



Project Summary

Corrosion and Calcium Carbonate Saturation Index in Water Distribution Systems

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Corrosion in water distribution systems was studied to gain a better understanding of the processes needed in developing control strategies. Equations and calculation methods for determining the pH_s (or the theoretical pH at which the water is saturated with CaCO₃) were developed using a chemical model with and without ionic speciation. Several calculation procedures for determining pH_s were analyzed and compared. Laboratory experiments using weight loss and electronic techniques for measuring corrosion rates were conducted in laboratory batch and continuously circulating systems using waters with different saturation indices (SI), pH, alkalinity, chlorides, sulfates, chlorine residual, dissolved oxygen, organic color, calcium, buffer capacity, and other water quality parameters. Changes in water quality were monitored in experiments with mild steel, galvanized steel, and copper coupons. Corrosion products obtained from coupons exposed to continuously circulated solution were analyzed by wet chemical techniques and X-ray diffraction. Increases in dissolved oxygen, chlorides, sulfates, chlorine residual, and hydrogen ion concentration accelerated corrosion of metal specimens. Higher pH, calcium content, buffer capacity, and organic color decreased the corrosion rate. A model was formulated that expresses corrosion rate in terms of chlorides, sulfates, alkalinity, dissolved oxygen, calcium, buffer capacity, saturation index, and immersion time. A four-variable corrosion rate model was de-

veloped from the multivariate analysis of corrosion data for mild steel in the batch studies. The model included total dissolved solids (TDS), dissolved oxygen, saturation index, and exposure time. Results indicate saturation index cannot be used alone to indicate the extent of corrosion or to measure the corrosivity of a water.

This Project Summary was developed by EPA's Water Engineering 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

Corrosion of pipes in community water supply systems has been recognized as a serious problem since the beginning of the 20th century. Economic estimates of corrosion costs in the water industry have increased from \$40 million in 1947 to as high as \$700 million in 1980. In addition to the economic consequences, as the metallic structure deteriorates, drinking water quality is degraded. The resulting corrosion products also pose potential health risks. Consequently, the U.S. Environmental Protection Agency (EPA) has amended the National Interim Primary Drinking Water Regulations to require that public water utilities carry out a corrosion control program. This program includes identifying the presence and sources of corrosion products and subsequently implementing effective corrosion control measures.

CaCO₃ deposition on the metal surface has been one of the better control strategies for combatting corrosion. Using the parameter pH_s (or the pH of CaCO₃ saturation) is commonly employed to ensure that the processed or treated water has sufficient protective property. Because most of the pH_s calculation methods are not accurate enough and provide only an approximate value, more precise methods are needed for determining pH_s. Likewise, further studies are still needed to assess the effects of important water quality parameters on corrosion of metals used in the distribution systems.

Research Objectives

This investigation was conducted:

- to derive a more accurate theoretical expression for evaluating pH_s;
- to make a comparative analysis of other methods for calculating pH_s;
- to develop a simplified method for accurately predicting the exact pH_s;
- to evaluate the corrosive behaviors of waters with different saturation indices;
- to study the effects of several water quality factors on the corrosion rates of mild steel, black steel, galvanized steel, and copper; and
- to analyze the corrosion data and develop empirical and statistical corrosion rate models.

Experimental Section

Different synthetic waters with different saturation indices were prepared by mixing appropriate quantities of the required reagents. A 24-hour equilibration test in which analytical reagent CaCO₃ was added to each water determined the actual saturation state with respect to CaCO₃. The changes in pH, Ca, and alkalinity were determined before and after the equilibration period.

