PART II TECHNIQUES PROJECT

MODELLING OF THE CORROSION OF BINARY ALLOYS

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Abstract

Neural networks offer a powerful means to model complex relationships between large numbers of variables. This allows for prediction of future results, as well as being able to illustrate the sensitivity of an output to influencing variables in a manner not possible experimentally. Neural network analysis is appropriate to a wide range of phenomena including welding, creep and fatigue behaviours, and the estimation of transformation times and temperatures. In this work a neural network method was employed to study how the rate of corrosion of Fe-based alloys was influenced by compositional and environmental factors as well as exposure time. The dataset was generated from measurements provided by the National Institute for Materials Science in Japan. Inclusion of sulphur in the alloy was seen to have the greatest impact, even though the concentrations were of the order of 0.001 wt% or less. Exposure of the sample to sun and rain, the level of atmospheric pollution, and the presence of certain other alloying elements were also seen to have important roles, generally in good accordance with the literature.

1. Introduction

The atmosphere is the corrosive environment to which alloys are most frequently exposed, and thus environmental corrosion is of widespread importance. Due to the complexity of the interdependent variables which determine corrosion reaction kinetics, it remains an area in which complete understanding is not held.

Research at the National Institute for Materials Science in Japan yielded data on the atmospheric corrosion of binary alloys of iron. These data were analysed using a neural network method, in order to create a model for weight loss as a function of composition, exposure time and exposure conditions.

2. Scientific background

The book by Shreir et al. [1] *was the main reference in researching this section.*

The corrosion of iron and steel has been the subject of study for more than a century. Bare iron and steel are liable to rust in most environments, with the extent of corrosion depending on a number of factors including the composition and surface condition of the metal, the corrosive medium itself and the local conditions.

2.1 Environmental effects

Where materials are left to rust in air, the main environmental factors are considered to be the availability of moisture and the extent of pollution. Other factors, such as temperature, must also be considered.

Work has shown that corrosion only occurs above a critical relative humidity and that in pure air these rates are generally very low for all humidity levels. However if pollutants, such as sulphur dioxide, are introduced the rate greatly increases, as does the variation of the rate with relative humidity. This is shown in Figure 1.

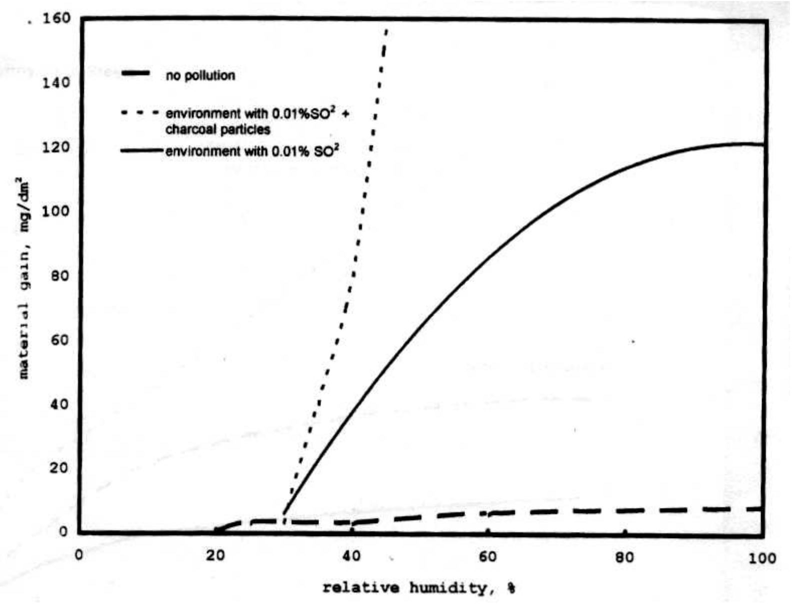

Figure 1: Effect of relative humidity and atmospheric pollution on the rusting of iron (*image from Cahn* et al.*)*

The most important impurity in industrial atmospheres has been shown to be sulphur dioxide, although chlorides may also have an effect. The SO_2 in the atmosphere is derived from the aerial oxidation of H_2S produced naturally and from the combustion of sulphur containing fuels. In densely populated countries the sulphur pollution levels are strongly related to the domestic heating cycle. There is typically a direct relationship between SO_2 in the atmosphere and the corrosion of exposed steel. Walton *et al*. showed that the actual amount of sulphur dioxide in contact with the steel is more important than the concentration.

The loss of iron as a sulphate accounts in only a small measure for the effects of sodium dioxide. It is thought that once ferrous sulphate is formed it is able to promote further rusting.

The predominant effects of temperature are thought to be largely indirect, having an effect on the relative humidity and the drying time of wet samples. In this way *variations* in temperature are also important.

2.2 Experimental set-up

The orientation of corrosion samples has also been shown to be important. It was found that on non-vertical samples the underside corrodes more quickly because it is shielded from the sun and takes longer to dry after rainfall. Previous tests on specimens at 45° found an increase in corrosion of 10-20% compared to vertical specimens, with 54% of the corrosion being on the underside.

The mass of the sample can have some effect because it will determine the rate at which the surface temperature adjusts to fluctuations in the ambient temperature.

2.3 Compositional effects

The mechanical properties of low-carbon steels are regularly improved by adding small amounts of other elements such as chromium, manganese, nickel and silicon. These 'low-alloy steels' are often found to rust several times more slowly than unalloyed mild steels. Indeed some low-alloy steels are specifically designed to resist corrosion and are called 'weathering steels'. The elements most commonly added for this purpose are chromium, nickel and copper.

