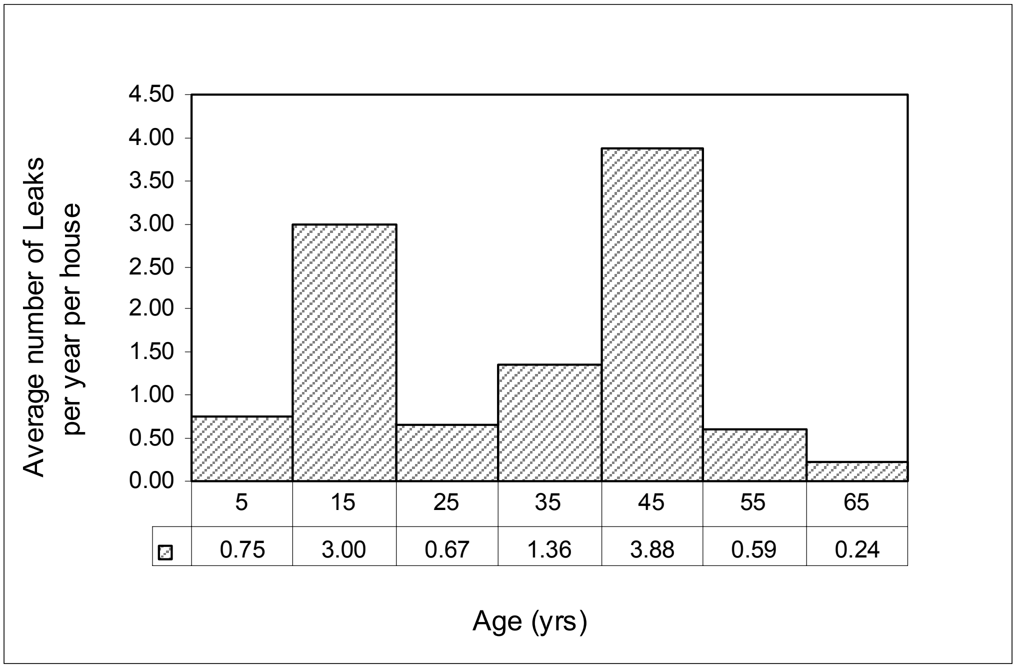

Figure 8 Average leak rates distribution with age of homes from homeowner survey.

It may be concluded that the information from the survey is limited, due to which no inference about the leak rates or the first leak time could be made. The data however is obtained from a nationwide survey and it contains information from some of the hotspots namely, unnamed communities in Florida and Ohio and parts of California, but because of its limited number of data points it may be assumed that it is partially representative of the pinhole leak patterns across the nation.

The Model

The basis of the model development is the bath tub curve that assumes an increase in the leak rate with age. From a model building perspective, the first two years of the plumbing are not considered, as it is assumed that this period is the burn in period, wherein failures related to poor workmanship or manufacturing defects in pipes may occur. The period of two years was chosen based on the time to first leak distribution from CDA data base. Hence, it is assume that the first two year of the plumbing system should be otherwise leak free, if the *burn in effect* does not come in play.

Since the leak rate varies with age of the plumbing, the leak rate is non stationary with time. In similar work a Non Homogeneous Poisson Process was used by Loganathan and Lee, (2005). In the paper, the leak rate curve was obtained using neural networks based on WSSC data. The methodology of building the model is quite similar to the one adopted by Loganathan and Lee, (2005), however, instead of using the WSSC data, the data from homeowner survey and the CDA database is used. The methodology used in the present study is explained in the following section.

The WSSC data is not considered for model building, as it is perceived that the data captures the extreme circumstances, wherein older homes where subjected to a sudden attack of pinhole leaks. It is very likely that due to this reason Loganathan and Lee, (2005) used a neural network approach with WSSC data. It follows that the situation in WSSC area was extreme and limited to a particular region; hence it is felt that a model based on WSSC data may not be suitable for use in other areas. In order to build a model that can be used on a nationwide basis, the data for the model should be based on surveys or databases wherein it has some intrinsic character of the leak patterns from different locations. Hence, the homeowner survey along with CDA database is chosen for the model building purposes.

The homeowner survey provides the leak patterns based on the nationwide survey, although due to lack of sufficient number of data points, the leak rate curve obtained from the survey does not provide a pattern suitable for model building. In order to use the data for the model, suitable pruning is required to obtain an increasing leak rate curve with the age. The pruning of data necessarily requires chopping the higher leak rates for each age group. Due to these exclusions, the number of data points would be reduced further. In order to obtain a reasonable leak rate curve for the model a different approach is used.

The pruned leak rates obtain from homeowner survey are initially used for NHPP simulations, the first leak distribution obtained from the simulations is then calibrated using the CDA time to first leak distribution, in an iterative environment by allowing the leak rate curve to change. This approach provides a leak rate curve at the end of calibration. The secondary advantage with the approach is that it ties the CDA time to first leak with the model, thus adding a nationwide flavor in the simulation results. The following steps are elaborated further.

Data pruning

The objective of data pruning is to obtain an increasing leak rate curve for the model. However, since the data used in NHPP simulations will be later calibrated, the pruned data is subjected to change with the calibration. For pruning the data, the upper limits for each age group was considered. The upper limit for the age group is based upon the hypothesis that for a particular age group the leak rates beyond a certain value will be unreasonable from homeowner’s perspective.

For instance, in the event of a leak the worst sequence of event can be perceived as follows. The homeowner would notice stains or water marks on walls, ceilings or floor that would indicate the leak in the pipes, the pipes are hidden within the structural elements. In order to detect the actual position of the leak, the homeowner would call a specialized agency that will figure out the approximate location of the leak. These leak detecting agencies may require removal of some drywalls, ceiling or floor elements to confirm the position of the leaking pipe. After the leak detection, the plumbers would fix the leaks. The homeowner would then engage a general contracting agency that will fix the dry walls, ceiling etc and do the finishing jobs. The entire procedure may take several days at the expense of the homeowner's time, money and stress. The leak may have caused additional damages to valuable items like carpet, tiles, paintings, furniture etc.

The above sequence of events suggests that even one leak in a two year (leak rate of 0.5 leak per year) is reasonably high from a homeowner's perspective. However, the above sequence of events may not happen in every home especially if the pipes are exposed. In order to account for this fact the generalization of the leak rates is kept slightly on the higher side. The upper bounds considered for pruning the data for each age group are presented in Table 3.

Table 3 Upper bounds of leak rates used for data pruning

Age Interval (years)		**Upper bound Leak Rate (number of leaks per year)**
5.01	15	0.5
15.01	25	0.5
25.01	35	1
35.01	45	2
45.01	55	2
>55		5

The data points in each group greater than the upper bound were pruned out. The average leak rate for each age group was recalculated based on the remaining data points. Since, the first two years are considered to be free of any leaks a leak rate of 0.0001 leaks/ year is used for the simulations; this is to ensure that the first leak time is always greater than 2 years. Since, there is only data point for age group of 5 years, a leak rate of 0.1 leak per year was assumed for age interval between 2 and 5 years. The leak rates obtained after pruning the data are presented in Figure 9.

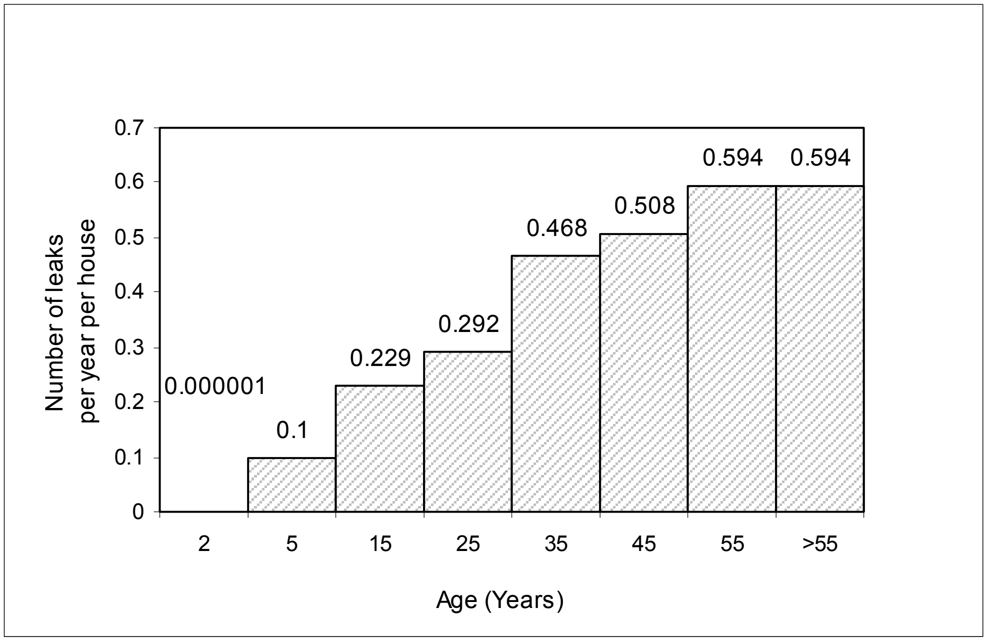

Figure 9 Average leak rates distribution with age after data pruning.

These leak rates are further divided into a two year time interval for using in NHPP simulation, this approximation is done to reduce the computational requirement in calibration.

NHPP simulation

A non-homogeneous Poisson process (NHPP) is used since the leak rates are non stationary with time. The NHPP model captures the variability of the leak rates with time. The model was used for defining optimal replacement criteria based on minimum cost by Loganathan and Lee, (2005). According to the NHPP process, if the counting of failure is started at $t = 0$, then the number of leaks $N(T_1)$ in the time interval $0 \le t \le T_1$ is defined by,

$$N(T_1) = \int_0^{T_1} \lambda(t)dt \tag{2}$$

The total number of leaks $N(T_2)$ at the end of another time interval, such that $T_1 \le t \le T_2$, will be the sum of the number of leaks in the time interval $0 \le t \le T_1$ and the number of leaks in the second time interval, hence,

$$N(T_2) = N(T_1) + \int_{T_1}^{T_2} \lambda(t)dt$$

Or

$$N(T_2) - N(T_1) = \int_{T_1}^{T_2} \lambda(t)dt \tag{3}$$

The stepwise approach used to perform NHPP simulation is presented, a sample calculation for the simulation is shown in Table 4. The approach for the simulation is same as used by Loganathan and Lee, (2005).

- The maximum leak rate is chosen for generation a time stationary Poisson process. Hence, $\lambda = \max\{\lambda(t)\}$. The inter event time is assumed to be exponential, with the parameter λ. Hence, for the exponentially distributed inter event time y_i, for any leak to arrive within x,

$$F(x) = \int_0^x \lambda e^{-\lambda y} dy = 1 - e^{-\lambda x}. \tag{4}$$

- Since $0 \le F(x) \le 1$, it is substituted by a uniform random number $U(0,1)$ (refer Col. 1 of Table 4). It follows from above,

$$x = -\left(\frac{1}{\lambda}\right)\ln(1-U) \tag{5}$$

- Since, x is the inter event time, it will be added to the previous time to get the leak time, hence,

$$t_{i+1} = t_i + x_{i+1} \tag{6}$$

- Following Loganathan and Lee, (2005) and Ross, (2000), any event that occurs at any time t as NHPP with parameter $\lambda(t)$, shall be equivalent to the event that occurred as a homogenous Poisson with a parameter λ and probability not exceeding $\lambda(t)/\lambda$. Hence, for each value of t_i the corresponding $\lambda(t)$ value is obtained from the leak rate curve (Col. 5).

- The leak ratio is calculated using the parameter λ, for each $\lambda(t)$ value (Col. 6). For the probability comparison, a uniform random number is generated $U(0,1)$ (Col. 7).

- The leak is counted if $U_i \le \dfrac{\lambda(t)}{\lambda}$, else the same is discarded for counting purposes (Col. 8).

The simulation was repeated 600 times, the entire simulation was set up in a spread sheet that enabled the calibration of the $\lambda(t)$ values in the next step. The leak times obtained from this step are for un-calibrated values of the leak rates, these leak rates are the same as presented earlier in Figure 9.

Table 4 Sample calculations for NHPP simulations

Col. 1	Col. 2	Col. 3	Col. 4	Col. 5	Col. 6	Col. 7	Col.8
U(0,1)	**1-U(0,1)**	**X = $(1/\lambda)$Ln(1-U)**	**Leak time**	**Leak rate**	**Ratio**	**U(0,1)**	**NHPP**
0.0212	0.9788	0.0361	0.0361	0.0000	0.0000	0.1667	-9999
0.2275	0.7725	0.4348	0.4709	0.0000	0.0000	0.6796	-9999
0.5402	0.4598	1.3085	1.7794	0.0000	0.0000	0.4467	-9999
0.3472	0.6528	0.7182	2.4977	0.1000	0.1684	0.0293	2.498
0.6016	0.3984	1.5499	4.0476	0.1000	0.1684	0.2217	-9999
0.2714	0.7286	0.5332	4.5808	0.1000	0.1684	0.1278	4.581
0.8355	0.1645	3.0395	7.6202	0.2292	0.3860	0.5043	-9999
0.7542	0.2458	2.3636	9.9838	0.2292	0.3860	0.8383	-9999
0.7754	0.2246	2.5156	12.4994	0.2292	0.3860	0.8231	-9999
0.3211	0.6789	0.6524	13.1518	0.2292	0.3860	0.7491	-9999
0.6632	0.3368	1.8330	14.9848	0.2292	0.3860	0.9338	-9999
0.7623	0.2377	2.4199	17.4047	0.2917	0.4912	0.8184	-9999
0.1384	0.8616	0.2509	17.6556	0.2917	0.4912	0.8753	-9999
0.5887	0.4113	1.4964	19.1521	0.2917	0.4912	0.1308	19.152
0.5940	0.4060	1.5181	20.6702	0.2917	0.4912	0.0277	20.670
0.4826	0.5174	1.1097	21.7798	0.2917	0.4912	0.6715	-9999
0.4791	0.5209	1.0984	22.8782	0.2917	0.4912	0.3291	22.878
0.2729	0.7271	0.5367	23.4148	0.2917	0.4912	0.5241	-9999
0.3306	0.6694	0.6760	24.0909	0.2917	0.4912	0.3060	24.091
0.4680	0.5320	1.0628	25.1537	0.4683	0.7886	0.3986	25.154
0.8141	0.1859	2.8341	27.9878	0.4683	0.7886	0.0756	27.988
0.8757	0.1243	3.5112	31.4991	0.4683	0.7886	0.8955	-9999
0.5562	0.4438	1.3683	32.8674	0.4683	0.7886	0.9736	-9999
0.3426	0.6574	0.7064	33.5738	0.4683	0.7886	0.4128	33.574
0.0486	0.9514	0.0840	33.6578	0.4683	0.7886	0.9662	-9999
0.1440	0.8560	0.2618	33.9196	0.4683	0.7886	0.1019	33.920

Calibration of leak rate curve

This step was introduced to obtain a leak rate curve. It is an alternative approach to Loganathan and Lee, (2005), who obtained the leak rate curve using neural network. In the following, the calibration of the first leak time is performed using the CDA time to first leak distribution. As presented earlier, an exponential distribution was fitted to CDA time to first leak data, although, the fit was not very good due to the statistical noise inherent in the dataset. For the purpose of calibration, the parameters for the fitted exponential are assumed to be valid. The parameters used for calibration are,

Mean = 9.06, and Standard deviation = 7.06.

