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Project Summary

Seattle Distribution System Corrosion Control Study: Volume VI. Use of a Rotating Disc Electrode to Assess Copper Corrosion

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The uniform corrosion of copper tubing used for transport of Tolt River water is characterized in this study as a heterogeneous rate process composed of metal oxidation and oxide film growth, interfacial chemical reactions, and mass transport in the liquid phase. Quantitative rate expressions were developed to characterize each of these rate processes. Experiments designed to measure the temperature and pH dependence of corrosion under rate control by each process were conducted using steady-state electrochemical techniques. The persistent and unexpected influence of solution transport of a reaction product, presumed to be OH^-, complicated characterization and identification of underlying rate process. Surface pH could be characterized empirically as a function of solution temperature, pH, and diffusion layer thickness.

This empirical correlation for surface pH along with solution mass transport models developed for turbulent and laminar pipe flow were combined to form a steady-state pipe flow model for uniform copper corrosion. Predictions made using the model under stagnant and low flow rate conditions show a stable and low corrosion rate of 0.2 mils per year (MPY) in water of pH > 6.0. At lower pH, predicted rates are substantially increased as the pH is reduced and temperature is increased. At high flow rates, tremendous acceleration of corrosion rate occurs, which again increases with increasing temperature and decreasing pH. Only at pH > 8.0 are the dramatic pH and temperature effects dissipated so that the rate is stabilized at a minimum value of approximately 0.2 MPY.

Steady-state electrochemical techniques gave rapid, reliable, and reproducible corrosion rate measurements and provided the versatility necessary to characterize quantitatively a heterogeneous rate process like aqueous copper corrosion.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Background

Corrosion of materials used to transport drinking water is both a public health concern and an enormous economic problem. In 1975, the estimated national cost for corrosion in industrial, commercial, and public establishments was $82 billion. This figure included monies spent for replacement of deteriorated parts and equipment, maintenance and repair, and direct expenditures for corrosion control. Costs as high as $375 million per year

have been estimated for replacement parts and repair of drinking water distribution systems transmitting corrosive water, with an additional cost of $27 million per year for water treatment to control corrosion. The Seattle Water Department has estimated repair costs to consumer plumbing systems to be 10 to 20 times higher than costs associated with the distribution system. Annual expenditures of $500,000 for corrosion control in Seattle are estimated to reduce consumer costs by $2 million.

Corrosion occurs in the distribution or plumbing system — the part of the drinking water cycle closest to the point of customer use. Water quality degradation and contamination occur because of the release of metal cations and other corrosion products into the water. Public health concerns involve ingestion and bodily accumulation of metal cations from drinking water. Dissolved lead and cadmium are two contaminants likely to be present above permitted levels as a result of aqueous corrosion in plumbing systems using galvanized steel or copper tubing with lead/tin solder.

Adverse aesthetic effects often result from the leaching of copper, iron, zinc, and manganese from corroding pipelines. For example, drinking water may be undesirable because it has an unpleasant taste or color, or because it promotes staining of porcelain bathroom and kitchen fixtures. All of these effects arise from a chemical reaction between a structural material and a chemical component of the transported natural water As the reaction proceeds, the metal is thinned and/or pitted, thus shortening its useful lifetime according to the rate of the overall reaction. Reaction products may also promote precipitation of solids, which accumulate on the metal surface and in some cases reduce water pressure and pipeline carrying capacity. Corrosion control efforts are then aimed at slowing down the reaction to an acceptable rate or stopping it completely without creating further ecological or water quality problems.

Purpose and Scope of Work

This study characterizes aqueous copper corrosion as a heterogeneous rate process by combining principles from various disciplines to develop quantitative rate expressions for each component rate process involved. Principles taken from solid-state, electrochemical, and corrosion sciences are combined with those of water chemistry and environmental engineering to describe and explain the overall corrosion process as a composite result of fundamental rate processes. Although the component rate processes are coupled, each is influenced by a distinct set of environmental variables that affects the rate at which it proceeds. Thus this work presents an overview of copper corrosion in drinking water as a composite result of several fundamental rate processes, and it determines through laboratory experiments which rate processes exert the greatest rate-controlling influence on the overall process. Environmental variables most important in influencing the rate-controlling processes are also evaluated.

