

Prediction of leachate pH for cement paste containing pure metal compounds

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Abstract

Neural network models, to predict the leachate pH for single batch extraction leaching tests conducted on Portland cement pastes containing pure compounds, were constructed using existing data from the literature. The models were able to represent the known non-linear dependency of pH on acid addition, and were used to show that Cu increases, and Zn and NO_3^- decrease, the leachate pH for addition of 8 meq acid/g dry cement (to achieve a mid-alkaline pH). Ba, Cd, Cr(III), Ni, Pb, Cl^- and OH^- had no detectable effect on the acid neutralisation capacity (ANC) of the cement pastes in the concentration ranges investigated. The laboratory where testing was conducted was found to be an important predictive variable, which acted as a surrogate variable for laboratory specific variables that were not adequately reported in the literature, such as cement characteristics, sample preparation details, and leaching test and pH measurement details. This work has shown that development of good empirical predictive models for solidified product leachate pH is feasible, and is limited only by the availability of data. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Stabilisation/solidification with Portland cement or other hydraulic binders is often suggested as the best treatment for wastes that can not be reduced or recycled. In a good solidified product, hazardous contaminants are chemically immobilised, by the alkaline environment and in the cement hydration products, and physically trapped, by encapsulation in the hydration products and in the overall bulk of the matrix. The pH and the ability of a solidified product to neutralise acid are important aspects both because solubility of contaminants is often pH dependent [1], and because the physical matrix is dissolved and

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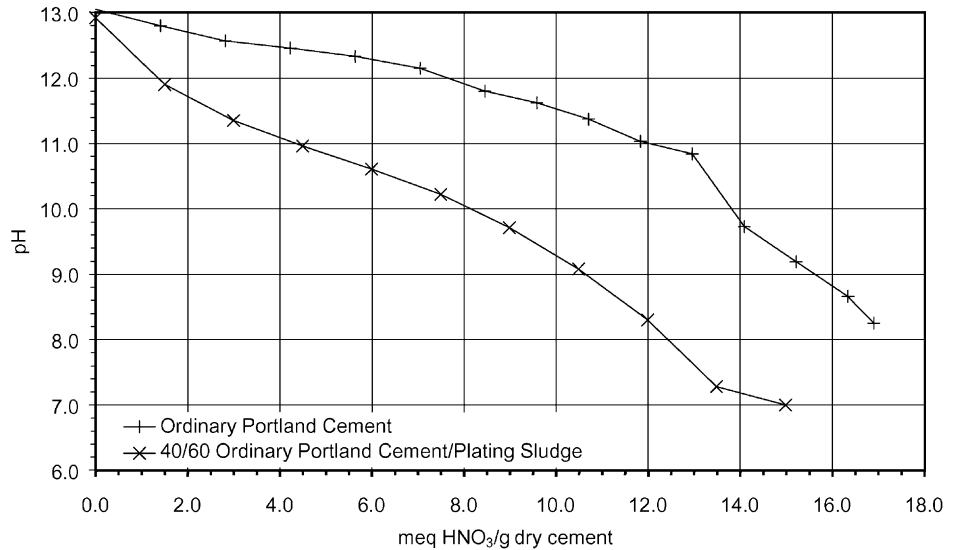


Fig. 1. Titration curves illustrating the effect of waste on the ANC of cement paste.

weakened by acid [2]. Thus, acid neutralisation capacity (ANC) should be a key part of any mechanistic leaching model.

The response of a hydrated cement to acid addition is dependent on the hydration products formed, and previous work has shown that these are affected by waste components [3]. The substantial effect that impurities can have on ANC is illustrated by Fig. 1, which shows titration curves for ordinary Portland cement and a solidified product containing ordinary Portland cement and metal plating sludge (with pH \sim 8), after 1 year of curing. Per equivalent mass of cement, the ANC to pH 9, where amphoteric contaminants increase in solubility, and below which a physically stable matrix can no longer exist, is 30% lower for the product containing waste than for the pure cement.

Unfortunately, although advances have been made in modelling the pH of pure systems [4–11] the changes to hydration products caused by the presence of impurities present in real cements, and contaminants in the wastes, are poorly understood, and it is not possible at this time to develop a mechanistic model of ANC of solidified products. However, the open literature contains results of many laboratory studies of leachability, including pH, and ANC. Whereas each of these studies presently stands on its own, without clear applicability to new situations, there is the potential to uncover trends in a number of studies taken together as a body of data, using empirical modelling techniques such as neural network analysis.

Neural network analysis has emerged over the past decade as a practical technique for identifying patterns in large data sets of many variables. Certain types of neural networks are useful for the construction of empirical regression models, i.e. for prediction of outputs based on inputs. Neural networks are most successful when used to model complex systems in which there is evidence of a relationship between the inputs and outputs, but the relationship can not be described mechanistically, and for which large amounts of data exist. Prediction

of solidified product pH and ANC is a good candidate for neural network analysis because it is clear that pH and ANC must be related to the hydration products formed, which in turn is related to solidified product composition, but the mechanisms are not understood, and the literature contains a large number of references with results of experiments to investigate these properties.

This paper reports on the construction of neural network models to predict the pH of a single batch extraction tests [12] conducted on products containing Portland cement and synthetic wastes. The objective of the work was to assess whether the development of useful predictive models is feasible, and investigate the variables that are important in predicting pH.

2. Approach

2.1. Neural network analysis

The application of neural network analysis to environmental and civil engineering problems has been the subject of a number of review articles in the past decade (e.g. [13]), and detailed information on neural networks is available in texts on the subject (e.g. [14]). The authors have prepared a glossary as an aid to studying this literature [15].

From the many different types of neural networks that have been developed with different objectives, the multilayer perception is particularly suited to regression problems and was chosen for application in this research. The objective of this type of neural network analysis is the same as that of polynomial regression, but the mathematical technique is different. By parallel processing of the inputs, multivariate non-linear functions are modelled as composites of simple non-linear functions (e.g. the sigmoid function), such that any multidimensional surface can be approximated [14]. The composite function is fitted to the data by modifying the parameters of the component non-linear functions in an iterative “training” process, which minimises the error between the predicted outputs and the target outputs.

To avoid overfitting of the neural network model to the data during iterative training, a separate data set is used to validate the model at intervals during training. Training is stopped when the error for the validation set begins to increase. A third set of independent data is used to test the network after completion of training and validation, to assess its performance on data to which it has never before been exposed.

