

# **The Use of Synthetic Environments for Corrosion Testing**

Francis/Lee, editors

STP 970 

# *The Use of Synthetic Environments for Corrosion Testing*

*P. E. Francis and T. S. Lee, editors*



Special Technical Publication (STP) 970

1916 Race Street, Philadelphia, PA 19103

ASTM Publication Code Number (PCN) 04-970000-27  
ISBN 0-8031-0977-6

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The quality of the papers in this publication reflects not only the obvious efforts of the authors and the technical editor(s), but also the work of these peer reviewers. The ASTM Committee on Publications acknowledges with appreciation their dedication and contribution of time and effort on behalf of ASTM.

## Foreword

The symposium on the Use of Synthetic Environments for Corrosion Testing was presented at the National Physical Laboratory, Teddington, Middlesex, England on 10-12 Feb. 1986. The symposium was sponsored by ASTM Committee G-1 on Corrosion, Deterioration, and Degradation of Materials and the National Physical Laboratory. P. E. Francis, National Physical Laboratory, and T. S. Lee, National Association of Corrosion Engineers, served as chairmen of the symposium and are editors of the resulting publication.

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# Introduction

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The most reliable indication of the corrosion performance of a material is its service history. However, there are many occasions when this is not available or it may be necessary to ascertain the influence of minor changes in the specification of a material or in the composition of the environment on the material's corrosion performance. The use of field trials can provide useful information, but such tests require a reasonable exposure time, and the experimental variables may not be precisely controllable, so that some speculation may be necessary on the interpretation of the outcome of the trials.

In most cases laboratory test methods can provide valuable information on the probable service performance and the influence of deviations from normal operating conditions. Furthermore, laboratory tests will allow a ranking of materials and enable the engineer to make a sensible selection of materials for service in a particular environment.

To avoid misleading results, standard procedures are increasingly used to specify the corrosion performance of metallic engineering materials. Many of these procedures rely on simulated natural environments and the specification of these synthetic environments is probably the most critical aspect of corrosion performance testing. In some instances the synthetic environment is chosen so that the corrosion process is accelerated. Other synthetic environments are formulated to simulate the natural environment as closely as possible, and sometimes a synthetic environment is only used because the natural environment is not readily accessible, for example, corrosion tests in body fluids and in seawater when natural seawater is not readily available.

The need for careful assessment of the effectiveness of the chemical composition of the synthetic environment in providing meaningful data is obvious. Some synthetic environments are specific to one industrial application, for example, steel in concrete, while others may relate to a range of industrial applications, for example, tests for stress corrosion cracking of metallic materials. Thus ASTM Committee G-1 on Corrosion, Deterioration, and Degradation of Materials in the United States jointly with the National Physical Laboratory in the UK sponsored a conference on the use of synthetic environments for corrosion testing that took place at the National Physical Laboratory. The aim of the conference was to provide a forum for an exchange of information on the effectiveness of synthetic environments in providing a prediction of long-term material performance.

The papers from this conference form the basis of this special technical publication (STP). They cover environments for tests relating to atmospheric corrosion, the food industry, body fluids, microbial corrosion, environmental fracture, potable waters, seawater, steel in concrete, flue gases, and so forth. The synthetic environments have been incorporated in test procedures involving exposure tests, electrochemical tests, erosion corrosion tests, and fracture tests.

Thus the 22 papers included in this STP provide the reader, with a very wide range of experience in the formulation and testing of synthetic environments and will familiarize them with the limitations and advantages associated with synthetic environments. For the reader unfamiliar to a particular application this STP will provide an excellent starting point.

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## Corrosion Studies in Complex Environments

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**REFERENCE:** Koch, G. H., Spangler, J. M., and Thompson, N. G., "Corrosion Studies in Complex Environments," *The Use of Synthetic Environments for Corrosion Testing*, ASTM STP 970, P. E. Francis and T. S. Lee, Eds., American Society for Testing and Materials, Philadelphia, 1988, pp. 3-17.

**ABSTRACT:** Corrosion studies have typically been performed in relatively simple environments where variations in corrosion behavior are determined as functions of one variable at a time. However, the desire to more closely simulate actual service environments requires more complex test environments. To study the effects of environmental variables on the corrosion behavior of materials, a statistical approach is highly desirable. In this paper, a sequential experimental design approach for complex experimental environments will be described. Examples are given where this approach is used to study the effect of solution variables in complex environments on the electrochemical parameters for different alloys.