Two sets of corrosion evaluations at room temperature (20±3°C) were conducted: jar tests and loop studies. In the jar tests (non-flowing system), several cleaned metal coupons were suspended and immersed by nylon cords in the plastic jars containing water with different chemical compositions and saturation indices. The jars were placed over a stirring apparatus (Figure 1), which can be used simultaneously for aerated and deaerated systems. The weight loss was used to calculate the corrosion rate:

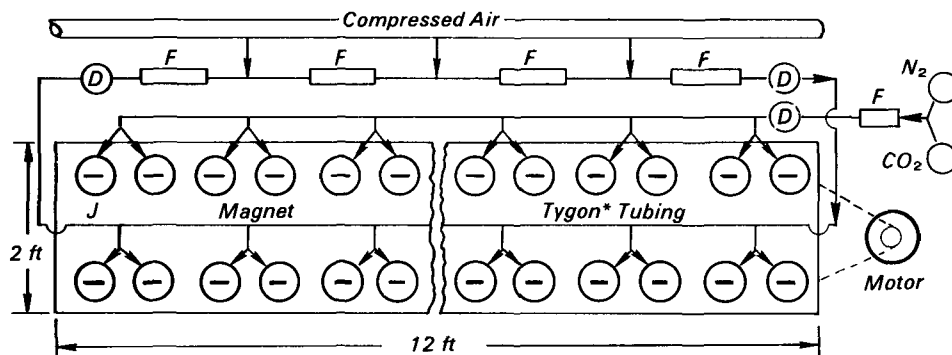


Figure 1. Stirring apparatus (D = deionized water; F = glass wool filter; J = jars).

before and after a specified immersion period, the oven dried weight of each coupon was determined. In addition to the weight-loss method, the corrosion rate in some experiments was electronically monitored at specific time intervals using a Magna Corratel Model 1120, which employed three-electrode probes.

Figure 2 shows the loop set-up constructed with nonmetallic materials to study corrosion of metals in contact with circulating water of different saturation indices. A Manostat Varistaltic* pump (advanced model) was connected to the water reservoir to feed the pipe sections and these regulate the water flow. Bypass tubes were provided to prevent disrupting the entire system operation when removing metal specimens for examination and analysis. Each PVC tube section in the loop system held four metal inserts. The corrosion rate of the exposed internal surface of each pipe coupon was determined by the weight-loss method. After each corrosion test, the loop set-up was flushed with acidified water and then rinsed twice with deionized water to remove any adhering corrosion products. An aliquot of the last wash water was analyzed for the presence of metal ions to ensure that no metallic substances still remained in the system.

Dried corrosion products obtained from loop studies of mild steel, black steel, and galvanized steel were analyzed by wet chemical methods and X-ray diffraction analysis. X-ray diffractograms of standard compounds were developed simultaneously during the sample analysis.

*Mention of commercial products or trade names does not constitute endorsement or recommendation for use.

Results

Theoretical Aspects

After presenting and reviewing several CaCO₃ saturation concepts and corrosivity indices, two alternative calculation methods for pH_s were derived. The first equation was a quadratic pH_s formula (QUAPHS) developed from a chemical model of CaCO₃ solubility equilibrium in which several ionic association equilibria were considered. The final form of the equation for hydrogen activity at CaCO₃ saturation was a function of the first and second thermodynamic dissociation constants of H₂CO₃ (K₁ and K₂), thermodynamic CaCO₃ solubility product constant (K_s), free calcium ion concentration, total equilibrium carbonate concentration, and activity coefficients of Ca²⁺, CO₃²⁻, and HCO₃⁻.

A computer program, constructed during the study, calculates QUAPHS through iterative calculation procedure whereby values of the variables, except equilibrium constants at a given temperature, initially are given approximate values. Solving for pH_s continues until both sides of the equation are almost numerically equal.

