MONTANA STATE UNIVERSITY

The effect of corrosion control treatments and biofilm disinfection on unlined ferrous pipes

by Calvin Glenn Abernathy

A thesis submitted in partial fulfillment Of the requirements for the degree of Doctor of Philosophy in Civil Engineering
Montana State University
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Abstract:
The occurrence of microbially related water quality problems has long been a concern to consumers and to water suppliers. Microbially related water quality problems are of particular interest because ferrous materials have been found to support larger populations of attached microorganisms (biofilms) even in the presence of disinfectants. These systems are now being required to implement corrosion control programs to reduce the quantities of lead and copper that leach from plumbing materials into the finished water. Many utilities have reservations about the implementation of a corrosion control program because most corrosion inhibitors contain phosphorus, which is an essential nutrient for microbial growth.

It is therefore the purpose of this research to investigate the numerous interactions between disinfectants (free chlorine and monochloramine) and several corrosion control methods and determine how they influence microbial growth in distribution systems.

To investigate these numerous interactions, studies were conducted using bench-scale and pilot-scale facilities, chemostats, and various other laboratory systems. Bench-scale facilities consisted of continuous flow annular reactors using unlined ductile iron or unlined mild steel materials. Pilot-scale facilities consisted of a 5-loop system of 4-inch mild steel pipe located at the Bozeman Water Treatment Plant. A series of experiments were conducted, using each type of facility, to evaluate the effect that various combinations of disinfectant and corrosion control treatments would have on distribution biofilms.

Results from these experiments have demonstrated that use of an effective corrosion control treatment will typically reduce microbial populations within the distribution system. Our studies have shown that corrosion products have a significant influence on the amount of microorganisms that a pipe material can support. Goethite (α-FeOOH), the most common corrosion product found in distribution systems, is of particular importance because it is able to adsorb and transform humic substances to more bioavailable forms, resulting in increased substrate for attached microorganisms. This study has demonstrated that an effective corrosion control program will reduce the amount of goethite formed on a ferrous pipe, and will consequently reduce the amount of bioavailable carbon on the surface and reduce habitat for problematic microorganisms.

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APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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The completion of this thesis represents the end of one dream and hopefully the beginning of a new career. The dream began in 1987 and has taken several stops, right turns, and wrong turns. The stops and right turns have proven to be inspirational moments that have identified who I am, while the wrong turns have proven to be the turns that directed back to my dream. In reality, the wrong turns were actually the right turns that helped me identify who I am and what I wanted out of life.

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ABSTRACT

The occurrence of microbially related water quality problems has long been a concern to consumers and to water suppliers. Microbially related water quality problems are of particular interest because ferrous materials have been found to support larger populations of attached microorganisms (biofilms) even in the presence of disinfectants. These systems are now being required to implement corrosion control programs to reduce the quantities of lead and copper that leach from plumbing materials into the finished water. Many utilities have reservations about the implementation of a corrosion control program because most corrosion inhibitors contain phosphorus, which is an essential nutrient for microbial growth.

It is therefore the purpose of this research to investigate the numerous interactions between disinfectants (free chlorine and monochloramine) and several corrosion control methods and determine how they influence microbial growth in distribution systems.

To investigate these numerous interactions, studies were conducted using bench-scale and pilot-scale facilities, chemostats, and various other laboratory systems. Bench-scale facilities consisted of continuous flow annular reactors using unlined ductile iron or unlined mild steel materials. Pilot-scale facilities consisted of a 5-loop system of 4-inch mild steel pipe located at the Bozeman Water Treatment Plant. A series of experiments were conducted, using each type of facility, to evaluate the effect that various combinations of disinfectant and corrosion control treatments would have on distribution biofilms.

Results from these experiments have demonstrated that use of an effective corrosion control treatment will typically reduce microbial populations within the distribution system. Our studies have shown that corrosion products have a significant influence on the amount of microorganisms that a pipe material can support. Goethite (α-FeOOH), the most common corrosion product found in distribution systems, is of particular importance because it is able to adsorb and transform humic substances to more bioavailable forms, resulting in increased substrate for attached microorganisms. This study has demonstrated that an effective corrosion control program will reduce the amount of goethite formed on a ferrous pipe, and will consequently reduce the amount of bioavailable carbon on the surface and reduce habitat for problematic microorganisms.

Chapter 1

Introduction

For the past 20 years, the United States government has been implementing drinking water regulations with the intent of reducing the health risk associated with drinking water. For the most part these regulations have focused on increased microbial disinfection, reducing the amount of disinfection by-products and reducing the leaching of lead and copper from distribution piping. In the years to come, new regulations will be promulgated that will not only lower the maximum contaminant levels (MCLs) of various disinfection by-products, but for the first time place a maximum limit on chlorine residuals found in distribution systems. In view of these new regulations, many utilities are concerned about maintaining chlorine residuals high enough to control biofilms and the possible impacts of increased microbial growth resulting from phosphorus based corrosion inhibitors.