The mean and standard deviation are the two parameters that govern the exponential distribution. The mean and standard deviation were calculated in the NHPP spread sheet for the 600 first leak times generated in NHPP simulation. The Excel solver function was used for calibration. Following steps define the calibration process,

- The sum of squares of the difference in mean and the standard deviation with the respective calibration values was minimized.

  $$Min(z) = \{(Mean)_{calibration} - (Mean)_{NHPP}\}^2 + \{(\sigma)_{calibration} - (\sigma)_{NHPP}\}^2 \tag{7}$$

- Since, the $\lambda(t)$ values were broken in a two year interval; a constraint for increasing $\lambda(t)$ values was imposed in the following manner

  $$\lambda(t+2) \geq \lambda(t) + \varepsilon \tag{8}$$

- The value of ε was varied in intervals of 0.001 in order to achieve the minimum value for the sum of squares.

- The changing functions were the $\lambda(t)$ values.

- The above steps were repeated iteratively, with different values of ε, till the standard deviation and the mean stabilized.

The calibration could not achieve a zero value for the sum of squared deviations; it is possibly due to the computational limitations of the machine. The mean and standard deviation of the NHPP stabilized at 9.488 and 6.063 years respectively. Beyond these values, the calibration started giving bigger deviations with change in ε. Hence, these values were adopted as the final values. The leak rate curve obtained from calibration is presented in Figure 10. The un-calibrated leak rate curve and the curve from Loganathan and Lee, (2005) are presented for comparison.

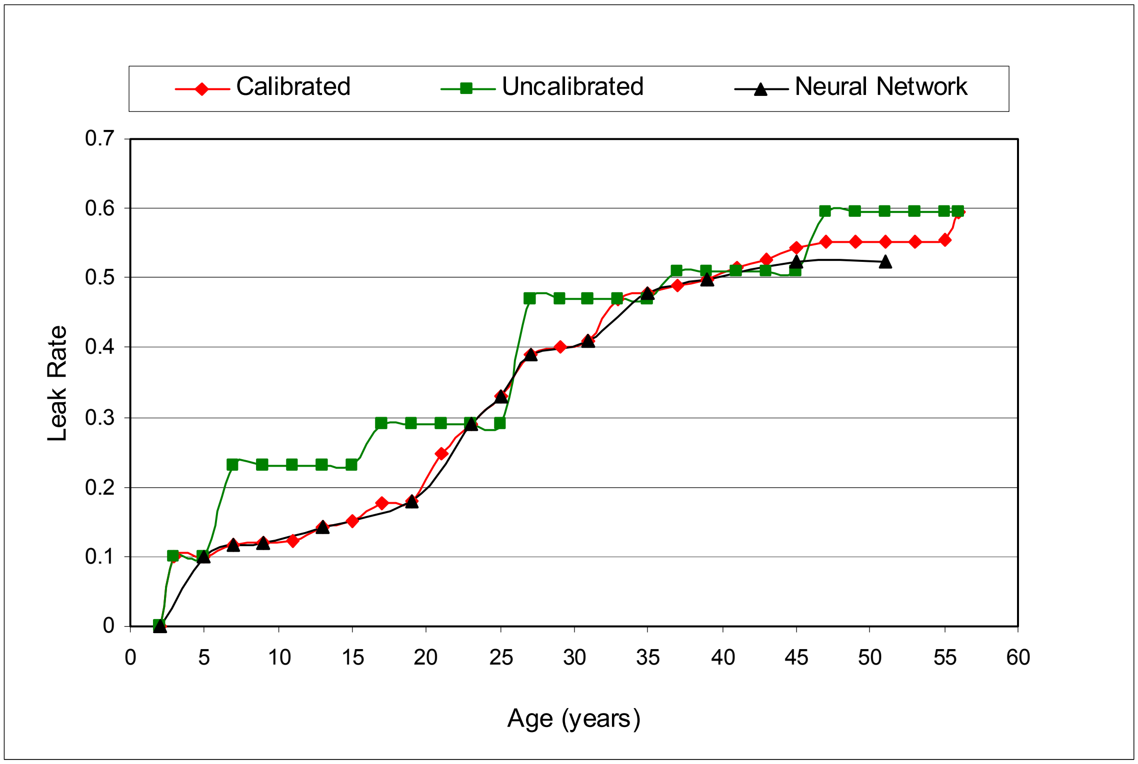

Figure 10 Calibrated leak rate curve for NHPP simulation.

From Figure 10, it may be inferred that the calibrated curve is similar to the one obtained by Loganathan and Lee, (2005). The leak rates in the last part of the calibrated curve are higher than the values obtained by Loganathan and Lee, (2005). Interestingly, the shape of the leak rate curve resembles the *useful life* and the *wear-tear period* of the bathtub curve, the useful life period is significantly shortened due to occurrence of pinhole leaks. The curve is adopted for calculation of other leak times from NHPP simulation.

The leak times obtained from NHPP simulation are presented in Table 5. The frequency distribution for the first five leaks is presented in Figure B-3.1 through B-3.5 (*Appendix B-3*).

Table 5 Summary of results for various leak times from NHPP simulations.

Leak #	**Min. (year)**	**Max. (year)**	**Mean (year)**	**Mode (year)**	**Median (year)**	**Stand. Dev. (year)**	**Diff. in Mode**	**Diff. in Mean**
1st Leak	2.019	31.051	9.488	3.793	7.862	6.067		
2nd Leak	2.645	34.498	15.664	13.617	15.147	6.752	9.824	6.176
3rd Leak	3.618	42.630	20.197	24.328	20.860	6.504	10.711	4.533
4th Leak	5.845	44.888	23.659	26.260	23.935	6.082	1.932	3.462
5th Leak	8.475	44.985	26.622	33.830	26.314	5.884	7.570	2.963
6th Leak	8.833	46.799	29.313	36.243	29.014	5.802	2.412	2.691
7th Leak	13.962	50.650	31.719	38.702	31.406	6.002	2.459	2.406
8th Leak	16.926	54.418	33.885	41.056	33.323	6.014	2.354	2.165
9th Leak	18.059	59.010	36.089	43.611	35.322	6.196	2.556	2.205
10th Leak	19.816	62.470	38.084	44.912	37.430	6.241	1.301	1.995
11th Leak	20.561	63.765	40.107	46.601	39.466	6.324	1.689	2.022
12th Leak	23.944	65.000	41.960	49.759	41.379	6.529	3.158	1.853
13th Leak	24.133	66.905	43.730	50.272	43.277	6.569	0.512	1.770
14th Leak	26.891	67.749	45.604	50.329	45.107	6.702	0.058	1.875
15th Leak	29.284	69.802	47.411	51.067	46.913	6.876	0.737	1.806
16th Leak	30.774	75.835	49.160	52.466	48.840	7.079	1.399	1.749
17th Leak	33.980	76.690	51.010	52.905	50.692	7.105	0.439	1.850
18th Leak	34.852	78.822	52.802	53.695	52.656	7.329	0.790	1.792
19th Leak	35.565	80.412	54.474	57.018	54.160	7.562	3.323	1.671
20th Leak	36.149	83.437	56.307	57.806	56.042	7.596	0.788	1.833
21st Leak	39.076	83.560	58.106	59.965	57.959	7.823	2.159	1.799
22nd Leak	39.935	87.981	59.801	60.545	59.295	7.944	0.580	1.695
23rd Leak	39.949	88.374	61.462	62.090	60.762	8.132	1.545	1.661
24th Leak	40.027	93.641	63.262	62.576	62.338	8.333	0.485	1.800
25th Leak	40.532	95.935	64.824	62.637	63.973	8.520	0.061	1.562

The basis of the model building was to aid the decision process for replacement of the plumbing system. The replacement criteria are discussed in the following section.

Replacement criteria

As discussed previously, the decision to replace the plumbing is subjective to one's choice. There may be several parameters that may govern the decision to opt for replacement. Most of the time, cost considerations dominate the replacement criteria but there may be other homeowners who may not like to consider the cost as a governing factor. This work presents the replacement criteria based on cost. This criteria is based on the minimum cost, the optimal replacement is determined so as to optimize the expenditure incurred by the homeowner considering the useful life period of the plumbing system.

In order to arrive at the said criteria, first an assessment of the repair and replacement cost is presented. The assessment of the cost is based on the Homeowner survey and the Plumber Survey-II. Both these surveys were conducted by Virginia Tech Survey Research Center. The surveys were conducted in 2005~2006 period, hence the cost data obtained from these surveys is very valid for present.

Repair costs

From a homeowner's perspective, the repair costs for the pinhole leak should not be limited to the cost of repairing the leaks only. The cost should include the cost incurred in getting the other damages repaired, cost of personal time spent, and cost of stress and any other cost incurred in getting one's life back to normal as it was before the leak. Unfortunately, such a data is not only difficult to obtain but also it has a lot of variability associated with it, especially in the cost of stress and cost of personal time. Hence, for estimation purposes the values that are considered may be subjected to change under special circumstances. The following cost data is based on 45 respondents from homeowner survey. These respondents had experienced pinhole leaks in copper pipes in their homes. The cost data presented in the following section represents the cost incurred by the respondents on all the leaks, the data does not provide costs incurred per leak.

Amongst 45 respondents, 60 percent reported no other damage from the pinhole leak and 40 percent reported other damages (Figure 11). Thirty eight percent respondents paid less than $ 100 for the repair of all the leak, about 29 percent paid between $ 101 ~ $ 500, fifteen percent between $ 501 ~$ 1000, thirteen percent between $ 1001~ $ 3000 (Figure 12) . Hence, there is considerable variability in the cost of repair.

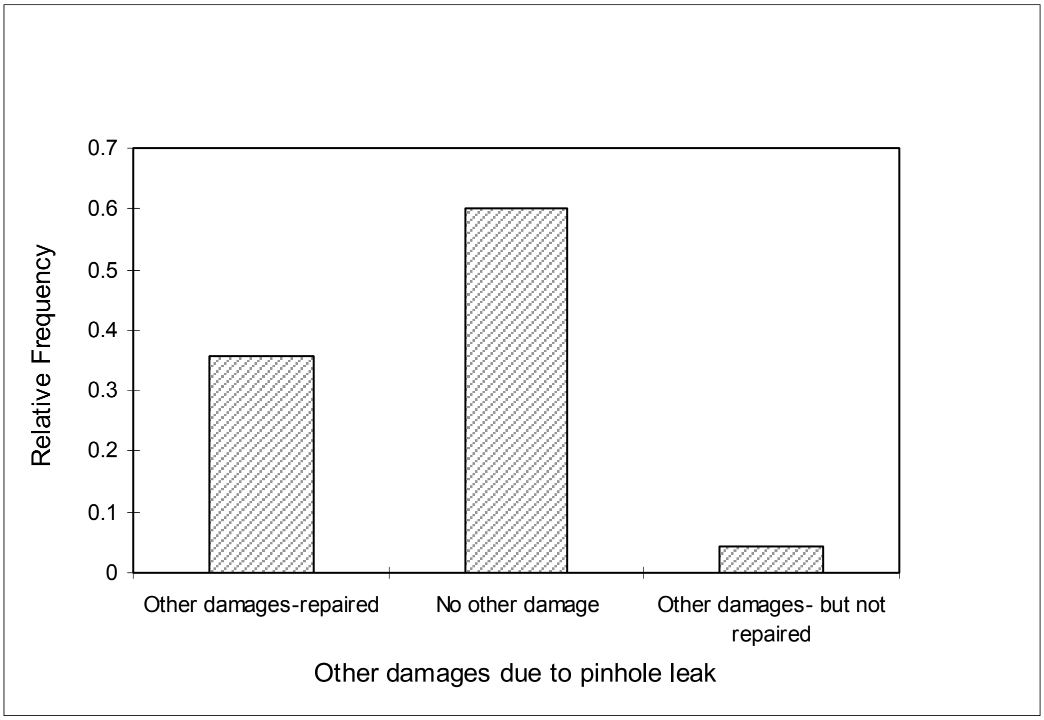

Figure 11 Analysis of damages due to pinhole leaks, based on 45 respondents from the survey.

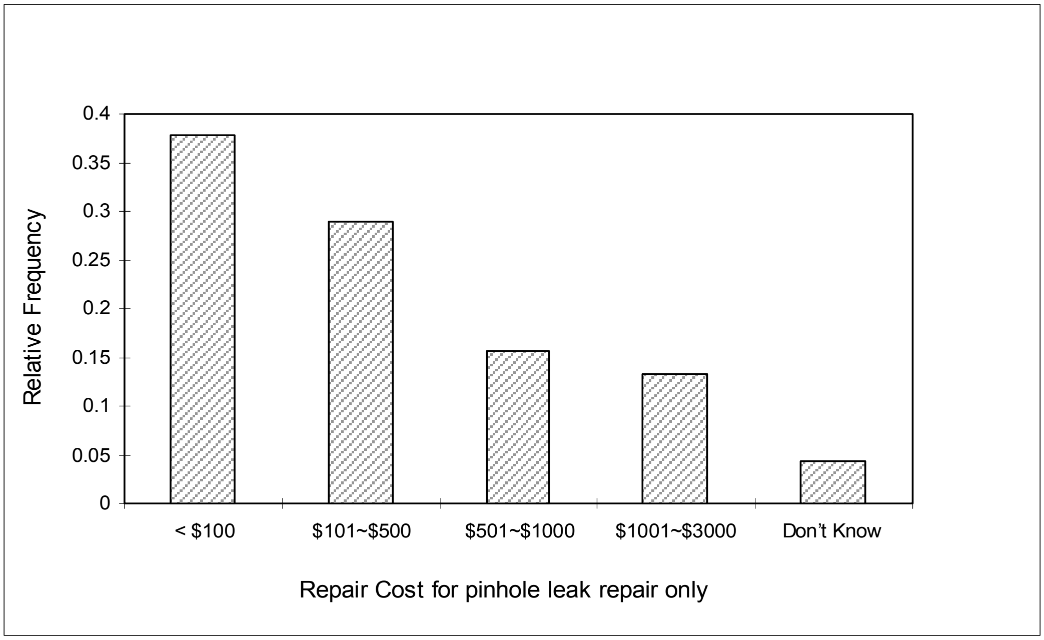

Figure 12 Analysis of repair cost incurred to homeowners for repair of pinhole leaks.

About fifty percent of the homeowners found the experience very stressful or somewhat stressful, twenty five percent found the experience not very stressful, while twenty percent did not respond to the question (Figure 13).

