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STATISTICS-BASED CLASSIFICATION OF MICROBIALLY INFLUENCED CORROSION IN FRESHWATER SYSTEMS

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Abstract—This paper describes work aimed at developing a statistics-based approach to classify water sites of an unknown biocorrosive class. Field surveys were performed at over 40 sites throughout Wisconsin for 2 years to investigate microbially influenced corrosion. More than 20 water-related variables were measured. Aerobic bacteria and sulfate-reducing bacteria were isolated and their numbers in the water sample were counted. Steel coupons were installed and the corrosion rates were estimated using a gravimetric method. A visual examination rating system was adopted to evaluate the microbial corrosion rate and results showed that the visual examination rating was in agreement with the measured corrosion rate. Based on the stepwise regression analysis and discriminant analysis results, a set of classification rules was developed. By using these practical rules, the biocorrosive tendency of freshwater sites could be predicted. Furthermore, some valuable implications obtained from field surveys were summarized and explored.

Key words—biodeterioration, discriminant analysis, microbially influenced corrosion, stepwise regression analysis, sulfate-reducing bacteria

INTRODUCTION

Microbially influenced corrosion (MIC) is one of many forms of corrosion. It may be defined as the deterioration of metal of corrosion processes which occur, either directly or indirectly, as a result of the metabolic activity of microorganisms (Uhlig, 1948). At the turn of the century, corrosion was usually considered to be related to the presence of oxygen. After the pioneering work of von Wolzogen Kuhr and van der Vlugt (1934), it was realized that many cases of metal deterioration were induced by microorganisms. More recent studies have shown that corrosion may arise from the presence of sulfate-reducing bacteria (SRB), slime-forming bacteria, nitrate reducers, sulfur bacteria, iron bacteria and other miscellaneous microorganisms such as algae, yeasts and molds (NACE, 1982; J. M. Montgomery Consulting Engineers, 1985). The role of these microorganisms in influencing corrosion in metal structures can be summarized as follows (Millers *et al.*, 1964; J. M. Montgomery Consulting Engineers, 1985; Tiller, 1986; Little and Wagner, 1987): formation of the concentration cell on a metal surface; production of high concentration of corrosive metabolites; removal of the corrosion reaction product, enhancing the kinetic forward reaction; reduction of the protective influence of surface film; increase in electrolytic concentration at surface sites, favoring electron transfer; and mediation of the oxidation of reduced species. In other words, microorganisms do not mediate a new corrosion mechanism but only accelerate the electrochemical processes which cause corrosion.

MIC is a widely recognized phenomenon in municipal sewage systems, metal objects buried in soil, fuel tanks and cooling equipment (Tatnall, 1981). It also occurs in metal structures in rivers and estuaries as a result of domestic or industrial pollution. Iverson (1972) reported that the cost of MIC of buried pipelines in the U.S.A. was approx. $500 million to $2 billion per year. There have been many studies on MIC, some of which have been conducted in pure culture to explore individually such variables as pH, temperature, number of bacteria, etc. Other studies used basic electrochemical techniques to evaluate MIC under special conditions. However, no distinguishing criteria have been proposed to predict corrosion tendencies resulting from the activity of water-related bacteria.

The Wisconsin Department of Transportation (DOT) has investigated corrosion, particularly of culvert pipes since 1965. Field observations and tests indicated that nearly half of the corrosion of steel culvert pipes was related to the activities of microorganisms. Corrosion was characterized by nodules of oxidation products overlying pits or perforations in the pipe (Patenaude, 1986). The DOT recognized that MIC on metal structures is a serious problem and initiated this project in 1989. The objectives of this

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research were to conduct extensive field surveys for a better understanding of MIC in Wisconsin and to develop a set of classification rules that can be used to classify water sites of unknown biocorrosive classes.

MATERIALS AND METHODS

Preparation of coupons

Steel coupons were used to measure the corrosion rate in field survey sites. Dimensions of the coupon were 7.5 × 7.5 cm × 1 mm with a total exposed surface area of approx. 115 cm^2. A 2-mm hole was punched next to the brim for installation. Analysis using inductively coupled plasma atomic emission spectroscopy showed that test coupons consisted of: Si < 0.01 wt%, P 0.012 wt%, Mn 0.12 wt%, S 0.017 wt%, C 0.031 wt%, Al 0.003 wt%, Cr 0.05 wt%, Ni < 0.01 wt%, Mo < 0.01 wt% and Fe > 99.737 wt%. Based on this test result, the grade of steel coupon is classified as AISI 1005 (American Society for Metals, 1990). The procedures to prepare the coupons for the experiment included (1) grinding with 240-grit SiC paper, followed by mechanical wet polishing with 320, 400 and 600 grit SiC paper until scratches were removed; (2) degreasing with 100% ethanol; (3) rinsing with acetone and then distilled water; and (4) drying with nitrogen blower and storing in a desiccator prior to use.