Although the federal regulations have changed significantly in the past 20 years and will continue to change well into the next millennium, microbial biofilms will still be present in water distribution systems. Biofilms have been shown to be responsible for positive coliforms in water samples along with causing taste and odor complaints from consumers(LeChevallier, et al 1996; van der Wende and Characklis 1990; AWWA 1996). In the years to come, the water industry will be implementing numerous treatment changes to stay one step ahead of the

regulations. In many cases, utilities will be using a trial-and-error approach to stay in regulatory compliance without knowing the impact a treatment change may have on the biostability of the finished water. Some questions that are frequently pondered by water suppliers are:

- Will the addition of phosphorus based corrosion inhibitors increase microbial growth of distribution biofilms?
- Will lower chlorine residuals be able to effectively control microbial regrowth in the distribution system?
- Will chloramines be strong enough to control microbial regrowth events even though it is a weaker disinfectant?

In view of the above listed concerns, a better understanding is needed about the interactions between pipe materials, disinfectants, and corrosion inhibitors, on distribution biofilms. It is therefore the purpose of this thesis to investigate and discuss many of these interactions, and hopefully provide better guidance on how treatment changes may affect distribution system biofilms.

1.1 Goals and Objectives

The main goal of this work is to gain a better working knowledge of the interactions between pipe materials, organics, corrosion inhibitors and how each of these influence the disinfection of distribution biofilms. Since the complete inactivation of distribution biofilms is not possible, this thesis will focus on the effect that corrosion control treatments have on the control of biofilms on unlined ferrous pipes.

1.2 Experimental Approach

To investigate the numerous interactions between corrosion control treatments and the disinfection of distribution biofilms, a four-step approach was implemented. This approach consisted of (a) a comprehensive literature review, (b) bench-scale studies utilizing annular reactors, (c) pilot-scale studies, and (d) ancillary laboratory experiments. Results from these four steps brought to light several new relationships between corrosion products, bioavailable carbon, and distribution biofilms. Regulation or control of the formation rates of corrosion products may prove to be a key factor in reducing water quality problems associated with distribution biofilms.

Chapter 2

Literature Review

The removal or inactivation of microorganisms in potable water is perhaps the leading health concern of consumers. Although the inactivation and removal of microorganisms from the finished water leaving a water treatment plant may appear to be simple, maintaining low levels of microorganisms in the distribution system is seldom, if at all, accomplished even in the presence of a disinfectant residual. The presence of microorganisms in water distribution systems is widespread because the microorganisms are able to accumulate and colonize on the interior surfaces of drinking water pipes. Once attached, they develop a physical and chemical structure that enables them to modify the microenvironment of the pipe surface in a manner that allows them to optimize their metabolism and become highly resistant to disinfectants (Characklis and Marshall 1990; LeChevallier, et al 1988).

In consideration of the numerous water quality problems associated with microorganisms in water supply, a better understanding of how implementation of processes to meet the federal regulations influences distribution biofilms so that water suppliers can develop more efficient ways to minimize water quality problems. It is therefore the purpose of this chapter to: (a) discuss the federal regulations and (b) discuss the numerous interactions between pipe materials,

organics, disinfectants, corrosion control methods and how each of these components affect the formation and inactivation of distribution biofilms.

2.1 Regulatory Impacts

The 1986 and 1996 Safe Drinking Water Act (SDWA) Amendments will require many water utilities to modify current treatment and distribution practices. The goal of these regulations is to reduce the microbial and chemical health risk of the finished water by increasing disinfection efficacy along with reducing the concentrations of lead and copper, disinfection byproducts, and disinfectant residuals within the distribution system. Although these regulations will result in lower health risk, many utilities will use a trial-and-error approach to compliance, and may actually increase water quality problems associated with the presence of microorganisms in the distribution system if improperly addressed.

In view of the above, it is therefore the purpose of this section to discuss the existing and proposed SDWA regulations, and define how irrational implementation may result in increased microbial related water quality problems. Regulations that will be addressed will include the Surface Water Treatment Rule, Lead and Copper Rule, and the Disinfectant and Disinfection Byproduct Rule.

2.1.1 Surface Water Treatment Rule

The assumption in developing the Surface Water Treatment Rule (SWTR) was that surface waters and groundwater under the direct influence of surface

waters are at risk of contamination by *Giardia lamblia* and other protozoa, viruses, and pathogenic microorganisms (Bryant, et al 1992). The goal of this rule was to provide a minimum level of protection from illnesses caused by these organisms by specifying a minimum 3-log (99.9 percent) inactivation and/or removal of *Giardia* cysts and a 4-log (99.99 percent) inactivation and/or removal of enteric viruses prior to final distribution. The SWTR also established a minimum disinfectant residual (either free or total chlorine) of 0.2 mg/L entering the distribution system and requires each utility to maintain a detectable residual throughout the distribution system.