For the prediction of solidified product leachate pH in this study, neural network analysis was conducted using the Trajan Neural Network Simulator [16]. Hundreds of different neural networks with different combinations of input variables were trained and evaluated in the course of this investigation. These regression models were evaluated initially on the basis of their root-mean-square errors for the training, validation and testing sets. The root-mean-square errors were compared with the interlaboratory experimental error, and the errors for linear models based on the same variables.

Three forms of visual analysis were conducted to examine the fit of the models.

1. The predicted values were plotted against the measured values, and correlation coefficients were calculated for the training, validation and testing sets.

2. Normal probability plots of the residuals, i.e. the differences between the target and predicted outputs, were created. In normal probability plotting, the cumulative frequency distribution of the residuals is mapped onto a plot with an ordinate whose scale is adjusted such that points that are normally distributed fall in a straight line. Normally distributed residuals are an indication that the model is accounting for all but random error. The normal probability plots were helpful in identifying outliers and systematic errors.
3. Response graphs of the predicted outputs as a function of each of the input variables were plotted. Unlike polynomial models, neural networks do not converge upon a unique solution. Thus, creating multiple neural networks for the same data set, each of which may model the system slightly differently, and plotting response graphs for each, can provide some perspective regarding the uncertainty associated with the predictions.

2.2. Data collection

The data set for neural network analysis was a subset from the MONOLITH database of cement-based product properties [17]. Of the approximately 1500 references in the database, only 13 references reported the leachate pH for single batch extraction tests for a total of 97 products composed of Portland cement and pure inorganic or toxic metal compounds [18–30]. Eighteen leachate pH values associated with a 14th reference [31] were obtained from the authors. ANC measurements for six different Portland cement control samples were also obtained [32–36]. The data from two references [22,23] were generated as part of the same project (Neural Network Analysis for Prediction of Interactions in Cement/Waste Systems, NNAPICS) [37], and one of the products from each were each tested in two other laboratories as part of the project quality control programme.

The compounds studied in each of these references are summarised in column 2 of Table 1, with the number of curing temperatures and ages in columns 3 and 4. Columns 5 and 6 show the number of products and pH measurements in each reference. From this table, it may be observed that Ba, Cd, Cr(III), Cu, Ni, Pb and Zn were each investigated in more than one reference, as oxides, hydroxides, chlorides and nitrates. As, Ca, Cr(VI), Hg, Fe, K, Mn, Na, SO_4^{2-} , and V were not included in the data set for neural network analysis because they were represented in too few examples. Therefore, the data from [18–20] could not be used, and only some of the data from [22,23,25,26,28,29,31], were included in the data set.

Thirty-five of the fifty-one pH measurements from [34] were also eliminated, because they were for generalised ANC tests using acetic acid, which sets up a buffer at low pH. Results for acetic acid extractions using less than 2 meq/g wet weight (e.g. the amount used in the USEPA TCLP), were retained because the extracts remained in the highly alkaline range.

Table 2 shows the variable ranges for the input and output variables in data set OPCpH1A. Although the cement composition might be expected to have an impact on the ANC, compositional information was not available for all the cements and could not be included as an input variable. All of the cements were ordinary Portland cements, and the effect of

Table 1
Summary of data collected for modelling of leachate pH of Portland cement containing pure compounds

Reference	Contaminants ^a	Number of curing		Number of products	pH
		Temperature (°C)	Time (days)		
[18]	CaCl ₂	1	1	6	30
[19]	Na ₂ HAsO ₄ , FeSO ₄	1	1	1	1
[20]	NiO, CdO, HgO, PbO	1	1	3	9
[21]	Cd(NO ₃) ₂	1	6	5	15
[22]	Cr ₂ O ₃ , Fe ₂ O ₃ , PbO, ZnO	1	1	10	123
[23]	Cr(NO ₃) ₃ , Pb(NO ₃) ₂ , Mn(NO ₃) ₂ , Zn(NO ₃) ₂	1	1	9	76
[24]	Ba(NO ₃) ₂ , Cd(NO ₃) ₂ , Cr(NO ₃) ₃ , Cu(NO ₃) ₂ , Ni(NO ₃) ₂ , Pb(NO ₃) ₂ , Zn(NO ₃) ₂	1	1	22	230
[25]	K ₂ CrO ₄ , Cr(NO ₃) ₃	3	3	3	6
[38]	Cd(NO ₃) ₂ , Cr(NO ₃) ₃ , CuCl ₂ , Pb(NO ₃) ₂ , K ₂ SO ₄ , NaCl, Zn(NO ₃) ₂	1	1	17	198
[3,15,17,27,37]	Ba(OH) ₂ , Cd(OH) ₂ , Cr(NO ₃) ₃ , Cu(OH) ₂ , Ni(OH) ₂ , Pb(NO ₃) ₂ , ZnCl ₂	1	1	16	176
[28]	Na ₂ Cr ₂ O ₇ , CdSO ₄ , NiSO ₄	1	1	3	3
[29]	CrCl ₃ , CrO ₃	1	1	2	2
[30]	NiCl ₂	1	1	1	1
[31]	Cd(NO ₃) ₂ , CrO ₃ , Na ₃ VO ₄	3	3	18	18
[32]	none	1	1	1	11
[33]	none	1	1	1	46
[34]	none	1	1	2	51
[35]	none	1	1	1	36
[36]	none	1	1	1	24

^a Not including waters of hydration.

the specific cement type, including the strength class, was confounded with the laboratory, which was included as a categorical variable with 15 categories in 1-of-*n* encoding. Except for the products from [25,29–31], the references cured and leached the products at room temperature. Therefore, temperature was also considered to be a part of the laboratory variable.

The product cement contents ranged from 73.7 to 100% of the total dry product mass (i.e. before water addition), but were not used in the analysis, as they were correlated with the contaminant contents. The water content was expressed as a percentage of the mass of dry cement and the concentrations of the pure compounds, separated into metals and anions (column 1 of Table 2), were expressed as mg/kg dry cement. The pure compounds were sometimes added individually, and sometimes in combinations with others. Product age (i.e. curing time) also had numeric values in the data set.