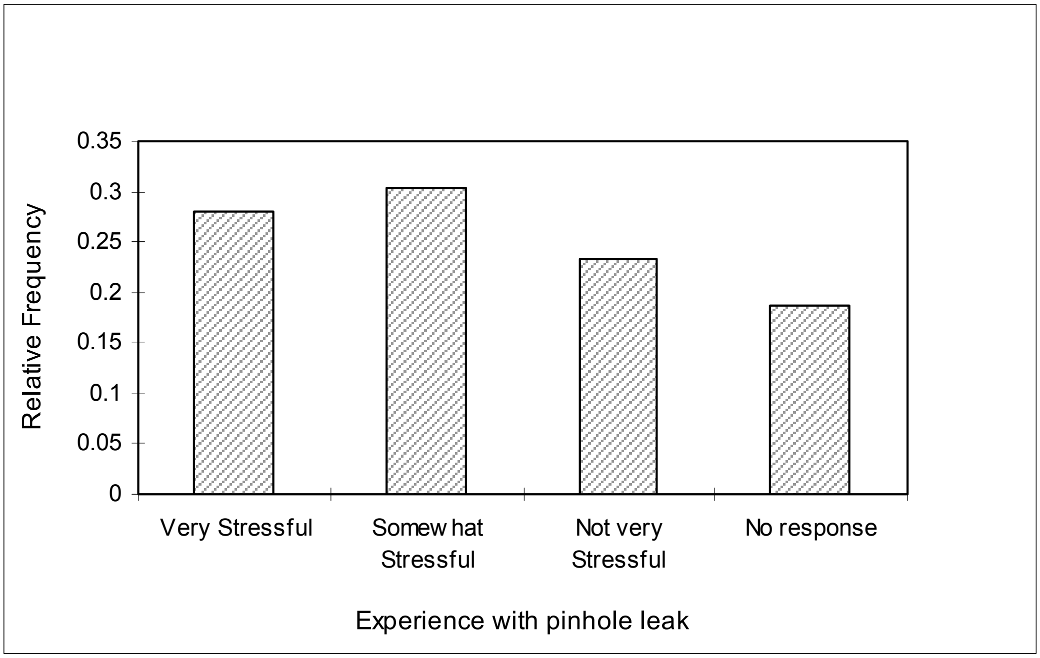

Figure 13 Analysis of stress experienced by homeowners in dealing with pinhole leaks.

Interestingly, majority of homeowners (50 percent) reported to have spent less than 10 hours on the repairs, about 25 percent spent 11~ 20 hours, fifteen percent 21~ 40 hours, less than five percent 41~ 80 hours and greater than 80 hrs respectively (Figure 14).

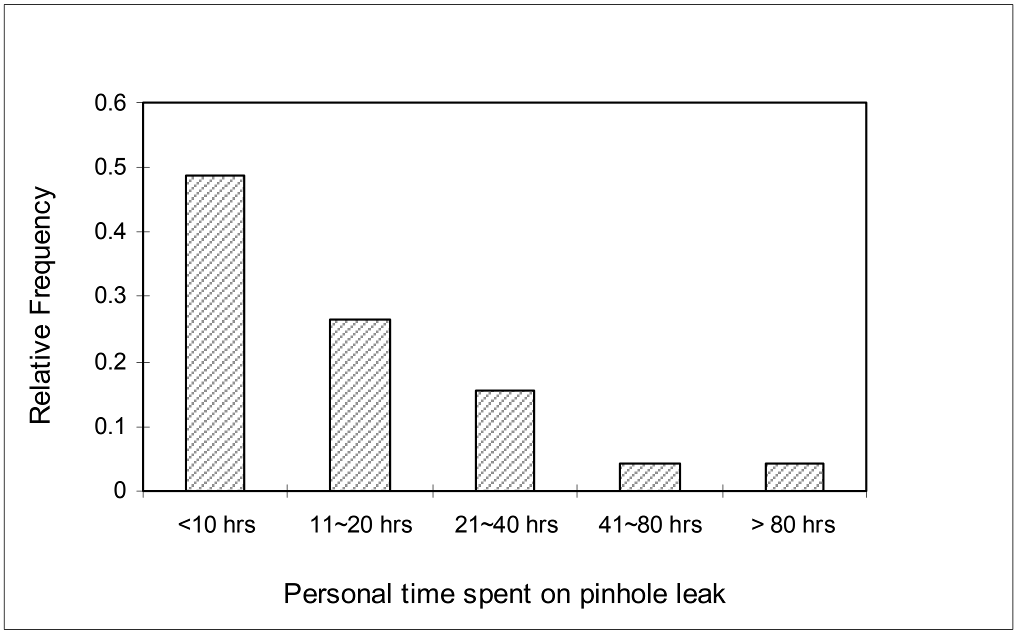

Figure 14 Analysis of personal time spent on repairs by homeowners in dealing with pinhole leaks.

Most of the homeowners could not provide any value for the total expenditure that was incurred due to the leak incident. Hence, a comprehensive figure for the repair cost of the pinhole leak cannot be obtained directly from the survey results. While majority of the homeowners reported to have spent less than $ 100 as repair cost on all the leaks. The variability in the cost is evident; the reason for the large variation in the cost may be due to small number of respondents that have experienced leak.

Since, the data does not provide the repair *cost data per leak*, suitable assumption needs to be made. If the cost of other damages, stress and personal time spent by the homeowner are taken into account the total cost of repair including these can be assumed to be $ 500 per leak. A repair cost of $ 500 per leak is used by Loganathan and Lee (2005).

Replacement cost

The modal value of the replacement cost or the cost of re-plumbing using copper pipes in a two bedroom two bath, two-level home obtained from Plumber survey-II is $ 3000. Although, there was a large variation in the cost of re-plumb but around 20 percent of the total 109 plumbers quoted the cost of re plumb between $ 2500 and $ 3000. Hence, the modal value of $ 3000 (quoted by 12 plumbers) can be considered as a reasonable estimate. This estimate is in agreement with the results of Plumber survey-I, where the quoted range was $ 2500 to $ 4000. Hence, an estimate of $ 3000 for re-plumb is justifiable.

With the available estimates of repair and replacement cost, an optimal replacement criteria is discussed. The other criteria based on the risk assessment, will be derived from the threshold value of inter event time.

Cost Based Optimal Replacement

The cost based optimality is required to optimize the expenditures for repair or replacement of the plumbing. Since, re-plumbing is about six times more expensive than repairing it is not the best alternative to prevent a homeowner from pinhole leaks. However, after certain leaks, the cost criteria may make the replacement viable from investment considerations. Hence, an optimal criterion is required to determine the threshold stage at which the replacement becomes viable.

Loganathan et al.(2002), derived the optimal replacement criterion based on the cost of repairs, cost of replacement and the discount rate. The criterion is presented below,

$$t_{n+1} - t_n < \frac{\ln\left(\frac{C_{n+1}}{F_n} + \frac{F_{n+1}}{F_n}\right)}{\ln(1+R)} \tag{9}$$

Where,

$t_{n+1} - t_n$ is the inter event time between the two successive failures.

C_{n+1} is the cost of repair for the $n+1^{th}$ failure

F_n is the cost of replacement at the time of the n^{th} failure

F_{n+1} is the cost of replacement at the time of the $n+1^{th}$ failure

The model was used by Loganathan and Lee, (2005), while determining the optimal replacement. If it is assumed that the cost of repair and the cost of re-plumb do not change with the failures, then it follows from above $F_n = F_{n+1} = \$3000$, $C_{n+1} = \$500$. Since, the cost of repair and the cost of replacement is considered independent of inflation, the nominal discount rate needs to be adjusted for inflation. A detailed discussion on the real rate, nominal rate and inflation is presented in *Appendix C-3*. For nominal discount rate of 6 % and inflation rate of 3.39 % the real rate is 2.61 % (*Appendix C-3*)

From Eqn (9), we get

$$t_{n+1} - t_n < \frac{\ln\left(\frac{500}{3000} + 1\right)}{\ln(1 + 0.0261)},$$

Or

$$t_{n+1} - t_n < 5.98 years \tag{10}$$

Hence, when the inter event time becomes less than 5.98 years, the option of replacement become viable from cost considerations. This result can be used with the NHPP model to determine the time of optimal replacement. From Table 5, if mean values for the leak times are considered, then the inter event time between the second and the third leak is 4.533 years, hence a replacement becomes viable at the second leak. The average age of the plumbing at the time of third leak is 15.664 years (From Table 5). Hence, from replacement considerations, the second leak or a fifteen year period after the installation, whichever is earlier should be used. The criteria should be used only for the plumbing systems that have experienced at least one leak.

Conclusions

The analysis provides two different kinds of criteria that may help the homeowner in the process of decision making. The leak rates are based on the CDA data and the homeowner survey, hence, the results are applicable on a nationwide basis. Since, the exact synergy of the causal factors that initiated the pinhole leaks are not understood, the model and the methodology are very beneficial from a homeowner's perspective.

The data and the criteria are applicable to the homes that have had at least one pinhole leak, it should not be used to evaluate the homes where pinhole leaks have not been a problem. In case, the plumbing system is replaced, the model should not be used for the new (replaced) system till such time pinhole leaks incidents start in the new system.

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APPENDIX A-3

Leak time Statistics and Distributions from CDA data base

Appendix A-3

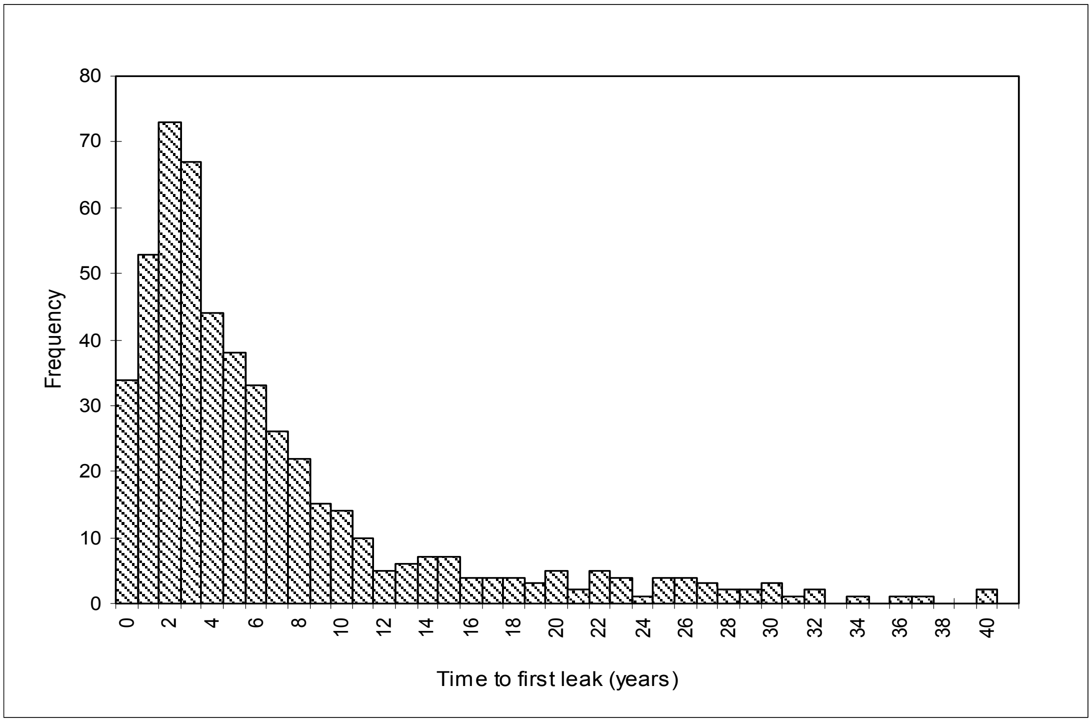

Figure A-3.1 Frequency distribution for time to first leak in cold water pipes from CDA data

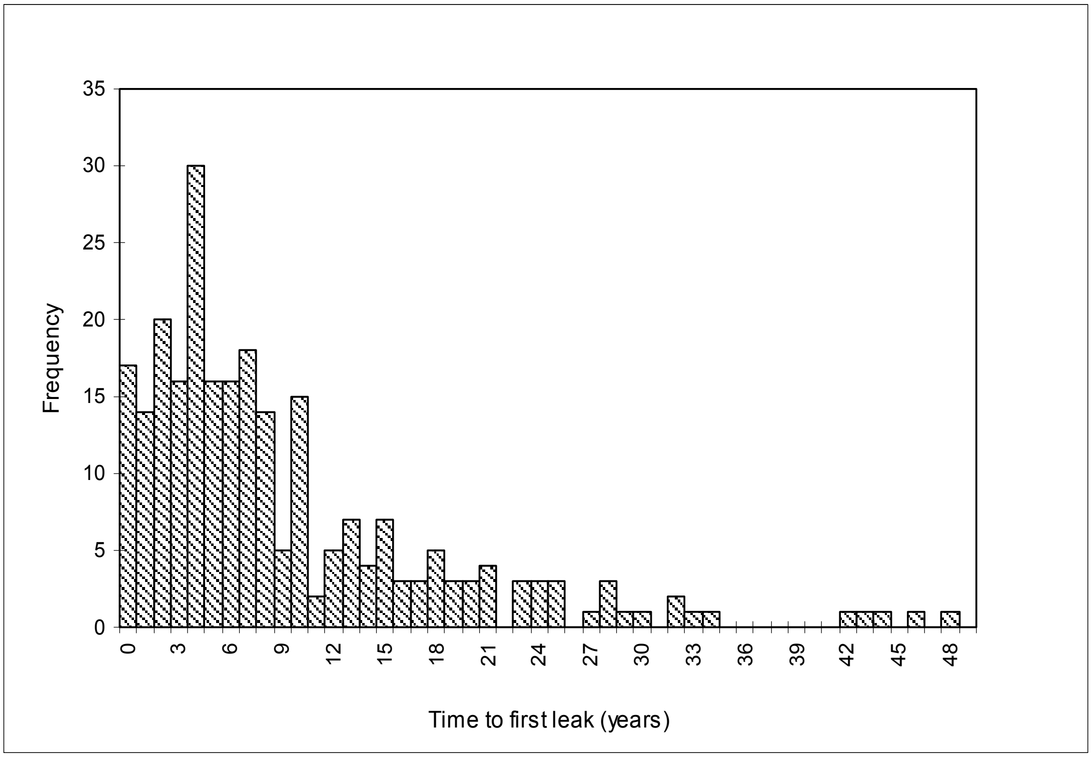

Figure A-3.2 Frequency distribution for time to first leak in hot water pipes form CDA data

Appendix A-3

Table A-3.1 Descriptive Statistics for time to first leak in cold water pipes categorized by failure causes

Cause of failure	**Count**	**Minimum**	**Maximum**	**Mean**	**Median**	**Mode**	**Standard Error**	**Standard Deviation**	**Sample Variance**	**Skew ness**	**Range**
Chloride/ Chlorine	236	0	37	6.26	4	3	0.410	6.29	39.64	2.146	37
Oxygen-differential	51	0	40	15.58	13	2	1.386	9.90	98.01	0.595	40
Failure initiated outside	67	0	40	4.87	3	0	0.838	6.86	47.06	3.329	40
Aggressive water	74	0	25	3.95	3	1	0.507	4.36	19.01	2.636	25
Erosion-Corrosion	43	0	32	6.60	4	1	1.098	7.20	51.86	1.760	32
Sulfide	16	1	34	9.25	8	8	1.762	7.04	49.67	3.135	33
Other minor [1]	25	0	31	7.04	3	1	1.796	8.98	80.71	1.495	31
Over All (average)	**512**	**0**	**40**	**6.73**	**4**	**2**	**0.325**	**7.36**	**54.17**	**1.992**	**40**

[1] Minor Causes include poor workmanship, microbial, no cause ascertained or a combination of above reasons.
All values reported are in years.