Another simplified pH_s (SIMPHS) expression similar to Langelier's equation was derived from equilibrium relationships in which ion pairing was neglected and a new salinity correction factor was added. The resulting pH_s equation was

$$\text{SIMPHS} = -\log \left[\frac{K_2}{K_s} [\text{Ca}^{2+}] (\text{Alk}) \right] + \frac{2.5\sqrt{I} + 3.63}{1.0 + 3.30\sqrt{I} + 2.61 I}$$

where: [Ca²⁺] = total calcium concentration, moles/L

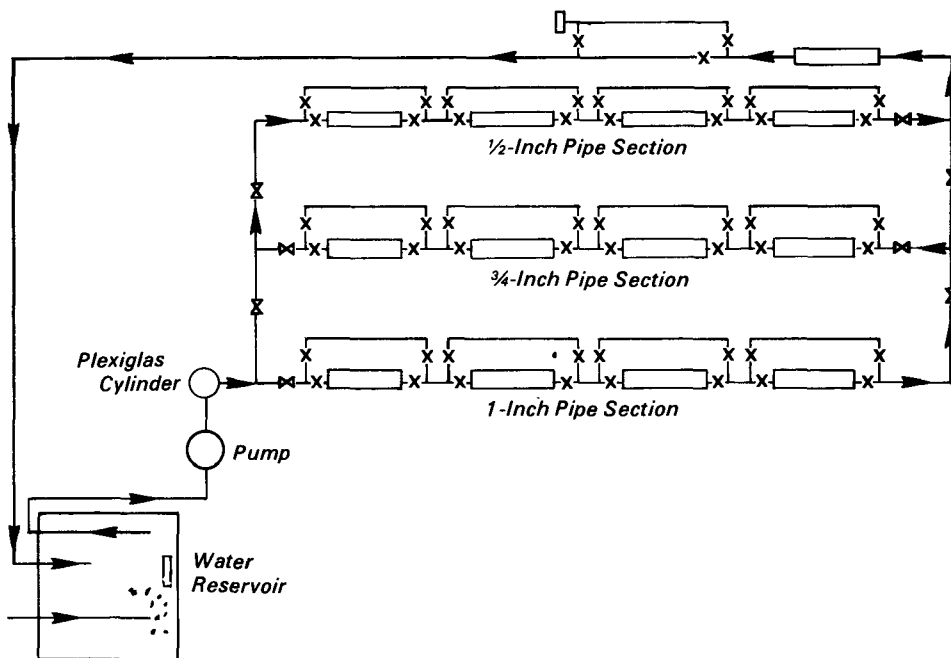


Figure 2. Set-up of the loop system for evaluating metal pipe corrosion in circulating water.

(Alk) = total alkalinity, equiv/L
I = ionic strength, moles/L

Several statistical predictive pH_s equations were analyzed and compared with the equations derived in this study. Two predictive equations, one containing 4 variables (STA4PHS) and the other, 5 variables (STA5PHS), were chosen. A comparative analysis was done among the two statistically derived predictive equations and among other calculation methods such as the WATSPEC2 computer program (WSP2PHS), Langelier's formula (LANGPHS), Larson-Buswell equation (LARBPMS), and graphical approximation of pH_s using Caldwell-Lawrence diagrams (CDLWPHS). The pH_s values of the 155 water samples (see Table 1) were calculated using each calculation procedure. When the pH_s values obtained via computer calculation of QUAPHS were compared with those derived from other methods, pH_s values for QUAPHS, SIMPHS, WSP2PHS, STA4PHS, and STA5PHS are generally close to one another. LANGPHS and LARBPMS are comparatively lower than the pH_s values obtained from QUAPHS and the first four aforementioned calculation methods. The highest values are those derived from the approximations in Caldwell-Lawrence diagrams.

Table 1. Mean Values and Ranges of the Analytical Parameters for 155 Samples of Florida Water

Parameter*	Mean	Range
TDS	456	44-1,774
Ca	71	4-260
Mg	16	0-111
Na	47	0-403
Cl	91	3-910
SO ₄	41	0-370
Fe	0.6	0-10.5
F	0.4	0-7.5
Hard†	247	14-774
Alk†	182	11-420
pH	7.45	6.20-9.20
pH_s^{**}	7.49	6.70-9.97

*All values in mg/L except Hard, Alk, pH, and pH_s .

†In mg/L as CaCO₃.