**KEY WORDS:** corrosion studies, experimental design, complex environments, screening experiments, main effects, interactions, regression analysis

Synthetic environments which have been used to simulate actual service environments in laboratory corrosion studies are usually relatively simple. An example is the 3.5% aqueous sodium chloride (NaCl) solution, which for years served to simulate seawater. In the last decade, researchers realized that actual environments are far more complex and that several of the trace elements present in actual environments can have considerable effects on the corrosion performance of materials. Complex laboratory environments are being used more frequently to simulate actual service conditions. However, in these complex environments, the effect on the corrosion performance of materials of changing one variable at a time is typically studied. This methodology not only may result in large numbers of corrosion experiments, but also, the observed effect may be due to synergistic effects between other constituents in the test environments, which go undetected.

In this paper, a methodology is developed to handle the effects of a large number of variables on the corrosion behavior of materials and to better simulate fluctuations of chemical species within these complex environments. By using an experimental design, a mathematical expression can be developed that relates a dependent variable or response, such as corrosion rate, to a number of independent solution variables or factors, such as species concentration, temperature, and pH. These expressions generally include main effect terms (linear), interactions (cross products), and quadratic terms. Higher-order terms, such as cubic and three-way interactions, could also be evaluated depending on their significance or prior physical evidence for their existence.

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## 4 USE OF SYNTHETIC ENVIRONMENTS FOR CORROSION

In this paper, a sequential and cost-effective approach for developing expressions that describe the corrosion behavior of materials in complex environments will be developed. Following a general outline of this experimental approach, some examples will be presented where experimental designs have been used successfully to describe corrosion of alloys in complex laboratory environments which closely simulated actual field environments.

### Experimental Design

#### *Screening Experiments*

During the initial investigation of a complex environment, it is likely that a large number of variables could have a significant effect on the corrosion performance of a material. With the aid of fractional factorial designs, it is possible to simultaneously evaluate a large number of variables with relatively few experiments. Subsequent regression analyses will then provide good estimates of the significance of each environmental variable for each measured corrosion parameter.

Initial screening can be performed by using a two-level saturated fractional factorial design of resolution III where  $k$  variables are evaluated in  $k + 1$  experiments [1,2]. For example, up to 15 variables may be evaluated with 16 experiments or up to 31 variables with 32 experiments. An example of a screening test is shown in Table 1 where 15 solution variables are tested in 16 experiments. The  $-$  and  $+$  symbols in the figure refer to low and high values of the various solution variables, e.g., species concentration in the test solution, or temperature. At least four midpoints with average values of the variables should be selected to provide an estimate of experimental error.

The resolution III design provides estimates of main effect terms influenced by one another. However, two variable (and higher) interactions are linked with the main effect terms. Therefore, a significant main effect cannot be differentiated from certain significant two variable interactions. Recent experience with complex chemical environments has confirmed the presence of numerous two-factor interactions. With large systems, the possible number of two-factor interactions increases rapidly. For example, with 15 solution variables (factors) there are 105 possible two-factor interactions; perhaps ten or more of these may be significant. If these interaction effects are confounded with main effects, then it is possible that nonsignificant variables will be carried to the next experimental design phase. The additional variables will result in artificially large designs for the next phase with a substantial increase in the number of required experiments.

To estimate the main effects of solution variables free and clear of other main effects and any interactions, a design of resolution IV is recommended (see Table 1). These resolution IV designs require approximately twice the number of experiments as a saturated (resolution III) design, but provide clear estimates of each of the variables and estimates of blocks of interactions between two variables. However, with a resolution IV design, three- and higher factor interactions are confounding the main effect terms. The higher-order interaction terms are generally small compared with main effects and two-factor interactions, so that a good estimate of the main effects can generally be obtained.

The screening approach described above can utilize any of various fractional factorial designs as taught by Box and Hunter [1,2], and numerous other authors [3-6]. These designs are useful in a variety of experimental environments and are a first choice. However, several limitations may reduce their usefulness under certain conditions. Two such conditions are given below:

- (1) Certain combinations of test variables or factor combinations are impossible to achieve. For example, at pH 7 or above, it is generally impossible to achieve high levels of Fe in solution. These constraints do not necessarily reduce the need to evaluate each variable over the intended range, but only to avoid specific combinations of variables.