Corrosion rate was measured with standard steady-state electrochemical techniques augmented with special instrumentation necessary for measurement in natural waters of low conductivity. Measurements were made under varying conditions of rate control to evaluate the dependence of component processes on temperature, fluid motion, and chemical composition of the system.

Results

General Observations

The likelihood of rate control by each of the component rate processes is shown in a comparison of the magnitude of the three types of data as a function of pH (Figures 1 and 2) at 25°C. The following general observations are made:

a) Corrosion rates measured at pH > 7.0 on electrodes without oxide films were much greater than those measured on oxide-covered electrodes.

b) Corrosion rates measured in stagnant solution were considerably lower than those made at 3000 RPM.

These observations demonstrate both the influence of oxide film growth and solution mass transport on the overall rate and, thus, suggest that a model of the overall process include the coupled effects of these two rate processes. Kinetic data may be important, but only at sites where the oxide film has been damaged or removed. The fact that solution mass transport control data were of smaller magnitude than the other two sets of data at corresponding pH and temperature values indicates that some species exist in solution whose diffusion affects the rate of the overall corrosion process

The rate of the process thus depends not only on the chemical reactions involved and the growth of oxide film, but also on the hydrodynamic flow regime of the corroding system since it inevitably influences the rate of solution mass transport. A definite solution mass transport influence exists, and the species exerting that influence may very well be OH^- diffusing away from the surface into bulk solution. In situations involving a reaction product that must diffuse away from the reacton site, a persistent influence is exerted on the overall process rate (even at very high Reynolds Numbers) to the point of masking the effects of the underlying process. A slow diffusion of OH^- away from the surface increases the pH of the solution adjacent to the oxide surface and reduces the oxide film growth rate. As the diffusion rate is increased (at higher Reynolds Numbers), the surface pH can drop, allowing a faster rate of oxide film growth and greater corrosion rate. The high pH values that arise at the oxide surface may promote precipitation of such solids as $Cu(OH)_2$, which have low solubilities. If such is the case, actual rate control of the corrosion process may occur in the solution adjacent to the oxide surface, not within or on the oxide itself. In addition, a variety of $Cu(OH)_n^{2-n}$ complexes may form in the solution adjacent to the oxide surface, reducing the "free OH^-" concentration and lowering the surface pH.

Pipe Flow Model

The principal value of corrosion research performed in the laboratory lies in its application to real-life corroding systems, such as copper tubing used for cold water plumbing. A simulation model is presented for predicting the rate at which copper tubing will corrode under a given set of environmental conditions. The model is based on (1) the presumption that mass transport of OH^- is the rate-controlling process and (2) the combined results of laboratory studies with quantitative models for mass transport in laminar and turbulent pipe flow. The result is an ability to predict the rate of uniform copper corrosion in cold water plumbing systems under varied conditions of flow, temperature, and pH of the water.

Results of the calculation for varying Reynolds Numbers at 25°C appear in Figure 3. The rates increase with flow rates at Reynolds Numbers greater than 2000. Effects of pH < 6 are apparent at all flow rates. Rates become very high at low pH and high flow rate.

The influence of temperature appears in Figure 4, which shows corrosion rates versus pH at a high Reynolds Number (50,000). The corrosion rate is much more pH dependent at 15°C and 25°C than at 5°C.