As a result of the SWTR, the microbial water quality supplied by water suppliers has improved, primarily from increased disinfection at the water treatment plant. Increased disinfection efficacy will minimize the possible "breakthrough" of microorganisms from the treatment system, and will likely reduce the quantity of microorganisms that enter the distribution system.

One possible adverse impact of the SWTR occurs when utilities increase disinfectant dosages or change primary disinfectants to comply with the "CT" requirements of the SWTR. In many cases it has been found that an increase in disinfectant dosage - particularly with the strong oxidants such as ozone, chlorine dioxide, and free chlorine - results in increased bioavailable organics in the finished water (Bryant, et al 1992). The increase of bioavailability of organics may result in increased microbial growth within the distribution system, even

though disinfection efficacy was increased at the water treatment plant. Additional information on this subject can be found in Section 2.4 of this chapter.

2.1.2 Lead and Copper Rule

The Lead and Copper Rule (LCR) was promulgated in June 1991 and requires utilities to maintain lead and copper concentrations at the consumer tap below an action level of 15 μg/L and 1.3 mg/L respectively (AWWA 1992). In the event that the lead and/or copper levels exceed the specified action limit, the water supplier must implement a response plan that will minimize the leaching of lead and copper from pipes and plumbing fixtures. The response plan is typically to implement a corrosion control program that interferes with the corrosion process, resulting in reduced leaching of lead and copper from piping and plumbing materials.

A corrosion control plan typically includes the use of pH adjustment of the finished water with sufficient alkalinity to promote the coating of the interior surface of pipes and plumbing materials with calcium carbonate ($CaCO_3$), or by applying a corrosion inhibitor (AWWA 1992). The selection and implementation of corrosion control programs should be done with caution, because they can have an impact on both the formation of disinfection byproducts and possibly increase microbial growth in the distribution system (AWWA 1992). Of particular concern of these corrosion control techniques are: (a) the increase in total trihalomethane (TTHM) formation resulting from higher pH values (Symons, et al 1982) and (b) the fact that most corrosion inhibitors contain phosphorus which is

an essential nutrient for microbial growth (Brock, et al 1994). It has also been demonstrated numerous times that the implementation of a corrosion control program reduces biofilm densities (Schreppel and Geiss 1996; Lowther and Moser 1984). Discussions about how these corrosion control techniques may increase microbial related water quality problems are presented in Section 2.6 of this chapter.

2.1.3 Disinfectant and Disinfection Byproduct Rule

The proposed Disinfectant/Disinfection Byproduct Rule (D/DBPR) is expected to lower the current THM levels and establish many new limits on various other disinfection byproducts and disinfectants in the finished water. This rule will likely have the most dramatic impact on water quality because it will apply to almost all water suppliers, regardless of size, and for the first time establish a maximum disinfectant residual in the distribution system. In summary, the goal of the D/DBPR is to optimize the removal of organic carbon, minimize the formation of disinfection byproducts, and to minimize disinfectant dosages. The implementation of the D/DBPR will drastically reduce the chemical health risk associated with disinfection, but may also reduce both primary and secondary disinfection efficacies.

The implementation of the D/DBPR may cause widespread microbial water quality problems if not addressed properly by water suppliers. Perhaps the highest at risk are the smaller utilities that currently serve less than 10,000 people. These utilities do not have to comply with current TTHM limits, but will

soon be required to meet TTHM levels as low as 80 μg/L and maintain disinfectant residuals less than 4 mg/L in the distribution system. Many of these utilities will struggle with coliform violations during the warmer months when microbial activity is at its highest level, and may not be able to control water quality problems with disinfectant residuals less than 4 mg/L and still comply with TTHM limits.

A second group of utilities that will possibly have adverse microbial water quality problems are those utilities that currently have TTHM levels between 80 and 100 μg/L. Many of these utilities will attempt to lower disinfectant residuals to reduce disinfection byproduct levels, only to result in reduced control of existing distribution biofilms.

A third group of utilities that may have problems with the delicate balance between disinfection byproducts and microbial inactivation will be the utilities that modify current primary disinfection practices by using more powerful disinfectants such as ozone or chlorine dioxide. The popularity of these powerful disinfectants is rapidly gaining because they are known to produce fewer regulated disinfection byproducts and are more effective at inactivating *Cryptosporidium.*(DeMers L.D. and Renner 1992; AWWA 1998). Although the use of these primary disinfectants will likely result in lower disinfection byproducts in the finished water, these disinfectants are known to increase the bioavailability of organics for downstream treatment processes or in the distribution system

(Pontius 1990; Langlais, et al 1991). Additional information on this subject can be found in Section 2.4 of this chapter.

