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NEURAL NETWORK MODELING OF THE ELECTROCHEMICAL BEHAVIOR OF STEEL IN CHLORIDE SOLUTIONS OF VARYING pH

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ABSTRACT

In order to provide boundary conditions for the numerical modeling of cathodic protection, a phenomenological model of the electrochemistry of steel in solutions or varying pH and pCl has been developed. Polarization curves have been measured for a range of solutions, and the results have been used to train neural networks to provide a predictor of the current density as a function of pH, pCl and applied potential. The resultant models produce predicted polarization curves that are reasonably similar to the measured curves, although interpolated curves tend to have rather unrealistic fluctuations in current density as a function of applied potential.

Keywords: polarization curve, modeling, chloride, steel.

INTRODUCTION

While cathodic protection is a well-established method of corrosion control, the detailed theoretical basis is rather limited. Most modern authors explain the mechanism of cathodic protection as the lowering the potential into the region of immunity on the E-pH diagram, but this fails to take account of chemical changes at the metal surface, notably the increase in pH and reduction in concentration of anions such as chloride. Suggestions by early workers [1] that the corrosion is limited by passivation in the alkaline conditions at the cathode also seem plausible. Current protection criteria are based as much on practical experience as on theoretical understanding. This is perfectly acceptable in many cases, but it does lead to problems in difficult situations. For example in the protection of high strength steel in concrete, the possibility of hydrogen embrittlement places a negative limit on the potential, and it is difficult to determine the acceptable range of potentials that can be applied. There is therefore a need to develop a better understanding of the combined effects of applied potential and changes in chemistry on the corrosion behavior of steel. A requirement for the development of such an understanding is a mathematical description of the electrochemical behavior of metal-solution interface as a function of the

local chemistry. Such a description can be developed from a theoretical model based on the underlying reaction kinetics [2], or it can be based on a phenomenological model, wherein many measurements are used to map the behavior and interpolation techniques are used to produce an estimate of the electrochemistry for any required conditions. The present study uses the second approach, with the polarization behavior of steel being determined as a function of pH and pCl (-log [Cl']). The interpolation has then been achieved by means of a neural network (see [3]).

EXPERIMENTAL

Specimen Preparation

In order to obtain reasonably stable mass transport conditions, and to minimize IR drop, a small diameter circular working electrode was used[1]. This was made from a 0.6 mm OD BS1052 mild steel wire, with the composition given in Table 1.

Table 1 Chemical Composition of the Working Electrode

Fe	C	Si	Mn	S	P
bal	0.030	0.038	0.230	0.017	0.013

In order to maintain a stable IR drop, the wire electrode and a Luggin capillary were embedded in epoxy resin in a glass tube (Figure 1). Before each experiment the end face of the electrode assembly was ground to 600 grit SiC paper, washed with ethanol and distilled water and dried.
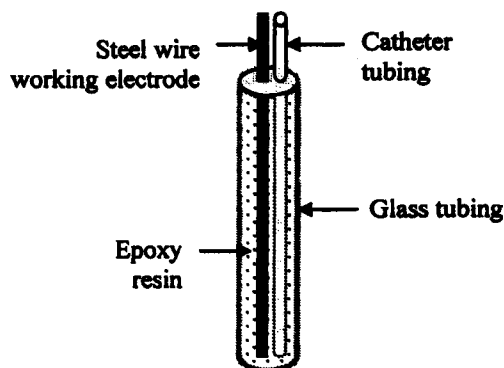

FIGURE 1 The test specimen for polarization experiment

In order to minimize crevice effects, a two-stage mounting procedure was used, with the wire being coated in epoxy resin before being cast into the glass tube. Prior to adopting this procedure, the polarisation results were not reproducible and showed a relatively high passive current.