**Evaluated via computer method using the quadratic pH_s formula.

Experimental Results

We experimentally evaluated the saturation states of the synthetic waters: 17 in the jar studies and 6 in the loop studies. Generally, water with negative saturation indices dissolved a certain amount of

added CaCO₃ during the equilibration experiments as indicated by the increase of calcium concentration in the solution. That the levels of calcium in waters with positive saturation indices in contact with solid CaCO₃ decreased suggests that CaCO₃ precipitation occurred.

The corrosive behavior of waters with different saturation indices were studied both in the jar tests and loop set-up. The sign and magnitude of the saturation indices were not directly related to the corrosion rates. Waters with positive indices were sometimes as corrosive or more corrosive than those with negative values (Figures 3 and 4). The correlation coefficient between corrosion rate and saturation index for corrosion data presented in Figure 3, for instance, was unacceptably low ($r = -0.20$). Hence, the corrosivity of a water cannot be evaluated simply on the basis of saturation index alone.

Other water quality factors significantly affected the aqueous corrosion of metals. Dissolved oxygen, as a powerful depolarizer, accelerated the corrosion rates of mild steel, black steel, galvanized steel, and copper. Likewise, acidic pH, chlorine residual, and increasing amounts of chlorides and sulfates increased the corrosion rates of the same metals. Higher calcium concentration, total alkalinity, and low water flow velocity retarded the corrosion of mild steel. Organic color, derived from a lake water, decreased the corrosion rates of mild steel and galvanized steel but enhanced the corrosion of copper. The corrosion products from mild steel and black steel pipe used in the loop studies were generally composed of goethite (α -FeOOH), lepidocrocite (γ -FeOOH), magnetite (Fe₃O₄), calcite [CaCO₃ (c)], and aragonite [CaCO₃ (a)] irrespective of the saturation index of the water used. Figure 5 shows a representative X-ray diffractogram of the dried corrosion products collected from black steel coupons in the loop studies. Both X-ray diffraction and wet chemical analysis of the corrosion products from galvanized steel specimens suggested that hydrozincite [Zn₅(CO₃)₂(OH)₆], aragonite, and hematite were present.

Several corrosion rate models were developed to describe the corrosion of mild steel in the batch studies as a function of important water quality parameters. An empirically constructed, nonlinear rate model consisting of eight variables (chloride, sulfate, dissolved oxygen, total alkalinity, calcium, buffer capacity, saturation index, and exposure

time) yielded a satisfactory graphical fit to the experimental data. Multivariate regression analysis of the correlation between the corrosion rate of mild steel and various water quality parameters presented in Table 2 revealed that the corrosion rate (CR4) is best predicted,

under the experimental conditions employed in the present study, by

$$CR4 = \frac{(TDS)^{0.253} (DO)^{0.820}}{(10^{SI})^{0.0876} (\text{time, day})^{0.373}}$$

The above predictive equation appears

to work well in waters with medium to high DO level (5.0-9.0 mg/L). Representative plots for comparing the observed and CR4-predicted values in three waters are shown in Figure 6. The experimental corrosion rates follow a decreasing trend with time as do the corrosion-time curves generated by the predictive equation.

Conclusion

Two equations for determining pH_s were developed. One was a quadratic expression derived from a $CaCO_3$ solubility equilibrium model, which incorporated interaction among the major ions. The other, derived without taking into account ion pairing, was similar in form to Langelier's equation but with a new ionic strength correction factor. A simpler method of computing pH_s was found in which pH_s is defined by a statistical predictive equation composed of a linear combination of the logarithmic values of total dissolved solids, total alkalinity, and analytical concentrations of calcium, magnesium, and sulfate. Although a more accurate method of determining the $CaCO_3$ saturation index was found, the traditional interpretation of the indices was not consistent with the experimental corrosion data obtained from the jar and loop studies. Analysis of X-ray diffractograms of the corrosion products suggested that $CaCO_3$ would still precipitate in waters with a negative saturation index while in contact with a corroding metal surface. Several water quality parameters influenced the corrosion of metals used in the study and would have to be taken into account when assessing corrosive behaviors of waters. An empirically constructed, eight-variable model indicates that the corrosion rate of mild steel under the experimental conditions used is affected not only by the water's tendency to precipitate or dissolve $CaCO_3$, but also by dissolved oxygen, chloride, sulfate, calcium, alkalinity, buffer capacity and immersion time. A four-variable model derived from multivariate regression analysis defines corrosion rate as a function of four parameters: total dissolved solids; dissolved oxygen; saturation index; and exposure time.