The different single batch extraction leaching tests conducted on the products were described by their liquid-to-solid ratios and acid additions, which were numeric variables. The type of acid was not included as an input variable, as most of the pH measurements were for nitric acid extractions; the other acids used in a small proportion of samples

Table 2
Summary of data set OPCpH1

Variable	Added as/with	Minimum	Maximum	Number of levels/ products
Water (% dry cement)	0	100	36/71 + 6	
Metals (mg/kg dry cement) ^a				
Ba	All but O ²⁻	278	10000	3/12
Cd	All but O ²⁻	1000	83000	12/22
Cr(III)	All	1000	68000	7/20
Cu	All but O ²⁻	1000	10000	4/15
Ni	All but O ²⁻	1000	68000	5/14
Pb	All	597	29000	7/19
Zn	All	1000	151000	6/19
Anions (mg/kg dry cement) ^a				
Cl ⁻	All but O ²⁻	1510	139000	4/12
NO ₃ ⁻	All but O ²⁻	598	121000	37/44
OH ⁻	All but O ²⁻	69	2070	14/15
O ²⁻	Cr(III), Pb, Zn	1610	49000	4/4
Age (days)		0	365	18/71 + 6
Liquid-to-solid ratio (g/g dry cement)	0.45	41	211/71 + 6	
Acid addition (meq/g dry cement)	0	31	620 + 133/71 + 6	
pH		0.01	14.0	620 + 133/71 + 6

^a Minima and numbers of levels do not include 0-addition controls.

were acetic, hydrochloric and sulphuric. The liquid-to-solid ratio was expressed as the ratio of the total mass of water, including the mixing water, to the dry mass of cement. Based on the characteristics of the tests, it was assumed that steady-state concentrations were attained in all the leachates, i.e. test duration, particle size and agitation were not included as separate variables, although in any case they were part of the “laboratory” variable. The acid addition was expressed as milliequivalents of acid per gram of dry cement.

Data set OPCpH1 contained 620 data points from references that studied the effects of pure compounds on ANC and 133 additional data points for ordinary Portland cement paste controls from other references, i.e. a total of 753 data points for 16 input variables. Testing was conducted using all 44 data points from [23], six data points from [31], four data points from [25], two data points from [28], two data points from [29,30], 21 data points from [33] and 34 data points selected at random from the remaining references. The remaining 527 data points were used in training.

Based on the results from initial network analysis, a subset of OPCpH1 was used in continued model development, which included only the data points with target pH values >9. This reduced the data set to 515 points and resulted in use of a subset of 72 of the previous points for validation, and a subset of 73 of the previous points for testing, leaving 370 training data.

3. Results and discussion

The performances of the best neural network models constructed for prediction of pH with data set OPCpH1 are summarised in Table 3. The number of “hidden cells” in column 4 is the number of simple non-linear multidimensional (sigmoid) functions that have been superimposed by the neural network to create the model.

3.1. General observations

In general, the root-mean-square errors of the neural networks in Table 3 are lower, and the correlation coefficients are higher, than for the linear models, which indicates that the neural networks are able to model non-linearities that cannot be modelled with a linear model. This is not a surprising result, because of the obvious non-linear dependence of pH on acid addition, whereby the curve of pH as a function of acid addition for a cement-based product appears as an initial series of plateaus at characteristic pH values for the alkaline solid phases, followed by a steep drop in the pH caused by the depletion of these phases at high acid additions.

A plot of the predicted versus target pH values for the best network constructed using all the variables and the full range of data, OPCpH1-1 (Fig. 2), shows good predictions at high and low pH, but relatively poor predictions for pH values between 2 and 10, which led to the appearance of strong tails in the normal probability plot (not shown). Below pH 10, the main solid hydration products have been depleted and small changes in acid addition have a proportionally larger affect on pH than in the alkaline region where acid additions are neutralised by the solid phases and the pH changes only gradually. Accordingly, small errors in acid addition have a greater effect once the solid phases are depleted, and

Table 3
Summary of neural network models constructed for data set OPCpH1

Model code	Inputs		Hidden cells	Root-mean-square error ^a			Correlation coefficient ^a		
	Number	Type ^b		Tr	V	Te	Tr	V	Te
Linear	16	1	–	1.61	1.70	2.E+14	0.92	0.92	0.23
Linear	16	2	–	0.27	0.24	1.E+14	0.97	0.98	–0.14
OPCpH1-1	16	1	3	0.73	0.87	1.28	0.98	0.98	0.94
OPCpH1-2	16	2	7	0.23	0.18	0.58	0.98	0.99	0.88
OPCpH1-3	10	3	11	0.23	0.18	0.65	0.98	0.99	0.87
OPCpH1-4	10	3	10	0.22	0.19	0.62	0.98	0.98	0.87
OPCpH1-5	10	3	4	0.24	0.19	0.53	0.98	0.99	0.92
OPCpH1-6	10	3	7	0.24	0.19	0.50	0.98	0.98	0.91
OPCpH1-7	10	3	3	0.21	0.19	0.45	0.98	0.98	0.93
OPCpH1-8	2	4	2	0.24	0.20	0.50	0.98	0.98	0.91
OPCpH1-9	1	5	13	0.52	0.46	0.54	0.90	0.90	0.90
OPCpH1-10	6	6	6	0.23	0.18	0.51	0.98	0.99	0.91

^a Tr: training set; V: validation set; Te: test set.

^b Input type: (1) all, for full data set; (2) all, with pH > 9; (3) all but Ba, Cd, Pb, Cl[–], OH[–] and O^{2–}, with pH > 9; (4) laboratory and acid addition only, with pH > 9; (5) acid addition only, with pH > 9; (6) laboratory, acid addition, water content, Cu, Zn, and NO₃[–], with pH > 9.

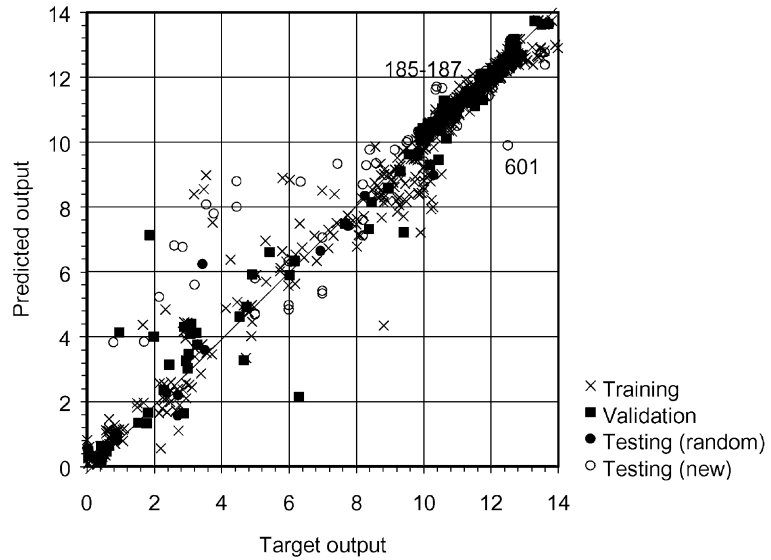


Fig. 2. Target vs. predicted pH values for neural network OPCpH1-1, based on all input variables, for full data set.