TABLE 1—Partial factorial design used for the screening experiments.

Variable	Al	Ca	Cr	Cu	Fe	Mo	N	P	Si	Br	I	H <sub>2</sub> S	O <sub>2</sub>	SO <sub>2</sub>	pH
DESIGN OF RESOLUTION III															
1	-	-	+	+	+	+	+	+	-	-	+	+	-	+	-
2	-	+	+	-	+	-	-	-	-	+	+	-	+	-	-
3	+	-	-	-	+	+	+	+	-	+	-	+	+	-	-
4	+	+	+	-	-	-	-	-	+	-	-	+	+	+	-
5	-	-	+	-	-	+	-	+	+	+	+	-	+	-	-
6	-	+	+	-	-	-	+	-	+	-	-	+	+	+	-
7	+	-	-	+	-	+	+	+	-	+	-	+	-	-	-
8	+	+	-	+	-	+	-	-	-	-	+	+	+	-	-
9	-	-	-	+	-	+	-	+	-	+	-	+	-	-	+
10	-	+	-	+	-	-	+	-	-	+	+	-	-	+	+
11	+	-	+	-	-	-	-	+	-	+	+	-	-	-	+
12	+	+	-	-	+	-	+	-	+	+	+	-	-	-	+
13	-	-	+	-	+	-	-	+	+	-	-	+	-	-	+
14	-	+	-	+	+	+	-	+	+	-	+	+	+	-	+
15	+	-	+	+	+	-	+	-	+	+	+	-	+	-	+
16	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
FOLD OVER DESIGN TO PRODUCE A RESOLUTION IV DESIGN															
1	+	+	-	-	-	-	-	-	+	+	+	+	+	+	+
2	+	-	-	+	-	+	+	+	+	-	-	-	-	-	+
3	-	+	+	+	-	+	-	-	+	+	+	+	+	+	+
4	-	-	+	+	+	+	+	+	+	+	+	+	+	+	+
5	-	+	-	+	+	-	-	-	-	-	-	-	-	-	+
6	+	-	-	+	+	+	+	+	+	+	+	+	+	+	+
7	+	+	+	-	+	-	-	-	-	-	-	-	-	-	+
8	-	+	+	+	+	+	+	+	+	+	+	+	+	+	+
9	+	-	+	+	+	+	+	+	+	+	+	+	+	+	+
10	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
11	-	+	+	+	+	+	+	+	+	+	+	+	+	+	+
12	-	+	+	+	+	+	+	+	+	+	+	+	+	+	+
13	-	+	+	+	+	+	+	+	+	+	+	+	+	+	+
14	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
15	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
16	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

(2) A significant quantity of previously generated hard data exists for the particular response, e.g., corrosion rate, and test variables. but the previous experimental plan does not fit the requirement of the proposed new design. In this case, it may be desirable to retain the original database and to build a new design around the previous work. This could provide a full evaluation of each of the proposed variables with significantly fewer additional experiments.

If either or both of the above conditions exists, then a customized screening design could be developed with the aid of an advanced computer algorithm. Recent work with such a computer program has shown that high quality designs can be produced by augmenting previous work while avoiding impossible factor combinations [7]. The computer algorithm used in this program is called COED® (Computer Optimized Experimental Design).<sup>4</sup> The COED program is an interactive computer program that selects an optimal subset of experiments to be carried out from the total number of possible experiments. The selection process is based on determinant optimality theory; that is, it determines the experiments which minimize the integrated error of prediction over all experimental design points. COED can be used to generate an entire experimental design or to augment an existing experimental design.

At the completion of the experiments based on the screening designs, the test variables are analyzed with respect to the corrosion parameters studied. The purpose of the analysis is

- (1) to determine which variables have a significant effect on a corrosion parameter of a particular material at a given probability;
- (2) to establish the magnitude and direction of the effect; and if possible, and
- (3) to determine the significance of groups of two-factor interactions.