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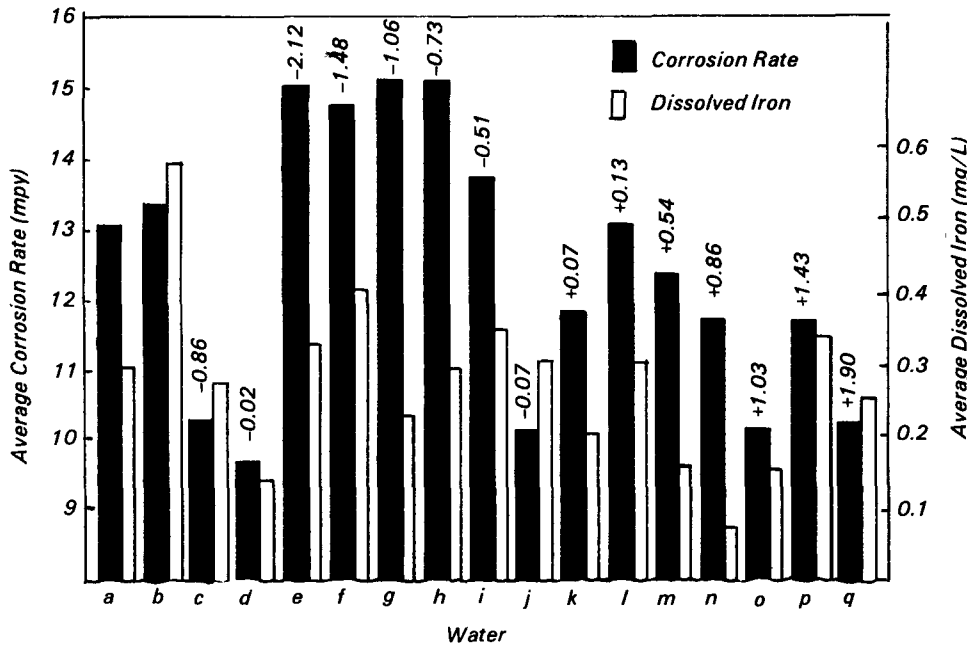


Figure 3. Bar graph of the average corrosion rate of mild steel and average total dissolved iron of the 17 test waters. Numbers above the corrosion rate bars refer to the saturation indices.