The improvement in corrosion resistance depends on the amount and nature of the alloying elements and on the nature of the corrosive environment. The distinguishing feature of the behaviour of the slow-rusting low-alloy steels is the formation of a protective layer.

Work has shown that the effects of the alloying elements are not additive, but with this in mind may be summarised as:

1. Copper additions up to 0.4wt% give a marked improvement, but further addition makes little difference.
2. Phosphorous, particularly combined with copper, may be highly beneficial, but levels above 0.10wt% adversely affect the mechanical properties.
3. Chromium, in fractional percentages, has a significant and apparently beneficial influence on corrosion rates.
4. Nickel also reduces corrosion rates, but to a lesser than the elements mentioned above.

3. Technique

Neural network modelling is a method of regression analysis in which a non-linear function is fitted to experimental data. Neural networks are able to discover complex relationships between input variables and the output which could not be deduced with traditional linear models. They are extremely useful in circumstances where the complexity of the problem is overwhelming from a fundamental perspective.

The structure of the network consists of many inputs (the experimental variables) and a single output with a layer of hidden units between (Figure 2). The input and output variables are normalised in the range ±0.5 as follows:

$$x_N = \frac{x - x_{\min}}{x_{\max} - x_{\min}} - 0.5$$

The hidden units are formed from hyperbolic tangent (tanh) functions of weighted combinations of the inputs, and the output is a weighted combination of the hidden units. This is described by the equation:

$$y = \sum_i w_{ij}^{(2)} h_i + \theta^{(2)},$$ where

$$h_i = \tanh\left(\sum_j w_{ij}^{(1)} x_j + \theta^{(1)} \right).$$

For an output y, inputs x_j, hidden units, h_i, weights w and biases θ.

The complexity of the function is thus related to the number of hidden units, and it can be seen that the resultant networks can model a function of great complexity.

In this work a method developed by MacKay [4] is used. The method is based on Bayesian probability theory and involves the algorithm inferring a probability density of weights rather than identifying the best set of weights. When making predictions this facilitates a process called marginalizing, whereby the variety of solutions corresponding to the sets of weights and their associated likelihoods can be considered and represented by error bars. This idea also leads to the use of the log predictive error when evaluating the performances of models, which places less penalisation on incorrect predictions if they are accompanied by large error bars.

A potential difficulty in neural network analysis is the possibility of overfitting the data. The problem is avoided by dividing the database into a training set and a testing set. The network is formed based on the training set and then tested. As the complexity of the model increases to produce curves fitting the training set more closely the model should also improve in describing the testing set. As overfitting begins to occur the model becomes less able to predict the testing set, because it is generating an overly complex function in trying to match the training set data too closely. This is illustrated in Figure 3.

Finally it is often found that combining networks which model a problem can lead to more accurate predictions. Thus it is normal to form a ‘committee’ of models. The non-weighted average value of the models’ predictions is used. Once the best committee of models has been chosen the models are retrained on the full data set.

The committee can then be used to predict an output for a set of inputs, as well as the sensitivity of the output to each input variable.

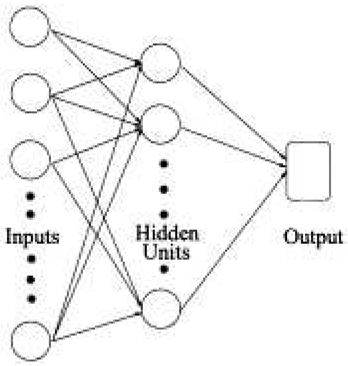

Figure 2: The structure of the network *(image from Yescas* et al.*)*

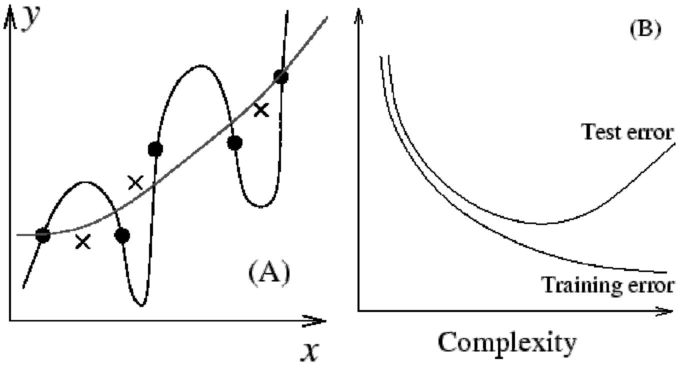

Figure 3: (A) when a model has overfitted the training data (■) the error on the test data (×) is larger than for an optimum model which fits the trend but not the noise (B) behaviour of error on training and testing sets as a function of complexity is illustrated (*image from Sourmail* et al.)

4. Source data

The database for the work was generated using data provided by the National Institute for Materials Science (NIMS) in Japan (NIMS Corrosion Data Sheet No. 0 and No. 1A, 2002). The data were collected by monitoring the corrosion weight loss of samples of alloy in an outdoor environment over a number of years. The testing is ongoing with results for other alloys and longer time durations planned.

In our data, identical tests were performed at three sites on thirteen alloys in sheltered (covered) and open conditions. Measurements were taken at five lengths of time. Assuming a full data set this allows for up to 390 data points.

The test specimens used were of the dimensions 50×150×5 mm and were subjected to grinding and degreasing prior to testing. The materials themselves are commercial alloys and melted alloys of known manufacturing history.

The samples were placed on outdoor test frames. Exposed frames were angled at 45° to horizontal and sheltered frames were covered by umbrella roofs to shield them from rainfall and solar radiation and were horizontal.

As well as the weight loss of the samples, weather data[1] were also recorded (as year averages).