2.2 Physical, Chemical and Biological Properties of Distribution Biofilms

Disinfectants such as free chlorine or monochloramine have been used for nearly 100 years to reduce microbial populations in potable water supplies. Both free chlorine and monochloramine can be highly efficient at inactivating microorganisms in the bulk fluid, but have been found to be up to 2400 times less efficient at inactivating distribution biofilms (LeChevallier, et al 1988; McMath, et al 1997; Geldreich 1996). Low inactivation efficacy of biofilms can be attributed to the physical and chemical properties of a biofilm which enable the microorganisms to accumulate nutrients and to develop resistance mechanisms to various disinfectants (Chen, et al 1993; van der Wende and Characklis 1990; LeChevallier, et al 1996; LeChevallier 1990; Geldreich 1996).

2.2.1 The Structure of Distribution Biofilms

In general, biofilms consists of four components. The first three components include a consortium of microorganisms, extracellular polymeric substances (EPS) excreted by the microorganisms, and water (Characklis and Marshall 1990). The fourth component can be classified as organic and inorganic particles that adhere to the EPS and may originate from the bulk fluid, the pipe surface, or from inactivated cells from within the biofilm (LeChevallier, et al 1996; LeChevallier 1990; van der Wende and Characklis 1990; LeChevallier, et al 1993). EPS production will vary in composition and quantity depending on

the bacteria present and may be influenced by environmental conditions (Koudjonou, et al 1997). The development and accumulation of these four components creates a variety of niches that favor the metabolisms of aerobic, facultative, and anoxic microorganisms (van der Wende and Characklis 1990; Geldreich 1996), EPS, and the accumulation of corrosion products and particulates exert a significant disinfectant demand and provides a shield that protects microorganisms from lethal levels of disinfectants (LeChevallier, et al 1996; van der Wende and Characklis 1990; Geldreich 1996; LeChevallier, et al 1993).

2.2.2 Types of Microorganisms Found in Distribution Biofilms

As result of the numerous niches formed within a biofilm, a distribution system can support a variety of microorganisms as described above. Microorganisms found in distribution biofilms may include coliforms, actinomyces, molds, fungi, nitrifying bacteria, iron oxidizing bacteria, sulfate reducing bacteria (SRBs), and possibly even *Giardia* cysts or *Cryptosporidium* oocysts (LeChevallier 1990; AWWA 1996; Geldreich 1996; Keevel 1997; Camper 1994). Possible water quality problems associated with these microorganisms are identified in Table 2.1.

Table 2.1 Problematic Microorganisms in Water Distribution Systems

Type of Microorganism	Infrastructure or Water Quality Problem
Coliforms	Positive samples may be a violation of the Total Coliform Rule for large utilities and a violation of the Total Coliform Rule for small utilities.
Actinomycetes, Molds, and Fungi	Produce earthy-musty-moldy taste and odor compounds. Commonly found in surface waters.
Iron Bacteria	Oxidize soluble iron to precipitate forms increasing the mass of corrosion products on pipe walls and pump casings. Excessive iron deposits causes increased pipe friction and lower pump efficacy.
Sulfate Reducing Bacteria (SRBs)	Reduces sulfate to hydrogen sulfide creating rotten egg taste and odor. Increases corrosion rates.
Nitrifying Bacteria	Oxidizes ammonia to nitrate. Consumes alkalinity, which may result in pH reduction.
Protozoans	Will not reproduce in biofilm, but may reside in biofilm.

2.3 Interactions Between Pipe Materials and Distribution Biofilms

Most water distribution lines constructed today utilize polyvinyl chloride (PVC), cement lined ductile iron, or prestressed concrete cylinder pipes (PCCP). However, prior to the 1940's when these modern materials were not universally available, most water distribution systems were constructed with unlined mild steel and unlined cast-iron pipes. Although these materials are seldom used today, they currently comprise about 22 percent of all distribution pipes in the

United States(LeChevallier 1997). For many of the larger water distribution systems (>50,000 people), the average age of the oldest section of the distribution system is typically greater than 50 years (Haas 1998). In view of this, it can be concluded that these distribution systems will have substantial quantities of unlined cast iron pipes. In many older cities, unlined cast-iron and unlined ductile-iron pipes may consist of more than 80 percent of the entire distribution system.

The materials used in water distribution systems appear to be one of the most important factors that influence the proliferation of distribution biofilms (Camper, et al 1996). In a recent survey (LeChevallier, et al 1996), it was found that water distribution systems that contain large quantities of unlined cast-iron and unlined ductile-iron pipes frequently experience problems with coliform violations and taste and odor complaints(LeChevallier, et al 1996; van der Wende and Characklis 1990; van der Kooij and Oorhuizen 1997). Researchers have also found that pipe materials support different quantities of microorganisms even when the influent water quality is the same for each material (Chen, et al 1993; Camper, et al 1996; Ollos, et al 1997; Delanoue, et al 1997). These researchers have documented that unlined mild steel, followed by unlined cast-iron, and unlined ductile-iron surfaces will support significantly higher biofilm densities than non-ferrous materials (LeChevallier 1997; Delanoue, et al 1997).