Statistical analytical tools include forward regression with extended analysis of variance. Typically, the statistical package calculates two useful statistics for each of the corrosion parameters, the  $F$  ratio and the adjusted  $R^2$  [8,10]. The  $F$  ratio is the ratio of two variances; i.e., the sum of squares explained by each factor when entered in the equation, divided by the residual mean square (error). In general, when the calculated  $F$  ratio for a variable is large, it indicates that a large amount of experimental variation is explained by this term compared to the error variation. If a calculated  $F$  ratio exceeds the appropriate tabulated  $F$  statistic, then it can be assumed that the solution variable has a statistically significant effect on a particular corrosion parameter. A 90% probability that a test solution variable is significant is usually acceptable for most experimental work, and implies that a 10% probability of being wrong can be accepted in assuming that the variable has a significant effect.

The adjusted  $R^2$  values indicates the percentage of the observed variation for the corrosion parameters that can be explained by the solution variables. An adjustment is made for the number of experiments and the number of parameters estimated in the regression.

### *Interactions and Higher Order Terms*

Once the main effects of solution variables on the corrosion behavior of a material are determined, an additional level of experimental design can be applied to examine interactions between two variables and higher order effects. At this design level, the following information is needed:

- (1) a list of environmental variables that are known by screening tests to have a significant effect on the corrosion performance of materials,
- (2) the maximum and minimum levels for each variable included,
- (3) a list of interactions between two variables that are suspected to affect the corrosion behavior,

<sup>4</sup>COED is a registered trademark of B. F. Goodrich Co.

- (4) any combination between variables that must be avoided (constraints), and
- (5) prior data that can be incorporated in the design.

With the above information available, the most cost effective approach can be developed for individual cases. A simple case would involve an environment with only a few (three or four) significant variables, no constraints, and no additional considerations. For this case, a Box-Behnken design [8] of 15 or 27 experiments would provide all the information needed to support a full quadratic equation for the three or four variables.

However, the following complexities may be encountered and require a more involved design:

- (1) A large number of variables (greater than 10) has been identified as significant.
- (2) There are several interactions between solution variables that are suspected to have significant effects of the corrosion behavior.
- (3) There are several constraints.
- (4) It would be desirable to use data from previous experimental programs.
- (5) Data are available from previous screening experiments.

An experimental design either for such a complex environment or to complement existing data, can be created using a sequential approach and an appropriate computer aided design program, such as COED. During the first iteration, a design can be developed to estimate main effect and interaction terms. This can be achieved by the computer program by augmenting the screening design and other forced design points while avoiding constraints. The number of additional experiments designed by the algorithm will be determined by the balance of the forced-in experiments, the complexity introduced by constraints, and the number of new terms that are to be estimated by the design.

After the additional experiments required by the experimental design have been performed, the results are analyzed using an appropriate statistical analysis. The analysis objectives are:

- (1) to determine and select the significant two-factor interactions;
  - (2) to reevaluate the significance of each of the main effect terms;
  - (3) to estimate the strength of the best model to predict the measured corrosion performance;
- and
- (4) to attempt to estimate the significance of the quadratic terms.

The results of the statistical analysis would to a large extent determine the next steps to be taken. For example, a mathematical expression with main effect and two-factor interaction terms may explain most of the experimental variation in the corrosion parameters measured. However, if these terms do not sufficiently explain the experimental variation of the measured parameter, a second design iteration would be performed to add quadratic terms to the final model. Results from the additional experiments would then be subject to appropriate statistical analysis.

The mathematical expressions describing corrosion parameters as functions of solution variables can be prepared with the aid of various statistics software packages such as SPSS [9], SAS [10] and Minitab [11]. These software packages provide many different multiple regression techniques. Forward step-wise regression is particularly useful. This technique starts with no variables in the model and adds variables one at a time. For each variable not in the model, an  $F$  statistic is calculated that reflects the variable's contribution to the model if it were to be included next. The variable which contributes most to the model is added provided that the  $F$  statistic is significant at the 90% significance level. Variables that are added to the model do not necessarily stay there. After a variable is added, a backward elimination is performed to delete any variable that does not contribute significantly to the model. This process continues until no variables can be added or deleted. The result of this regression analysis is a model in which the selected corrosion parameters are a function of significant solution variables. Such an empirical model will take on the form of:

$$Y = a_0 + \sum a_1 x_i + \sum a_2 x_i^2 + \sum a_3 x_i x_j \quad (1)$$

where

$\sum a_1 x_i$  and  $\sum a_2 x_i^2$  represent the main and quadratic effects of solution variables  $x_i$ , and  $\sum a_3 x_i x_j$  represent the interactions.