Table A-3.2 Descriptive Statistics for time to first leak in hot water pipes categorized by failure causes

Cause of failure	**Count**	**Minimum**	**Maximum**	**Mean**	**Median**	**Mode**	**Standard Error**	**Standard Deviation**	**Sample Variance**	**Skew ness**	**Range**
Erosion-Corrosion	84	0	30	6.87	5.5	4	0.631	5.781	33.42	1.67	30
Excessive Heating of water	64	0	48	13.19	10	7	1.382	11.05	122.2	1.17	48
Failure initiated outside	40	0	43	6.85	4.5	4	1.234	7.804	60.9	3.01	43
Chloride/ Chlorine	24	0	29	7.5	5	4	1.556	7.621	58.09	1.72	29
Oxygen-differential	16	0	33	11.94	9	2	2.857	11.43	130.6	0.97	33
Other minor [2]	23	0	46	9.96	7	7	2.19	10.52	110.8	1.99	46
Over All (Average)	**251**	**0**	**48**	**9.14**	**6**	**4**	**0.571**	**9.049**	**81.89**	**1.82**	**48**

[2] Minor Causes include poor workmanship, aggressive water, no cause ascertained or a combination of above reasons.
All values reported are in years.

Table A-3.3 Descriptive statistics for *time to first leak* in cold water and hot water pipes after data pruning

Cause of failure	**Count**	**Minimum**	**Maximum**	**Mean**	**Median**	**Mode**	**Standard Error**	**Standard Deviation**	**Sample Variance**	**Skew ness**	**Range**
CDA- time to first leak (after pruning)	561	2	48	9.06	6	2	0.345	8.16	66.60	1.78	46

Table A-3.4 Calculations for exponential fit -CDA first leak time

Class Inter.	**Freq.** x_i	**Relative Freq. Density** y_i	**Exponential Fit** (for $x_i \geq 2$) $\hat{y}_i = \left(\frac{1}{7.06}\right)\exp\left\{-\left(\frac{1}{7.06}\right)(x_i - 2)\right\}$	**SSE=** $\left(y_i - \hat{y}_i\right)^2$	**SST=** $\left(y_i - \bar{y}_i\right)^2$
0	0				
1	0				
2	81	0.144385	0.141630901	7.59E-06	0.015156
3	71	0.126559	0.122927344	1.32E-05	0.011085
4	56	0.099821	0.10669375	4.72E-05	0.006169
5	46	0.081996	0.092603939	0.000113	0.003687
6	40	0.071301	0.080374807	8.23E-05	0.002502
7	37	0.065953	0.069760635	1.45E-05	0.001996
8	33	0.058823	0.060548154	2.97E-06	0.00141
9	18	0.032085	0.052552259	0.000419	0.000117
10	27	0.048128	0.045612289	6.33E-06	0.000721
11	12	0.021390	0.039588801	0.000331	1.29E-08
12	8	0.014260	0.034360765	0.000404	4.92E-05
13	12	0.021390	0.029823136	7.11E-05	1.29E-08
14	11	0.019607	0.025884739	3.94E-05	2.78E-06
15	14	0.024955	0.022466441	6.2E-06	1.35E-05
16	7	0.012477	0.019499557	4.93E-05	7.74E-05
17	7	0.012477	0.016924476	1.98E-05	7.74E-05
18	7	0.012477	0.014689456	4.89E-06	7.74E-05
19	6	0.010695	0.012749589	4.22E-06	0.000112
20	8	0.014260	0.011065898	1.02E-05	4.92E-05
21	6	0.010695	0.009604553	1.19E-06	0.000112
22	4	0.007130	0.008336191	1.45E-06	0.0002
23	7	0.012477	0.007235326	2.75E-05	7.74E-05
24	3	0.005347	0.00627984	8.69E-07	0.000254
25	7	0.012477	0.005450534	4.94E-05	7.74E-05
26	4	0.007130	0.004730745	5.76E-06	0.0002
27	2	0.003565	0.00410601	2.93E-07	0.000314
28	5	0.008912	0.003563777	2.86E-05	0.000153
29	3	0.005347	0.00309315	5.08E-06	0.000254
30	4	0.007130	0.002684674	1.98E-05	0.0002

Table A-3.4 Calculations for exponential fit -CDA first leak time

Class Inter.	**Freq.** x_i	**Relative Freq. Density** y_i	**Exponential Fit** (for $x_i \geq 2$) $\hat{y}_i = \left(\frac{1}{7.06}\right)\exp\left\{-\left(\frac{1}{7.06}\right)(x_i - 2)\right\}$	**SSE=** $\left(y_i - \hat{y}_i\right)^2$	**SST=** $\left(y_i - \bar{y}_i\right)^2$
31	1	0.001782	0.00233014	3E-07	0.00038
32	4	0.007130	0.002022425	2.61E-05	0.0002
33	1	0.001782	0.001755347	7.39E-10	0.00038
34	2	0.003565	0.001523538	4.17E-06	0.000314
35	0	0	0.001322342	1.75E-06	0.000453
36	1	0.001782	0.001147716	4.03E-07	0.00038
37	1	0.001782	0.00099615	6.18E-07	0.00038
38	0	0	0.0008646	7.48E-07	0.000453
39	0	0	0.000750422	5.63E-07	0.000453
40	1	0.001782	0.000651323	1.28E-06	0.00038
41	0	0	0.00056531	3.2E-07	0.000453
42	1	0.001782	0.000490656	1.67E-06	0.00038
43	0	0	0.000425861	1.81E-07	0.000453
44	1	0.001782	0.000369622	2E-06	0.00038
45	0	0	0.000320811	1.03E-07	0.000453
46	1	0.001782	0.000278445	2.26E-06	0.00038
47	0	0	0.000241674	5.84E-08	0.000453
48	1	0.001782	0.000209759	2.47E-06	0.00038
$\sum x_i = 561$				**SSE= 0.001831**	**SST= 0.052246**
$\bar{y}_i$ = **0.021276**				$R^2 = 1 - \frac{SSE}{SST} = \boldsymbol{0.96496}$	

APPENDIX B-3

Frequency distribution of leak times from Non-Homogenous Poisson Process Simulations

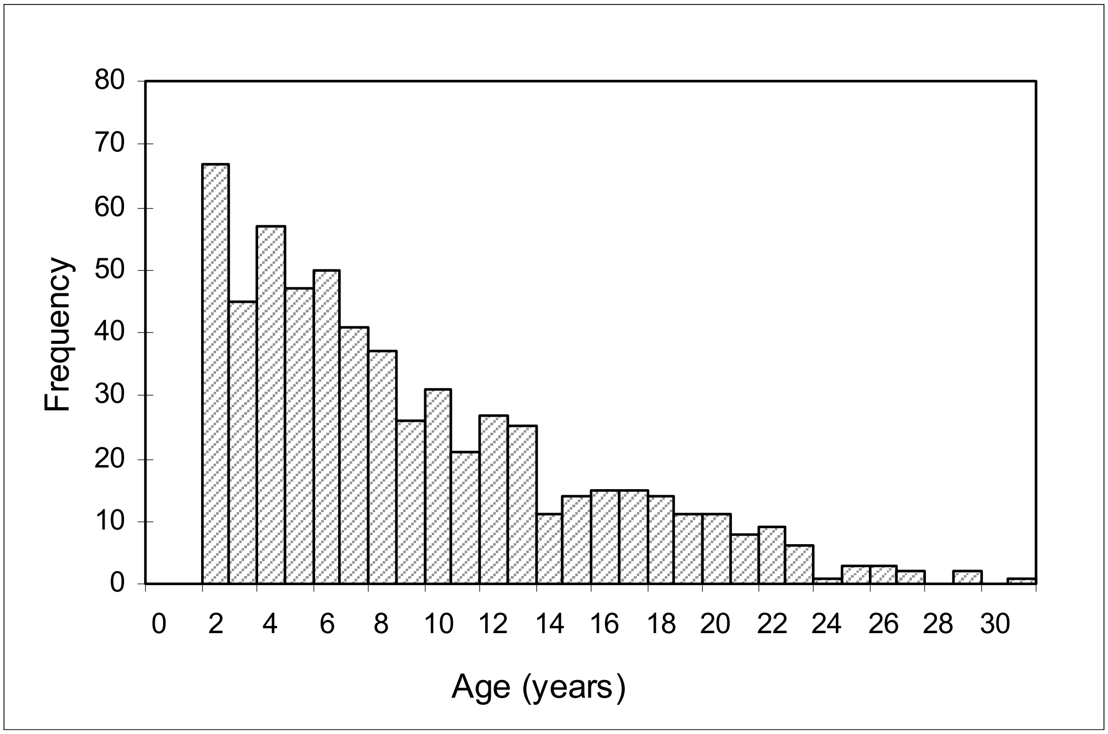

Figure B-3.1 Frequency distribution for time to first leak from NHPP simulations.

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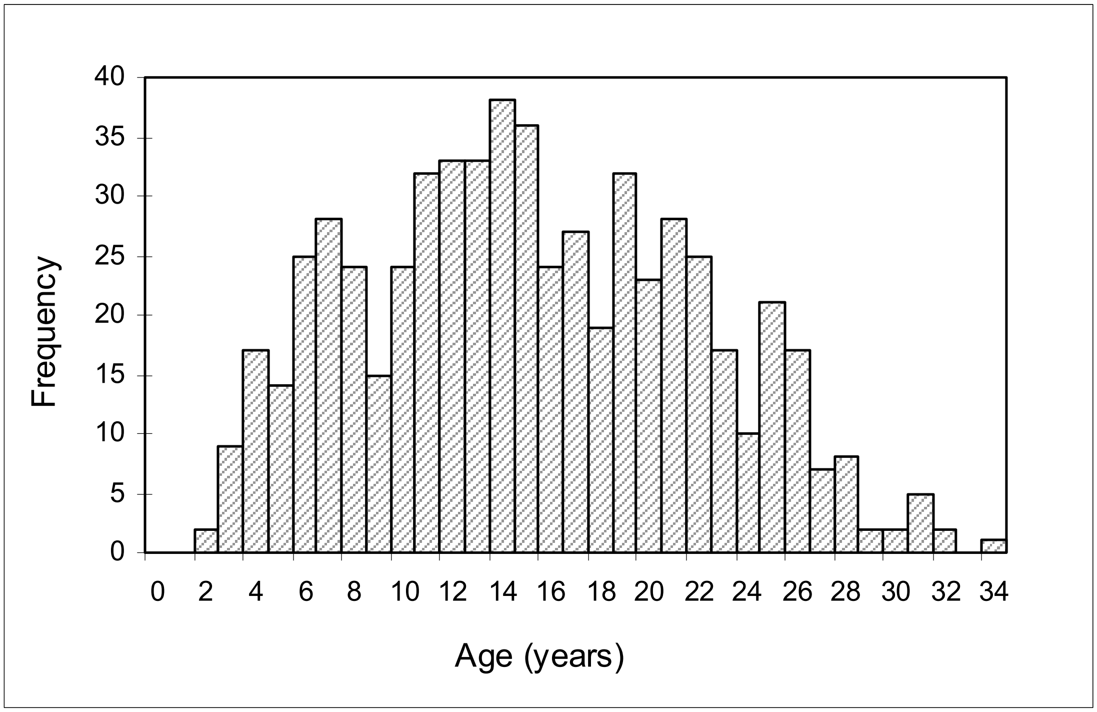

Figure B-3.2 Frequency distribution for time to second leak from NHPP simulations.

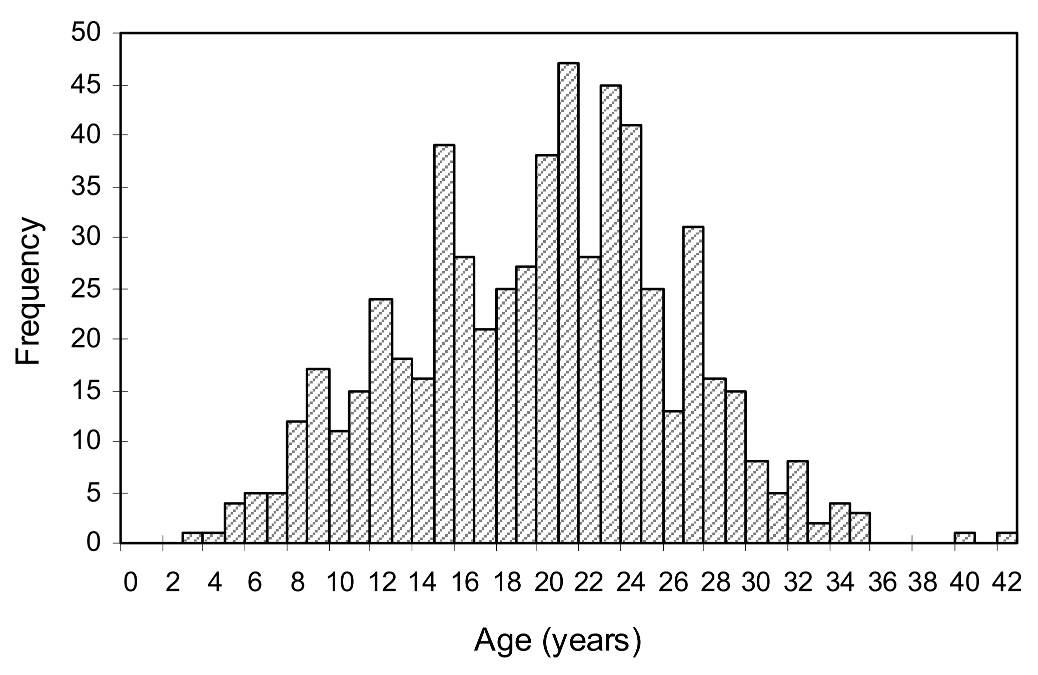

Figure B-3.3 Frequency distribution for time to third leak from NHPP simulations.

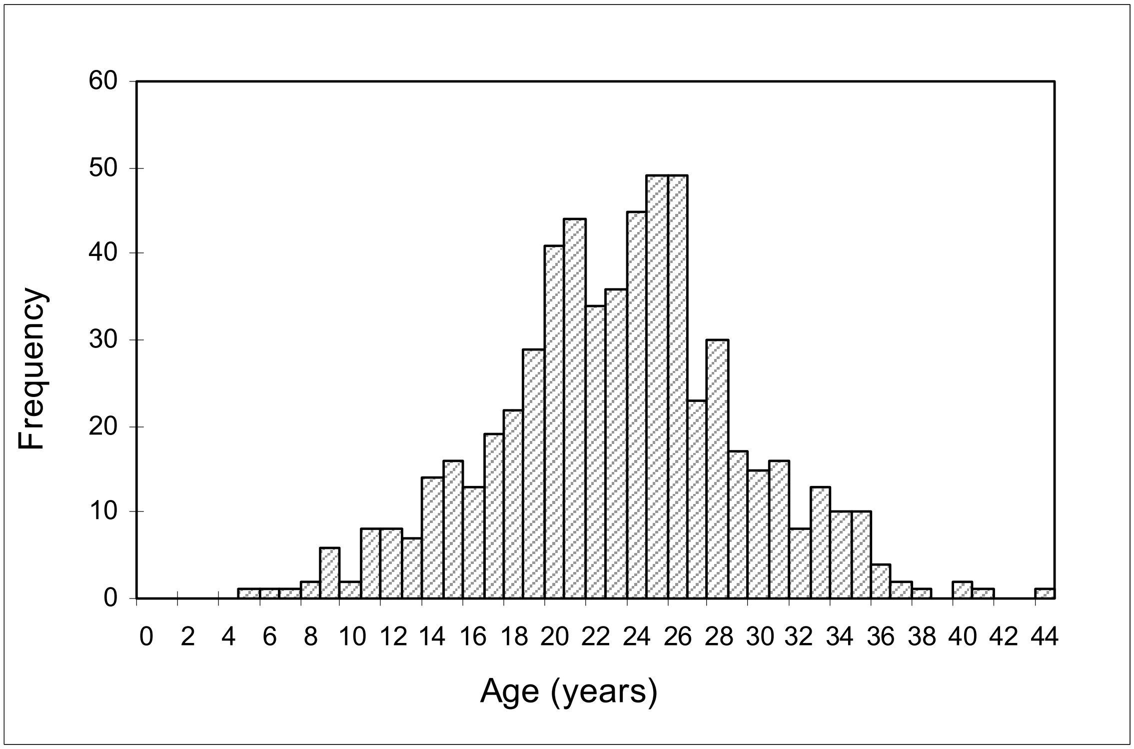

Figure B-3.4 Frequency distribution for time to fourth leak from NHPP simulations.