2.3.1 Pipe Material Properties

In consideration of the facts presented above, one must ponder why unlined mild steel, unlined cast-iron and unlined ductile-iron pipes are capable of supporting higher biofilm densities than non-ferrous materials. The answer to this question is likely to be related to the amount iron present in each material. A typical mild steel will contain approximately 99.12 percent iron by weight, while cast-iron and ductile-iron contain 93.18 and 92.66 percent respectively (Singley and Ahmadi 1985). Although the differences between these percentages may appear to be insignificant, the amount of exposed iron surface area is substantial when the specific gravity of the non-ferrous materials are taken into consideration. The exposed non-ferrous materials amount to 1.1 percent of the total area for mild steel and 17 and 18.5 percent for cast-iron and ductile-iron pipes, respectively (Singley and Ahmadi 1985). Exposed iron is critical because the formation of iron based corrosion products is directly related to release of dissolved Fe^{2+} from the pipe surface. Corrosion products exert a chlorine demand and can accumulate nutrients for the growth of microorganisms (van der Wende and Characklis 1990; LeChevallier, et al 1996; LeChevallier, et al 1993). Corrosion products are of interest because systems with significant quantities of corrosion product mass have been found to have substantially higher microbial densities (Rice, et al 1991; Herson, et al 1991; van der Kooij and Oorhuizen 1997; McMath, et al 1997; Crayton, et al 1997; Martin, et al 1982; LeChevallier, et al 1991; LeChevallier, et al 1993; Camper 1994).