The main effect of a solution variable on a corrosion parameter represents the net effect of this variable in the presence of all other variables at an average value. Thus, an observed main effect represents the effect of a species by itself on the corrosion of an alloy. If the measured synergistic effects are significant, the variation in corrosion parameter cannot be explained by the main effects only and the interactive terms should be entered into the empirical model. Interactions between  $x_i$  and  $x_j$  occur when the rate of change of  $y$  with increasing  $x_i$  is different at low and high values of variable  $x_j$ . This is illustrated schematically in Fig. 1.

### Complex Simulated Environments

In this section of the paper, examples are discussed in which experimental designs were applied to study the effect of complex environments on the corrosion performance of alloys. The different levels of the experimental design will be discussed.

#### *Example 1, Corrosion of Stainless Steels in Condensates of High-Efficiency Domestic Furnaces [12,13]*

There is an increased interest in the use of residential high-efficiency gas furnaces and boilers. For maximum efficiency, residential heating equipment must be designed to operate in the condensing mode. Flue gas condensate is corrosive with respect to stainless steels [12]. The principal variables of the flue gas condensate that may affect the corrosion of stainless steels are pH, chloride, fluoride, nitrite, nitrate, sulfate, and reduced sulfur oxyanions (i.e.,  $S^x$  where  $x = -2$  to  $+3$ ). To determine which of these variables had a significant effect on the corrosion of stainless steel, a fractional factorial design was selected for the experimental evaluation. The selected design included 19 experimental conditions of condensate composition. Of these, three test solutions, numbers 17, 18, and 19, were duplicated to test the reproducibility of the experimental results. The test matrix using the seven variables at the various concentrations is given in Table 2. Potentiodynamic anodic polarization experiments were used to determine the corro-

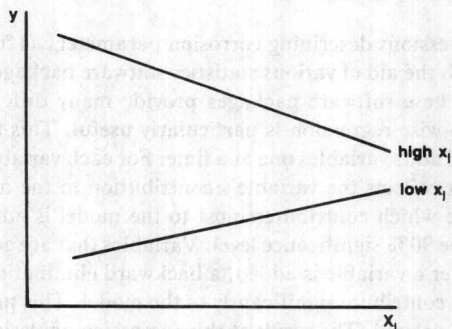


FIG. 1—Schematic diagram showing interaction between  $x_i$  and  $x_j$ .  $Y$  is the measured corrosion parameter and  $x_i$  and  $x_j$  are the solution variables.



TABLE 2—*Partial factorial design test matrix to study the effect of solution variables of condensates from high-efficiency domestic furnaces on the corrosion of stainless steels [13].*

Solution No.	pH	Temperature °F <sup>a</sup>	Concentration, log of concentration (g/m) <sup>3</sup>					
			SO <sub>4</sub> <sup>-2</sup>	Cl <sup>-</sup>	F <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	S <sub>2</sub> O <sub>3</sub> <sup>-2</sup>
1	0.4	120	4.7	0	0	4	3.3	3
2	4.0	180	0.7	0	0	1	0.3	3
3	4.0	120	4.7	4	0	1	0.3	0
4	0.4	180	0.7	4	0	4	3.3	0
5	4.0	120	0.7	0	2.7	4	3.3	0
6	0.4	180	4.7	0	2.7	1	0.3	0
7	0.4	120	0.7	4	2.7	1	0.3	3
8	4.0	180	4.7	4	2.7	4	3.3	3
9	4.0	180	0.7	4	2.7	1	0.3	3
10	0.4	120	4.7	4	2.7	4	3.3	0
11	0.4	180	0.7	0	2.7	4	3.3	3
12	4.0	120	4.7	0	2.7	1	0.3	3
13	0.4	180	4.7	4	0	1	0.3	3
14	4.0	120	0.7	4	0	4	3.3	3
15	4.0	180	4.7	0	0	4	3.3	0
16	2.9	120	0.7	0	0	1	0.3	0
17	2.2	150	2.7	2	1.3	2.5	1.8	1.5
18	2.2	150	2.7	2	1.3	2.5	1.8	1.5
19	2.2	150	2.7	2	1.3	2.5	1.8	1.5

$$^{\circ}\text{C} = \frac{5}{9} (^{\circ}\text{F} - 32).$$

sion behavior of Type 304L and 316L stainless steels in the simulated flue gas condensate solutions listed in Table 2. The corrosion parameter selected for analysis in this study was the "pitting margin" defined as  $\Delta E_{\text{pit}} = E_{\text{pit}} - E_{\text{pas}}$  (Fig. 2).