Figure B-3.5 Frequency distribution for time to fifth leak from NHPP simulations.

APPENDIX C-3

Discussion on nominal and real interest rates

Interest Rate

The fee charged by the lender to the borrower is known as *interest*. It is generally expressed as annual percentage of the *principal amount*. The principal amount is the amount borrowed. For instance, if a person A borrows a sum of $ 100 from person B at an annual interest rate of 10%, then the principal amount is $ 100 and at the end of one year period, person A needs to pay $ 110 to person B to clear his debts. This method of calculation of interest is also known as *simple interest*. In simple interest calculation, the interest is calculated only on the principal, hence if the money is borrowed for 2 years, the amount that the person A needs to pay in order to clear all the debts will be $ 120. No interest is charged on the amount accrued due to interest at the end of the first year. The relationship between the simple interest and the principal amount is given by,

$$I = \frac{prt}{100} \tag{C-1}$$

Where,

I is the interest in dollars

p is the principal amount in dollars

r is the rate of interest in annual percent

t is the time in years

Another method of calculating interest is the *compound interest*. In this method additional interest is charged on the amount accrued due to interest at the end of every year. The total amount payable by person A at compound interest is given by

$$A = p\left(1+\frac{r}{100}\right)^{n} \qquad \text{(C-2)}$$

Where

A is the total amount to be paid by person A at the end of n years to clear all debts, in dollars

p is the principal amount in dollars

r is the rate of compound interest

Hence, if a person A borrows $ 100 from person B at a rate of 10% compound interest, then the amount that the person A needs to pay at the end of one year in order to clear all his debts will be

From Eqn (C-2)

$$A = 100\left(1+\frac{10}{100}\right)^{1} = 110$$

Which is same as the amount to be paid by person A, had the money was borrowed on simple interest. At the end of two year period, the amount to be paid by person A, will be

From Eqn (C-2)

$$A = 100\left(1+\frac{10}{100}\right)^{2} = 121$$

This is more than the amount that the person A would have paid, had he borrowed the money on simple interest. The difference of $ 1 is due to added interest that is calculated on the interest accrued at the end of the first year (i.e. $ 10).

Importantly, the rate of interest r does not account for *inflation*. Inflation is the measure of increase in price of the goods or decrease in purchasing power of the currency with time, and is expressed as annual percentage. Let us assume that the person A borrows \$ 100 from person B for a period of one year at 10% interest rate. For simplicity, let us assume a one year period as it does not affect the method of calculation of interest (simple or compound). Hence, at the end of one year period the person A returns \$ 110 to person B to clear all his debts.

Apparently, the amount that the person B earned from the deal is \$ 10 at the end of one year, although during this 1 year period the prices of the good might have increased by some percentage say 4% (assumed). Hence, the goods that were available at a price of \$ 100 at the time the money was lend are costing \$ 104 at the time the money is returned, hence the net gain to person B at the end of the deal should be \$ 6 (= \$10 - \$ 4 or = interest – inflation). Thus, the actual earning of person B from the deal is at 6% interest, if the inflation is accounted. By this conclusion, we can define *nominal* and *real* interest rate. The nominal interest rate is the rate stated on bond, it does not account for the inflation. The real interest rate is defined as the current interest rate minus the current inflation rate. The nominal interest rate can be expressed in terms of the real interest rate and the inflation, by *Fisher* equation, hence mathematically,

$$(1+r_n) = (1+r_r)(1+i_n) \qquad \text{(C-3)}$$

Where

r_n is the nominal rate of interest

r_r is the real rate of interest

i_n is the rate of inflation

By expanding Eqn (C-3) we get,

$1 + r_n = 1 + r_r + i_n + r_r i_n$

Or

$$r_n = r_r + i_n + r_r i_n \qquad \text{(C-4)}$$

Since $r_r + i_n > r_r i_n$, we can neglect $r_r i_n$,

Hence, Eqn (C-4) can be approximated by

$$r_n = r_r + i_n \qquad \text{(C-5)}$$

The inflation rate varies depending upon the Consumer Price Index (CPI) and Producer Price Index (PPI), these indices are generally calculated on a monthly basis. The averaged inflation rate for the year 2005 is 3.39 %

http://inflationdata.com/Inflation/Inflation_Rate/HistoricalInflation.aspx

The current discount rate or the nominal rate is 6 %, based on Federal Reserve Bank of San Francisco http://www.frbsf.org/banking/data/discount/index.html

Hence, using Eqn (C-5), the real rate will be

$$6 = r_r + 3.39$$

Or

$r_r = 2.61\ \%$

Since, the cost of repair and cost of re-plumbing is assumed constant with time, real interest rate should be used instead of the nominal rate.

CHAPTER-4

PINHOLE LEAKS- MECHANISTIC MODELLING

Corrosion Thermodynamics

Corrosion is the electrochemical degradation of a metal when exposed to the environment. The phenomenon leading to corrosion is usually described using the laws of thermodynamics and electrochemistry. The objective of most of the studies is to understand the kinetics of the corrosion. Even during studying the kinetics, the rate of change must obey the stoichiometric relationship. Much of the following description is based on Tretheway and Chamberlain (1995). Most of the metals exist in impure (ore) state in nature. Thermodynamically the natural state of any metal or element corresponds to its lowest energy state. The process of extraction and refining of metals require a set of processes where substantial energy is consumed. The energy consumed may vary in magnitude and form depending on the metal and the extraction process itself.

This energy may be supplied to the process in the form of heat energy for blast furnaces, electrical energy for electrochemical separation or any other form of energy such as nuclear energy. A major part of the energy consumed in the purification process is stored in the metals in the form of free energy. Hence the pure state of a metal corresponds to higher energy state, and according to the laws of thermodynamics there exists an inherent tendency for substances at higher energy state to transform to their lower energy states.

Thus pure metals are at higher energy states and are less stable, they are prone to transformations to products that are at lower energy states and hence more stable. This tendency of the metals is the driving force behind the corrosion phenomenon. The energy state of the corrosion product is generally similar to the energy state of the metal ore, in some cases even comparable. Figure 1, shows the relative difference in free energies of a metal and its lower energy states on an arbitrary scale.

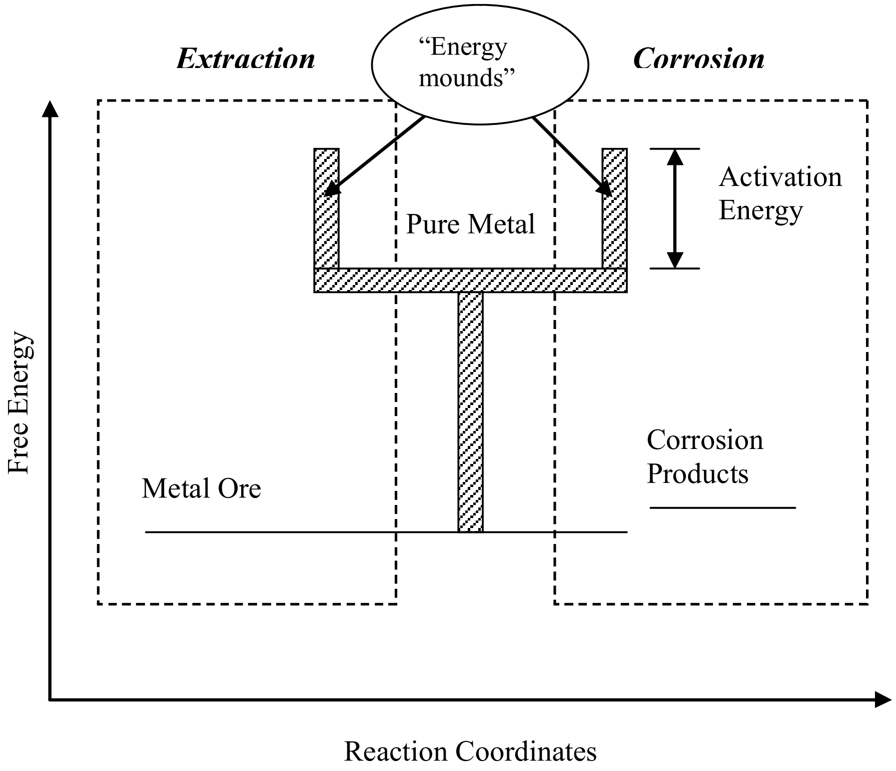

Figure 1 Schematic diagram showing Energy profile of metal and its corrosion products

The above definition of corrosion may altogether question the stability and hence the existence of pure metals but in reality metals exists in pure form. The existence of metals in pure state can be supported by the fact that there exists an energy barrier between any of the three states (i.e. the metal ore, pure metal and the corrosion products).

Figure 1, shows the energy barrier in form of “energy mound”, which helps the metals to stay in the pure states even though there is a strong tendency to corrode. Thus, for a metal in pure state the energy barrier is the minimum activation energy that is needed to trigger a reaction, which can take it to a lower energy state. According to the laws of thermodynamics, for the reaction to occur spontaneously, the change in free energy for the reaction $(\Delta G)_{reaction}$ should be negative. The change in free energy for a reaction is defined as the difference between the free energies of the products and reactants. Mathematically, it can be written as

$$\Delta G_{reaction} = \Delta G_{products} - \Delta G_{reac\tan ts} \tag{1}$$

Figure 1, shows a negative free energy change for the corrosion process, hence corrosion is a spontaneous process. Most of the metals exist in thermodynamically stable states, hence are already corroded, this can be explained by the presence of a thin oxide film on the surface of the metals, the presence of this film offers resistance to corrosion by protecting the metal from its environment. The film is known as passivating film and the phenomenon is known as passivation.

However, if the surface of metal is scratched with a sharp edged object, the film will get damaged and the surface of the metal will be exposed to the environment. Upon exposure to environment the damaged film can reinstate itself and hinder corrosion or it may get destroyed and corrosion may propagate, the behavior of the passivating films in metals is extremely complex and is very often dependent on the environmental conditions.

Corrosion and Electrochemistry

From electrochemical perspective, corrosion may be defined as a phenomenon where the metal loses electrons (oxidized) to its environment. For conservation of charge, the environment should accept the same number of electrons (reduced). The corrosion reactions are characterized by the presence of two oppositely charged electrodes, the oxidation takes place at anode while the reduction takes place at cathode. At anode the corroding metal loses electron and hence moves to higher oxidation states, thermodynamically these oxidation states should correspond to lower energy. It implies a direct correlation between the thermodynamics and the electrochemical reaction involved in the corrosion phenomenon. The electrochemical behavior of the corrosion reactions may be best described by using the electrochemical series. The concepts to develop and arrive at electrochemical series are presented below.

Consider a rod of metal *A* dipped into an aqueous alkaline solution, since the metal has a tendency to corrode, it will tend to lose electrons and move to higher oxidation state, mathematically the reaction may be expressed as,

$$A \longrightarrow A^{z+} + ze^{-}$$

Where

z is the number of electrons involved in the reaction (also equal to the change in oxidation state or is the number of electrons given up by the atom)

The metal ions tend to enter the electrolyte leaving behind a negatively charged metal surface, thus by bringing the electrode to a negative potential. A setup of electrode and the electrolyte put together is often named as a half cell and the reaction at the electrode is referred as the half cell reaction. In order to overcome the difficulties associated with the measurement of absolute value of the potential, hydrogen electrode is universally accepted as a reference electrode. The electrode potential for hydrogen is arbitrarily accepted as zero at 298 K (25^{o}C) and 1 atmospheric pressure. Hence the electrode potentials for all the electrodes are expressed either above (positive) or below (negative) of the hydrogen electrode under standard conditions. These are also known as standard electrode potentials. As a conventional practice, the electrode potentials may either be expressed for oxidation or reduction reactions. For example,

$$A \longrightarrow A^{z+} + ze^{-} \qquad E^{0} = +B \text{ Volts.}$$

The above equation shows oxidation of metal *A*, hence the electrode potential when measured under standard condition with reference to hydrogen electrode, will be known as *Standard Oxidation Potential*. If the same equation is expressed as a reduction equation, then the electrode potential when measured under standard condition with reference to the hydrogen electrode is known as *Standard Reduction Potential*. The corresponding reduction equation may be expressed as

$$A^{z+} + ze^{-} \longrightarrow A \qquad E^{0} = -B \text{ volts.}$$

Both the conventions are equally acceptable, however the present work will follow the Standard Reduction Potentials. The Standard Reduction Potentials are standard values, which are constant for a metal under standard conditions; these values may be tabulated in a descending order to obtain a series. The series is known as the *electrochemical series* and is considered as a benchmark for all the corrosion reactions. The electrochemical series is presented below in Table 1.

Table 1 Electrochemical series Standard Reduction Potential
(*Source: http://en.wikipedia.org/wiki/Standard_electrode_potential_%28data_page%29*).

Electrode reaction	$E^0(Volts)$
$Au^+ + e^- = Au$	+1.83
$Hg^{2+} + 2e^- = Hg$	+0.85
$Ag^+ + e^- = Ag$	+0.80
$Cu^+ + e^- = Cu_s$	+0.52
$Cu^{2+} + 2e^- = Cu$	+0.34
$Cu^{2+} + e^- = Cu^+$	+0.16
$2H^+ + 2e^- = H_2$	0.00
$Pb^{2+} + 2e^- = Pb$	-0.13
$Sn^{2+} + 2e^- = Sn$	-0.13
$Ni^{2+} + 2e^- = Ni$	-0.26
$Cd^{2+} + 2e^- = Cd$	-0.40
$Fe^{2+} + 2e^- = Fe$	-0.44
$Cr^{3+} + 3e^- = Cr$	-0.74
$Zn^{2+} + 2e^- = Zn$	-0.76
$Al^{3+} + 3e^- = Al$	-1.68
$Mg^{2+} + 2e^- = Mg$	-2.38
$Na^+ + e^- = Na$	-2.71
$Ca^{2+} + 2e^- = Ca$	-2.76
$K^+ + e^- = K$	-2.93

The table is an abbreviated version of the table available on http://en.wikipedia.org. The information related to copyright permission is available on http://en.wikipedia.org/wiki/Wikipedia:Copyrights.

An electrochemical cell necessarily consists of four elements, an anode, a cathode, an electrolyte and a physical connection for passage of current. The Standard Reduction Potential or the relative placement of a metal in the electrochemical series determines whether it will act as an anode or as a cathode for that particular pair of electrodes. For example, let us consider iron and zinc, since zinc is more noble to copper it shall act as anode, hence in a cell consisting of zinc and iron electrodes, corrosion will occur at zinc while deposition will occur at iron. This is the reason why zinc is used for galvanizing iron.