the result is that the variance of the pH measurement is not constant over the full pH range. This is demonstrated clearly by the plot of the variances measured in the NNAPICS quality control programme [17,37] (Fig. 3); the interlaboratory standard deviation calculated for $\text{pH} > 9$ was 0.28; that for $\text{pH} < 9$ was 9.0. Also, an early study of the properties of cement-based solidified wastes [49] found the following comparable interlaboratory

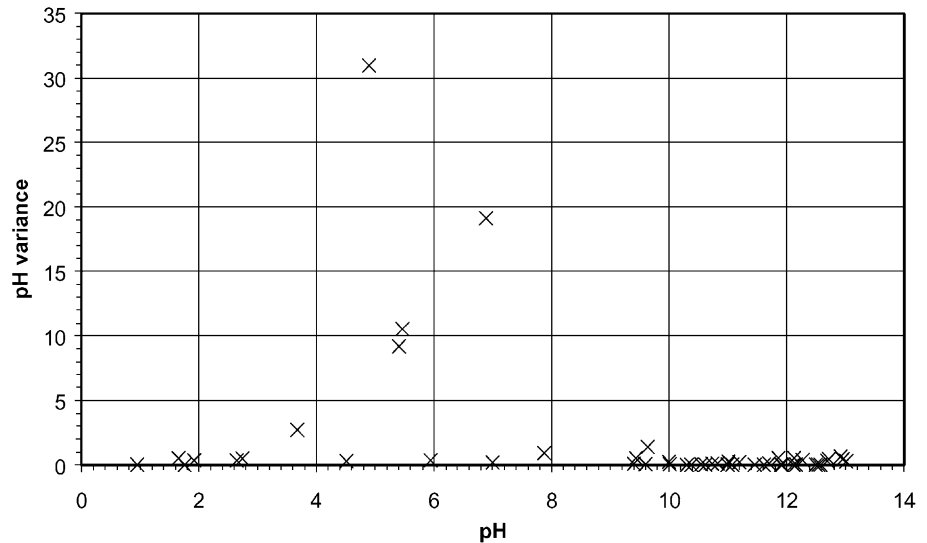


Fig. 3. Variance as a function of pH for NNAPICS quality control data.

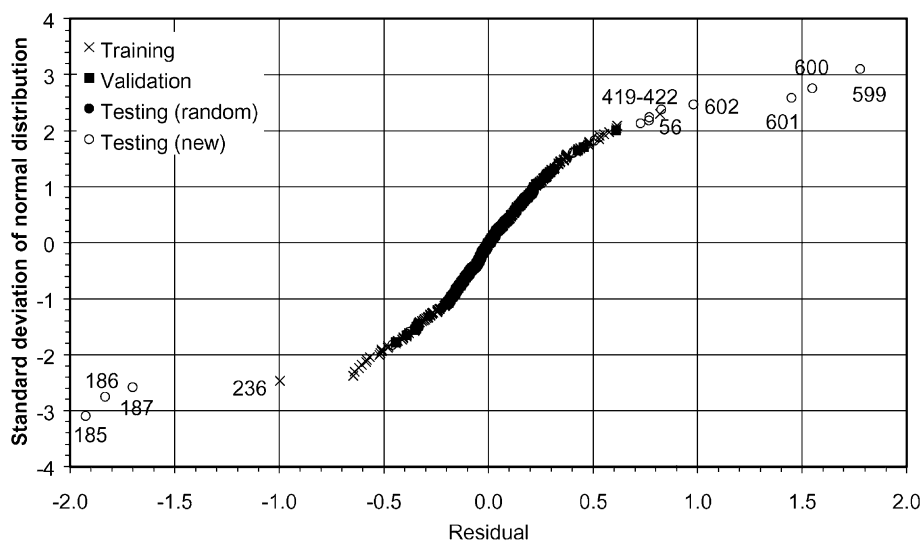


Fig. 4. Normal probability plot of residuals for neural network OPCpH1-2 based on all input variables, for data with target pH > 9.

standard deviations for pH:

1. 0.51–1.0, for a distilled water extraction with a median pH of 12;
2. 0.77–1.2 for the USEPA TCLP with a median pH of 9; and
3. 1.2 for the ANC test (over the entire pH range).

Thus, a normal distribution of residuals over the full pH range can not be expected.

For this reason, neural network development was continued with the data for pH measurements >9 only. The normal probability plot of the residuals for the best network constructed using all the variables (OPCpH1-2) is shown in Fig. 4. A much smaller systematic error was visible in this plot than in the normal probability plot for OPCpH1-1. Since very alkaline pH solutions are prone to carbonation from the atmosphere, and most solid phases have been depleted by pH 9, it is possible that the variance associated with the pH measurement is in fact slightly greater at either end of the training range. These phenomena could be responsible for the observed systematic error.

Fig. 4 also shows a number of outliers for new test data, and for one of the training data points, which have been labelled with their identifying indices. Training data point 236 (from [24]) had a target pH of 9.04, near the end of the training range, and is probably simply a point with an unusually high measurement error. For the new test data, one of the primary causes of poor predictions is the strong dependence of the network on the laboratory as an input variable. Since all of the new test data points were from laboratories unfamiliar to the network, it is encouraging that many of them were well-predicted, rather than surprising that some were not. Those that were poorly predicted tended to have strong differences from the training set: data points 185–187 [31] had estimated product water contents, elevated curing temperatures, and were tested using acetic acid at liquid-to-solid ratios that were

out of the training range; data points 419–422 [25] were obtained at elevated curing and leaching temperatures; data points 601 and 602 [29,30] had liquid-to-solid ratios that were out of the training range, and also contaminant concentrations that were out of the training range, as did 599 and 600 [28]. These outliers demonstrate that neural network models are poor at extrapolating outside of the training range, and are responsible for the higher overall root-mean-square error on the test set; the remaining test data were well-predicted.

The differences between the root-mean-square errors for the training and validation sets indicate that the data set is relatively small to describe the system.