5. Computing methodology

A database consisting of composition, weather and time variables was created. Composition and time were straightforward to input. A {ln(*time*)} variable was also added. This is a normal practice in this type of study since a relationship with {ln(*time*)} in a corrosion problem would be sensibly anticipated and thus including it explicitly as an input can help the network to simply deduce this relationship. To avoid biasing the model, and as there may be other unknown effects of *time*, both variables were included.

Initially the weather variables were simply the average temperature, chloride deposition and humidity for the three sites from the year 2000, and a binary yes/no for sheltered condition. This made all three sites useable in terms of complete data, giving datasets for all 367 recorded outputs, but made the effects of the weather variables impossible to separate. A method whereby the variables were time averaged over the period of exposure was then employed (so for instance a two-year exposure beginning towards the end of 1998 had the average temperature given by the equation:

$$T = \frac{1}{8}\left(T_{1998} + 4T_{1999} + 3T_{2000}\right)).$$

In this manner the network was given the opportunity to isolate the weathering variables, but the number of data points was reduced to 243 as the tabulated weather information was incomplete for the Tsukuba site and so the model could only be given data from two sites to work on. In this instance the weathering variables chosen were the average temperature, humidity, chloride deposition rate (per day), sulphur dioxide deposition rate (per day), solar radiation rate (per year) and rate of precipitation (per year). The latter two variables were set to zero for the covered samples.

In these models the sulphur content of the alloy was identified as the input variable of greatest significance. The trained committee was used in a predictor program to illustrate how variations in input variables would be

1. Point of note: humidity readings were taken as a relative humidity. This is defined as the percentage ratio of the water vapour pressure in the atmosphere compared with that which would saturate the atmosphere at the same temperature.

Exposure time (yrs)	0.5	1.0	1.5	2.0	3.0
Corrosion loss (mg cm^{-2})	43.688	58.471	171.741	67.876	112.653

Table 1: Corrosion loss data for Fe-3wt%Cr at Miyakojima in sheltered conditions

expected to affect the output. It was noticed that if the inputs were set to combinations of values unlike those in the dataset negative corrosive losses could be predicted.

Following the work of Yescas *et al.* [6], the output variable, {*weight loss*}, was replaced with {ln[-ln(*weight loss*)]}. This avoids the problem of predicting negative outputs. The model was re-run and re-examined for predictions. The most surprising result was the prediction that increasing SO_2 deposition rate would *decrease* the corrosion rate. This contradicted a wealth of strong evidence in the literature, and also the neural network analysis of Cai *et al.* [7].

Upon re-examination of the source data, it was noted that a large number of data entries appeared highly anomalous. This was most obvious comparing results for five samples of the same alloy, in the same location and exposure, for different lengths of time. Although most of these sets showed an increase in the amount of corrosion with time, many did not, with there often being one particular reading spectacularly bucking the trend. An example of such a dataset is shown in Table 1.

It was proposed that these large amounts of ‘noise’ in the input data might be confusing the analysis and causing the unusual predictions being observed. The approach adopted was to remove such data from the database and see how this affected the development of the model. Any sets of data found which recorded a reduction in corrosion with time between any two successive samples were removed entirely from the database (so for instance the five data points given in Table 1 were removed). The neural network analysis was then performed on the remaining 158 data entries. Although it had fewer data points to train and test with, the analysis provided by the model was now much more sensible.

The maximum and minimum values of inputs in this data set are given in Table 2. Figure 4 gives an idea of the distribution of each input against corrosion weight loss.

One notable feature of Table 2 is that all of the data for the three significantly silicon-containing alloys were removed as being ‘noisy’.

Input variable	Min.	Max.	Mean	Standard deviation
C (wt %)	0.0010	0.0060	0.0020	0.0018
Si (wt %)	0.000	0.000	0.000	0.000
Mn (wt %)	0.00	0.12	0.0531	0.0491
P (wt %)	0.0003	0.0010	0.0006	0.0002
S (wt %)	0.0001	0.0011	0.0004	0.0004
Cu (wt %)	0.00	0.43	0.0517	0.1403
Cr (wt %)	0.00	5.03	0.8437	1.6211
Ni (wt %)	0.00	9.06	2.2811	3.1137
Ave. T (^{o}C)	14.96	23.95	19.08	4.28
Ave. humidity (%)	77.83	80.13	78.81	0.86
Ave. precipitation rate (mm year^{-1})	0	2317	994	957
Ave. solar radiation rate (MJ m^{-2} year^{-1})	0	5397	2687	2488
Ave. chloride deposition rate (mg (NaCl) m^{-2} d^{-1})	0.2865	0.4660	0.3661	0.0743
Ave. SO_2 deposition rate (mg (SO_2) m^{-2} d^{-1})	0.0200	0.0615	0.0387	0.0162
Time (years)	0.5	3.0	1.5728	0.8481