The total electrochemical cell potential is defined as the difference of cathodic and anodic reduction potential, we may express cell potential as

$$E_{cell}{}^{0} = E_{cathode}{}^{0} - E_{anode}{}^{0} \tag{2}$$

Faradays related the change in free energy with the electrochemical cell potential by following expression

$$\Delta G^{0} = -(zF)E_{cell}{}^{0} \tag{3}$$

Where

ΔG^{0} is the change is free energy under standard conditions.

z is the number of electrons involved in the reaction (also equal to the change in oxidation state)

$E_{cell}{}^{0}$ is the standard cell potential.

For reaction to be spontaneous the net change in free energy should be negative, it follows from Eqn(3)

$$\Delta G^{0} < 0$$

Hence,

$$-(zF)E_{cell}{}^{0} < 0$$

Or $$E_{cell}{}^{0} > 0 \tag{4}$$

Or $$E_{cathode}{}^{0} - E_{anode}{}^{0} > 0 \tag{5}$$

The above inequality states that the electrode with lesser reduction potential in the electrochemical series will act as anode for the reaction to be spontaneous. Since, the potential of the half cell depends upon number of physical parameters like temperature, pressure, concentration of electrolyte etc, and most of the reactions encountered in real life do not take place under standard conditions, it is important to evaluate and arrive at an expression that can take into account for all these parameters. Consider a reaction under non-standard conditions

$$X^{z+} + Y \longrightarrow X + Y^{z+}$$

Using thermodynamics, the free energy change under non standard conditions, ΔG may be expressed as

$$\Delta G = \Delta G^{0} + RT\ln\frac{[X][Y^{z+}]}{[Y][X^{z+}]} \tag{6}$$

Where

ΔG is the change in free energy under non standard conditions

ΔG^{0} is the change in free energy under standard conditions

R is the universal gas constant.

T is the absolute temperature in Kelvin

$[X]$ & $[Y]$ are the concentrations of solid X and Y respectively. (Generally taken as unity, because it is assumed that the reaction is not limited by the concentration of these species)

$[X^{z+}]$ is the concentration of ion from metal X under non-equilibrium conditions.

$[Y^{z+}]$ is the concentration of ion from metal Y under non-equilibrium conditions.

It follows from Faradays law stated above in Eqn(3),

$$\Delta G \ = -(zF)E_{cell}$$

and

$$\Delta G^0 = -(zF)E_{cell}{}^0$$

Substituting the values for change in free energy in Eqn(6), we get

$$-zFE = -zFE^0 + RT \ln \frac{[X^{z+}]}{[Y^{z+}]}$$

Or

$$E = E^0 - \frac{RT}{zF} \ln \frac{[X^{z+}]}{[Y^{z+}]} \qquad (7)$$

Eqn(7) is called the *Nerst equation* and has great theoretical and practical significance.

Corrosion Kinetics

Electrochemical reactions involve flow of electron from a negatively charged site (anode) to a more positively charged site (cathode). As the current flow in the external circuit, the metal ions flow from anode to cathode in the electrolyte. The flow of electrons can be measured as electrical current, where 1 ampere is equal to 1 coulomb charge (6.2 x 10^{18} electrons) per second. Faradays' law relates the corrosion current and the mass reacted, by following expression

$$m = \frac{Ita}{zF} \tag{8}$$

Where

m is the mass transferred from anode in *g*

I is the current measured in *coulombs per second*

a is the molar mass of the metal in *g per mol*

z is the number of electrons participating in the reaction (also equal to the change in oxidation state)

F is the Faraday's constant in *coulombs per mol-electrons*

t is the time in *seconds*

Defining rate of reaction as r, then we may write

$$r = \frac{m}{tA} \tag{9}$$

Where

A is the surface area

Substituting the value of m from Eqn(9), we have

$$r = \frac{m}{It} = \frac{Ia}{AzF}$$

Defining $\frac{I}{A} = i$ (current density) and substituting in the above expression we get,

$$r = \frac{ia}{zF} \tag{10}$$

Since a, z and F are constants for a metal in a particular cell reaction, it follows that

$$r \propto i$$

The dimensional units of r in Eqn(10) are $\left[ML^{-2}T^{-1}\right]$. The units may be converted to units of penetration $\left[LT^{-1}\right]$. The conversion of the units to r to mili-inches per year (mpy) reduces the Eqn(10) to

$$r = 0.129\frac{ai}{zD} \tag{11}$$

Where,

r is the rate of corrosion measured in (mpy)

a is the molar mass of the metal $g\ per\ mol$

D is the density of the metal gm/cm^3

i is the corrosion current density $\mu A/cm^2$

z is the number of electrons participating in the reaction (also equal to the change in oxidation state)

Hence, the kinetics of the corrosion is solely dependent on the nature and variation of the corrosion current density. The corrosion current density is defined as the difference between the anodic and the cathodic current densities. Hence,

$$i_{meas} = i_a - i_c$$

Where

i_a is the anodic current density , and

i_c is the cathodic current density.

$i_{meas} = i$ is the corrosion current density that is equal to the difference in anodic and cathodic current densities.

At equilibrium the magnitude of the net corrosion current density becomes zero, although there exists a current that flows in both the direction but it cannot be measured. This is called the exchange current density and is denoted by i_0. Hence at equilibrium,

$$i_a = i_c = i_0$$

Due to surface defects, a metal can behave as its own anode and cathode when placed in an electrolyte. Thus a single piece of metal may have anodic and cathodic sites that are connected with the metal surface. When such a metal piece is dipped in an electrolyte it forms an electrochemical cell. The anodic sites on the surface of the metal tend to lose electron, as the current flows through the metal surface; there is a loss of positive metal ions at anode. Let us analyze the process in terms of the corrosion current density and the change in free energy.

Consider a metal *A* placed in some electrolyte, Figure 2 shows the energy profile, at the start of the reaction ΔG^* is the energy barrier for the metal to undergo corrosion. Please note that Figure 2 shows only the corrosion process from Figure 1, the other half that shows the metal extraction is not shown. Initially the difference in the energy states of the metal and the corrosion products is large. As the reaction proceeds the two states approach each other and hence ΔG^* increases, while ΔG decreases. Thermodynamically, the rate of the anodic (forward) reaction can be expressed in terms of the energy barrier ΔG^*.

$$r_a = \lambda \exp\left(-\frac{\Delta G^*}{RT}\right) \tag{12}$$

Where

ΔG^* is the activation free energy for the forward reaction.

λ is a proportionality constant

R is the universal gas constant

T is the absolute temperature in Kelvin

Analysis of Eqn(12) suggests that as ΔG^* increases the rate of the anodic reaction decreases. Since the current density is directly proportional to the rate of the reaction, it would imply that the anodic current density decreases as the reaction proceeds.

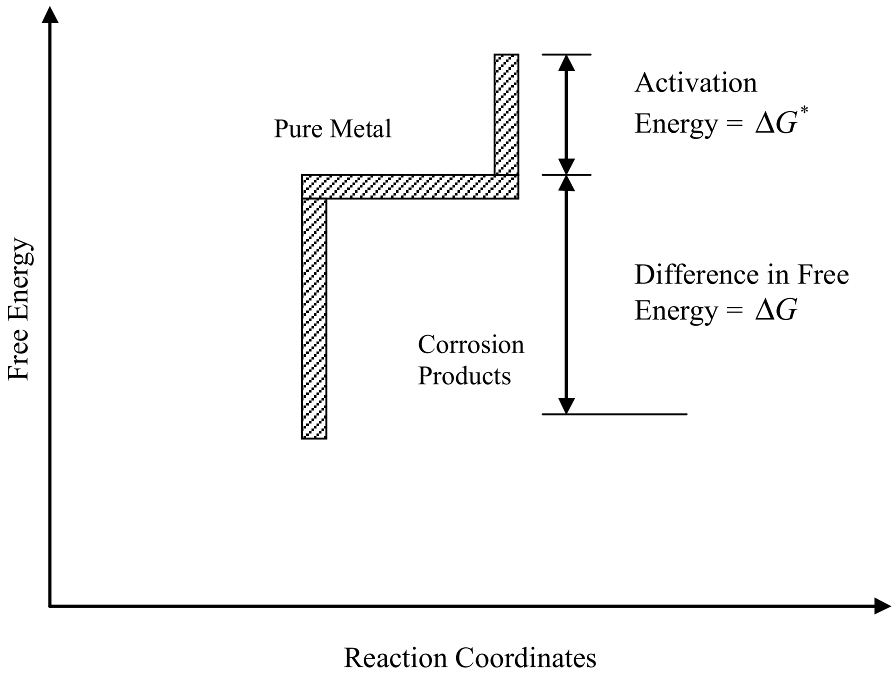

Figure 2 Schematic diagram showing activation energy of corrosion mechanism

Similarly the activation free energy for the backward reaction in the beginning of the process is $(\Delta G^* + \Delta G)$, as the reaction proceeds ΔG decreases and ΔG^* increases, and as both the energy states of the metal becomes closer to each other the magnitude of $(\Delta G^* + \Delta G)$ decreases. Thermodynamically, the rate of cathodic reaction may be written as

$$r_c = \lambda \exp\left(- \frac{(\Delta G^* + \Delta G)}{RT} \right) \qquad (13)$$

Where

$(\Delta G^* + \Delta G)$ is the activation free energy for the reverse reaction.

Since the rate of reaction is related to the current density, by analogy the rate of the anodic and cathodic reactions should be related to anodic and cathodic current densities. It is evident from Eqn(13) that the magnitude of $(\Delta G^* + \Delta G)$ decreases as the reaction proceeds and hence the magnitude of cathodic current density increases. Hence, during the initial stages of the reaction $i_a > i_c$, as the reaction proceeds the magnitude of i_a decreases and the magnitude of i_c increases, hence the corrosion current i decreases with the progress of the reaction.

Eventually a condition of thermodynamic equilibrium is achieved, under equilibrium conditions, the activation free energies for forward and reverse reactions are equal; hence the anodic and cathodic current densities will be equal. The magnitude of the anodic and cathodic densities under such condition is equal to the exchange current density i_0. The values of i_0 are determined experimentally.

From the above analysis it is clear that the pure metal and the corrosion products themselves do not remain in the same energy state, as the reaction proceeds the pure metal moves into lower energy state while the corrosion products moves into higher energy state. Hence the equilibrium between the metal and its corrosion product is disturbed, due to which the electrode potential differs from the equilibrium potential, this difference is known as *over potential* or the *polarization* (η). Polarization is a useful parameter in determining the kinetics of the corrosion phenomenon. We further define α as the polarization proportionality, the parameter α ranges between 0 and 1, it defines the extent of polarization of anode and cathode. If the total polarization is η, then we can define $(\alpha\eta)$ as the anodic polarization and $(1-\alpha)\eta$ as the cathodic polarization. At equilibrium the rate of the reaction and hence the exchange current density may be expressed as

$$i_0 = \lambda_0 \exp\left(-\frac{\Delta G^*}{RT}\right) \tag{14}$$

Where

λ_0 is a constant of proportionality and undetermined.

We can convert the anodic and cathodic overpotential into activation free energy using Faradays law and hence

New activation energy for anodic reaction = $\left(\Delta G^* - \alpha\eta zF\right)$

New activation energy for cathodic reaction = $\left(\Delta G^* + (1-\alpha)\eta zF\right)$

So, the anodic current density may be written as,

$$i_a = \lambda_0 \exp\left(-\frac{\left(\Delta G^* - \alpha\eta zF\right)}{RT}\right) = \lambda_0 \exp\left(-\frac{\Delta G^*}{RT}\right)\exp\left(\frac{\alpha\eta zF}{RT}\right) \tag{15}$$

Substituting i_0 from Eqn(14) in Eqn(15), we get

$$i_a = i_0 \exp\left(\frac{\alpha\eta zF}{RT}\right) \tag{16}$$

Similarly the cathodic current density may be written as,

$$i_c = \lambda_0 \exp\left(-\frac{\left(\Delta G^* + (1-\alpha)\eta zF\right)}{RT}\right) = \lambda_0 \exp\left(-\frac{\Delta G^*}{RT}\right)\exp\left(\frac{-(1-\alpha)\eta zF}{RT}\right) \tag{17}$$

Substituting i_0 from Eqn (14) in Eqn (17), we get

$$i_c = i_0 \exp\left(-\frac{(1-\alpha)\eta zF}{RT}\right) \tag{18}$$

So for a non-equilibrium condition

$$i_{meas} = i_a - i_c$$

Substituting i_a and i_c from Eqn (16) and Eqn (18) we get,

$$i_{meas} = i_0\left[\exp\left(\frac{\alpha\eta zF}{RT}\right) - \exp\left(-\frac{(1-\alpha)\eta zF}{RT}\right)\right] \tag{19}$$

Eqn (19) is known as *Butler-Volmer Equation*. This equation can be used to determine the corrosion current and hence the rate of corrosion. The equation has two unknown parameters η and i_0 that needs to be determined experimentally. Both these parameters are specific function of particular redox reaction and are dependent on many physical parameters such as concentration of electrolyte, temperature, ratio of the oxidized and reduced species which makes it impossible to determine them theoretically. However, if these two parameters are available then Eqn (16) may be considered as a strong approach for calculating the corrosion rates.

Corrosion kinetics: Linear Polarization Approach

In order to arrive at an expression that is useful from analytical perspective, a simplified approach is presented. The approach is based on the correlation between polarization and the corrosion current density. In the previous section it was demonstrated that the activation free energies change with the progress of the corrosion reaction. The anodic and the cathodic current densities also change as the activation free energy changes. Since the rate of anodic and cathodic current densities are related to the anodic and cathodic polarization (refer Eqn (15 & Eqn (17)), the polarization should also vary with the corrosion current density. A plot of polarization vs the current density, is known as polarization curve. Figure, 3 shows a typical polarization curve. For small magnitudes current density, the polarization curve is almost linear (shown in dotted rectangle).