Following the experimental work, a multiple regression analysis was conducted for the values of  $\Delta E_{\text{pit}}$  and the corresponding environmental variables from the test matrix. The results of this analysis, presented in Table 3, show the probability of significance based on the calculated  $F$  ratio and the regression coefficients for those variables with the highest probability of significance. The results of the regression for Type 316L stainless steel indicated that chlorine (Cl) and temperature had the most significant effect on the pitting margin while chlorine and the ratio of nitrate and nitrite ( $\text{NO}_3^-/\text{NO}_2^-$ ) significantly affected the pitting margin of Type 304L stainless steel.

Based on the results of these experiments, two solutions were selected to study a range of additional alloys. Solution number 13 was found to be an aggressive pitting solution, whereas solution number 17 was not aggressive.

#### *Example 2, Stress-Corrosion Cracking in Continuous Digesters [14]*

Stress-corrosion cracking has recently been observed in the welds and near-weld regions of continuous digesters. Continuous digesters are large carbon steel vessels used in the paper industry to convert wood chips or sawdust into a cellulose pulp by a reaction with a hot solution containing primarily sodium hydroxide (NaOH) and sodium sulfide ( $\text{Na}_2\text{S}$ ). Additional chemicals in this solution are elemental sulfur,  $\text{S}^0$ , sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ), sodium chloride (NaCl) and sodium sulfite ( $\text{Na}_2\text{SO}_3$ ). In many metal-environment systems, including carbon steel in caustic solutions [15], stress-corrosion cracking occurs in a narrow region of potentials corresponding to the active-to-passive transition region of anodic polarization curves. Often, various species present in the environment can move the free-corro-

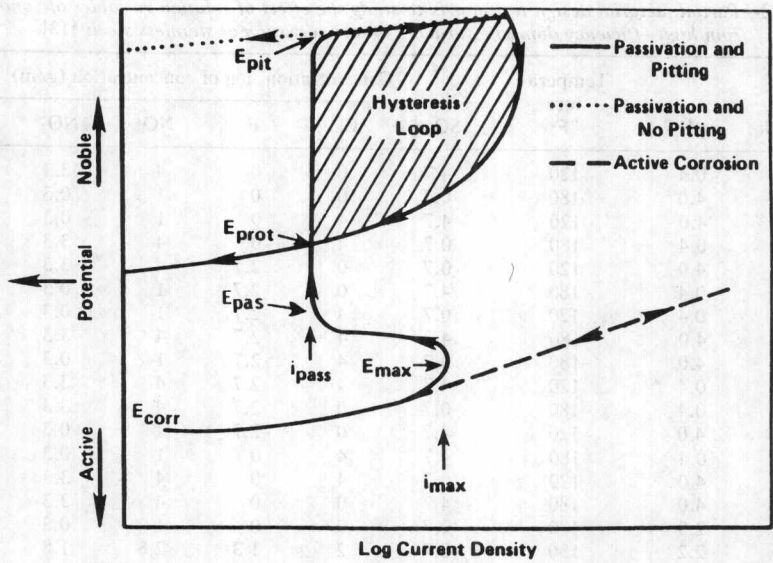


FIG. 2—Schematic diagram of typical anodic potentiodynamic polarization curves showing important polarization parameters:  $E_{corr}$  = corrosion potential;  $E_{pit}$  = potential at which pits initiate on forward scan;  $E_{prot}$  = potential at which pits repassivate on reverse scan;  $i_{max}$  = current density at active peak;  $i_{pass}$  = current density in passive range.  $\Delta E_{pit} = E_{pit} - E_{pas}$ .