Table 2: Various inputs in the dataset

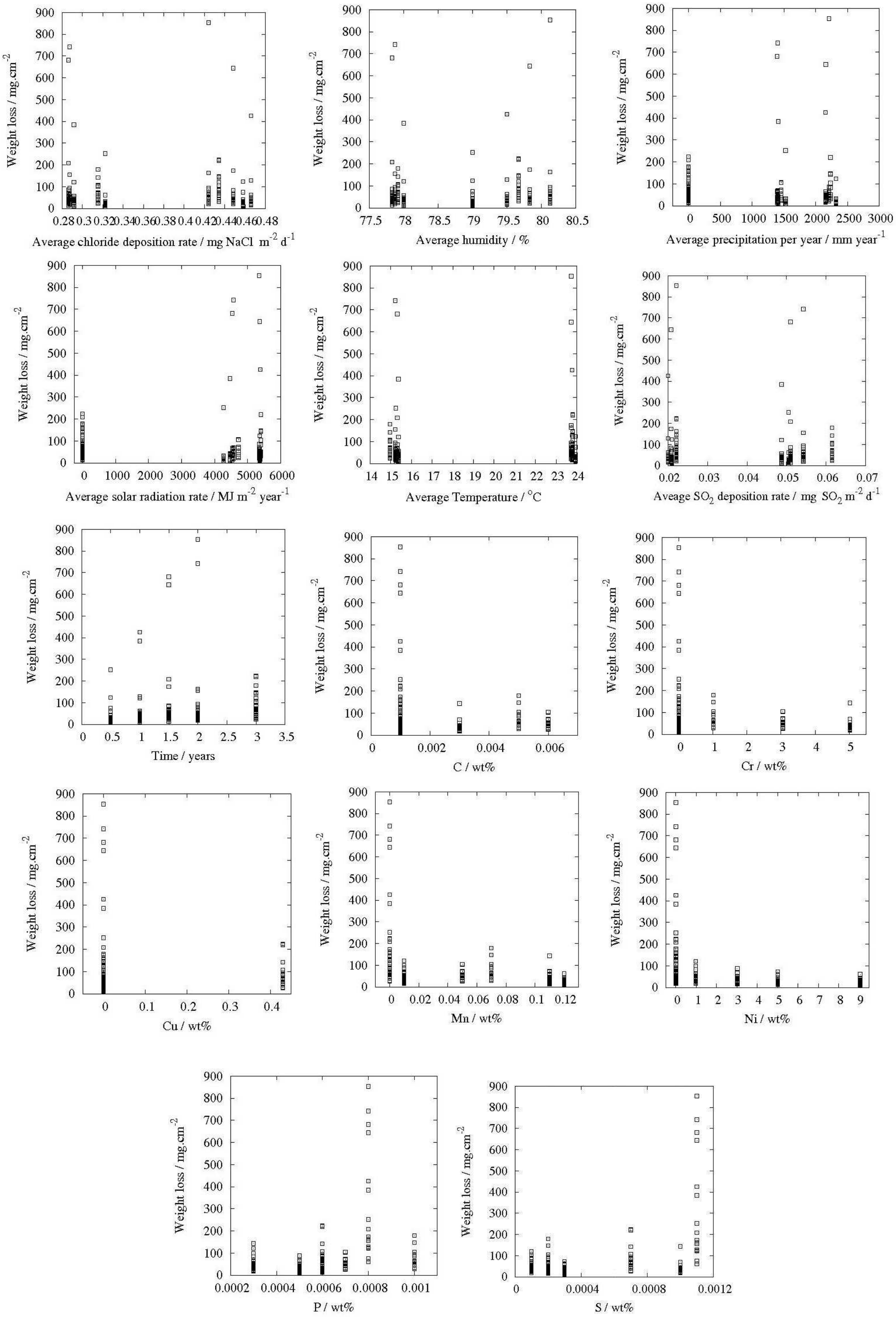

Figure 4: Distribution of the different inputs plotted against weight loss for the final dataset used in the analysis

6. Software Implementation and Results

A large number of networks were trained with up to 20 hidden units. As expected the perceived level of noise generally decreased with an increasing number of hidden units (Figure 5a). A selection of committees were built as discussed above, with a committee of two models being found to give the lowest combined test error (Figure 5c).

The perceived significances of these two models are shown in Figure 6. They represent the extent to which a particular input explains the variation in the output. Thus, the significances are not necessarily an indication of the *sensitivity* of the output to an input and are best considered alongside prediction data. Figures 7, 8 and 9 show the predicted effect of adjusting the input variables individually on a given ‘base’ set of input variables. This base set was one chosen from the dataset and is shown in Table 3. The plot showing the variation with time shows the effect of adjusting the {*time*} and {ln(*time*)} input variables simultaneously.