Test Solutions

The solutions used in the experiment were chloride-containing solutions with concentration of 1, 10^{-2}, 10^{-4} and 10^{-6} M, described hereafter in terms of pCl, where pCl = $-\log_{10}$ [Cl'], so the above concentrations translate to pCl 0, 2, 4, and 6 respectively. These solutions were prepared at pH values of

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[1] It is recognised that the use of an electrode with better-controlled mass transport, such as the rotating disk, would improve the measurement. However, this was not feasible with the resources available to us, and the simple approach described here is based on reducing mass transport effects as much as possible (by the use of the small electrode diameter, and by stirring), with the control of the mass transport (to permit some correction for mass transport effects) being a secondary objective.

4, 6, 8, 10, 12, and 13. They were prepared using de-ionized water and reagent grade NaCl, HCl and NaOH. Table 1 shows the matrix of test solutions for both aerated and de-aerated conditions:

TABLE 1
pH AND CHLORIDE CONCENTRATION OF THE TEST SOLUTIONS

pH	Chloride Concentration (M)			
	1×10^{-6} (pCl=6)	1×10^{-4} (pCl=4)	1×10^{-2} (pCl=2)	1×10^{0} (pCl=0)
4			√	√
6		√	√	√
8	√	√	√	√
10	√	√	√	√
12	√	√	√	√
13	√	√	√	√

The ticked cells corresponded to the pH-pCl combinations that were tested. The blank cells corresponded to the pH-pCl combinations that were not tested. For pCl 6 test solution at pH 4, it would be impossible to prepare the solution at this pH-pCl combination since pCl cannot be greater than pH unless a second anion, such as sulfate, is also added.

Experimental Set up

A conventional electrochemical configuration was used, with the addition of a platinum microelectrode that was used to determine the limiting current density for oxygen reduction, and hence estimate the oxygen concentration (in the case of the deaerated solution). Also a platinum electrode was connected in parallel with the reference electrode in order to minimize system noise.

A magnetic stirrer was placed below the specimen so as to give a reproducible mass transport. The position of the stirrer and the distance of the specimen from the stirrer were pre-determined from studies of the limiting current for oxygen reduction on a platinum microelectrode. The location was selected that gave the minimum sensitivity of the limiting current density to electrode position and stirrer rotation speed.

For tests in aerated conditions air was bubbled through the solution throughout the polarization experiment. The air was passed through 1M NaOH to remove CO_2. Prior to immersing the steel specimen into the test cell, it was ground using a 600-grit size grinding paper, washed with ethanol for about one minute, rinsed with de-ionized water, and dried. The specimen was subjected to a cathodic potential of –800 mV (SCE) for 30 minutes to reduce the air-formed oxide film. Then the potential was swept from –1500 mV (SCE) to 1500 mV (SCE) with a sweep rate of 10mV/min.

For tests in deaerated conditions the procedure was similar, except that the air was replaced by oxygen-free nitrogen. The concentration of oxygen was monitored during the de-aeration process, using the platinum microelectrode polarized at -600 mV (SCE) for alkaline solution and -400 mV (SCE) for acid solution. The test solution was de-aerated for at least four hours before the specimen was introduced into the test cell.

For both aerated and de-aerated conditions, the experiment was repeated using freshly-prepared specimens until at least two reproducible results were obtained for each point in the test matrix.

NEURAL NETWORK MODELLING

In order to use the data obtained in the experimental measurements as inputs into a numerical model of the cathodic protection process, it is necessary to perform an interpolation process, so that the current density can be derived as a continuous function of pH, pCl and potential. The grid of measured points was not completely regular, and became less regular if the bulk solution pH were corrected to allow for mass transport effects during the measurement of the polarization curves (although this has not been done for the data reported here). For these reasons, interpolation methods relying on a regular arrangement of data points (such as the inbuilt Matlab[2] interpolation functions) could not be used. A neural network was therefore used to model the electrochemical behavior.[32] The EasyNN[3] program was used for this work. This uses conventional multi-layer perceptron network trained by the back-propagation algorithm.

The original data consisted of 27,267 examples (an example is one current density associated with defined potential, pH and pCl); to reduce the time to iterate through the training, this was reduced by random selection to one quarter (6817 examples) for training.