Isolation and enumeration of bacteria

Aerobic bacteria (i.e. sulfur-oxidizing bacteria, iron-oxidizing bacteria and slime-forming bacteria) and anaerobic bacteria (i.e. SRB) have been related to corrosion-causing reactions on metal surfaces. Therefore, numbers of the aerobic bacteria and SRB were selected as the water-related variables in this research.

The counting of the aerobic bacteria of the field sample was done by using six serial dilutions from 10^{-1} to 10^{-6} without duplicate. A dilution factor was obtained and multiplied by the number of colonies on a specific plate. The plates counted were those that contained between 30 and 300 colonies. Plates containing more or less than this were considered inaccurate. For this research, three different types of media, MacConkey's agar, nutrient agar and lactic acid agar (ASM, 1981), were used. The highest plate count from these three media was selected as the number of aerobic bacteria.

Water samples, collected under hydrogen to maintain an anaerobic environment, were brought to the laboratory to attempt to isolate sulfate reducers. Portions of these samples were inoculated into an appropriate medium containing all of the right growth factors while maintaining an anaerobic environment. The simple sulfate reducing medium (Widdel and Pfennig, 1977) was used for this research. The medium was a mixture of part A [i.e. 0.3 g KH_2PO_4, 0.3 g K_2HPO_4, 0.3 g $(NH_4)_2SO_4$, 0.6 g NaCl, 0.12 g $MgSO \cdot 7H_2O$, 0.08 g $CaCl_2$, 2.84 g Na_2SO_4, 0.08 g ascorbic acid and 500 ml distilled water adjusted to pH 7.5] with part B (i.e. 0.5 g $FeSO_4 \cdot 7H_2O$, 5 ml 60% of sodium lactate and 500 ml distilled water adjusted to pH 7.0). This was brought to a boil and sparged under nitrogen. Then, the medium was portioned into Balch tubes under nitrogen gas. The Balch tube is a modified test tube which allows a butyl rubber stopper and crimp to be placed over the top to contain the nitrogen gas and maintain an anaerobic environment. To inoculate the tube of medium, the needle from a syringe was pushed through the butyl rubber stopper to dispense the test sample into the tube. The needle first had to be reduced, however, by pushing it into a sterile tube of medium and collecting nitrogen into the syringe. In this way the bacteria would not be killed by encountering oxygen already in the syringe. After inoculating the medium with 0.1 ml of the sample, the medium was incubated at 13°C for 2 days. The presence of a black precipitate in the Balch tube at the end of the two days indicated that sulfate reducers were isolated. The most probable number (MPN) method (ASM, 1981) was then used to count the number of SRB obtained in a culture.

Table 1. Visual examination ratings

Rating	Condition of pipe
0	No corrosion, galvanizing or cladding intact
1	Discoloration or superficial rusting, no pitting
2	Moderate rusting, rust flakes tight, possible tubercles, minor pitting
3	Fairly heavy rusting and rust flakes tight, some scale, tubercles, some pitting
4	Heavy rusting, rust scale easily removed, deep pitting but metal is sound
5	Heavy rusting, deep pitting and unsound area easily penetrated with pick end of geology hammer
6	Small perforation in pipe
7	Large perforation in pipe

Visual examination

Visual examination of the test coupon surface provided clues to the types of corrosion. Certain surface changes were attributable to the presence of specific bacteria; for example, surface biodeposits may indicate MIC. Discrete mounds and tubercles on the surface often contain large populations of bacteria. Those kinds of deposits are usually soft and easy to deform. Thus far, however, there is no good method of specifically estimating the biocorrosion rate in an aqueous system. Therefore, a visual examination rating system was adopted to evaluate the microbial corrosion rate. This system was modified over a period of 25 years of field observation of steel culvert pipes (Patenaude, 1988). Eight different extents of biocorrosion ratings of metal pipe are listed in Table 1.