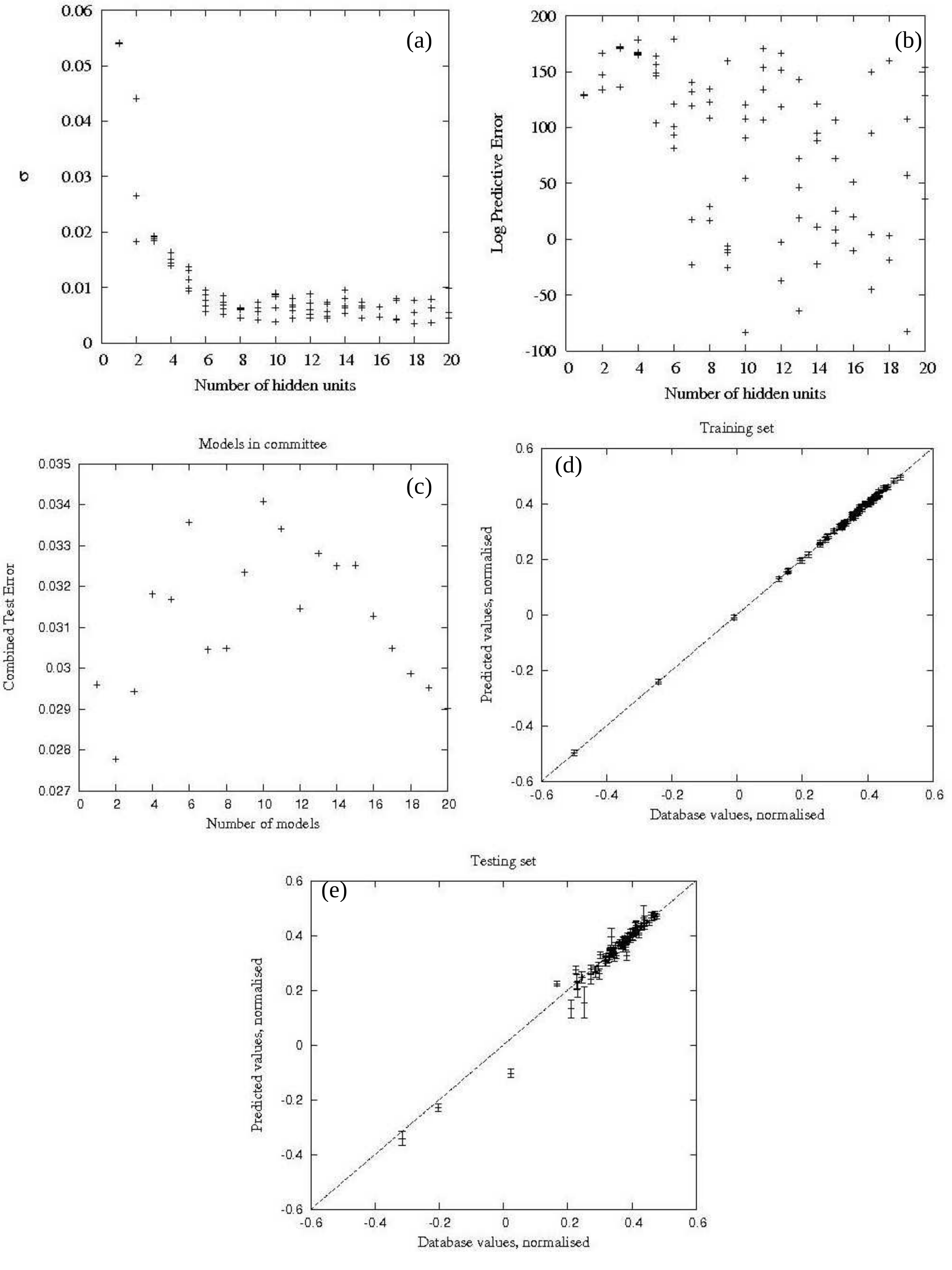

Figure 5: (a) Perceived level of noise, (b) log predictive error, (c) combined test error for number of models in committee, performance of the best single model on predicting the training (d) and testing (e) sets of data

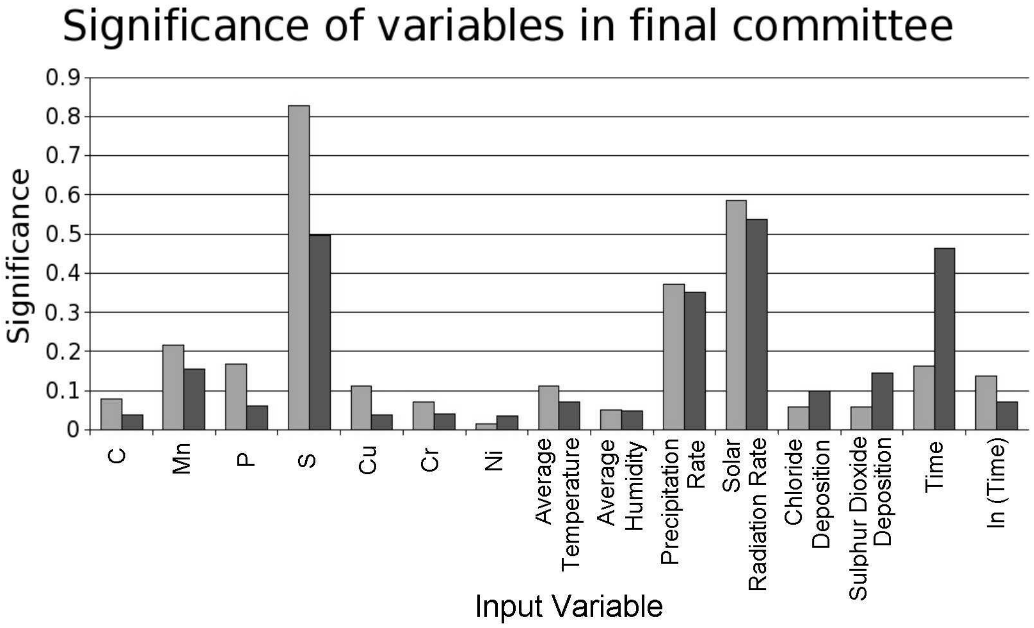

Figure 6: Perceived significances for the two networks constituting the final committee model

Input variable	Value
C	0.0010 wt %
Si	0.000 wt %
Mn	0.01 wt %
P	0.0005 wt %
S	0.0002 wt %
Cu	0.00 wt %
Cr	0.00 wt %
Ni	3.02 wt %
Ave. T	23.73 ºC
Ave. humidity	80.13 %
Ave. precipitation rate	2209.49 mm year^{-1}
Ave. solar radiation rate	5340.46 MJ m^{-2} year^{-1}
Ave. chloride deposition rate	0.424 mg (NaCl) m^{-2} d^{-1}
Ave. SO_2 deposition rate	0.022 mg (SO_2) m^{-2} d^{-1}
Time	2.0 years

Table 3: 'base' dataset used for predictions

6.1 Predicted effect of altering time on corrosive weight loss

Figure 7 shows a plot of the predicted effect of exposure time on the corrosive weight loss. The time variation was made to the 'base' set of variables listed in Table 3.