Of the reduced data set, 80 percent (5,454 examples) were used as the training set and 20 percent (1,363 examples) as the validation set.

Two neural network architectures, namely 3-50-50-1 (3 input nodes, 50 nodes in the first and second hidden layers and 1 output node, with a total of 2700 weights) and 3-60-60-1 (as before, but 60 nodes in each of the hidden layers, with a total of 3840 weights), were trained using the polarization data for the aerated and de-aerated test conditions.

The input and output values, namely pH, pCl, potential and current density, were automatically normalized (linearly transformed to values between 0 and 1) by the program. However, the inherently logarithmic character of current densities leads to a domination of the training by the high current densities at the extremes of the polarization curve. For this reason, the values of current densities were manually normalized using the following sigmoidal function:

$$i_{trans} = \frac{1}{1+e^{-i^{0.2}}} \qquad\qquad (4.5)$$

The value 0.2 was used to adjust the values of i_{trans} to give a reasonable balance between high and low currents. Figure 2 shows a plot of sigmoidally transformed current values for one test condition. An ideal transformation from the perspective of neural network training would lead to a straight line relationship between potential and transformed current density. This is clearly not going to be achieved for all data, but the result in Figure 2 implies that there is a reasonably good linear relationship (the sigmoidal function is designed as 'the next best thing' to a logarithmic transform, since the logarithmic transformation fails as the current density goes through zero).

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[2] Matlab is a trade name of The Mathworks Inc.
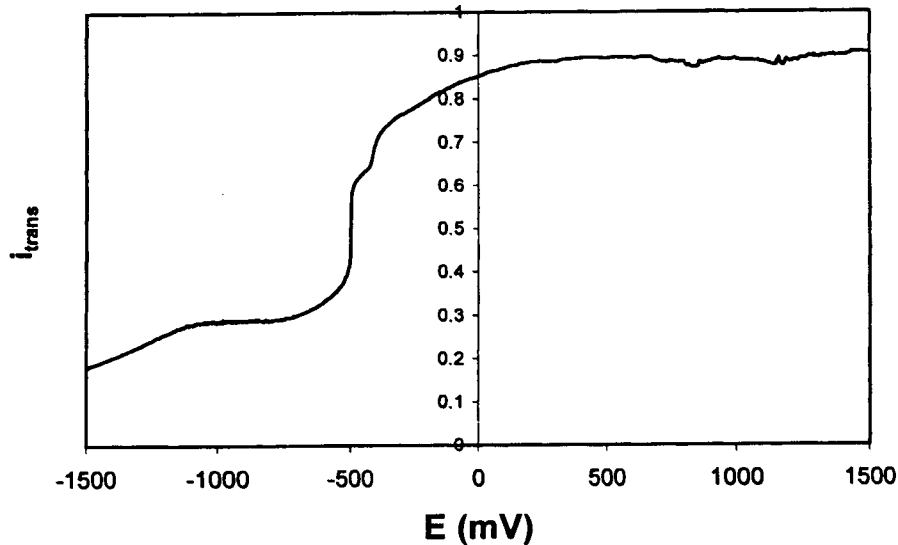[3] EasyNN is a trade name of Steven Wostenholme

FIGURE 2 Sigmoidal transform of current densities for a pH10 and pCl =2 test

Network Training

Several training runs were performed (since the network is initialized with random weights, each training produces a different result). The trained networks were assessed on the following criteria, and the best network selected for each of the network dimensions:

1. The ability of the networks to curve-fit the original data at a particular pH and pCl. Three pH values at a particular pCl were selected, pH 6 (representing active behavior), pH 10 (representing pitting), and pH 13 (representing passive behavior). The predicted polarization curves were compared with the measured curve at pCl 4.

2. The ability of the networks to interpolate the original polarization curves by pH and pCl. The interpolated pH values were pH 5, 7, 9, and 11, and the interpolation was made at pCl 2. The interpolated pCl values were pCl 1, 3, and 5, and the interpolation was made at pH 10. The quality of the interpolation was assessed in terms of the 'reasonableness' of the predicted polarization curve (i.e. its lack of unexpected peaks and troughs and its fit between adjacent experimental curves).

