

INVESTIGATION OF THE PITTING CORROSION OF LOW CARBON STEEL CONTAINERS*

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ABSTRACT

The present study was undertaken because the prediction of the degradation rate of low carbon steel containers over long time frames is one of the crucial elements in the development of a source term model for low-level shallow land burial. The principal data base considered is that of the NBS corrosion measurements of ferrous materials buried in the ground for periods of up to 18 years. In this investigation, the maximum penetration in mils, h_m , due to pitting corrosion was found to conform closely to the relation $h_m = kt^n$ where t is the exposure time of the sample in years, k is the pitting parameter in mils/(years)ⁿ, and $n > 0$ is a parameter related to the aeration property of the soil. The central objective of the present investigation is the determination of the dependence of the pitting parameters k and n on the soil properties. The result of a detailed linear correlation analysis of k on one hand, and the pH value and the resistivity of the soil on the other hand revealed that k is principally influenced by the pH value of the soil. The resistivity of the soil is found to play a minor role. Based on a linear regression analysis, the following two relationships were derived:

$$k_a = 5.74(9.9 - \text{pH}) \text{ and } k_b = 5.05(2\text{pH} - 10.3)$$

for acidic and alkaline soils, respectively. The two linear relationships intersect at a point specified by $\text{pH} = 6.9$ and $k = 17.3$.

INTRODUCTION

Because of low cost due to easy fabricability and relative durability, carbon steel containers are being considered as one of the alternatives for nuclear waste packages. However, such containers are susceptible to general as well as localized corrosion in natural environments. The prediction of the degradation rate of carbon steel containers over long time frames (hundreds of years) is a crucial element in the development of a source term model. As a first approximation, localized corrosion as represented by pitting corrosion will be assumed to be the major degradation mechanism for carbon steel containers. The central points which need to be addressed for pitting corrosion are the following:

- a) kinetics of pit growth in terms of depth and radius,
- b) the distribution of pit depths,
- c) the number of pits/cm² as a function of time, and
- d) physical corrosion constants for application in mechanistic modeling. In the present study, the focus of attention is placed on metallic corrosion in a soil environment with emphasis on the development of a rela-

tion between maximum pit depth and exposure time with physical parameters applicable to specific soils.

The extensive and detailed metallic-corrosion investigations of the National Bureau of Standards (NBS) (1) provide a primary source data base to answer some of these questions directly. Furthermore, other sources of information obtained from corrosion measurements carried out under more controlled conditions in the laboratory were surveyed in order to supplement the information derived from the field.

LOCALIZED CORROSION DATA PIT GROWTH KINETICS

One of the main objectives of the present study is the determination of the physical parameters which are required in the present modeling effort (2). This is achieved by carrying out a correlation analysis between the rate constants for pit growth and other variables such as the resistivities, the pH values, the porosity, and the moisture and clay contents of the various soils. A new finding of this study is the strong dependence of the pitting rate constant on pH value signifying that localized corrosion is most probably ohmic-driven. In addition, the n value is parameterized in terms of the clay and moisture contents of the soils. The extensive soil corrosion investigations for ferrous and

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nonferrous materials buried in the ground for periods up to 18 years provides a rare and valuable source of degradation data (1) for study and analysis. The ferrous pipes have been exposed to 125 representative soils, characterized by a wide range of resistivities (64-45,000 ohm-cm), pH values (3.1-9.8), moisture contents (2.8-58%), air-pore spaces (1.1-57.8%), clay contents (0.6-87.8%), drainage, and aeration properties. The soils, classified (1) according to aeration, are designated as: good (G), fair (F), poor (P), and very poor (VP).

A measure of the susceptibility of a metal to pitting is the rate of pit penetration. The maximum pit depths of corroded samples were determined (1) as a function of time.

$$h_m = kT^n \quad (1)$$

where, h_m = maximum penetration of the pit expressed in mils and averaged over two samples, T = exposure time of the sample in years, and k = pitting parameter for maximum pits in mils/year ^{n} .

To investigate the systematics of the parameters k and n and their dependence on soil properties, the various k values along with the pertinent soil properties are compiled and stored on a computer disk for easy accessibility and quantitative manipulations

Parameterization of the n Value

A weighted average performed in the present study of the individual n values determined in Ref. 1 gives the following values for the time exponent, n ; 0.26 ± 0.03 , 0.39 ± 0.03 , 0.44 ± 0.04 , and 0.59 ± 0.10 for good, fair, poor, and very poorly soils, respectively.