Field surveys

Over a 2-year period, field surveys were conducted twice each year at more than 40 sites throughout Wisconsin. Figure 1 shows the location of these sites by county and Wisconsin DOT district. Pretreated steel coupons were

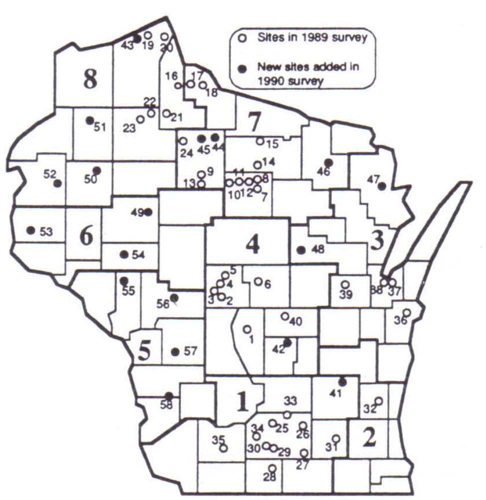

Fig. 1. Location of field sampling sites in Wisconsin.

installed during the first survey and collected during the second survey. They were suspended under water by a plastic-covered wire attached to a wooden pole or frame and were located within 1 m of a culvert pipe on the downstream end. Water-related parameters such as pH, temperature, resistivity of water and soil, dissolved oxygen (DO), redox potential (redox) and sulfate concentration of water were measured in the field. Water samples were taken for further laboratory analysis. Condition of the nearby culvert pipe was observed and a visual examination rating was assigned.

All the analytical methods were standard (APHA, 1989): total dissolved solids (TDS), 209C; total organic carbon (TOC), 505; dissolved organic carbon (DOC), 505; total Kjeldahl nitrogen (TKN), 420A; ammonium nitrogen, 417A; alkalinity, 403; bicarbonate, 403; and sulfate, 426C. Chloride, DO and water resistivity were measured with a Bulcher–Cotlove chloridometer, DO meter and resistivity meter, respectively. Minerals (P, K, Ca, Mg, S, Zn, Mn, B, Cu, Fe, Na and Al) were measured using an inductively coupled plasma emission spectrometer. The number of aerobic bacteria and SRB were counted from water samples taken in the field.

The coupons were exposed to the water for about 70 days and were brought back to the laboratory to measure the weight loss. The step for reweighing coupons was conducted following ASTM G1-81 (1988). The corrosion rate, expressed in mg/dm^2/day (mdd), was calculated by:

$$\text{corrosion rate} = \frac{\text{weight change (mg)}}{\text{area of coupon (dm}^2) \times \text{days of exposure}} \quad (1)$$

The unit "mdd" can be converted to mpy (mils/yr), which is the most commonly used corrosion rate expression in the United States. One mpy is equal to 1.44 mdd/D, where D is the density of the metal in g/cm^3.

RESULTS

Field survey results

The concentrations of alkalinity, TDS, sulfate, Ca and Mg at the southern sites were higher than at the northern sites while, conversely, the TOC concentrations and water resistivity at the southern sites were generally lower than at the northern sites [all data are contained in Peng (1992)]. Also, it was found that the corrosion rates at the southern sites were generally lower than at the northern sites except for two low pH sites ($4 < pH < 5$) and four low DO sites ($DO < 2.5$ mg/l).

According to Dutton and Bradley (1970), Wisconsin can be divided into five major physiographic divisions: (1) Central Plain (CP), (2) Eastern Ridges and Lowlands (ERL), (3) Lake Superior Lowland (LSL), (4) Northern Highland (NH) and (5) Western Upland (WU). The different physiographic divisions are underlain by different materials which influence the quality of surface water. For example, southern divisions such as ERL and WU are similar in that they both are underlain by dolomites. Natural fresh waters in these two divisions always contain higher concentrations of alkalinity, TDS, Ca and Mg than the other divisions. This fact explains why concentrations of alkalinity, TDS, Ca and Mg at the southern sites were obviously higher than at the northern sites.

Under a given set of conditions, the difference in the rates of corrosion when microorganisms are present or absent can be attributed to MIC. From the field surveys, it is not possible to quantitatively measure corrosion rates caused by activities of microorganisms alone, because MIC is typically complicated by conventional corrosion and biological fouling. In this research, a visual examination rating was adopted to evaluate the MIC and proved to agree with the measured corrosion rate.

Figure 2 shows the relationship between the corrosion rate and the visual examination rating. It is evident that the visual examination rating was rela-