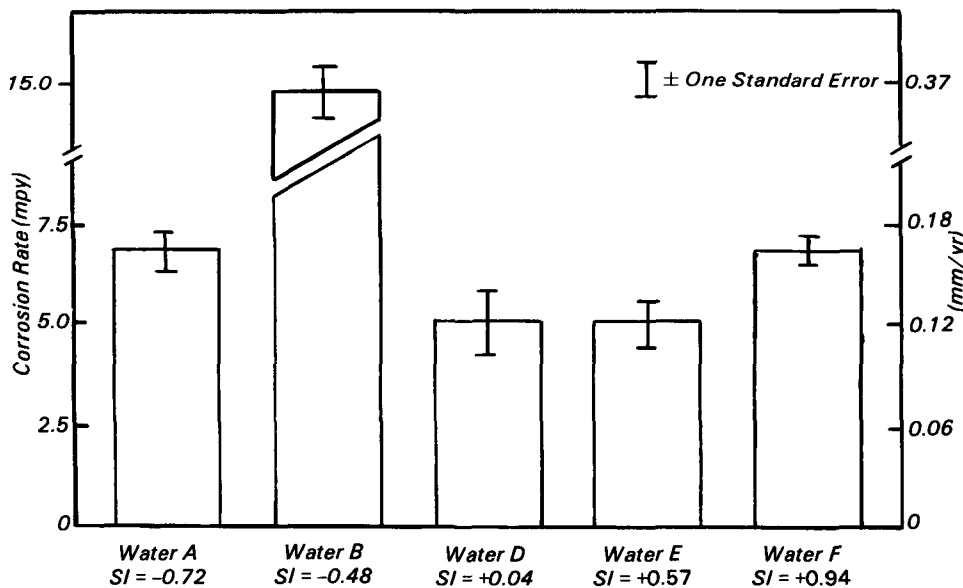


Figure 4. Bar graph showing the corrosion rates of black steel pipes after 21 days in the loop system (DO = 5.0 + 0.2 mg/L) using five waters of different saturation indices.

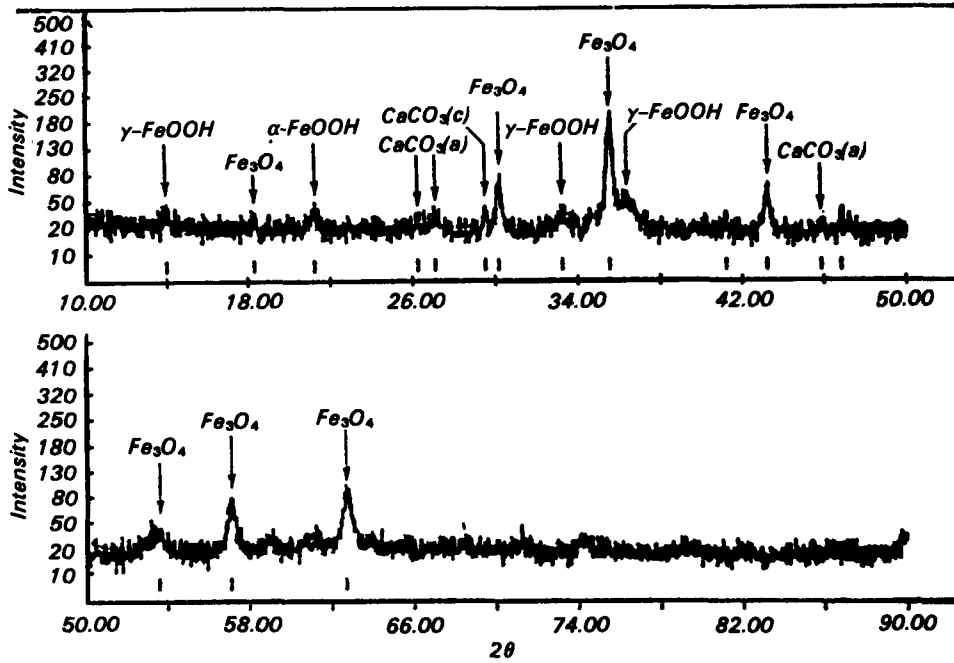


Figure 5. X-ray pattern of corrosion products from black steel pipes in contact with water B (SI = -0.46).

Table 2. Means and Ranges of Analytical Variables* for the 17 Waters Used in the Mild Steel Batch Corrosion Studies

Parameter	Mean	Range
TDS	473	116-791
Ca	68	10-120
Mg	16	2-52
Na	64	7-130
Cl	119	18-213
SO ₄	79	16-208
Alkalinity, mg/L as CaCO ₃	116	21-232
β (mg/L as CaCO ₃ /pH)	16	3-42
pH, units	7.77	6.70-8.95
pH _s , units	7.79	7.60-9.07
Saturation Index, units	-0.02	-2.12-+1.90
Ionic Strength, mole/L	0.0081	0.0001-0.0198
Dissolved Oxygen	5.1	1.4-9.1
Corrosion Rate (mpy)	11.9	2.1-36.6
Corrosion Rate (mm/yr)	0.301	0.053-0.930

*All values are expressed in mg/L except as indicated.