Model predictions provide valuable insight into identification of principal variables affecting the overall process,
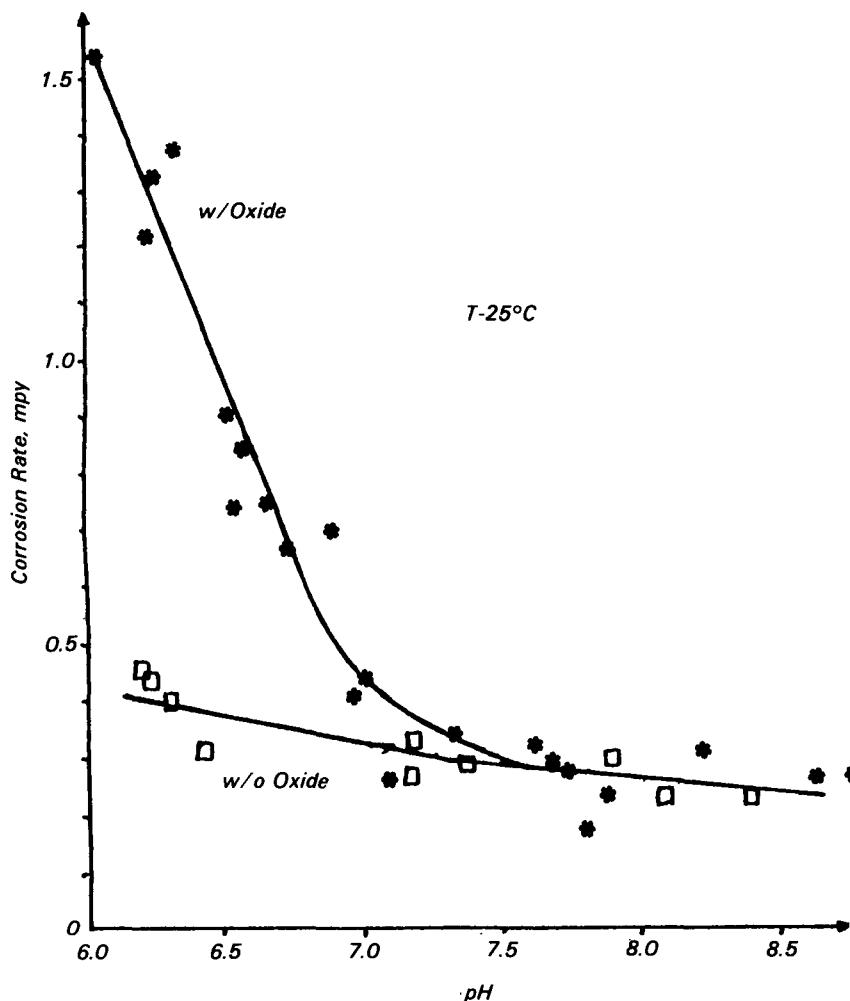
Figure 1. Comparison of corrosion rates measured with and without Oxide film at 25°C.

the extent to which each variable exerts an influence, and the range of magnitude in which the maximum effect is manifested. Possible strategies for corrosion control (or at least corrosion rate reduction) are also suggested.

Conclusions

Over the pH range of 6.0 to 8.5, the rate of copper corrosion is reduced as pH is increased. Over the temperature range of 5°C to 25°C, the rate of copper corrosion is reduced as temperature is reduced. The presence of a Cu_2O film on the copper surface reduces the corrosion rate at all pH and temperature values studied.

The transport of a reaction product (presumed to be OH^-) away from the oxide/solution interface is the principal process controlling the overall corrosion rate. At low pH (6.0), rate control by mass transport is nearly complete. At higher pH

values (>8.0), the influence of the underlying rate process exerts a greater influence on the overall rate.

In pipe flow under stagnant or low rate (laminar flow) conditions, the corrosion rate of copper is stabilized for pH > 6.0 at a value of 0.2 MPY. Only when the pH is reduced below 6.0 do the accelerating effects of low pH and high temperature manifest themselves. At high (turbulent) flow rates in pipe flow, corrosion rates are accelerated dramatically with reduced pH and increased temperature. Under these conditions, only at pH >8.0 is the corrosion rate stabilized to an acceptably low value of 0.2 MPY.