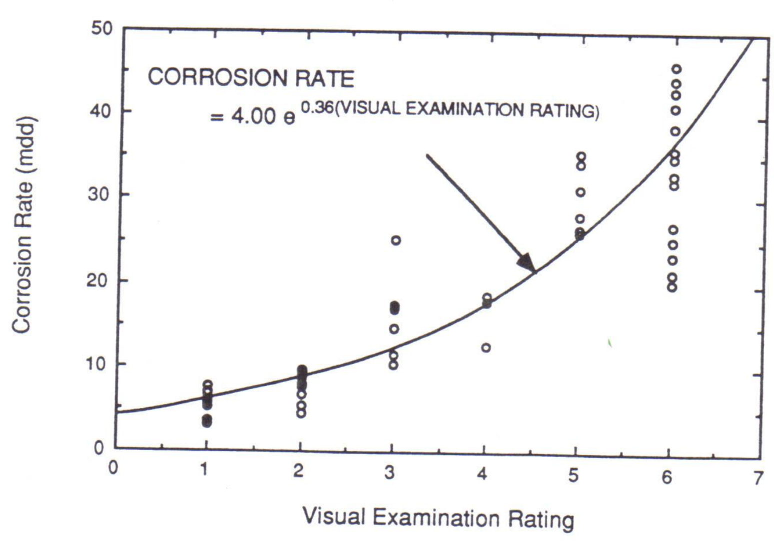

Fig. 2. The relationship between visual examination rating and corrosion rate.

tively accurate when the corrosion was small; however, as the visual examination rating increased, the variability of the corrosion rate increased. A regression model was used to relate these two variables:

$$\text{corrosion rate} = 4.00\, e^{0.36(\text{visual examination rating})} \quad (2)$$

Equation (2) had a coefficient of determination (R^2) of 0.85. The visual examination rating used in this study generally had a strong relationship to the corrosion rate.

Empirical observation

The following summarizes the empirical observations from the investigations completed in 1989 and 1990:

(1) There was little corrosion or little deposition between pH 4.0 and 4.5.
(2) When water was stagnant with DO of about 1–2.5, there was only a black film on the surface of the coupons.
(3) When coupons were installed vertically in the water, brown tubercles appeared on both sides of the coupons. When the tubercles were removed, a black film and the beginning of a pit developed beneath the tubercle.
(4) If the coupon was horizontal on the stream upon subsequent visits, the upper surface was often covered with brown tubercles and the lower surface was often covered with a black film. If the coupon was vertical in the water–sediment interface, the upper portion of the coupon in the water was often covered with tubercles, while the lower portion in the sediment was commonly covered with a black film.
(5) The fouling deposit accumulations at higher alkalinity sites were much less than at lower alkalinity sites.
(6) Pitting was most severe in a culvert pipe in the zone where the water level fluctuated. If the sediment covered the invert of the pipe, the metal surface that was covered by the sediment did not have tubercles but commonly had a black film.
(7) The tubercles dried out during periods of low water. Later, when high water conditions returned, the dried shell of the tubercles was pushed out of the culvert pipe. New tubercles formed at the sites of former tubercles rather than at new sites.

Stepwise regression analysis

The stepwise regression method was used to determine subsets of water-related variables that best describe the visual examination rating or corrosion rate. Note that the water-related variables used in the regression analysis excluded P, K, Zn, Mn, Fe, Cu and Al because many samples were below the detection limit. Also, the water test sites used in the regression analysis excluded two low pH sites and four low DO sites. The information from the few coupons that had shifted from their initial installation position to become partially embedded in the sediment was also not used for data analysis. Furthermore, a log transformation (base 10) was used to adjust the range of the two variables, the amount of SRB and aerobic bacteria, because of the wide range of observations from 15 to 2.4×10^7 (cells/ml) and from 380 to 6.2×10^9 (cfu/ml), respectively. On the other hand, the variables such as alkalinity, TDS, Ca and Mg were highly correlated with each other (i.e. high colinearity). High colinearity can yield large estimated variances and make it difficult to detect the "significant" regression coefficients (Johnson and Wichern, 1988). Since they are highly correlated, each may be placed into a regression model with all the other water-related variables one at a time. This technique yielded four regression models each containing only one of the alkalinity, TDS, Ca or Mg variables. Stepwise regression results from the field study data are summarized in Table 2. All of the water-related variables shown in Table 2 are significant at the 0.05 level.

Results listed in Table 2 show regression equations for the visual examination rating had greater R^2 values than those for corrosion rate. The R^2 values of the visual examination rating and corrosion rate for each regression model were very close. Furthermore, one should note that alkalinity, TDS, Mg or Ca was

Table 2. Stepwise regression results form field data

VE† = 5.681 − 0.012 Alkalinity* + 0.002 TOC	$R^2 = 0.801$
VE = 5.111 − 0.009 TDS + 0.073 DOC + 0.053 Na^+ + 0.008 SO_4^{2-} + 0.080 TKN	$R^2 = 0.732$
VE = 5.479 − 0.062 Ca + 0.046 DOC + 0.010 SO_4^{2-} + 0.090 TKN	$R^2 = 0.802$
VE = 5.389 − 0.010 Mg + 0.033 DOC + 0.007 So_4^{2-} + 0.067 TKN	$R^2 = 0.848$
CR† = 32.625 − 0.074 Alkalinity	$R^2 = 0.604$
CR = 31.282 − 0.069 TDS + 0.101 SO_4^{2-} + 0.463 Na^+ + 0.780 TKN	$R^2 = 0.579$
CR = 28.483 − 0.371 Ca + 0.077 SO_4^{2-} + 0.741 TKN + 0.219 Na^+	$R^2 = 0.604$
CR = 27.386 − 0.581 Mg + 0.051 SO_4^{2-} + 0.702 TKN	$R^2 = 0.618$