TABLE 3—Results of multiple regression analyses for Type 316L and Type 304L test in simulated condensates of high-efficiency domestic furnaces [13].

316L, $\Delta E_{pit}$			304L, $\Delta E_{pit}$		
Solution variable	% Probability of significance	Coefficient <sup>a</sup>	Solution variable	% Probability of significance	Coefficient
Cl <sup>-</sup>	100	-173	Cl <sup>-</sup>	98.0	-127
Temp.	93.7	64	NO <sub>2</sub> <sup>-</sup> /NO <sub>3</sub> <sup>-</sup>	89.7	+84
SO <sub>4</sub> <sup>2-</sup>	74.8	...	SO <sub>4</sub> <sup>2-</sup>	50.0	...
S <sup>+</sup>	59.1	...	S <sup>+</sup> x	41.5	...
NO <sub>2</sub> <sup>-</sup> /NO <sub>3</sub> <sup>-</sup>	56.8	...	Temp.	32.6	...
pH	45.3	...	pH	18.6	...
F <sup>-</sup>	35.5	...	F <sup>-</sup>	11.8	...
Constant	...	528	Constant	...	464

<sup>a</sup>A negative sign indicates that an increase in solution variable has a detrimental effect on corrosion behavior, a positive sign indicates a beneficial effect.

sion potential ( $E_{corr}$ ) into or out of the cracking range, thereby inducing or eliminating stress-corrosion cracking. An experimental design was set up to determine what chemical variables in the digester liquor would significantly affect  $E_{corr}$ , and thus the susceptibility of carbon steel to stress-corrosion cracking.

A Box-Behnken factorial design [8] was employed to make 25 different solutions containing NaOH, Na<sub>2</sub>S, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and S<sup>0</sup> as variables. The selected ranges of concentrations of these four components were based upon those reported for digesters [15] and are shown in the test matrix



TABLE 4—Solution compositions of simulated continuous digester liquids based on a Box-Behnken experimental design [14].

Number	Solution Concentration in g/L Composition			
	NaOH	Na <sub>2</sub> S	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	S <sup>0</sup>
1	80	50	7	1
2	80	10	7	1
3	20	50	7	1
4	20	10	7	1
5	50	30	11	2
6	50	30	11	0
7	50	30	3	2
8	50	30	3	0
9	50	30	7	1
10	80	30	7	2
11	80	30	7	0
12	20	30	7	2
13	20	30	7	0
14	50	50	11	1
15	50	50	3	1
16	50	10	11	1
17	50	10	3	1
18	50	30	7	1
19	80	30	11	1
20	80	30	3	1
21	20	30	11	1
22	20	30	3	1
23	50	50	7	2
24	50	50	7	0
25	50	10	7	2
26	50	10	7	0
27	50	30	7	1

in Table 4. The table indicates that the matrix was designed at three levels for each solution component. Three of the 27 solutions, 9, 18, and 27, were identical, and were intended to test the reproducibility of the data. After measuring  $E_{\text{cor}}$  for a set period of time in each of the designed test solutions, the results were analyzed using a multiple regression routine. The multiple linear regression analysis of the results indicated that there was a strong correlation between  $E_{\text{cor}}$  and the Na<sub>2</sub>S and S<sup>0</sup> contents of the test solutions. The NaOH and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> contents were gave less significant results. The regression equation obtained was:

$$E_{\text{cor}} = -659 - \text{NaOH} - 15.8 \text{ Na}_2\text{S} - 24.2 \text{ S}^0 + 35.5 \text{ Na}_2\text{S}_2\text{O}_3 \\ + 0.129(\text{Na}_2\text{S})^2 + 2.63 \text{ Na}_2\text{S} \cdot \text{S}^0 - 2.54(\text{Na}_2\text{S}_2\text{O}_3)^2 \text{ in V SCE} \quad (2)$$

Using this equation, the free-corrosion potential can be predicted for various chemistries, and these agreed with the potentials measured in the liquor near areas where stress-corrosion cracking was observed.

### Example 3, Effect of SO<sub>2</sub> Scrubber Environments on the Corrosion of Alloys [7,17]

Coal-fired power plants provide an increasingly important source of energy. Sulfur dioxide (SO<sub>2</sub>) is a major ecological concern resulting from the increased use of coal. Scrubbing of the