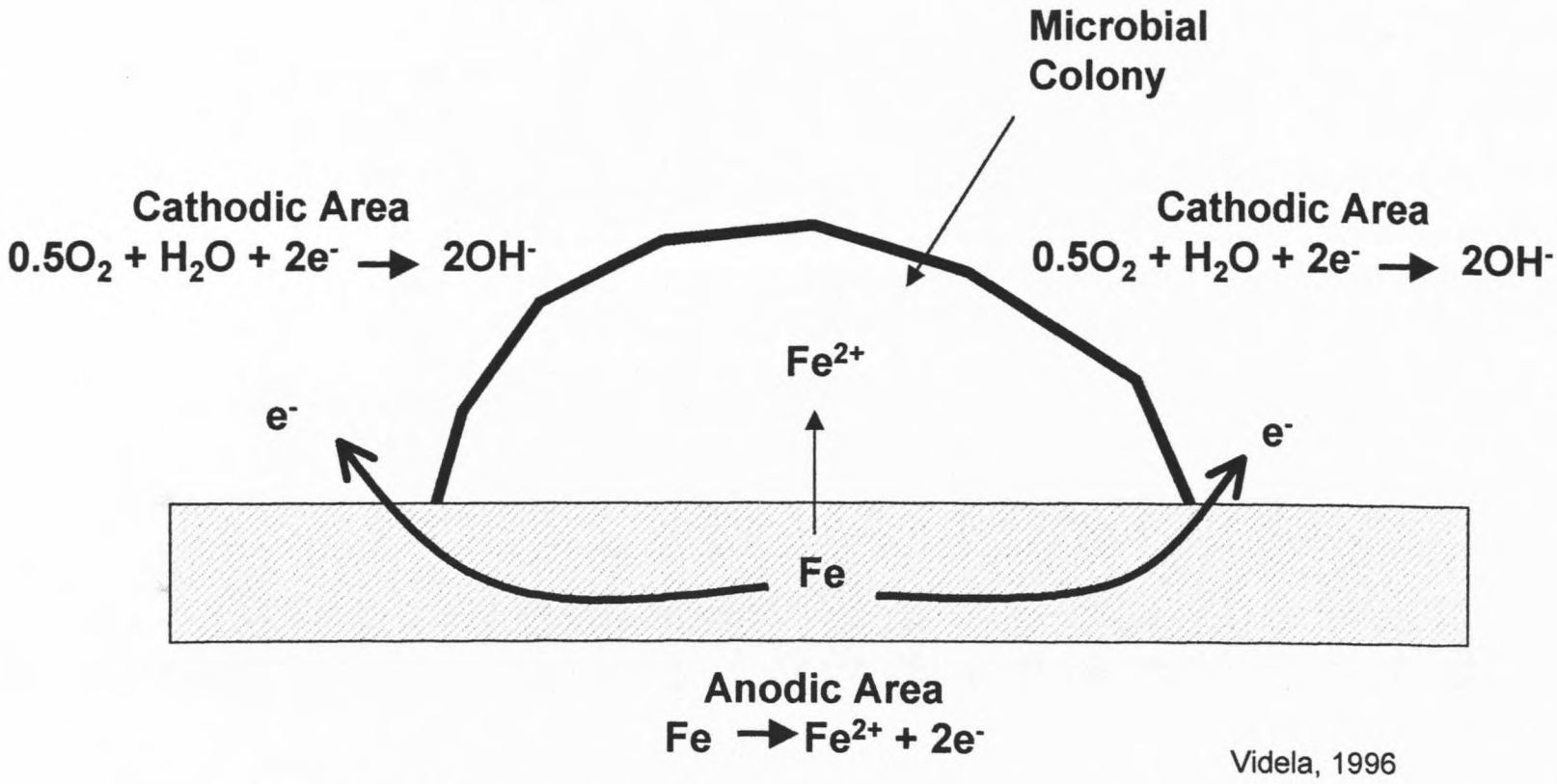
2.3.2 Formation of Corrosion Products

The formation of corrosion products in water distribution systems results from the release of Fe^{2+} ions from the pipe surface that react with various electron acceptors such as carbonate, oxygen, and free chlorine in the bulk fluid (Singley and Ahmadi 1985). Dissolved iron (Fe^{2+}) can be released from the pipe by either microbiologically influenced corrosion (MIC) or by chemical induced corrosion. MIC is caused by the chemical gradient that develops between the pipe surface beneath a microbial colony and the bulk fluid. The oxygen gradient creates an electrochemical cell that causes the pipe to release a Fe^{2+} ion and two electrons as illustrated in Figure 2.1 (Videla 1996).

Chemically induced corrosion is the result of an electrochemical potential differences between the ions present in the bulk fluid and the pipe surface, which promotes the release of the more thermodynamically stable form of iron (Fe^{2+}) and electrons from the pipe surface. Once Fe^{2+} is released, it reacts with various electron acceptors to form precipitated corrosion products, or chelates with organic compounds in the bulk fluid or the biofilm matrix (Gu, et al 1994; Parfitt, et al 1977; Benjamin, et al 1990; Weber 1988).

2.3.3 Physical/Chemical Properties of Corrosion Products

Goethite (α-FeOOH) and magnetite (Fe_3O_4) are the most common types of corrosion products found on iron pipe surfaces in water distribution systems (Singley and Ahmadi 1985; Smith, et al 1996). The presence of goethite, the



Videla, 1996

Figure 2.1 Microbially Influenced Corrosion

most abundant corrosion product, is of interest because it is capable of adsorbing organics from the bulk fluid (Gu, et al 1994; Chang, et al 1997; Benjamin, et al 1993; Benjamin and Li 1997; Benjamin, et al 1990; Parfitt, et al 1977; Tipping and Cooke 1982; Characklis 1989). There have even been a few studies where iron oxides have been used as a filter medium to remove natural organic matter (NOM) from water supplies (Benjamin, et al 1993; Benjamin and Li 1997). Considering that corrosion products are iron oxides, the corrosion products on a pipe surface are capable of adsorbing organics from the bulk fluid, hence, providing a higher concentration of carbon on the pipe surface than in the bulk fluid (van der Wende and Characklis 1990). It is hypothesized that these adsorbed organics exert a substantial chlorine demand along with increasing the bioavailability of carbon substrates for microorganisms. The interactions between organics and corrosion products are discussed in more detail in Section 2.4.

2.4 Interactions Between Organics and Distribution Biofilms

The role and significance of organic compounds in drinking water is of concern because many are precursors for various disinfection byproducts such as THM's, and that many of the microorganisms present in distribution biofilms require the use of organic carbon for metabolism and/or cell synthesis (Camper 1994). This section will discuss the role of dissolved organic compounds typically found in finished water and discuss how they influence the formation of distribution biofilms.

2.4.1 Types of Organics in Finished Water

The amount of total organic carbon (TOC) in finished water is often used as a measure for appraising a water's potential to form disinfection byproducts and to support microbial growth in the distribution system. In many situations this appraisal works reasonably well for assessing the disinfectant byproduct potential of a water, but can be inaccurate for predicting a water's ability to promote excessive growth of microorganisms in the distribution system. The shortfall of using TOC as an indicator of a water's ability to support biofilms is that only a small fraction of TOC can be used as a carbon source for microbial growth and energy (Geldreich 1996). This small amount of TOC can be classified as the bioavailable portion of TOC, and will change after rain events and seasonally (Trussell 1998). In view of this, it is possible to have a decrease in TOC and have an increase in bioavailable carbon in the distribution system.

In an attempt to quantify the bioavailable portion of TOC, several researchers have developed methods that measure the bioavailability of carbon in water. Results from these studies can be used to assess a water's potential to support microorganisms in the distribution system. These methods utilize bioassays and are defined as the biodegradable organic carbon (BDOC) and assimilable organic carbon (AOC). An overview of these bioassays are described by Huck and Camper (Huck 1990; Camper 1994).