Given the data rejection criterion set in Section 5, the prediction that the weight loss increases with time was assured, however it is noted that the rate of corrosion appears to decrease after about one year. This fits with a theory of the initial oxide formed offering some protection to the underlying material and slowing the corrosion rate.

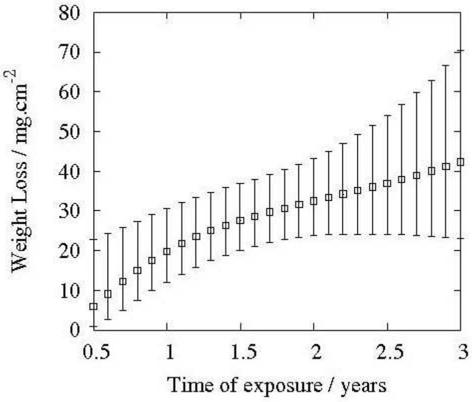

Figure 7: Predicted variation of weight loss with time

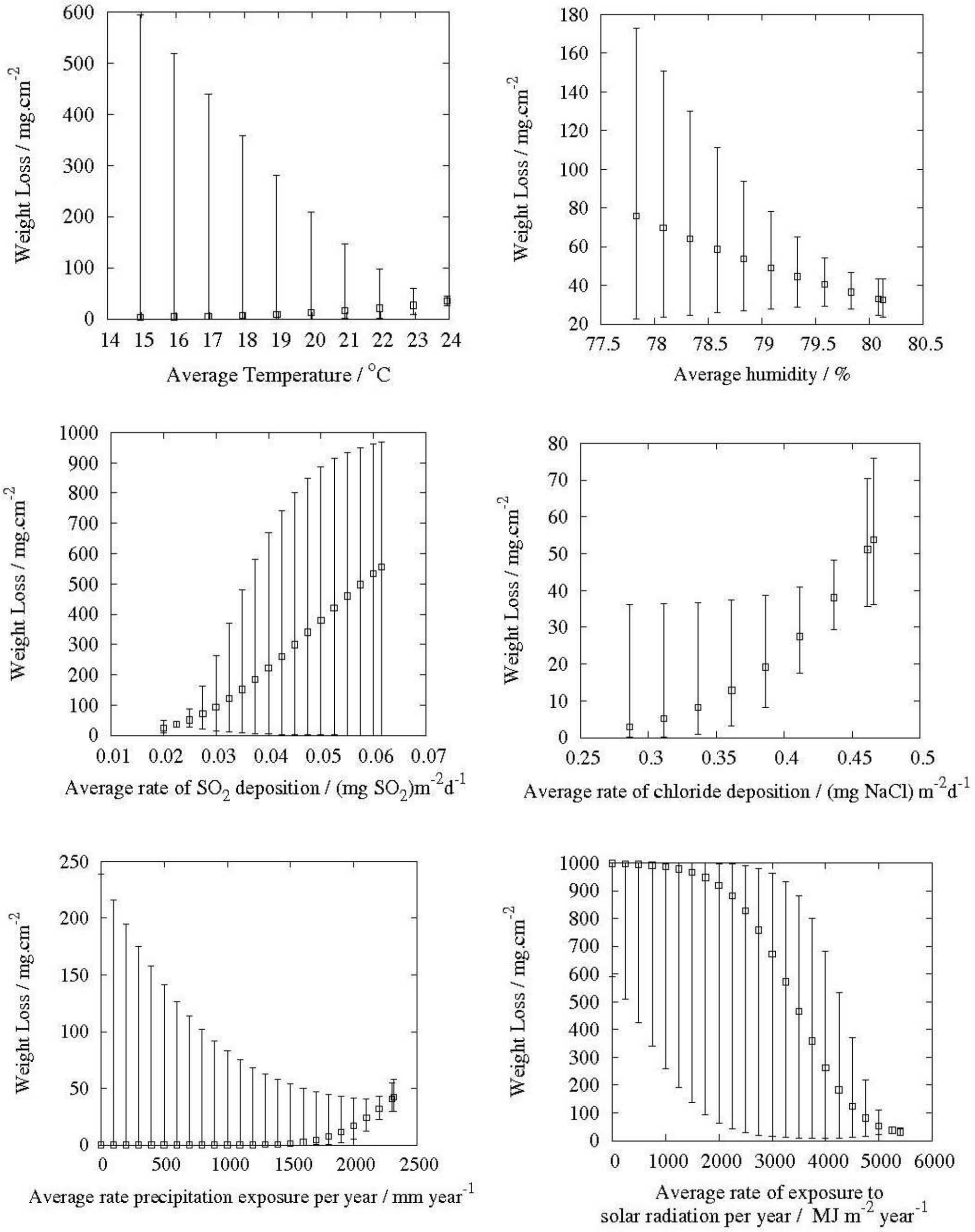

Figure 8: Predicted variation in weight loss with environmental variables

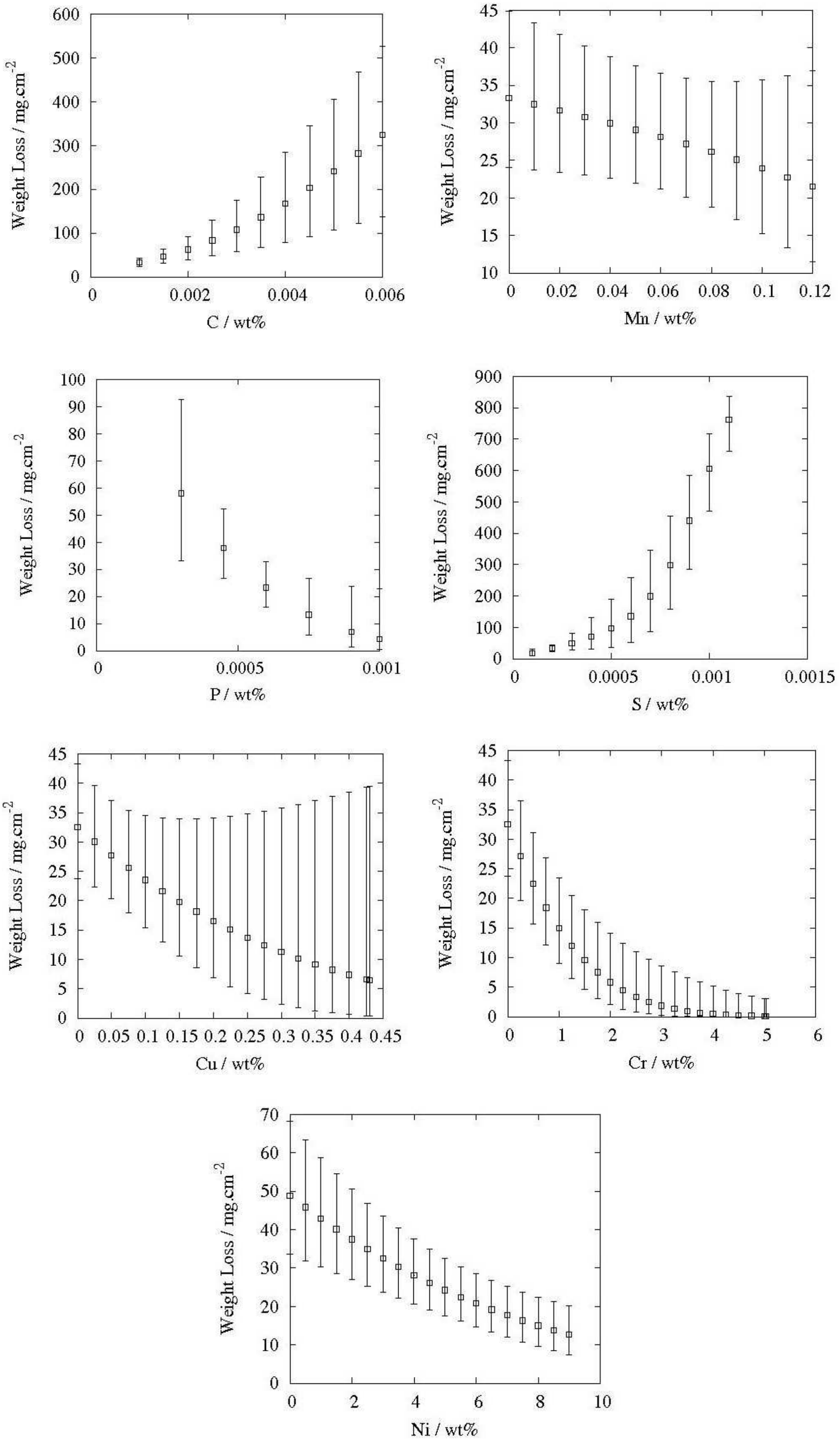

Figure 9: Predicted variation in weight loss with compositional variables

6.2 Predicted effect of adjusting the weather input variables on corrosive weight loss

Figure 8 shows the results of sensitivity analyses conducted on the trained committee whereby the effect of the weather variables on the resultant weight loss was determined. The alterations were again made to the ‘base’ set of variables listed in Table 3.

The prediction of the model is that rising temperature has an effect to slightly increase corrosion, whereas rising humidity will slightly reduce it.

These effects could be seen as unexpected – like most reactions the kinetics of corrosion (i.e. the rates of reaction) increase with temperature, but the increase of temperature is also likely to hasten the evaporation of surface moisture. According to the literature increasing humidity should increase corrosion (see also Figure 1). The low significances and large error bars leave some doubt about the legitimacy of these trends. The use of annual averages for weather variables in this type of study has been questioned elsewhere, in the literature as well as in the similar work of Cai *et al.