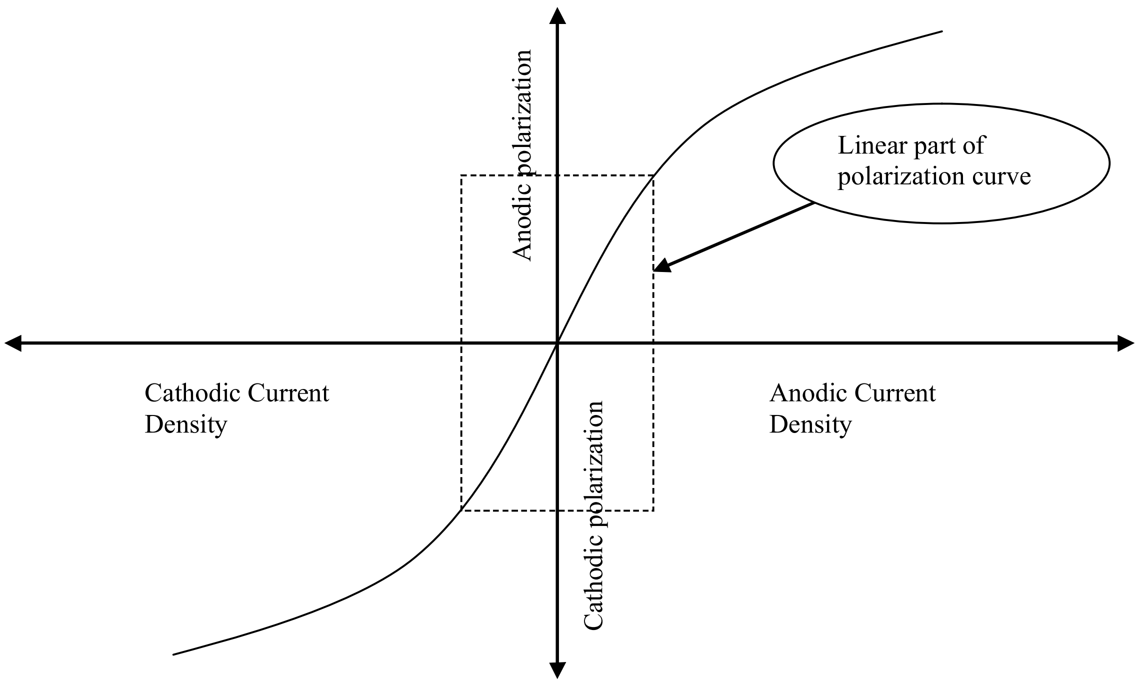

Figure 3 Typical polarization curve, showing linear zone between polarization and current density

In order to arrive at a simplified expression for calculating the current density, it is assumed that the corrosion takes place in the linear part of the polarization curve. Hence, a new parameter polarization resistance R_p is defined as the slope of the polarization curve in this region. We may write,

$$R_p = \frac{\Delta\eta}{\Delta i} = \frac{d\eta}{di} \tag{20}$$

The quantity $\frac{d\eta}{di}$ can be obtained from Butler-Volmer equation (Eqn (19)).

We have,

$$i_{meas} = i_0 \left[\exp\left(\frac{\alpha \eta z F}{RT} \right) - \exp\left(- \frac{(1-\alpha) \eta z F}{RT} \right) \right] \text{ (Butler-Volmer Equation)}$$

Differentiating Eqn (19) with respect to η, we get

$$\frac{di_{meas}}{d\eta} = \left[\left(\frac{\alpha z F}{RT} \right) i_0 \exp\left(\frac{\alpha \eta z F}{RT} \right) \right] - \left[\left(\frac{-(1-\alpha) z F}{RT} \right) i_0 \exp\left(\frac{-(1-\alpha) \eta z F}{RT} \right) \right] \tag{21}$$

From Eqn (16) and Eqn (18), we have,

$$i_a = i_0 \exp\left(\frac{\alpha \eta z F}{RT} \right)$$

$$i_c = i_0 \exp\left(- \frac{(1-\alpha) \eta z F}{RT} \right)$$

By reverse substitution of i_a and i_c, in Eqn (21) we get

$$\frac{di_{meas}}{d\eta} = \left[\left(\frac{\alpha z F}{RT} \right) i_a \right] - \left[\left(\frac{-(1-\alpha) z F}{RT} \right) i_c \right] \tag{22}$$

Let us define two more parameters, β_a and β_c as the anodic and cathodic Tafel coefficients. We define,

$$\beta_a = \frac{2.303 RT}{\alpha z F} \tag{23}$$

$$\beta_c = \frac{2.303RT}{(1-\alpha)zF} \tag{24}$$

Substituting the values of R_p, β_a and β_c in Eqn (22) we get,

$$\frac{1}{R_p} = \frac{2.303 i_a}{\beta_a} + \frac{2.303 i_c}{\beta_c} \tag{25}$$

For linear behavior of Tafel equation at both anode and cathode, the anodic and the cathodic current densities should be approximately equal to the corrosion current density (independently).

Hence,

$$i_a \sim i_{meas} \tag{26}$$

And

$$i_c \sim i_{meas} \tag{27}$$

Substituting i_{meas} from Eqn (26) & Eqn (27) in Eqn (25) we get,

$$i_{corr} = i_{meas} = \frac{1}{2.303 R_p \left(\frac{1}{\beta_a} + \frac{1}{\beta_c} \right)} = \frac{\beta_a \beta_c}{2.303 R_p (\beta_a + \beta_c)} \tag{28}$$

Or

$$i_{corr} = \frac{K}{R_p}\text{, where } K = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)}$$

Eqn (28) is known as the *Linear Polarization equation*, notice that the Tafel constants β_a and β_c are fixed parameters for a reaction at a particular temperature, hence, the corrosion current becomes the function of one variable R_p.

Examples

Example1

A single family residential home is located in an area that is prone to pinhole leaks. Knowing that pinhole leak is inevitable, the homeowner wants to know when he should expect the first leak in his house. The homeowner knows that the pipes used in his plumbing system are $(1/2)''$ & $(3/4)''$ nominal diameter, M-type copper.

With this information he approaches a consultant, who is doing research on the pinhole leaks in single family homes; the consultant has some historical data collected from a nationwide survey. However, due to busy schedule, the consultant could not offer his services to the homeowner, but as a gesture of goodwill he handed over some valuable information that can be used to calculate the time to first leak. The information given by the consultant is presented in the Table 2.

The homeowner contacts a graduate student, for getting the time to first leak calculated, demonstrate how the student would do his calculations? Assume the trend of pinhole leaks is same nationwide and is truly reflected in the data provided by the consultant. List all assumptions.

Table 2 Data from consultant's research

Molar mass of copper	63.546 gm/mol
Temperature of cold water	285 K
Temperature of hot water (in hot water pipes and hot water recirculation system)	403 K
Density of copper	8.94 gm/cm^3
Polarization proportionality (α)	0.3
Faraday's constant	96485 Coulomb/ mol
Number of electron exchanged during reaction (also equal	2
The modal value of polarization resistance R_p for a single	0.12 Ωm^2
Thickness of M- type $(1/2)^{"}$ nominal diameter pipe	0.028 inches
Thickness of M- type $(3/4)^{"}$ nominal diameter pipe	0.032 inches
Universal gas constant	8.314 J/mol-K

<u>Solution:</u> Since the data provided by the consultant is representative of the single family homes on a nationwide scale, it is assumed that the polarization resistance for the home will be same as the modal value of polarization resistance obtained from the survey. A stepwise solution to the problem is provided below:

Step 1: Calculating the Tafel coefficients from given data

The anodic and the cathodic Tafel coefficients β_a and β_c are given by,

$$\beta_a = \frac{2.303(RT)}{\alpha zF} \tag{E1-1}$$

And

$$\beta_c = \frac{2.303(RT)}{(1-\alpha)zF} \tag{E1-2}$$

Where,

R = universal gas constant in *J/mol-k*

α = polarization proportionality

T = absolute temperature in *Kelvin*

z = number of electron participation or the change in oxidation state.

F = Faradays' constant in *Coulomb/ mol*

From the consultant's data we have,

R = 8.314 *J/mol-k*

α = 0.3

T = 285 K (cold water)

T = 403 K (hot water)

z = 2

F = 96485 *Coulomb/ mol*

For cold water pipes

Substituting the values in Eqn (E1-1) & Eqn (E1-2), we get

$$\beta_a = \frac{2.303(8.314)(285)}{(0.3)(2)(96485)} = 0.094262$$

And

$$\beta_c = \frac{2.303(8.314)(285)}{(1-0.3)(2)(96485)} = 0.040398$$

For hot water pipes

Substituting the values in Eqn (E1-1) & Eqn (E1-2), we get

$$\beta_a = \frac{2.303(8.314)(403)}{(0.3)(2)(96485)} = 0.13329$$

And

$$\beta_c = \frac{2.303(8.314)(403)}{(1-0.3)(2)(96485)} = 0.057124$$

Step 2: Calculating the corrosion current density using Linear polarization equation

The linear polarization equation relates the corrosion current density and the polarization resistance by following expression:

$$i = \frac{\beta_a \beta_c}{(2.303)(R_p)(\beta_a + \beta_c)} \tag{E1-3}$$

Where,

i is the corrosion current density in A/m^2

β_a is the anodic Tafel coefficient

β_c is the cathodic Tafel coefficient

R_p is the polarization resistance in $\Omega - m^2$

For cold water pipes

We have,

$\beta_a = 0.094262$ (from Step-1)

$\beta_c = 0.040398$ (from Step-1) and

$R_p = 0.12\Omega m^2$ (from consultants' data)

Substituting β_a, β_c and R_p in Eqn (E1-3), we get

$$i = \frac{(0.094262)(0.040398)}{2.303(0.12)((0.094262)+(0.040398))} = 0.10232 \ A/m^2$$

For hot water pipes

We have,

$\beta_a = 0.13329$ (from Step-1)

$\beta_c = 0.057124$ (from Step-1) and

$R_p = 0.12\Omega m^2$ (from consultants' data)

Substituting β_a, β_c and R_p in Eqn (E1-3), we get

$$i = \frac{(0.13329)(0.057124)}{2.303(0.12)((0.13329)+(0.057124))} = 0.144692 \ \ A/m^2$$

Step 3: <u>Calculating the corrosion rate using Faraday's Law</u>

Faraday's law relates the current density and the corrosion rate by the following expression:

$$r = 0.129(\frac{ai}{zD}) \qquad \text{(E1-4)}$$

Where,

r = corrosion rate in *mpy*

a = molar mass of copper in *gm/mol*

D = density of copper in *gm/cm*^{3}

z = number of electrons participating or the change in oxidation state.

i = corrosion current density in *micro-amp/ sq-cm*

From consultants' data we have,

$a = 63.546 g/mol$
$z = 2$
$D = 8.94 gm/cm^3$

<u>For cold water pipes</u>

$i = 0.10232 \ \ A/m^2$ (from Step-2)

For hot water pipes

$i = 0.144692 \ A/m^2$ (from Step-2)

Converting i in $\mu A/cm^2$

For cold water pipes

$$i = 0.10232 \ A/m^2 = 0.10232\left(\frac{10^6}{10^4}\right) \ \mu A/cm^2 = 10.232 \ \mu A/cm^2$$

For hot water pipes

$$i = 0.144692 \ A/m^2 = 0.144692\left(\frac{10^6}{10^4}\right) \ \mu A/cm^2 = 14.469 \ \mu A/cm^2$$

Substituting a, i, D and z in Eqn (E1-4), we get

For cold water pipes

$$r = (0.129)\frac{(63.546)(10.232)}{(2)(8.94)} = 4.691 \ mpy$$

For hot water pipes

$$r = (0.129)\frac{(63.546)(14.469)}{(2)(8.94)} = 6.6336 \ mpy$$

Step 4: Calculating the time to first leak from the corrosion rate

Assuming the rate of corrosion is same for both the pipe sizes. The rate may be expressed as the thickness of incision through the pipe wall, divided by the time. If t is the pipe wall thickness in inches and T is the time to first leak in years, and r be the rate of corrosion in mili-inches per year (mpy), then

$$r = \frac{1000t}{T} \tag{E1-5}$$

Solving for T, we have

$$T = \frac{1000t}{r} \tag{E1-6}$$

The rate in Eqn (E1-6) is equal to the one calculated in Step-3, hence the time to first leak will depend on the thickness of the pipe. For thick walled pipes, the time to first leak will be more as compared to thin walled pipes.

We define

t_1 as the thickness (in inches) of $(1/2)^{"}$ nominal diameter

t_2 as the thickness of (in inches) $(3/4)^{"}$ nominal diameter

T_1 as the time to first leak (in years) for $(1/2)^{"}$ nominal diameter

T_2 as the time to first leak (in years) for $(3/4)^{"}$ nominal diameter

Then from Eqn (E1-6) we have,

$$T_1 = \frac{1000t_1}{r} \tag{E1-7}$$

And

$$T_2 = \frac{1000t_2}{r} \tag{E1-8}$$

We have

t_1 = 0.028 inches (from consultant's data)

t_2 = 0.032 inches (from consultant's data)

For cold water pipes

$r = 4.691 \ \ mpy$

Substituting t_1 and r in Eqn (E1-7) we have,

$$T_1 = \frac{1000(0.028)}{(4.691)} = 5.968 \ \ years.$$

Similarly, substituting t_2 and r in Eqn (E1-8) we have,

$$T_2 = \frac{1000(0.032)}{(4.691)} = 6.821 \ \ years.$$

For hot water pipes

$r = 6.6336 \ \ mpy$

Substituting t_1 and r in Eqn (E1-7) we have,

$$T_1 = \frac{1000(0.028)}{(6.6336)} = 4.220 \ \ years.$$

Similarly, substituting t_2 and r in Eqn (E1-8) we have,

$$T_2 = \frac{1000(0.032)}{(6.6336)} = 4.824 \ \ years.$$

Hence, in cold water pipes, the first leak in $(1/2)''$ pipe will occur after 5.97 years and the first leak in $(3/4)''$ inch pipe will occur after 6.82 years. For hot water pipes, the first leak in $(1/2)''$ pipe will occur after 4.22 years and the first leak in $(3/4)''$ inch pipe will occur after 4.824 years. The results from the above approach suggest that an increase in temperature increases the corrosion rate however this is highly subjective to water chemistry. As discussed previously in chapter 2, the effect of temperature can be deleterious specially if the water has low alkalinity and low DIC (dissolved inorganic carbon).

Example 2

You are a corrosion scientist and you live in a community that is developing very fast. Unfortunately, the community had several incidences of pinhole leaks in the recent past. A real estate builder, who has got major contracts for building new homes, is interested in knowing the time to first leak for M-type copper pipes, so that he may give an option of other plumbing materials to his new clients. He has set up a laboratory to run experiments and obtain information that may be utilized to calculate the time to first leak. The builder has accumulated some data which is shown in Table 3.

The builder approaches you with a set of parameters and requests your services as a consultant. He also requests you to show all the calculations and assumptions as a part of the consultancy report. Calculate the time to first leak for $(1/2)''$ and $(3/4)''$ nominal diameter pipes and show what calculations you shall be putting in your report?

Table 3 Corrosion data provided by the builder

Temperature of water	285 K
Polarization proportionality (α)	0.3
Faraday's constant	96485 Coulomb/ mol
Over- potential (η)	0.16 Volts
Exchange current density (i_0) for Cu electrode in 0.1 N HCL solution (*Fontana, 1986*)	0.2 $\mu A/cm^2$
Thickness of M- type $(1/2)''$ nominal diameter pipe	0.028 inches
Thickness of M- type $(3/4)''$ nominal diameter pipe	0.032 inches
Universal gas constant	8.314 J/mol-K
Molar mass of copper	63.546 gm/mol
Density of copper	8.94 gm/cm^3

Solution: Since the builder has provided the values for exchange current density (i_0) and the over- potential (η), we may use the Butler-Volmer equation for calculating the corrosion current density. Once the corrosion current density is obtained, Faradays' law can be used to get the corrosion rate. A step wise approach is presented below:

Step-1: Calculating corrosion current density from Butler-Volmer Equation

The Butler-Volmer equation may be written as

$$i_{meas} = i_0\left[\exp\left(\frac{\alpha\eta zF}{RT}\right) - \exp\left(\frac{-(1-\alpha)\eta zF}{RT}\right)\right] \tag{E2-1}$$

Where

i_{meas} is the corrosion current density

i_0 is the exchange current density (at equilibrium).

α is the polarization proportionality

z is the number of electron exchanged (also equal to change in oxidation state)

R is the universal gas constant

F is the Faraday's constant.