For the networks constructed using the full data set, as well as those constructed using only data with target pH > 9, it was noted that the root-mean-square errors on the training and validation sets were lower than the relevant interlaboratory standard deviations from the NNAPICS quality control programme and previous investigations. There are two possible explanations for this.

1. The interlaboratory standard deviations from the NNAPICS quality control programme and the previous investigations were measured for products containing real wastes, whereas OPCpH1 contained only data from products containing pure compound additions. The interlaboratory reproducibility of the ANC measurements for products containing pure compounds may be better than that for products containing real wastes because the variability of the starting material was lower.
2. The neural networks may have overfitted the data. This would also provide another explanation of the systematic errors observed in the normal probability plots.

The latter explanation was judged to be unlikely on the basis that:

1. the test data were predicted as well as the training and validation data (with the previously explained exceptions);
2. dependence of the residuals on the pH accounted for the systematic error; and
3. a progression in the shape of the normal probability plot can be observed as more input variables are added from Fig. 5 (acid addition only), to Fig. 6 (acid addition and laboratory), to Fig. 4 (all input variables). The same shape is observed in each, but the spread of the distribution becomes smaller.

3.2. *Effects of input variables*

Sensitivity analysis of OPCpH1-1 and -2, and a group of four additional neural networks constructed with the same input variables for each, was conducted by observing the effect of omission of each of the input variables in turn on the root-mean-square error [17]. The results suggested that acid addition was the most important variable for the prediction of pH, but the performance of neural network OPCpH1-9 (Table 3 and Fig. 5) based on acid addition only showed that the other input variables improved the pH predictions substantially. Sensitivity analysis also showed that the laboratory was an important predictive variable. Such a result might be expected because of the many experimental variables that would remain consistent within a laboratory, but might vary from one laboratory to another, such as: cement type, protection of samples from carbonation during batch preparation, curing, drying and comminution, drying temperature, and particle size, leaching vessel type,

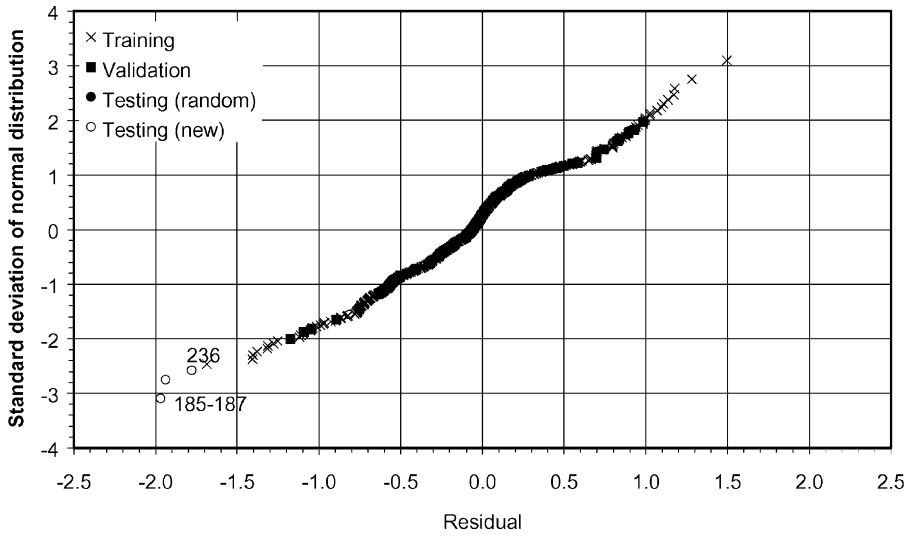


Fig. 5. Normal probability plot of residuals for neural network OPCpH1-9 based on acid addition only, for data with target pH > 9.

solid/leachant contact time, leaching reagent purity, acid addition mechanisms, agitation, solid/leachate separation procedures and pH electrode maintenance and calibration for the leaching tests. Liquid-to-solid ratio, curing time and water content were also identified as important predictive variables.

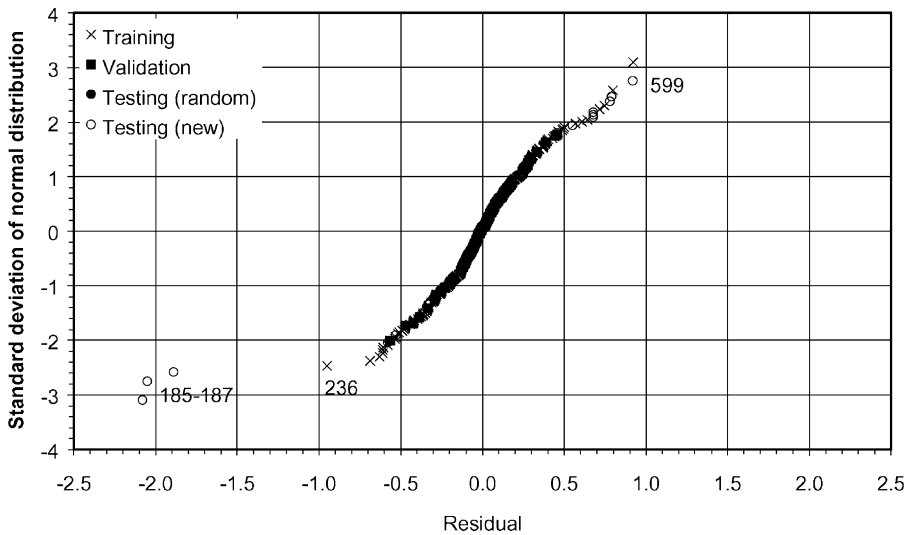


Fig. 6. Normal probability plot of residuals for neural network OPCpH1-8 based on acid addition and laboratory, for data with target pH > 9.

Response graphs were constructed for the groups of five networks trained with the same data as OPCpH1-1 and -2, to better evaluate the effects of the numeric variables on the pH predictions [17]. For each group, the maximum and minimum pH values predicted by the five networks were plotted for an acid addition of 8 meq/g dry cement, to try to achieve a mid-range alkaline pH, as each input variable was varied over its range in the data set in 10 steps. For each plot, the values of the other input variables were held constant at their mean concentrations.

The response graphs (not shown) showed:

1. high variability of the pH predictions on the basis of curing time and liquid-to-solid ratio;
2. a decrease in the median pH of about half a unit going from a water-to-cement ratio of 0–1;
3. no effect of Ba, Cd, Pb, Cl^- or OH^- over the concentration ranges investigated;
4. small effects for Cr(III), Cu, Ni, Zn and NO_3^- , but without agreement between the two groups of neural networks; and
5. increasing variability of the pH predictions as a function of the O^{2-} and Zn concentrations.