All water-related variables with the unit of mg/l, except as noted.
*Alkalinity: mg/l as $CaCO_3$.
†VE, visual examination rating; CR, corrosion rate, mdd.

always included first in the regression equations for visual examination rating and explained around 73% of the variability in the data.

A sensitivity analysis of the regression models was conducted using a forward selection stepwise regression method at the significant level of 0.15 to discern the relative importance of individual parameters. The R^2 value of 0.779 was obtained by including only alkalinity in the model. Further addition of TOC, water resistivity, redox potential, and SO_4^{2-} yielded R^2 values of 0.801, 0.806, 0.811 and 0.817, respectively. It should be noted, however, that the inclusion of more parameters did not always improve the prediction accuracy of the visual examination ratings. Because of this, the stepwise regression analysis at the significance level of 0.05 suggested the inclusion of only alkalinity and TOC as shown in Table 2.

When alkalinity was used as a parameter, TOC was the next important factor affecting the visual examination rating. While when TDS, Ca or Mg was used as a predominant factor, DOC and TKN as substitutes for TOC became the important factors as carbon and nitrogen sources for SBR along with SO_4^{2-}. TDS had the lowest Pearson correlation coefficient with respect to alkalinity compared with Ca and Mg. Because of this, in addition to TDS, Na^+ had to be included in the regression equation to match the effect of alkalinity, Ca, or Mg on MIC. Therefore, Na^+ appeared to be indirectly related to MIC.

The eight Wisconsin DOT districts were grouped to two areas (see Fig. 1). The area covering Wisconsin DOT districts 1, 2, 3 and 4 were described as Southern Wisconsin, while the area covering Wisconsin DOT districts 5, 6, 7 and 8 were described as Northern Wisconsin. A second stepwise regression analysis based on location of each site in Wisconsin DOT district was carried out and results are listed as follows:

For districts 1, 2, 3 and 4

$$\text{corrosion rate (mdd)} = 57.844 - 0.006\ \text{water resistivity (ohm-cm)} - 0.122\ \text{alkalinity (mg/l as } CaCO_3) \quad (3)$$

For districts 5, 6, 7 and 8

$$\text{corrosion rate (mdd)} = -42.736 - 0.122\ \text{alkalinity (mg/l as } CaCO_3) + 2.161\ \text{temperature (°C)} + 1.304\ SO_4^{2-}\ \text{(mg/l)} + 6.365\ \log(\text{SRB}) \quad (4)$$

where SRB is the number of sulfate-reducing bacteria, cells/ml. The equations given above had the R^2 of over 0.77. Equations (3) and (4) suggested that water resistivity and alkalinity were significant in districts 1, 2, 3 and 4. On the other hand, alkalinity, temperature, sulfate concentration and log(SRB) were significant in districts 5, 6, 7 and 8. Again, although only alkalinity appeared in the models among TDS, Ca and Mg, it did not mean that these three variables were not important in corrosion. In fact, they were highly correlated. For districts 5, 6, 7 and 8, sulfate concentration and log(SRB) were essential to corrosion rates, indicating the susceptibility of these districts to MIC. The Pearson correlation coefficient of SO_4^{2-} and log(SRB) was −0.085, implying that there was little colinearity between them; thus, either SO_4^{2-} or log(SRB) alone did not appear to explain MIC entirely.

Discriminant analysis

Discriminant analysis is a process of deriving classification rules from samples of classified objects (observations). Based on these rules, new objects of an unknown class can be allocated to previously defined groups (Johnson and Wichern, 1988). In this study, canonical discriminant analysis in the SYSTAT® statistical package was used to find linear combinations of the quantitative variables that best summarize the difference between the classes. The visual examination rating was used to characterize the process and to classify conditions as "slightly biocorrosive sites", "moderately biocorrosive sites" and "very biocorrosive sites". Three classifications based on visual examination rating were created using the following rules:

visual examination rating ≤ 2	slightly biocorrosive
$2 <$ visual examination rating < 4	moderately biocorrosive
visual examination rating ≥ 4	very biocorrosive