The BDOC is that portion of the TOC in water that can be mineralized by heterotrophic microorganisms (Camper 1994). BDOC can be determined by

measuring the difference in TOC between the influent and effluent of a packed bed bioreactor (Lucena, et al 1990). The change in TOC is defined as the BDOC and is typically less than 0.6 mg/L and may be less than 0.1 mg/L for a high quality water. Due to the low levels of BDOC, the accuracy of TOC equipment must be very high and all glassware must be thoroughly cleaned to obtain statistically reliable results.

The AOC has been defined as the portion of BDOC that can be converted to cell mass and is expressed as μg/L acetate equivalents (van der Kooij and Hijnen 1984). The procedure to measure biomass production uses prepared cultures of *Pseudomonas fluorescens* (P17) and *Spirillum* (NOX) (van der Kooij and Hijnen 1984). The procedure is time consuming and can take up to 20 days to obtain results. This procedure is considered by many to be excessively labor intensive and may not be entirely representative of the bioavailable carbon, because it only uses two specific microorganisms which may not have similar metabolisms as the microorganisms in the distribution system.

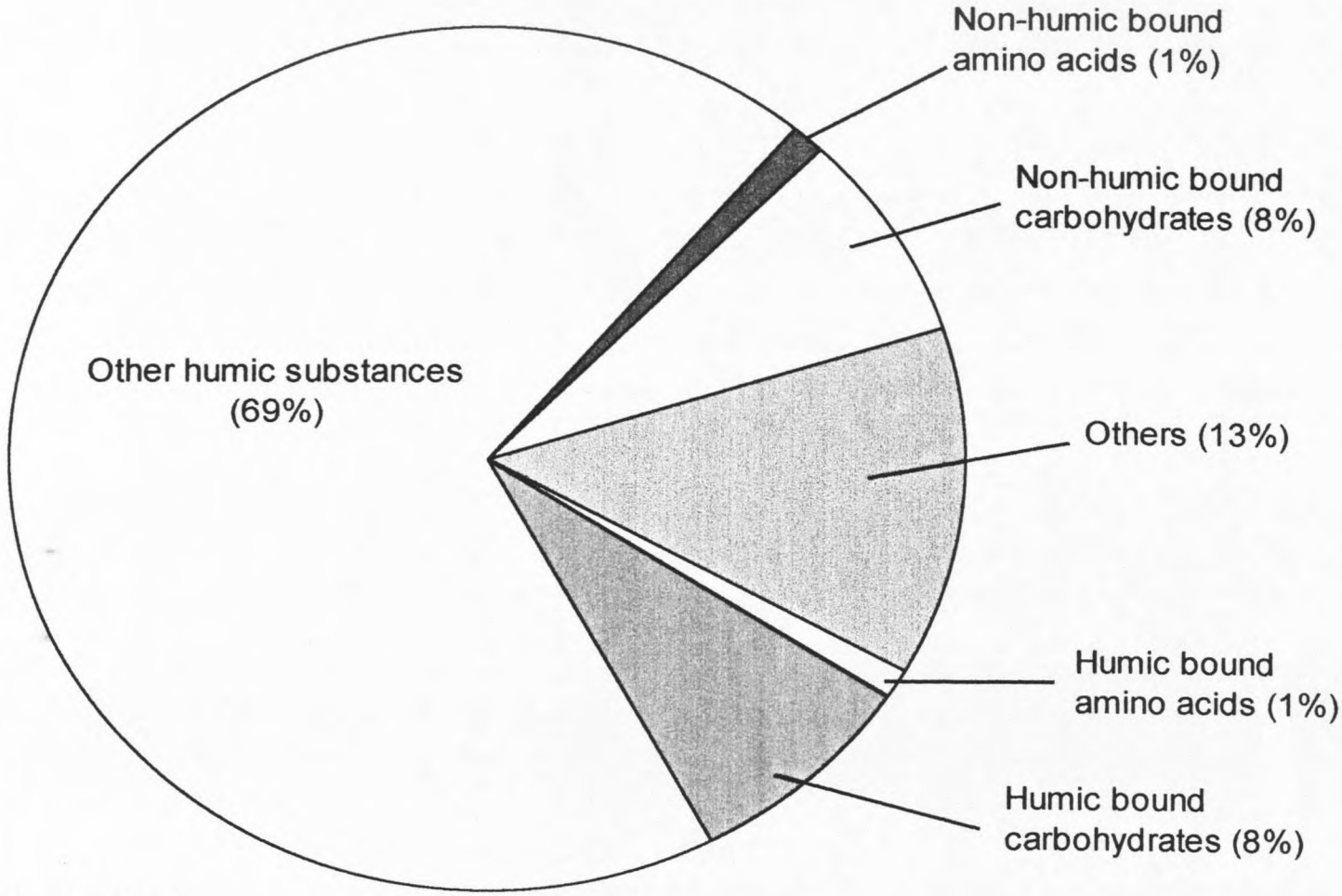
Many researchers and water suppliers have used these to determine relationships between BDOC and AOC concentrations and the occurrence of coliforms in distribution samples. These studies have found that AOC levels greater than 10-15 μg/L typically supported heterotrophic microbial growth in distribution systems (van der Kooij 1992), while AOC levels greater than 50 μg/L always supported heterotrophic growth (LeChevallier 1990; Laurent, et al 1997).