As would be expected, both groups of response graphs confirm the importance of acid addition for pH prediction. The constant acid addition of 8 meq/g dry cement used to generate the response graphs for the other input variables resulted in a median pH of 11.6 for the networks constructed using the full data set and 11.4 for the networks constructed with data for target pH values >9 . Table 4 shows the equilibrium pH values of the pure phases present in cement-based products. Comparison with the tabled values suggest that at the median predicted pH values, calcium hydroxide and high Ca:Si ratio calcium silicate hydrate (C–S–H) would have been depleted. Given the uncertain stability and unknown effects of the numerous solution components and solid phase substitutions (caused by both manufacturing impurities in the cements, and the added contaminants) on the equilibrium, lower Ca:Si ratio C–S–H, ettringite, monosulphate and hydrogarnet may or may not have dissolved at this pH, and low Ca:Si ratio C–S–H, gehlenite hydrate, hydrotalcite and brucite will not have dissolved. Thus, a predicted decrease in the pH for an acid addition of 8 meq/g dry cement may be due to a reduction in the quantity of calcium hydroxide or high Ca:Si ratio

Table 4
Equilibrium pH values for pure cement phases

Pure phase	pH	Reference
Calcium hydroxide, $\text{Ca}(\text{OH})_2$	12.5	[40]
High Ca:Si, C–S–H	12.3	[41]
Intermediate Ca:Si, C–S–H	11.9	[41]
Ettringite, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$	9.8–12.8	[42–47,5]
Monosulphate, $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$	12	[42]
Hydrogarnet, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$	10.5–12.0	[5,40]
Low Ca:Si, C–S–H	9.9	[41]
Gehlenite hydrate, $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot 8\text{H}_2\text{O}$	9.2–11.2	[5]
Brucite, $\text{Mg}(\text{OH})_2$	10.3	[48]
Hydrotalcite, $4\text{MgO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$	6.8–9.3	[5]

C–S–H, and/or lower quantities of lower Ca:Si ratio C–S–H, ettringite, monosulphate and hydrogarnet, and/or a decrease in the equilibrium pH of these latter phases, caused by the pure compound addition. The converse is true for an increase in the pH predicted for this acid addition.

Since the sensitivity analysis and response graphs for the networks developed using all input variables agreed that Ba, Cd, Pb, Cl^- and OH^- had no predictive value, these variables were omitted as inputs for subsequent neural network development. O^{2-} was also omitted, as examination of the data set revealed its presence at higher concentrations to be correlated with higher concentrations of Zn, Pb and Cr(III). Because of different assignments of responsibility by the different networks used to generate the response graphs, this correlation was responsible for the increase in model uncertainty observed as a function of concentration for Zn and O^{2-} . Continued neural network development was also restricted to the data set with target pH values >9 , in part because it was assumed that the better interlaboratory reproducibility in this range would make it easier to identify effects. However, acid neutralisation behaviour in the alkaline range was also of greater interest, because the stability pH values for the phases found in cements (Table 4) show that the solid matrix will have disintegrated at $\text{pH} < 9$. Thus, prediction of lower pH values is of little importance for solidified products, although $\text{pH} < 9$ is common in the natural environment.

The normal probability plot of the residuals for the best neural network constructed with the selected input variables, OPCpH1-3, in Fig. 7 is very similar to that for OPCpH1-2 constructed using all the inputs (Fig. 4), and the performance indicators in Table 3 are equivalent. On the other hand, the normal probability plot for the best network constructed using only the laboratory and acid addition as inputs, OPCpH1-8 (Fig. 6), was less smooth,

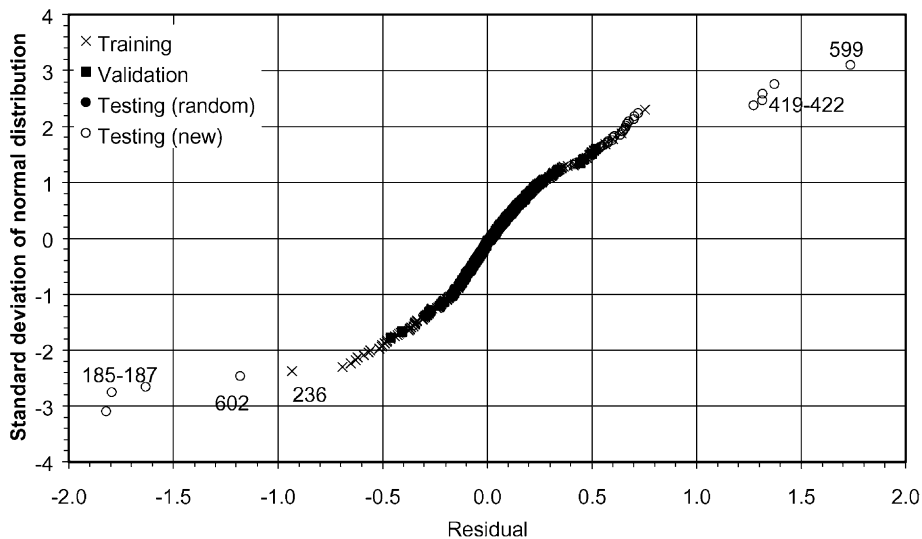


Fig. 7. Normal probability plot of residuals for neural network OPCpH1-3 based on selected input variables, for data with target pH > 9 .

and its performance was slightly worse. Together, these observations suggest that although acid addition and the laboratory may be the most important predictors of leachate pH, the other selected input variables have some predictive value.

Response graphs for the five best neural networks constructed with selected input variables, OPCpH1-3 to -8, are shown in Figs. 8–10. The observations noted above for the networks constructed with all the input variables are confirmed to a large extent. In the cases of curing time and liquid-to-solid ratio, model uncertainty remained higher at either end of the ranges of these variables. Since the liquid-to-solid ratio for all tests in a particular laboratory remained the same, this variable was confounded with the laboratory variable, and the uncertainty associated with it is a consequence of different apportioning of responsibility between the laboratory and liquid-to-solid ratio by each of the neural networks used to plot the response graphs. Nevertheless, it is interesting to note a drop in the median pH of 0.3 units between a liquid-to-solid ratio of 0.5 (for pore-water expression) and 25. Dilution of an unbuffered solution with pH 11.4 by a factor of 50 would reduce the pH to 9.7. However, in these systems the pH is controlled by dissolution of the solid phases, so a large drop in pH would not be anticipated, and the observed reduction in median pH of 0.3 units could be related to a decrease in the ionic strength. Curing time was also somewhat confounded with the laboratory, so that a separate effect on pH as a function of curing time could not be discerned. In theory, continued hydration over time might be expected to increase ANC. However, this effect might be partially or wholly offset by carbonation of inadequately protected samples over the curing period.