The discriminant coefficients obtained from the canonical discriminant analysis were used to compute the discriminant scores as follows:

$$\text{Factor(1)} = 0.514\ \text{pH} + 0.169\ \text{temperature} - 0.217\ \text{DO} + 0.034\ \text{water resistivity} + 0.118\ \text{redox} - 1.306\ \text{alkalinity} + 0.061\ \text{TOC} + 0.386\ \text{DOC} + 0.200\ \text{TKN} - 0.404\ Cl^- - 0.357\ SO_4^{2-} - 0.072\ \log(\text{aerobic bacteria}) - 0.224\ \log(\text{SRB}) + 0.375\ Na^+ \quad (5)$$

$$\text{Factor(2)} = -0.795\ \text{pH} + 0.367\ \text{temperature} + 0.746\ \text{DO} - 0.258\ \text{water resistivity} + 0.053\ \text{redox} + 0.383\ \text{alkalinity} - 0.039\ \text{TOC} + 0.540\ \text{DOC} + 0.185\ \text{TKN} + 0.463\ Cl^- + 0.100\ SO_4^{2-} - 0.097\ \log(\text{aerobic bacteria}) + 0.805\ \log(\text{SRB}) - 0.295\ Na^+ \quad (6)$$

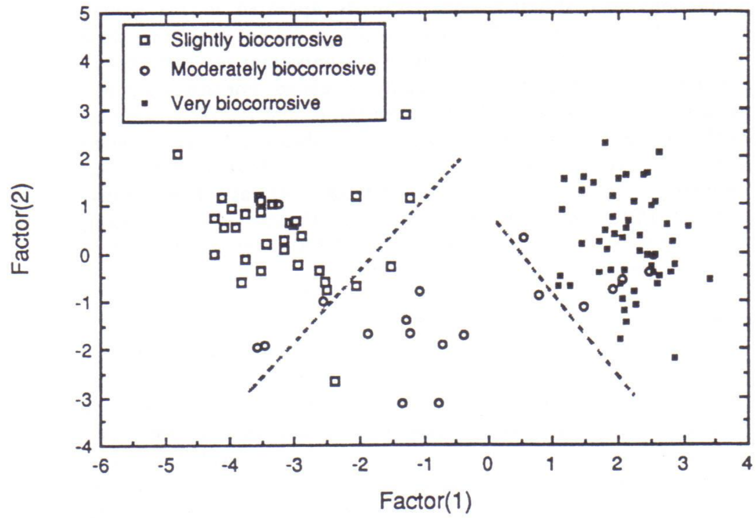

Fig. 3. Plot of discriminant scores for three-group classification (dotted lines express the boundary between groups).

The coefficients in the two equations above were standardized using the within-group standard deviations, so the magnitude across variables having different scales can be compared. Since they are not raw coefficients, there is no need for a constant in the linear combination functions (Wilkinson, 1987).

Factor(1) was dependent largely on pH, alkalinity, DOC, Cl^-, SO_4^{2-} and Na^+. Factor(2) was mainly dependent on pH, temperature, DO, alkalinity, DOC, Cl^- and log(SRB). The canonical correlation coefficient for Factor(1), 0.922, was much larger than the corresponding canonical correlation coefficient for Factor(2), 0.512. This illustrated that Factor(1) had the most discriminatory power between the two discriminant functions. Substituting each set of field data into Factor(1) and Factor(2) as shown in Fig. 3 can be divided into three different groups.

The number of misclassified sites was determined and the misclassification rates are given in Table 3. None of the very biocorrosive sites were misclassified. Nine out of eighteen moderately biocorrosive sites were misclassified. Five moderately biocorrosive sites were wrongly classified as very biocorrosive sites. The misclassification rates for slightly biocorrosive sites, moderately biocorrosive sites, and very biocorrosive sites were 9.4, 50 and 0%, respectively. The misclassification of slightly biocorrosive sites and moderately biocorrosive sites as very corrosive sites may not be a serious problem, since the few unnecessary control adjustments are inexpensive. However, misclassification of very biocorrosive sites can be damaging because the design engineer loses the opportunity to prevent heavy MIC which leads to perforation of the culvert pipes. Fortunately, in this study, the discriminant analysis gave the correct classification of the culvert pipes heavily affected by MIC.