Since there is a wide variation in the n values in each soil population an attempt to parametrize the n value in terms of soil physical properties is made. At first sight, the average n values appear to be strongly correlated with the average moisture for the various soil groups. One preliminary parametrization is:

$$n = n_0 MC(1.00 - CL)^{0.4} \quad (2)$$

where MC is the fraction of Moisture Content, CL is the fraction of Clay Content, and $n_0 = 1, 1.5, 2, 2.5$ for G, F, P, and VP soils.

To compare with the Harwell measurements (3), the k and n values are averaged over all soils to give the following result:

$$h_m = 29T^{0.39} \text{ mils} \quad (3)$$

This empirical relation predicts a maximum pit depth of 1.1 cm to develop over a period of 1000 years. It is emphasized that these results are applicable only to samples of surface area 0.4 ft^2 . Procedures for the extrapolation of the present result to samples of significantly different sizes such

as, for example, those of 55 gallon drums have been discussed previously (1,3).

Dependence of k on pH and Resistivity of the Soil

The possible dependence of k and n on the various soil properties (pH, resistivity, porosity, moisture content, chloride and sulfate ion concentrations, etc.) can be disentangled in principle by a multivariate analysis. However, a more revealing and simpler approach, which is followed in the present study, is the calculation of the linear correlation coefficient of two variables x and y , defined by:

$$\rho(x,y) = \frac{\sum_i (x_i - \bar{x})(y_i - \bar{y})}{(\sum_i (x_i - \bar{x})^2 \sum_i (y_i - \bar{y})^2)^{1/2}} \quad (4)$$

where \bar{x} and \bar{y} are the mean values.

In the present study, the dependence of k on two variables, the pH value and the resistivity of the soil, R , is considered. The results of the present correlation analysis applied to the four populations of k values (classified by the aeration of the soil) are summarized in Table I. Included in this table are both the k range and the average value of k . The correlation coefficients of k and soil conductivity, σ , are given in the column headed $\rho(k,\sigma)$ and for k and pH in the column headed $\rho(k,\text{pH})$. As described by the fifth column, a weak and insignificant correlation between k and the conductivity is found. However, one possible interesting result is that the present correlation coefficients are all positive and seem to follow a trend of increasing magnitude with decreasing aeration of the soil.

In contrast, the dependence of k on the pH value, presented in the last column exhibits the following features. For the poor-aerated soils, complete negative correlation exists. The 95% confidence interval for this statistical sample size computed by the method of a Fischer transformation is (-0.94-1.0). The other soil types did not reveal any apparent significant dependence on the pH value. A linear regression analysis of k and pH values for VP soils yielded the following equation (when expressed in terms of one multiple of the pH value).

$$k_a = 5.74 (9.87 - \text{pH}) \quad (5)$$

for pH values in the range of 3.1-6.8.

Such a relationship is similar to the Flade potential, E_f , for iron (4), which is the potential above which pitting takes place: $E_F = 0.058(10 - \text{pH})$.

A close examination of the alkaline soils indicated that the dependence of k on pH follows a different pattern. The correlation of k and pH for the population of alkaline soils ($\text{pH} > 7.5$) yielded a positive correlation coefficient:

TABLE I

Statistical Properties of the Reaction Parameters of Localized Corrosion.

Soil Type	Statistical Sample Size	k range	\bar{k}	$\rho(k, \sigma)^a$	$\rho(k, \text{pH})$
a) <u>NBS classification:</u>					
Good aeration	15	17.5-60.7	37.1±14.7	+0.189	+0.139
Fair aeration	11	19.1-51.4	34.0±10.1	+0.127	-0.04
Poor aeration	17	11.8-37.8	20.4±6.8	+0.30	+0.125
Very poor aeration (3.1 < pH < 6.8)	4	18.5-38.0	26.7±9.4	+0.653	-0.994
b) <u>Specialized cases:</u>					
pH > 7.5	7	11.8-47.2	32.9±12.9	+0.509 +0.413 ^b	+0.801
Fair Aeration (3.8 < pH < 6.2)	7	19.1-51.4	35.1±13.3		-0.664

a) σ is the soil conductivity.
b) This value represents $\rho(kR^{0.5}, \text{pH})$ where R is the soil resistivity

$$\rho(k, \text{pH}) = +0.801 \text{ (99.4\% confidence level)}$$

A linear regression analysis for these alkaline soils yielded:

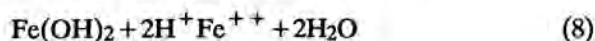
$$k_b = 5.05(2 \text{ pH} - 10.3) \quad (6)$$

for pH values in the range 7.5-9.7.