* [7]. These sources suggest that the variation in these inputs is of greater importance. It is also possible that the model might have difficulty separating the effects of these two variables, since even with the time-averaging method they tend to change in tandem.

Although the significances of the pollutant variables (particularly SO_2) may not have been as great as anticipated, the sensitivity analyses highlight their effects. In particular we see the effect of sulphide deposition (between the max. and min. values from the database) as being an order of magnitude greater than that of chloride deposition and of comparable size to the highly significant sulphur content (for equivalent ranges).

When assessing the predictions for varying rainfall and solar radiation we bear in mind that the variable not being altered is fixed to an ‘open condition’ value, thus we are not surprised by the very high corrosion rates estimated for zero solar radiation (since there will be very long drying times) or the very low weight loss for intermediate and low rainfall (the solar radiation is still high and so the time of wetness will fall greatly). These two variables were identified as having high significances in Figure 6. The trends predicted are for rainfall to worsen corrosion and for exposure to solar radiation to reduce it, which is consistent with the notion that corrosion rates are influenced most directly by the time of wetness.

6.3 Predicted effect of altering alloy composition on corrosive weight loss

Figure 9 shows plots of the predicted variation in corrosive weight loss upon altering compositional variables (balanced with iron) in the ‘base’ set of variables listed in Table 3.