Classification rule

Based on the second stepwise regression analysis results and the discriminant analysis results, a set of classification rules was developed. These practical rules can be used to classify new sites of an unknown biocorrosive class. A flow chart for the decision making procedure of classification rule is shown in Fig. 4. By using this flow chart, design engineers can forecast the biocorrosive tendency of a site and select appropriate control actions. For example, galvanized pipes can be used if the class is predicted to be "slightly biocorrosive", aluminized pipes can be used if the class is predicted to be "moderately biocorrosive", and aluminum or concrete pipes should be used if the class is predicted to be "very biocorrosive". The classification guideline has not been validated using

Table 3. Classification table of discriminant analysis

		(Predicted) Slightly	Moderately	Very	Total
(Observed)	Slightly	29	3	0	32
	Moderately	4	9	5	18
	Very	0	0	53	53
	Total	33	12	58	103

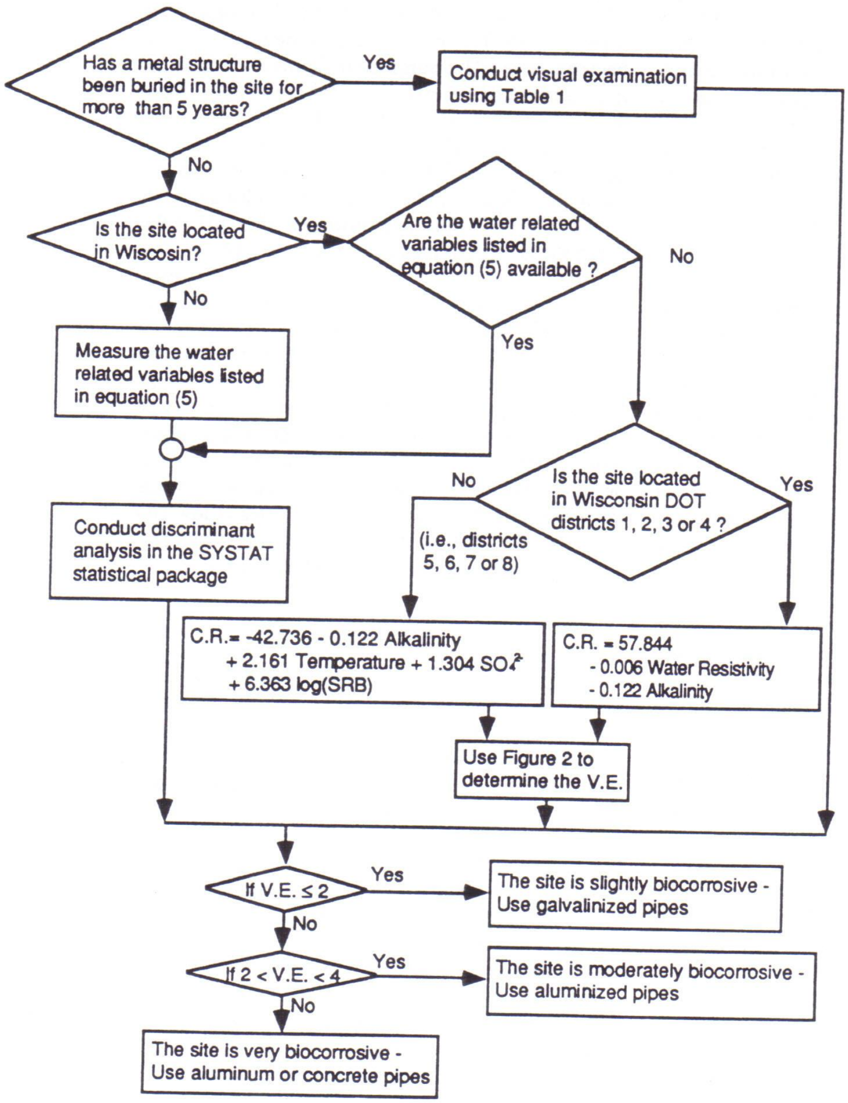

Fig. 4. A flow charge of classification rule.

the data outside Wisconsin; thus, the guideline should be used at the user's discretion.

IMPLICATIONS

Effect of $CaCO_3$ precipitation

Field survey results showed that water sites with higher alkalinity, TDS, Ca and Mg always had a lower visual examination rating and corrosion rate. Stepwise regression analysis also showed that alkalinity, TDS, Ca and Mg were the most important variables explaining the variability of the visual examination rating and corrosion rate. The implication of this result is important because this may suggest that these water quality factors can directly or indirectly influence biocorrosion. In an aqueous environment, microorganisms will affect the surface chemistry of a metal if there are no inhibitors. Alkalinity, TDS, Ca and Mg are directly related to the $CaCO_3$ precipitation which may act as an inhibitor to MIC. Field observations of this research found that the biofouling deposit accumulations at the southern sites were much fewer than those at the northern sites. This illustrates that the $CaCO_3$ film coated on metal may prevent corrosion and biofouling deposit accumulations which directly results in a reduction of the MIC. To date, the interactions between the biofouling deposit and the $CaCO_3$ precipitation are poorly understood. A further experiment has been conducted to investigate the effect of $CaCO_3$ precipitation on MIC (Peng, 1992). The result confirmed that the $CaCO_3$ precipitation played a significant role in influencing the biocorrosion tendency of steel under both aerobic and anaerobic conditions.