It has also been shown that some coliforms are unable to grow in waters containing AOC concentrations less than 50 μg/L (LeChevallier 1990).

In view of the above, it is clear that the amount of bioavailable carbon present in the bulk fluid may have a profound affect on a water's biostability. However, as addressed in the Section 2.3 and in the concluding sections, the biostability of a water should be based on numerous factors that include material composition of the substratum, organics, disinfectant type and residual, and ions present in the finished water (Laurent, et al 1997; Trussell 1998).

To obtain a better working knowledge of BDOC and AOC, the types of organics that are utilized by microorganisms in water distribution systems must be considered. The types of organics commonly found in finished water include humic and non-humic substances. Typically, up to 90 percent humic substances are fulvic acids, with the remaining components consisting of humic acids and humin (Benjamin, et al 1993; Beckett 1990; Chang 1992). The non-humic substances may include carbohydrates, proteins, and lipids (Ollos, et al 1997).

As illustrated in Figure 2.2, humic substances and humic-bound organics comprise the majority of organics found in a finished water (Kaplan, et al 1994). Humic substances are naturally occurring organic materials that result from the decomposition of vegetative material and residues (Benjamin, et al 1993; Lovley, et al 1996; Stumm and Morgan 1996; Owen, et al 1993). They are long-chain molecules having molecular weights ranging from 500 to 5,000 g/mole (Stumm and Morgan 1996). In the bulk fluid, humic substances are found in tightly coiled



Kaplan 1994

Figure 2.2 Major Groups of TOC Available for Microbial Growth in Drinking Water

structures, which decreases their bioavailability to suspended microorganisms (Chang 1992). However, there are several physical/chemical pathways that are capable of transforming the structure of humic substances to forms that increase the bioavailability of these compounds, resulting in an increase in BDOC and AOC levels without an increase in TOC.

2.4.2 Transformation of TOC Bioavailability by Disinfectants

The use of disinfectants to inactivate pathogens and control microbial water quality is widespread in most of the world. Disinfectants such as ozone, chlorine dioxide, and free chlorine are used in water treatment processes for a variety of reasons. Although these disinfectants can be highly efficient at inactivating suspended microorganisms, they also react with various organic and inorganic compounds present in the water. The reactions of these disinfectants with humics substances are of concern because; (a) they may lead to the formation of trihalomethanes, and (b) they may transform the structure of humics to smaller more bioavailable molecules (Bryant, et al 1992). As a result, the BDOC and AOC levels increase, perhaps leading to elevated microbial growth in the distribution system (Volk, et al 1997; van der Kooij, et al 1998). The transformation of TOC to a more bioavailable form by disinfectants provides one explanation of why the addition of a disinfectant sometimes increases microbial populations in downstream processes or in the distribution system.

2.4.3 Transformation of TOC Bioavailability by Corrosion Product Adsorption

Adsorbed humic substances is perhaps the most overlooked component of corrosion products. Humic substances are some of the most powerful metal-binding agents found in natural organic matter (NOM) (Glaus, et al 1995). The mechanisms by which humic substances adsorb to corrosion products have been proposed to involve: (a) anion exchange, (b) ligand exchange-surface complexion, (c) hydrophobic interaction, (d) hydrogen bonding, (e) cation bridging, and (f) electrostatic interactions (Gu, et al 1994; Glaus, et al 1995; Varadachari, et al 1997; Chang 1992; Stumm and Morgan 1996; Kummert and Stumm 1980; Davis 1982; Weber, et al 1983; Tipping 1981; Tipping and Cooke 1982; Parfitt, et al 1977; Tipping, et al 1981).

The most common adsorption mechanism is thought to be ligand exchange between the hydroxyl (OH^-) molecule of goethite (α-FeOOH) and the carboxylate groups (COO^-) of humic substances as illustrated in Figure 2.3 (Parfitt, et al 1977; Gu, et al 1994; Varadachari, et al 1997; Chang, et al 1997). Once adsorbed, humic substances collapse on the surface, allowing for maximum points of interaction and ligand exchange with goethite (Gu, et al 1994; Chang 1992; Stumm and Morgan 1996). As a result of this collapse, the humic molecules becomes uncoiled, increasing the bioavailability of sugars and peptides previously unavailable to microorganisms (Gu, et al 1994). The tails of the adsorbed humic substances may also bond with other humic molecules in the bulk fluid, increasing the mass of humics at the corrosion product-bulk fluid