Of all the input variables, sulphur was identified as having the greatest significance in one of the two models forming the committee, and is very close to having the greatest significance in the other (Figure 6). Our sensitivity studies also predict a very large effect – increasing sulphur content worsening corrosion – with relatively small error bars. The sulphur in these alloys is an impurity, rather than a deliberate addition, but we see that an increased presence of as little as 0.0001 wt% can have a voracious effect on corrosion. This is discussed further in Section 6.4.

Of the other elements carbon addition is seen to cause worsening corrosion whereas manganese, phosphorous, copper, chromium and nickel additions all improve corrosion resistance. In Section 2 we identified the inclusion of manganese, phosphorous, copper and chromium in ‘low-alloy’ and ‘weathering’ steels for this very reason. The class of ‘stainless’ steels are characterised by the inclusion of at least 10 wt% chromium. The effect of nickel addition is also in agreement with the literature.

6.4 The role of sulphur on corrosive weight loss

In Section 6.3 sulphur was identified as having a powerful influence on corrosive weight loss. The role of sulphur included in the bulk alloy has been well studied and recorded in the literature. The accepted mechanism is one whereby sulphur is able to accumulate at the interface between the metal and the passive oxide layer. The interfacial enrichment is caused by selective dissolution of elements diffusing through the passive film. Sulphur is not transported due to its low solubility in the oxide and its negative charge, and consequently it remains at the metal/oxide boundary. Above a critical concentration of sulphur at the interface, shown to be one monolayer, the passive film breaks down and

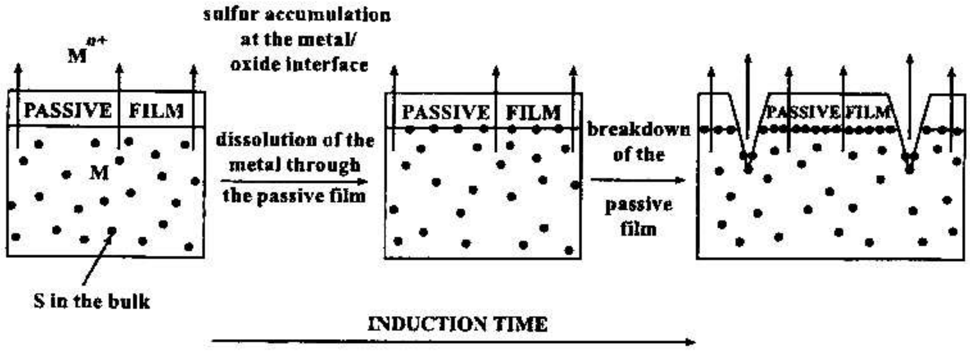

Figure 10: Breakdown mechanism of the passive oxide film induced by the enrichment of sulphur at the metal-passive film interface (*image from Cahn* et al.)

pits grow, with the presence of sulphur preventing repassivation. This breakdown mechanism is illustrated in Figure 10.

7. Summary and Conclusion

The application of neural network methods can provide a means to create accurate, quantitative models of problems in a wide range of areas. The strengths of the technique become apparent when the problem is of great complexity and involves a large number of interdependent influencing factors. The trained network may be used to predict future results, and may also be interrogated to yield valuable sensitivity analyses.

The difficulty in the technique, which was highlighted in this report, is often the need for a large number of entirely quantitative data to work with. With a sufficiently large dataset, the network can be highly effective at following trends accurately whilst ignoring noise in the data. However such large numbers of datasets (from several hundred to several thousand) are difficult to obtain, particularly as the method requires that there must be no empty fields in the database. Very often there is a compromise between the desire to include a large number of variables (leading to fewer ‘full’ data entries) and the need to establish a large dataset (whereby neglect of an important variable can lead to more noise rather than less).

Neural network techniques are appropriate to a wide range of phenomena including welding, creep and fatigue behaviours, transformation times and temperatures and mechanical properties as well as corrosion rates. Thus the usefulness of this tool is apparent in both industry and academia.

In this work a neural network method was employed to study how the corrosion of binary alloys was influenced by compositional and environmental factors as well as exposure time. The main difficulties experienced were related to the relatively small dataset which was used. The similar work of Cai *et al.* [7], which studied only environmental input variables, used a database of around 400 entries. In this work a database of 367 entries was available, which became reduced to 243 when it became apparent that the weather variables needed to be time averaged to make their effects separable, rather than simply fixing one value for each variable per site for all exposure times.

Initially the network was seen to produce unusual predictions. In order to ‘help’ the network cope with the large amounts of noise in the input data, some highly anomalous series of data were removed from the database by hand. The network created with the remaining 158 data entries provided much more confident predictions, which were generally in good accordance with the literature. The removal criterion for data ensured the prediction that corrosion increased with time, but should not have biased the predictions made for the other 12 variables.

In the committees produced for 367, 243 and 158 data entries, inclusion of sulphur in the alloy was always seen to have the greatest impact, even though the inclusions were of the order of 0.001 wt% or less.

Exposure of the sample to solar radiation and rainfall, the levels of atmospheric pollution, and the inclusion of certain other alloying elements were also seen to have important roles.

There is scope for further work which would broaden these sensitivity analyses using a different base dataset. The set chosen might be one in a sheltered condition or using a different composition. In this manner it would be possible to see more clearly the interactions between variables – for instance it is expected that with increasing carbon content, addition of chromium is less effective in influencing corrosion behaviour.

In order to better assess the flexibility of the model, it would be advantageous to test it on further datasets lying outside the ranges of the training data. The paper by Cai *et al.* includes a wealth of references providing atmospheric corrosion data for a particular composition. These include studies conducted in more than 30 countries, and thus a variety of climates.

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