Training Results - Aerated Test Conditions

Table 2 gives the final values of the validation percentage (the percentage of examples in the validation set that lie within a specified deviation, in this case 10%, from the predicted value) and the maximum error (the standard deviation of the percentage difference between the predicted value and the training value) on stopping training as well as the maximum validation percentage achieved during the training for the 3-50-50-1 and 3-60-60-1 neural networks, trained using the aerated test condition data.

TABLE 2

NETWORK TRAINING PERFORMANCE – AERATED SOLUTION

Neural Network	Maximum Error (%)	Validation Percentage	Max. Validation Percentage
3-50-50-1	6.89	75.44	77.93
3-60-60-1	5.83	75.59	84.82

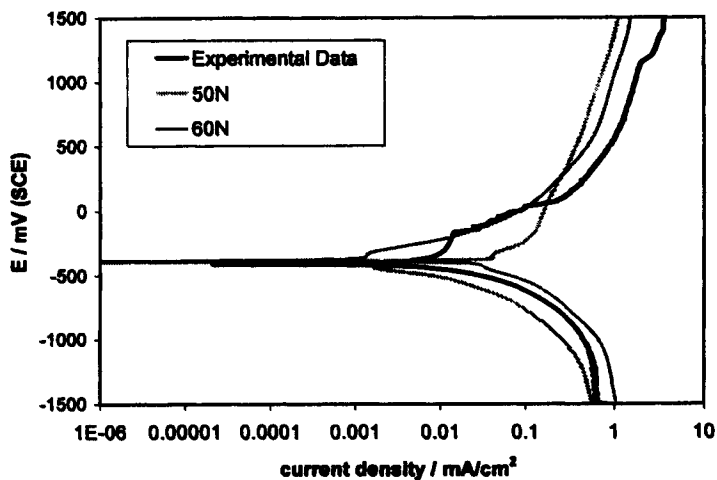Figure 4 shows the fit of the two networks to the experimental curves at pH 10 and pCl 4.

FIGURE 4 Performance of Trained Network (Aerated Solution, pH 10 and pCl 4)

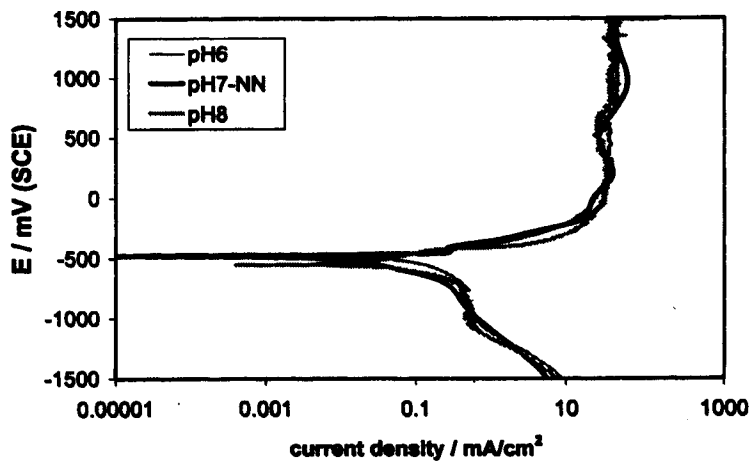Figure 5 shows the fit to the measured data for pH 7 and pCl 2.

FIGURE 5 Interpolation of Polarization Curves for pH 7 and pCl 2 for
Aerated Test Conditions (3-60-60-1 network)

Deaerated Conditions

Table 3 gives the final values of the validation percentage and the maximum error at the end of the training as well as the maximum validation percentage achieved during the training for the de-aerated data.