The term in parentheses of Eq. 6 appears to correspond to the negative value of the expression:

$$\log [\text{Fe}^{++}] = 10.23 - 2 \text{ pH} \quad (7)$$

This relation between Fe^{++} ion concentration and pH is derived (5) on the basis of the law of mass-action applied to the reaction at equilibrium



which is applicable in the same pH range as that of Eq. 6.

A summary of the results of the present analysis is illustrated in Figs. 1-2 for the acidic and alkaline soils. The variation of $\rho(kR^n, \text{pH})$ as a function of n is shown at the top of Figs. 1-2, while at the bottom the pH dependence of k is depicted. The correlation coefficient ρ is maximized for n values close to zero indicating the insignificant played by the resistivity of the soil.

The present findings embodied in Eqs. 5-6 reveal the source of lack of observation of a significant correlation between k and pH for all except the very poor-aerated soils. The data shows that five out of eleven of the good-aeration soils are characterized by pH values in the range 6.8-7.3, where changes in pH have a minor influence on k, while two others have pH values equal to or larger than 9.5. The latter soils give a positive canceling contribution to $\rho(k, \text{pH})$.

Similarly, the fair aerated soils contain three cases with pH values in the range 6.8-7.3 and an additional one with pH = 9.4. If soils having a pH in the range of 6.8-7.3 are excluded in a correlation analysis, a value $\rho(k, \text{pH}) = -0.664$ (98.4% confidence level) is derived for this subset of soils. A linear regression analysis gives:

$$k_a = 6.75(10.23 - \text{pH}) \quad (9)$$

for the fair aerated soils with pH values in the range 3.8-6.6.

Finally, the population of poorly aerated soils is characterized predominantly by pH values in the region where k is insensitive to changes in pH. Such a situation renders the observation of a significant correlation between k and pH difficult, if not impossible.

A summary of the present findings for the pitting parameter k as a function of soil pH is described in Fig. 3. The two straight lines labelled by k_a and k_b for acidic and alkaline soils, respectively, exhibit a different pH dependence and join at an intersection point specified by pH = 6.85

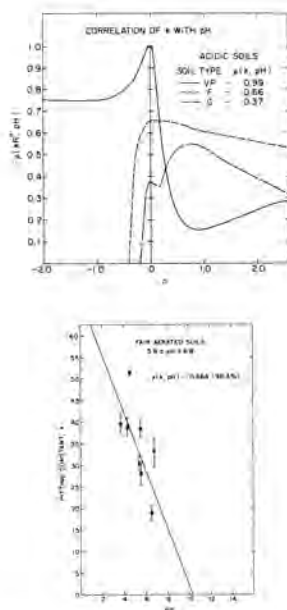


Fig. 1 Correlation and Regression Analysis for the Acidic Soils of the NBS Data. At the Top is Shown the Variation of $-\rho(kR^n, pH)$ as a function of the n Value. The Bottom Figure Represents the k Dependence on the pH Value.

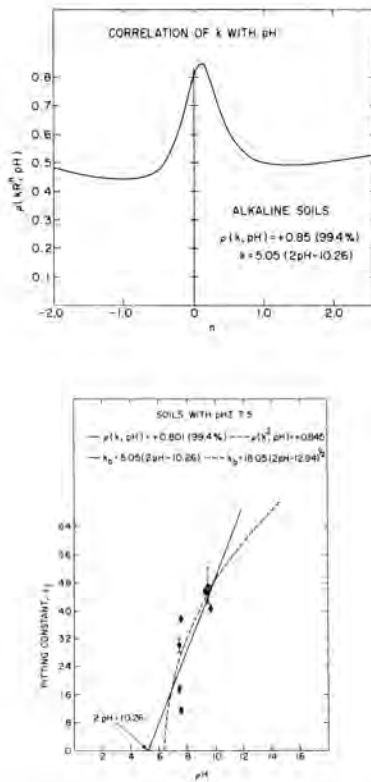


Fig. 2. Correlation and Regression Analysis for the Alkaline Soils of the NBS Data. At the Top is Shown the Variation of $+\rho(kR^n, pH)$ as a Function of the n Value. The Bottom Figure Illustrates Two Possible Relations Representing the Dependence of k on pH.