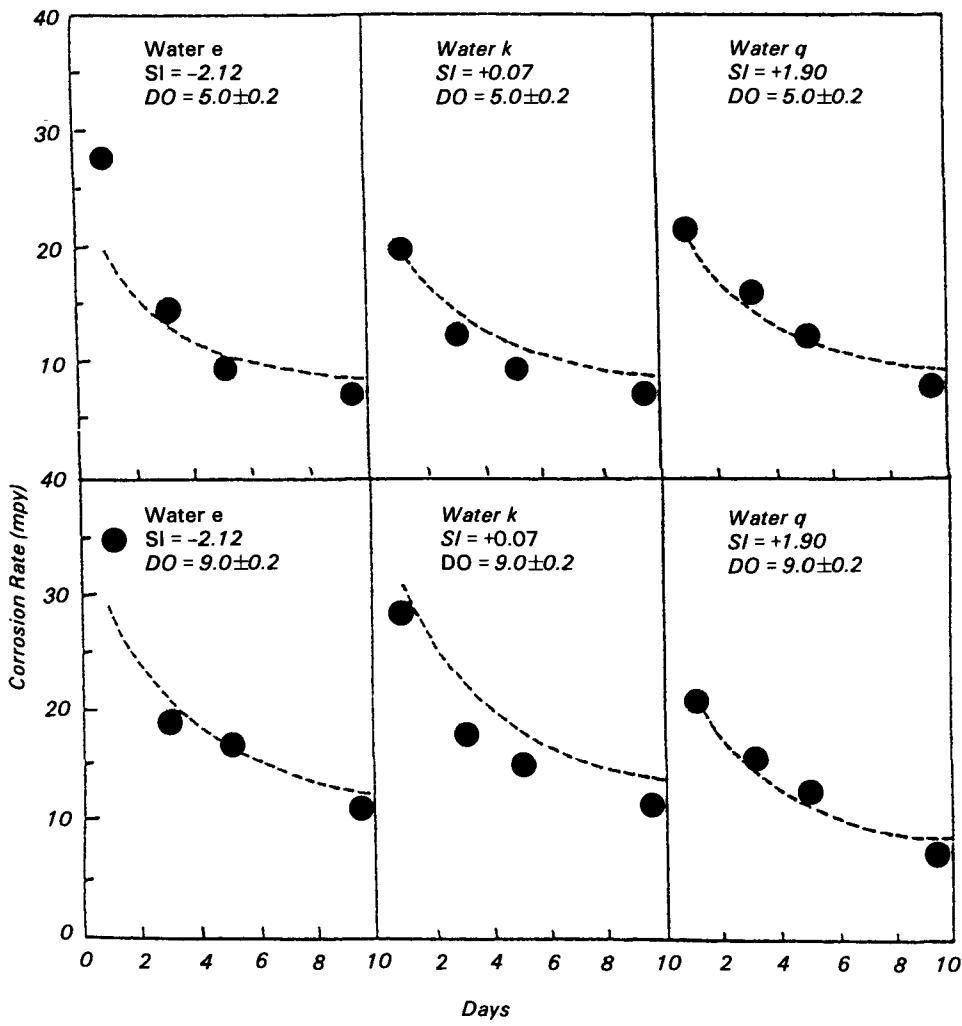


Figure 6. Predicted corrosion-time curves and experimental values (●) for corrosion of mild steel in waters e, k, and q.

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Marvin Gardels is the EPA Project Officer (see below).

The complete report, entitled "Corrosion and Calcium Carbonate Saturation Index in Water Distribution Systems," (Order No. PB 85-228 112/AS; Cost: \$22.00, subject to change) will be available only from:

National Technical Information Service

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