The decrease of the predicted pH as the water-to-cement ratio increases from 0 to 1 is interesting. It must be remembered that acid addition has been expressed as milliequivalents per gram of dry cement to be able to compare all products on an equal basis. Closer examination of the data shows that the great majority of the water-to-cement ratios lie between 0.3 and 0.5, so the definition of the data space at higher and lower water-to-cement ratios is poor. Only a single study investigated a range of water-to-cement ratios [24]. This study did show a decrease in ANC with increasing water content and is largely responsible for the behaviour of the model. Knowing this still leaves open the question of why this particular study might have found such a result, but the reasons are likely to be operational rather than related to changes in the hydration chemistry. For example, examination of the data from this study shows the moisture content to have been measured at 29 days, whereas the ANC of the product was tested at 110 days. If the product was not dried thoroughly before ANC measurement, the test would have contained a smaller amount of cement per mass than assumed in the calculations, and this effect would have been greater for higher water contents. An alternative explanation is that the products were exposed to carbonation, which could have affected the higher water content products to a greater extent. The more limited opportunity for carbonation of several products in which unhydrated cement was added directly into the leaching vessel which was then immediately sealed, i.e. which corresponded to a water-to-cement ratio of 0 [33,34,38], may also have resulted in a higher pH, which contributed to the modelling results.

As regards the contaminants, the response graphs showed no effect for Cr or Ni. Predicted pH increased by 0.2 over 0.15 mol Cu/g dry cement, and decreased by 0.5 over 2 mol NO_3^- /g dry cement. Increasing the Zn concentration from 0 to 2.3 mol/g dry cement decreased the pH by 0.2 units.

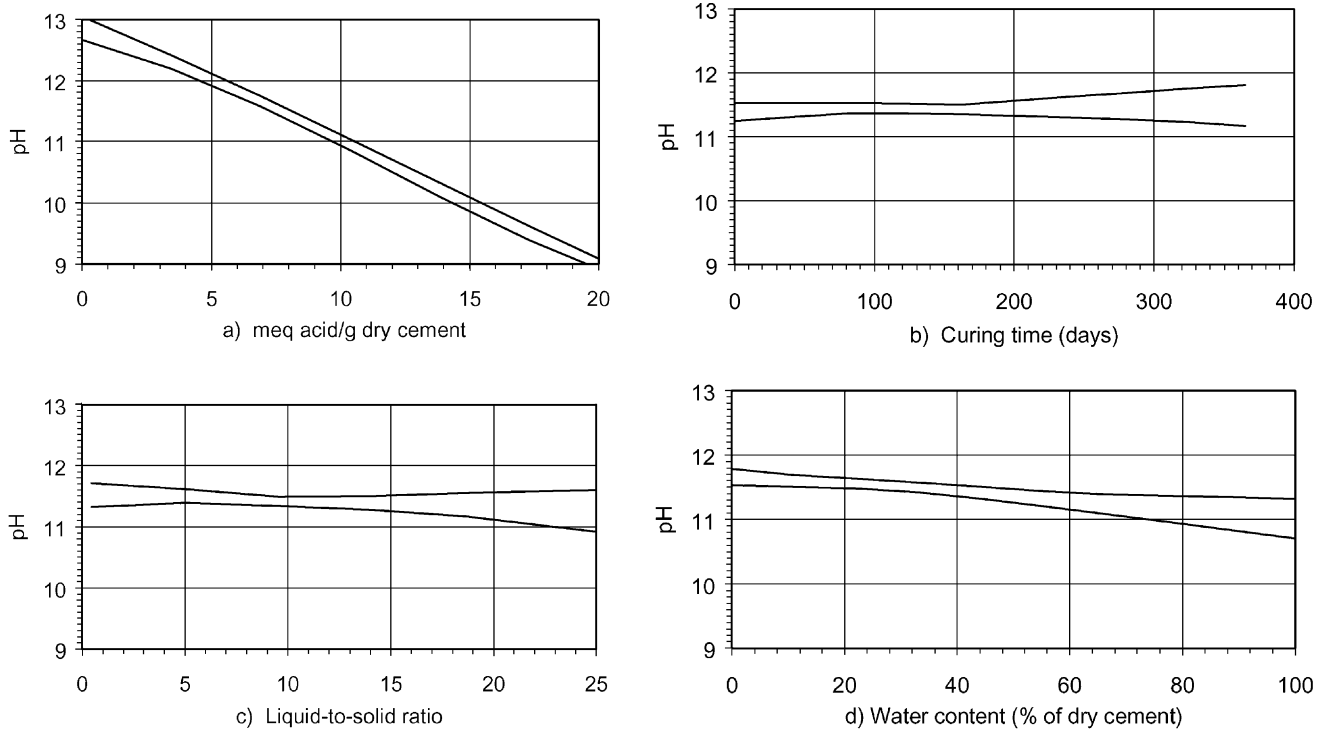


Fig. 8. Plots of predicted pH as a function of (a) acid addition with other variables at their means, and (b) curing time, (c) liquid-to-solid ratio and (d) water content at an acid addition of 8 meq/g dry cement for neural networks OPCpH1-3 to -8.