TABLE 3
ERROR CHARACTERISTICS FOR TRAINING WITH DEAERATED TEST DATA

Neural Network	Maximum Error (%)	Validation Percentage	Max. Validation Percentage
3-50-50-1	15.41	81.4	88.88
3-60-60-1	65.92	59	87.78

Figure 6 shows the match of the predicted and measured curves at pH 10 and pCl 4.
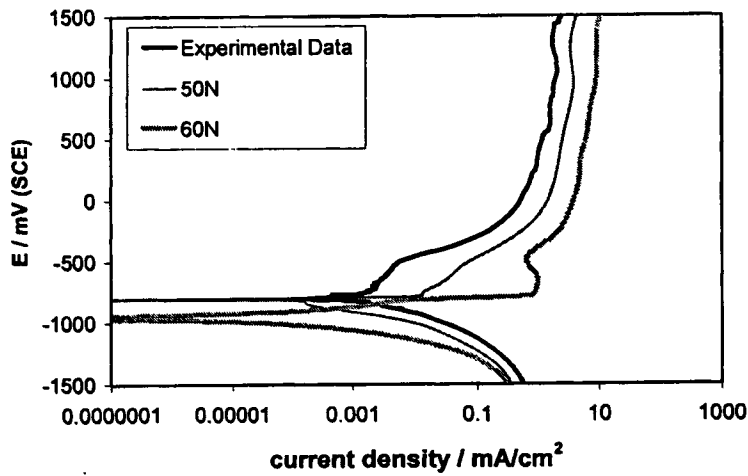

FIGURE 6 Performance of Networks (De-aerated Chloride Solution at pH 10 and pCl 4)

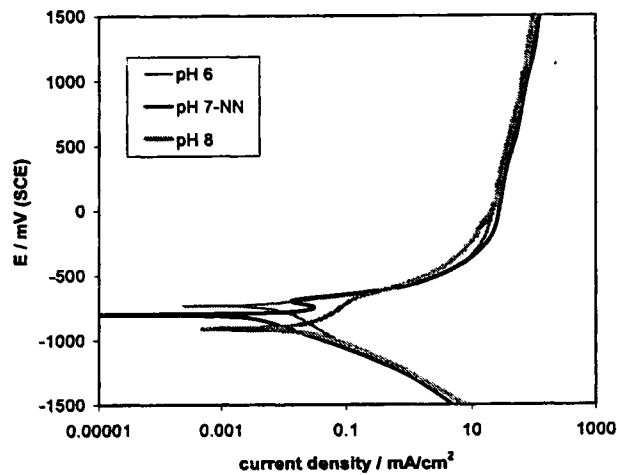Figure 7 shows an example of the interpolation behavior for pH 7 and pCl 2.

FIGURE 7 Interpolation of Polarization Curves at pH 7 and pCl 2 for
De-aerated Conditions (3-50-50-1 network)

DISCUSSION AND CONCLUSIONS

Overall the results indicate that the 3-60-60-1 network generalized better for the aerated test conditions, while for the de-aerated test conditions, the 3-50-50-1 network generalized better. As can be seen from the figures presented here, the fit to the experimental data is reasonable, but not perfect, and the interpolation results similarly seem moderately good (it should be appreciated that there are several other curves a similar 'distance' for the interpolated curve, and the network may be making the best of a difficult job). Bearing in mind that the current density is plotted on a logarithmic scale, the errors are often quite large, and more work is needed to improve the quality of the model. At present the training data is derived from polarization curves determined in 17 combinations of pH and pCl. The data in the potential dimension are very densely packed, but the data are widely spaced in the pH and pCl dimensions. Thus it is not entirely surprising that the interpolation behavior is relatively poor.

The neural network models that have been obtained in this work have been converted to Matlab functions for use as boundary conditions in finite element modeling. This has proved successful, although the large number of weights involved does mean that the computation is very slow, and improved performance may be achieved by using the neural network model to compute a dense regular array of points, and then use the Matlab interpolation functions within the finite element calculations.

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3. R.A. Cottis, L. Qing, G. Owen, S.J. Gartland, I.A. Helliwell and M. Turega, "Neural network methods for corrosion data reduction", *Materials and Design* (UK), vol. 20, no. 4, pp. 169-178, Aug. 1999.