The use of steady-state electrochemical techniques gave reliable and reproducible corrosion rate measurements, even in water of low conductivity. In addition, they provide the versatility needed for experimental design of adequate sophistication to provide data that can be used

in mechanism determination and model development. These qualities greatly enhance the research capabilities of the investigator.

Recommendations

The ability to characterize complex metal-oxide-solution systems as heterogeneous rate processes is an important step in determining the dependence of the corrosion rate on system variables. Crucial to the development of aqueous corrosion science is the gathering of appropriate multidisciplinary information to develop quantitative rate expressions for processes involved in the general corrosion of metals other than copper used in the transport of drinking water.

The model presented for aqueous copper corrosion should be extended and refined. Extension to a broader range of aqueous species and concentrations to include species involved in water treatment processes such as chlorination seems advisable. Also in order are (1) more sophisticated mathematical modeling of the oxide/solution interfacial interactions controlling the solution pH just next to the interface, and (2) precipitation studies involving Cu^{2+} and OH^- species. An evaluation could then be made of the effect of precipitated hydroxide and carbonate solids in altering the corrosion rate by depositing on the metal surface.

The steady-state methods used here should be further applied to the study of other metal-oxide-solution systems along with the testing and development of transient electrochemical techniques such as the A.C. impedance method. The latter, because of its possibility for instantaneous measurement, can provide invaluable insight into the coupled rate processes involved in aqueous corrosion.
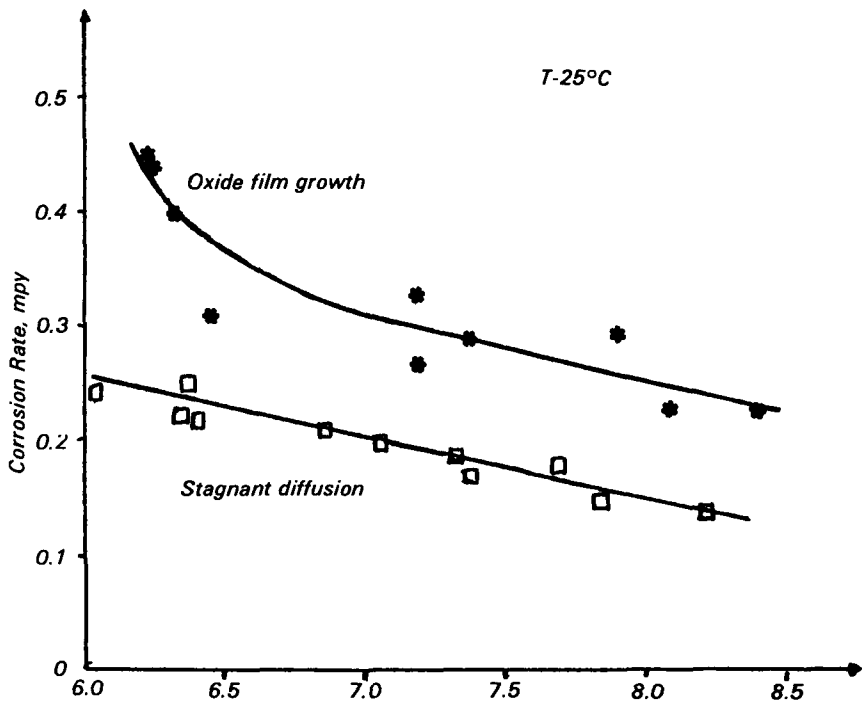
Figure 2. Comparison of corrosion rates measured with and without solution mass transport effects at 25°C.
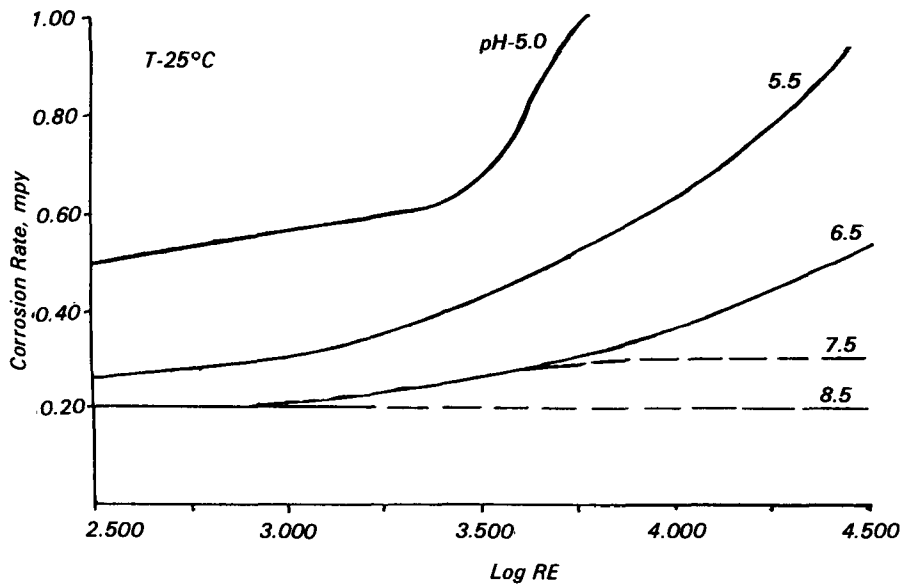