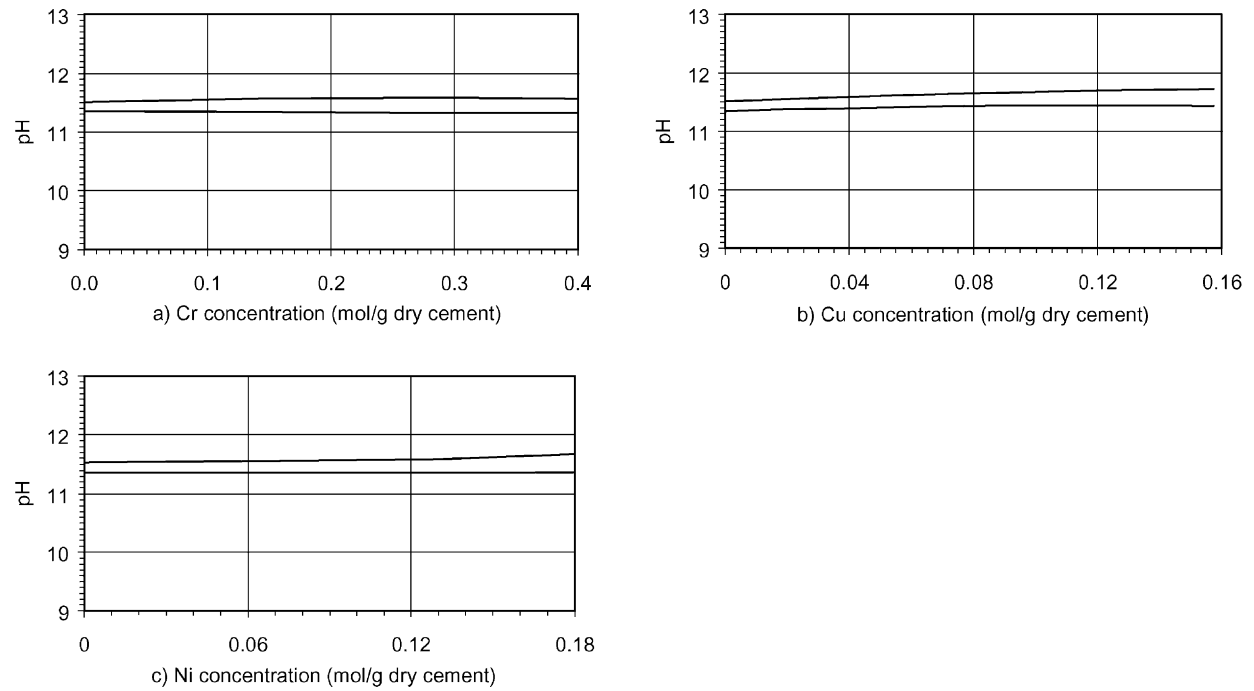


Fig. 9. Plots of predicted pH as a function of (a) Cr, (b) Cu, (c) Ni concentrations at an acid addition of 8 meq/g dry cement for neural networks OPCpH1-3 to -8.

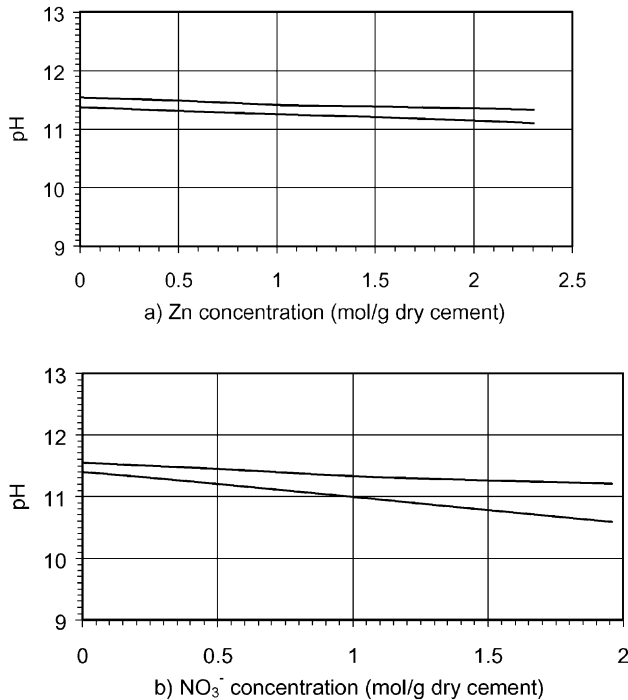


Fig. 10. Plot of predicted pH as a function of (a) Zn and (b) NO_3^- concentrations at an acid addition of 8 meq/g dry cement for neural networks OPCpH1-3 to -8.

Thus, it appears that neural network analysis has tentatively identified that Cu increases, and Zn and NO_3^- decrease, ANC to a pH of approximately 11.4. Response graphs for a final group of networks trained with only acid addition, laboratory, Cu, Zn and NO_3^- indicated the same trends [17]. Equivalent performance by the best of these networks, OPCpH1-10 (Table 3) suggests that the omitted variables really did not have a significant effect. Likewise, the slight degradation in performance when Cu, Zn and NO_3^- were left out of neural network OPCpH1-8 suggests that they do have a real effect. At the same time, these conclusions can not be absolutely firmly stated, since the observed differences are small and result in pH changes of only the order of the interlaboratory standard deviation, over the concentration ranges investigated.

It is interesting to note that one of the studies that contributed data for neural network analysis found that ZnCl_2 and $\text{Cr}(\text{NO}_3)_3$ decrease ANC [27]. This study also showed small effects for Cu and Pb, and indicated the possible presence of interaction effects between Zn and Cr as did another study [38]. Interaction effects between contaminants were not investigated in the work reported here, as even the main effects were difficult to identify.

For the studied contaminants, the literature indicates that Cr(III) acts as an accelerator and is taken up into the structure of C-S-H, whereas the other metals are thought to act as retarders by forming hydroxide hydration barriers around hydrating cement grains, and are not quantitatively taken up into C-S-H. It is thought that Cl^- is taken up into monosulphate,

and literature on the subject of NO_3^- is scarce [39]. Whereas, any of these interactions could be anticipated to have effects on pH and ANC, neural network analysis indicates that any effects of the pure compounds are quite small. A significant difference between adding pure compounds and real wastes is that the acid/base contribution of the pure compounds in the range investigated is low, whereas wastes are added in large enough quantities that acidic wastes may consume ANC while alkaline wastes may contribute to it.

4. Conclusions

Neural network analysis was able to represent the known non-linear dependency of pH on acid addition, and indicated that Cu increases, and Zn and NO_3^- decrease, the pH of the leachate, for addition of 8 meq acid/g dry cement. Ba, Cd, Cr(III), Ni, Pb, Cl^- and OH^- had no detectable effect on the ANC of the cement pastes in the concentration ranges investigated. Laboratory-specific variables, such as cement characteristics, sample preparation details, and leaching test and pH measurement details, were not well-reported in the literature, but the laboratory was used as a categorical surrogate for these input variables, and found to be important for making successful predictions. It was clear that the variance of the pH measurement is dependent on the pH value, and the model error over the pH range was found to be similar to the experimental error.

This work has shown that development of good predictive models for leachate pH of cement-based products is feasible, and is limited only by the availability of data regarding laboratory-specific variables, as well as wider concentration ranges and combinations of variables.

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