Effect of sulfate concentration

SRB are probably the most important anaerobic bacteria influencing microbial corrosion. Under reducing conditions, these bacteria may successfully change sulfate to sulfide. At this point, the sulfide reacts with the ferrous ions produced at the anode to form the black ferrous sulfide. This indicates that higher sulfate concentrations may enhance the corrosion rate. Initially, field results apparently did not support this. The concentrations of sulfate at the southern sites were obviously higher than at the northern sites; conversely, corrosion rates at the southern sites were generally lower than at the northern sites. However, referring to equation (4), sulfate concentration and log(SRB) were essential to corrosion rates at Northern Wisconsin. This suggests that the effect of sulfate on MIC is significant only at lower alkalinity, TDS, Ca and Mg sites. Even though sulfate concentrations were higher in southern Wisconsin, without a suitable environment for biofilm accumulations on metal surface the corrosion rate was still quite low.

Effect of low pH and dissolved oxygen

During the field surveys, it was observed that little corrosion or deposition occurred at pH between 4.0 and 4.8. When water was stagnant with DO < 2.5 mg/l, there was only a black film on the surface of the coupons. Field results of those two low pH sites and four low DO sites are summarized in Table 4. It is evident that corrosion rates of those sites were very low.

At a pH of 4 or more, the principal cathodic reaction of corrosion is the reduction of oxygen (J. M. Montgomery Consulting Engineers, 1985). For these two low pH sites, their pH values ranged from 4 to 5 and their DO concentrations were higher than 4.5 mg/l. However, their corrosion rates were lower than 7.5 mdd. This may be due to the fact that most bacteria have pH optima near neutrality and minimum and maximum pH values for growth near 5 and 9, respectively. MIC, notably by SRB, usually occurs in an abundance of sulfate aqueous environment at pH between 5.5 and 8.5. Compared to other sites, the numbers of SRB at these two sites were also quite low (<930 cells/ml). This demonstrated that pH influenced the growth of microorganisms of these two low pH sites, resulting in the reduction of the corrosion rates. Field survey results showed corrosion rates at the low DO sites were all below 5 mdd. DO is one of the most important factors influencing the corrosion rate of steel because it is a direct participant in the corrosion reaction. Therefore, corrosion rates may be reduced with lower levels of DO in the bulk solution. Also, in the absence of DO conditions, the SRB becomes the most important microorganism in the microbial corrosion. Low corrosion rates at low DO sites may be due to the fact that the anaerobic corrosion rate caused by SRB is relatively low.

CONCLUSIONS

More than 20 water-related parameters were measured at over 40 sites in Wisconsin to determine the corrosion rate and the dominant parameters affecting MIC. The overall corrosion rate was found to be strongly correlated with a visual examination rating developed herein which allows the evaluation of MIC. Empirical relationships were developed by the stepwise regression and discriminant analyses. Based on these results, a set of classification rules was developed. Design engineers could use these rules to forecast the biocorrosion tendency of a site and select appropriate control actions.

Biodeterioration at the southern sites (high alkalinity; high $CaCO_3$ deposit) was found to be much less than at the northern sites (low alkalinity; low $CaCO_3$ deposit), implying that $CaCO_3$ precipitation played a significant role in influencing the microbial corrosion tendency. The effects of sulfate concentration and bacteria on biocorrosion were significant only for a freshwater undersaturated with $CaCO_3$. Low pH (<4.8) resulted in low corrosion rates. At low DO (<2.5 mg/l), the corrosion appeared to be controlled

Table 4. Field results of those low pH sites and low DO sites

	Low pH sites			Low DO sites		
Site No.	11	13	6	21	42	45
pH	4.5	4.4	6.7	7.2	7.3	6.6
Temperature (°C)	16.0	13.5	22.0	22.0	24.0	17.0
DO (mg/l)	6.4	4.8	1.5	2.2	1.5	1.5
Alkalinity	1.7	0	37.9	57.9	97.4	41.4
Redox (mV)	515	545	370	260	420	440
TDS (mg/l)	196	151	132	106	212	124
TOC (mg/l)	44.3	44.5	23.3	8.8	45.1	13.5
SO_4^{2-} (mg/l)	2.1	2.8	13.1	3.4	5.5	3.3
VE	1	1	6	4	4	6
CR (mdd)	7.06, 8.37	4.85, 5.36	0.46, 0.54	3.34, 4.95	1.11, 1.62	1.10, 1.26

by SRB, which led to low corrosion rates at the initial stages of corrosion.

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