Figure 3. Corrosion rate estimates for 1/2-in. copper tubing at varied flowrates and 25°C.
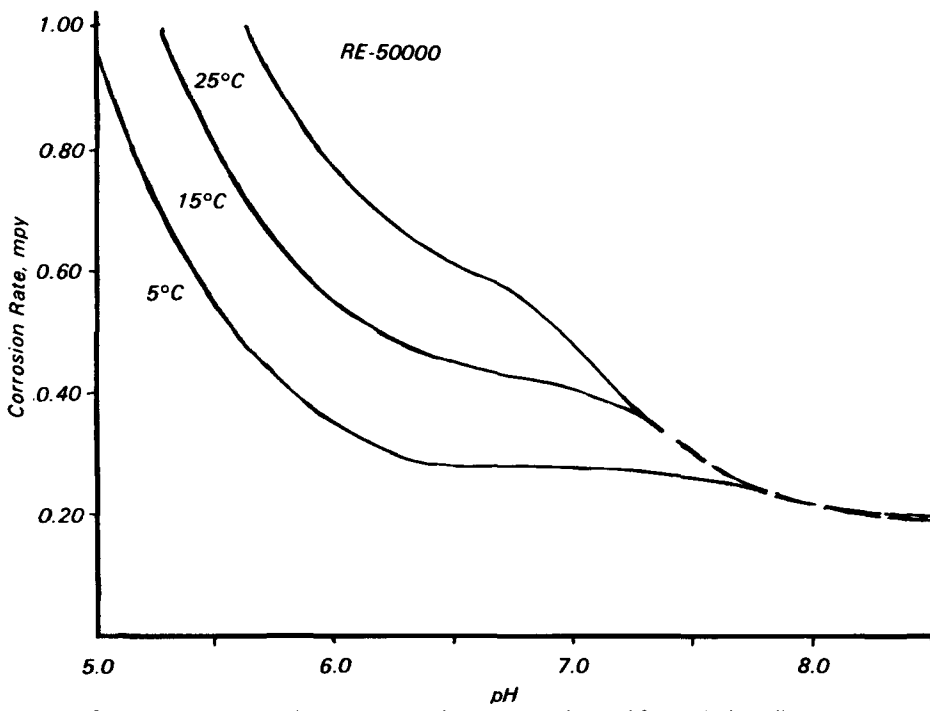
Figure 4. The pH dependence of corrosion rates estimated for turbulent flow conditions.

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