T is the temperature in Kelvin

Assumptions:

- Copper oxidizes only to +2 oxidation state by the following reaction:

  $Cu \longrightarrow Cu^{2+} + 2e^-$, the value of z may be taken as 2.

- The i_0 value is true representative value for the water supplied in the community; the value remains constant through out the distribution system and does not change with time.

From the information provided by the builder we have,

$i_0 = 0.2\ \mu A/cm^2$

$\eta = 0.16$ Volts

$\alpha = 0.3$

$R = 8.314$ J/mol-K

$F = 96485$ Coulomb/ mol

$T = 285$ K

z =2 (from our assumption)

Substituting in Eqn (E2-1) we get,

$$i_{meas} = (0.2)\left[\exp\left(\frac{(0.3)(0.16)(2)(96485)}{(8.314)(285)}\right) - \exp\left(\frac{-(1-0.3)(0.16)(2)(96485)}{(8.314)(285)}\right)\right]$$

$$i_{meas} = i(say) = 9.9707\ \mu A/cm^2$$

Step-2: Calculating corrosion rate using Faraday's Law

Faraday's law relates the current density and the corrosion rate by the following expression:

$$r = 0.129\left(\frac{ai}{zD}\right) \tag{E2-2}$$

Where,

r = corrosion rate in *mpy*

a = molar mass of copper in *gm/mol*

D = density of copper in gm/cm^3

z = number of electrons participating or the change in oxidation state.

i = corrosion current density in *micro-amp/ sq-cm*

From the builders' data we have,

$a = 63.546 g/mol$
$D = 8.94 gm/cm^3$

And

$i = 9.9707 \mu A/cm^2$ (from Step-1)

z =2 (from our assumption)

Substituting the values in Eqn (E2-2), we get,

$$r = (0.129)\frac{(63.546)(9.9707)}{(2)(8.94)} = 4.571 \ mpy$$

Step 3: <u>Calculating the time to first leak from the corrosion rate</u>

Assuming the rate of corrosion is same for both the pipe sizes. The rate may be expressed as the thickness of incision through the pipe wall, divided by the time. If t is the pipe wall thickness in inches and T is the time to first leak in years, and r be the rate of corrosion in mili-inches per year (mpy), then

$$r = \frac{1000t}{T} \qquad \text{(E2-3)}$$

Solving for T, we have

$$T = \frac{1000t}{r} \qquad \text{(E2-4)}$$

The rate in Eqn (E2-4) is equal to the one calculated in Step-2, hence the time to first leak will depend on the thickness of the pipe. For thick walled pipes, the time to first leak will be more as compared to thin walled pipes.

We define

t_1 as the thickness (in inches) of $(1/2)''$ nominal diameter

t_2 as the thickness of (in inches) $(3/4)''$ nominal diameter

T_1 as the time to first leak (in years) for $(1/2)''$ nominal diameter

T_2 as the time to first leak (in years) for $(3/4)''$ nominal diameter

Then from Eqn (E2-4) we have,

$$T_1 = \frac{1000t_1}{r} \tag{E2-5}$$

And

$$T_2 = \frac{1000t_2}{r} \tag{E2-6}$$

We have

$t_1 = 0.028$ inches (from consultant's data)

$t_2 = 0.032$ inches (from consultant's data)

$r = 4.571 \ mpy$ (from Step-2)

Substituting t_1 and r in Eqn (E2-5) we have,

$$T_1 = \frac{1000(0.028)}{(4.571)} = 6.125 \ \ years.$$

Similarly, substituting t_2 and r in Eqn (E2-6) we have,

$$T_2 = \frac{1000(0.032)}{(4.571)} = 7.00 \ \ years.$$

Hence, the first leak in $(1/2)^{"}$ pipe will occur after 6.125 years and the first leak in $(3/4)^{"}$ inch pipe will occur after 7.0 years.

Further discussion on linear polarization

The equation has been used by various scientists to evaluate corrosion rates of different metals. Zhang et al. (2002) used the linear polarization approach to study the instantaneous corrosion rates of naturally patinated copper during continuous rain using the electrochemical impedance spectroscopy. Abhijit and Pehkonen (2000) used the linear polarization approach to assess the performance of corrosion scales in corrosion inhibition in copper pipes in water distribution system. Hiromoto et al. (2000) used the approach in studying the effect of pH on the polarization behavior of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$, as amorphous alloy due to presence of chloride ion.

The strength of the polarization approach is that the corrosion rates can be obtained by knowing just a single parameter (R_p). Hence, if the distribution of R_p is known with age of the plumbing, the corrosion rates and time to failures can be obtained using Eqn (28) and Eqn (11). In all of the above cited works, the laboratory setups were used to establish the R_p values. Hence, the *linear polarization* approach though reduces the number of variables as compared to *Butler-Volmer* equation, but it needs some experimental support to establish the pattern of R_p with variation of age of the metal and water chemistry.

The following section demonstrates a possible method of analysis based on linear polarization method. The pitting phenomenon necessarily involves two steps, the pit *initiation* and the pit *propagation*. The initiation of the pit may be immediate upon exposure or may be delayed (Melchers, (2005)). Also, the rate of propagation of the pits vary, some of the pits propagate faster and cause early failure, some pits propagate at a slower rate and cause a relatively delayed failure, while some other pits stop propagating after certain time, the phenomenon is often known as *meta- stable* pitting (Melchers,(2005)). The *meta- stable* pits may reactivate after some time and propagate to cause failure. Thus the exact modeling of pit growth based on corrosion current is fairly complex and it requires experimental data under different hydraulic and water quality conditions. From modeling perspective, the variation of corrosion current with age of the plumbing is of interest. Considering the complexity in calculation of corrosion rates due to varied initiation and propagation, the corrosion current distribution based on only the first leak time is presented. The distribution is obtained using *the time to first failure distribution* from chapter-3.

If the time to first failure is known, then the corrosion rate equation can be used to obtain corrosion current using Eqn (11), for a given pipe thickness. Once the corrosion current is known, the polarization resistance (R_p) can be calculated in terms of corrosion current and the

Tafel slopes. Hence, if the pipe of thickness t_1 (inches) is considered that developed the first leak after T_j years of installation, then the rate of corrosion can be expressed as

$$r = \frac{1000t_1}{T_j} \text{ mili-inches per year} \tag{29}$$

From Eqn (11) we have,

$$r = 0.129\frac{ai}{zD}$$

Where,

r is the rate of corrosion for the first leak, measured in (mpy)

a is the molar mass of the metal $gm\ per\ mol$

D is the density of the metal gm/cm^3

i is the corrosion current density $\mu A/cm^2$

z is the number of electrons participating in the reaction (also equal to the change in oxidation state)

By substituting the value of r in Eqn (29) we get,

$$0.129\frac{ai}{zD} = \frac{1000t_1}{T_j}$$

Or

$$i = \frac{(1000t_1)(zD)}{T_j(0.129a)} \tag{30}$$

Eqn (30) provides the corrosion current in terms of pipe thickness; age of plumbing, molar mass of copper, density of copper and the number of electrons lost by copper during the corrosion reaction. The corrosion current can be used to obtain the polarization resistance R_p, using Eqn (28),

From Eqn (28) we have

$$i = i_{corr} = \frac{K}{R_p}, \text{ where } K = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)}$$

However, the units of i in Eqn (28) are A/m^2, hence by changing the units of i to $\mu A/cm^2$ using the conversion, 1 $\mu A/cm^2$ = 10^{-2} A/m^2 and substituting i in Eqn (30) we get,

$$\frac{K}{R_p} = \frac{(10^{-2})(1000t_1)(zD)}{T_j(0.129a)}$$

Or

$$R_p = \frac{KT_j(0.129a)}{(10t_1)(zD)}$$

$a = 63.546$ gm/ mol (the molar mass of copper)

$D = 8.94\ gm/cm^3$ (density of copper)

$z = 2$ (number of electrons lost, as copper changes from 0 to +2 oxidation state)

Hence,

$$R_p = 0.0459 \frac{K(T_j)}{t_1} \tag{31}$$

where $K = \dfrac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)}$

$$\beta_a = \frac{2.303RT}{\alpha zF}$$

$$\beta_c = \frac{2.303RT}{(1-\alpha)zF}$$

Hence, if α, T and t_1 is assumed, then using the distribution for first leak time (chapter 3), the distribution for R_p can be calculated.

For a M-type ½- inch copper pipe, the thickness $t_1 = 0.028$ inches,

for $\alpha = 0.3$

$T = 285$ K,

$R = 8.314$ J/mol-K

F = Faraday's constant= 96485 Coulomb/ mol

T_1= 3.79 years, modal *time to first leak* from chapter-3, we have

$$\beta_a = \frac{2.303(8.314)(285)}{(0.3)(2)(96485)} = 0.0942$$

$$\beta_c = \frac{2.303(8.314)(285)}{(1-0.3)(2)(96485)} = 0.040398$$

$K = 0.01227$

From Eqn (31),

$$R_p = 0.0459\frac{(0.01227)(3.79)}{0.028} = 0.076\ \Omega m^2$$

The distribution of corrosion current and polarization resistance for the first leak is shown in Figure 4 and 5.

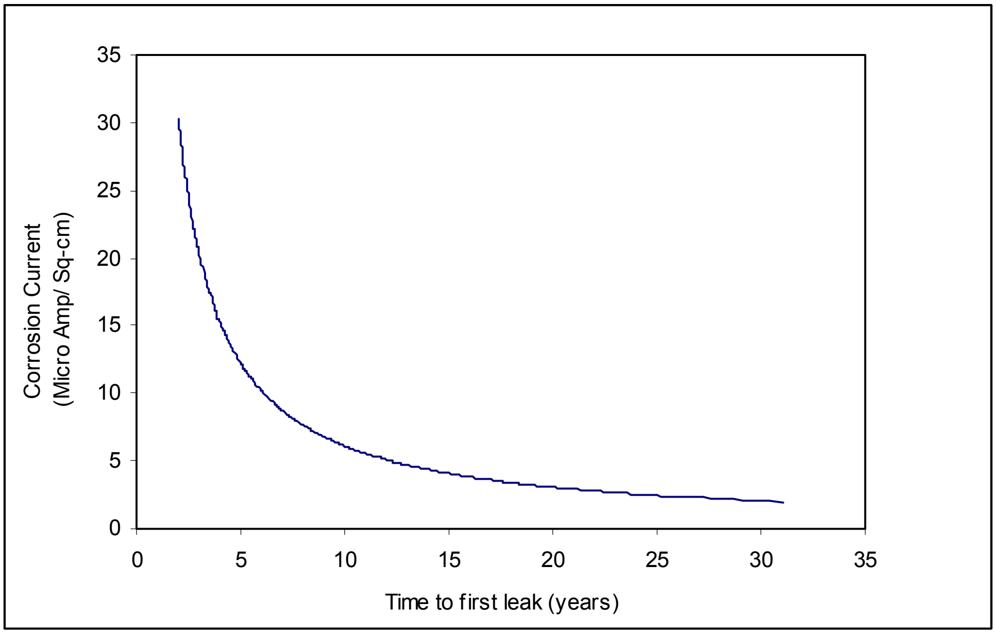

Figure 4 Distribution of corrosion current with age of the plumbing for first leak.

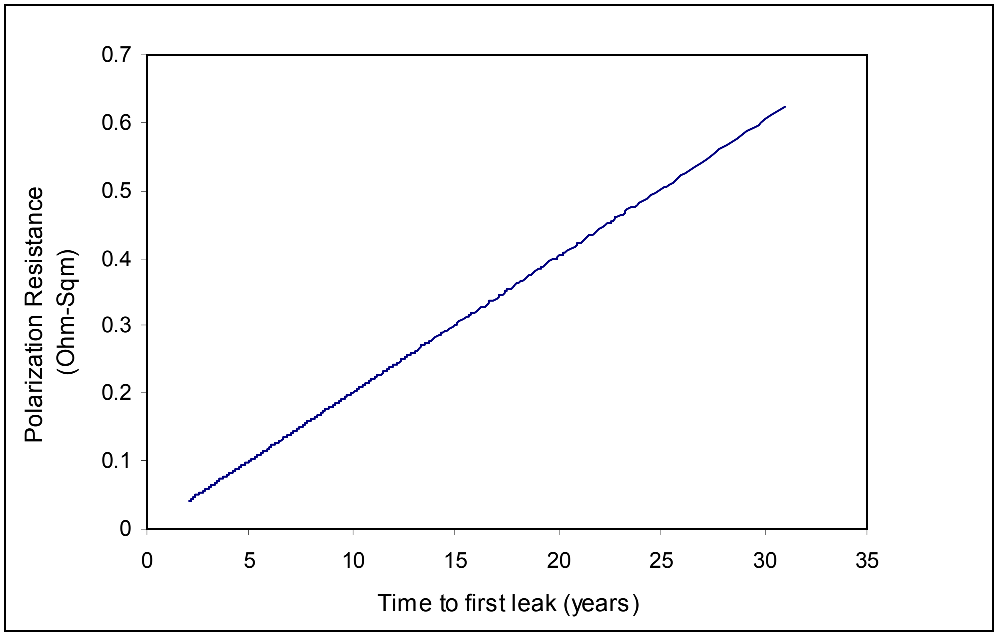

Figure 5 Distribution of polarization resistance with age of the plumbing for first leak.

The distributions in Figure 4 and 5 are based on the first leak time distribution from chapter-3. The corrosion rate decreases hyperbolically with age for the first leak distribution; the corresponding polarization resistance shows a linear increase with age. Due to complexities associated with delayed initiation and meta-stable pitting, the other leak times cannot be used directly to obtain similar distributions of corrosion rate with age. For simulating conditions similar to home plumbing systems, the variation of corrosion current and the polarization resistance with age is needed for different hydraulic and water quality conditions. This needs experimental support and can be useful for further research.

Conclusions

The two approaches namely *Butler-Volmer equation* and *linear polarization approach* can be used for mechanistic modeling of copper corrosion. Both the approaches require experimental data based on anion chemistry, pH and temperature for obtaining parameters that are needed to model copper corrosion. The linear polarization approach requires lesser parameters than the Butler-Volmer equations, however, the former is derived based on certain assumptions and hence the results from the former would be less accurate.

From modeling perspective, the distribution of corrosion parameters with age of the plumbing is needed. The distribution of polarization resistance and corrosion current is presented based on first leak distribution; however the distribution of other leak times could not be used directly due to complexities associated with delayed initiation and meta-stable pitting. The approach needs experimental support for obtaining distribution of corrosion current with age, under different hydraulic and water quality conditions.

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Owais was born on June 4th, 1975 in India. It was his interest in mechanics that led him to *University of Roorkee* (now IIT-Roorkee) to pursue Engineering. He completed his Bachelors degree in Civil Engineering in 1998 and joined *Maruti-Suzuki* as an engineering trainee. His career in Maruti-Suzuki was marked by achievements and accolades. He designed and implemented *rainwater harvesting system* in Maruti-Suzuki, the project was a pioneering effort by the organization towards the arrest of the depleting ground water table. The success of the project and his noble motives to serve the human kind brought him to United States to pursue Masters Degree in Civil Engineering (Water Resources). His interests include studying and designing BMPs, optimizing BMPs and forecasting. After completing his degree he will move to Maryland to join a leading consulting firm in water industry. He intends to start a non-profit organization at a later part of his career. He firmly believes in "*think big- achieve big*" philosophy. He is a big fan of English and Urdu poetry.