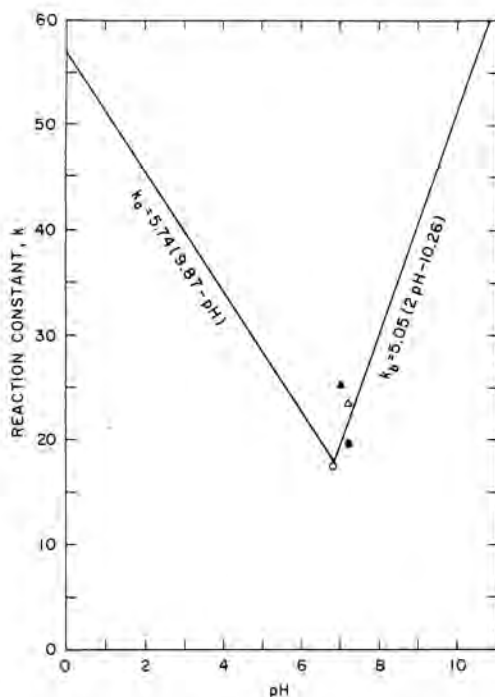


Fig. 3. Summary of the Dependence of k on the pH Value of the Soil for the Acidic and Alkaline Soils. See the Text for Details.

and $k = 17.3$. To compare with the present predictions, the average k values for soils in the range 6.8-7.3 are also included. As shown, in Fig. 3, the agreement between measurements and predictions is reasonably good to give further support to the present parameterization.

COMPARISON WITH HARWELL MEASUREMENTS

It is of particular interest to carry out a comparison of the NBS data (1) with more recent measurements such as those of the Harwell investigations of the growth kinetics of maximum pit depth, pit depth distribution, and uniform (general) corrosion rates (3). Long term immersion tests of low carbon steel cylinders (8 cm² exposed surface area) in 0. M NaHCO₃ (pH 8.4) containing 1000 ppm Cl⁻ at 90°C were conducted at 0 and -200 volts applied potential. Pit depths and the number of pits/cm² were determined by the incremental grinding and counting technique. The observed maximum pit depths for the 0 and -200 V measurements were fit by a single relation:

$$h_m = 3.11 T^{0.44} \quad (10)$$

where T is in years and h_m is in mm,

To take into account the size of actual nuclear waste containers (3.8 m²), the individual measured pit depths were adjusted by the application of extreme value statistics. The correction factors for the maximum pit depths were

found to be in the range of 2.6-3.7 (3). On the other hand, the linear logarithm prescription (6) gave a factor of 3.7. An expression for the area-corrected data thus becomes:

$$h_m = 8.35 T^{0.46} \quad (11)$$

It is noteworthy to point out that this result is approximately one order of magnitude larger than that of the NBS study after taking into consideration the area effect and the pH influence (Eq. 6). The source of the discrepancy can be attributed to temperature effects and possible time-dependent corrosion rates. The average temperature of the NBS sites is about 20°C while that of the Harwell (3) study is 90°C. A temperature change from 20°C to 90°C results in about a threefold increase in the pitting corrosion rate according to the results of Tait (7).

The observed pit size distribution conducted in the Harwell studies for a period of 10,000 hours appears to consist of two components: a main one which can be described by an approximate exponential function, and a minor one whose maximum is located at larger pit depths and which resembles half a bell-shaped curve merging with the main component. This is somewhat similar to the results of the pit size distribution studies of Aziz (6). This information is required in the estimation of the corroded area for a specified time (8).

SUMMARY

A model has been developed to predict the maximum pit depth on carbon steel containers in soil environments.

In this model, the pit depth, h_m , is expressed by the relation $h_m = kt^n$ where k is the pitting parameter, mils/yearsⁿ, t is the exposure time in years, and the exponent n is related to the degree of aeration of the soil.

Using the NBS data on corrosion in soils a linear regression analysis was performed to determine the pitting parameter, k , as a function of pH and soil resistivity. The results of this analysis shows that k is principally influenced by the pH. Resistivity was found to be relatively unimportant. From this linear regression analysis, the following two relationships were derived:

$$k_a = 5.74(9.9 - \text{pH}) \text{ and } k_b = 5.05(2\text{pH} - 10.3)$$

for acidic and alkaline soils, respectively.

The value of the exponent n as a function of aeration was also determined with the following results: $n = 0.26$; 0.39 ; 0.44 ; and 0.59 for good, fair, poor, and very poorly aerated soils, respectively. Within the data there were significant variations in the exponent n for the same degree of aeration. To account for these variations, a linear regression analysis was performed to determine the relationship between n and the soil moisture content, MC , and the clay fraction of the soil, CL . The results of this analysis lead to the following expression for n :

$$n = n_0 MC(1 - CL)^{0.4}$$

where $n_0 = 1, 1.5, 2, 2.5$ for good, fair, poor, and very poorly aerated soils, respectively.

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