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Prediction of unconfined compressive strength of cement paste with pure metal compound additions

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Abstract

Neural network analysis was used to construct models of unconfined compressive strength (UCS) as a function of mix composition using existing data from literature studies of pure compound additions to Portland cement paste. The models were able to represent the known nonlinear dependency of UCS on age and water content, and generalised from the literature data to find relationships between UCS and contaminant concentrations, resulting in the following ranking of the UCS values predicted for addition of the contaminants, on an equimolar basis: at 7 days, Cl $\approx$ Cr(III) > NO_3^- $\approx$ Cd > control > Zn $\geq$ Ni > Pb > Cu >> Ba; at 28 days, Cl > Cr(III) > NO_3^- $\approx$ control $\geq$ Zn $\geq$ Cd > Ni > Pb > Cu >> Ba. Application of the best neural network to other data suggested that Cs is a retarder and Cr(VI) has no effect. No trends could be discerned for Hg, K, Mn, Na and SO_4^{2-}. The root-mean-square error for the best neural network seems to be an estimate of the interlaboratory error for UCS. © 2002 Published by Elsevier Science Ltd.

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1. Introduction

From its development in the late 19th century, Portland cement has been the principal cement used in construction applications worldwide. Its popularity is deserved, as it is a standardised material with well-defined final properties that can be easily produced from widely available raw materials. Although the chemistry of Portland cement is complex and the mechanisms underlying its characteristics are not completely understood, problems with its use are avoided through adherence to strict experience-based quality standards and specifications. In particular, the presence of impurities in Portland or other types of commercially manufactured cements is traditionally minimised, as impurities can have variable and significant effects on product quality, which are difficult to predict [1,2]. Nevertheless, introduction of impurities into cement-based products is inherent to use of chemical and mineral additions and admixtures in cement and concrete, treatment of industrial wastes by cement-based solidification prior to disposal and in recycling of industrial wastes by utilisation in cement-based building materials. In these products, impurities are blended with cement in order to obtain specific desired characteristics in the final product, for instance, to control setting characteristics, improve durability, reduce cost or (in the case of solidified wastes) provide a chemical and physical environment that controls leaching of contaminants into the environment.

The consequences of design of cement-based products without proper consideration of the potential interactions between cementing components and impurities may be serious. Handling difficulties, failure to set, improper strength development, deterioration over time and provision of a chemical and/or physical environment in which contaminants are not immobilised (in the case of solidified wastes) are typical problems encountered. Due to the potential practical and financial implications of these effects, considerable research has been done on the effects of admixtures and additions on cements of different types. Currently, most of these studies stand on their own, without clear relationship to the others, and there is often disagreement between

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their results [2]. The work reported here is part of a project to try to make use of the wealth of information in the literature by collecting data about cement-based products containing impurities and using neural network analysis to perform data mining to identify useful general relationships in them, which can be used to predict cement-based product properties of interest [3].

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 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 cannot be described mechanistically, and for which large amounts of data exist. Cement-based products fulfil these criteria, in that their behaviour is complex, but there are known trends, e.g., for strength as a function of water/cement ratio, and the literature contains a large number of references with results of experiments to investigate their properties [4].

Along with setting time [5] and leachate pH [6], unconfined compressive strength (UCS) was chosen as one of the primary variables of interest for prediction, as it affects the structural suitability of a cement-based product for utilisation or disposal, and is related to durability. UCS can also be thought of as an indicator of whether hydration reactions in Portland cement systems are proceeding normally, or have been retarded or accelerated. Because of the higher likelihood of successful model development for simple systems, and the prevalence of data for products containing synthetic wastes in the literature [7], it was decided to work initially with Portland cement pastes containing synthetic wastes. This work is reported here, and work with real wastes is reported in a second paper [8]. The objective of the work was to assess whether development of useful predictive models is feasible, and to investigate the variables that are important in predicting UCS.

2. Approach

2.1. Neural network analysis

The history and concepts of neural network analysis are described in detail in texts on the subject (e.g., Ref. [9]), and the use of neural networks for civil and environmental engineering applications has been the subject of a number of review articles in the past decade (e.g., Ref. [10]). The authors have prepared a glossary as an aid to studying this literature [11].

There are many different types of neural network. The multilayer perceptron used in this research is the most commonly used neural network type for engineering applications, and is particularly suited to regression problems. 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 nonlinear functions are modelled as composites of simple nonlinear functions (e.g., the sigmoid function), such that any multidimensional surface can be approximated [9]. The composite function is fitted to the data by modifying the parameters of the component nonlinear 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 prediction of the UCS of cement-based products in this study, neural network analysis was conducted using the Trajan Neural Network Simulator [12]. 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 [13]. Of the approximately 1500 references in the database, only 12 references reported UCS for products composed of ordinary Portland cement and pure inorganic or toxic metal compounds. Data for a total of 75 products at various ages were available [14–25]. Data from two references [17,18] were generated as part of the same project (Neural Network Analysis for Prediction of Interactions in Cement/Waste Systems, NNAPICS [3]), and one of the products from each was 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. Column 5 shows the number of UCS 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, Cr(VI), Cs, Fe, Hg, K, Mn, Na and SO_4^{2-} were insufficiently common to allow their inclusion in the data set for neural network analysis. Therefore, only some of the UCS measurements from five references [14,15,17,18,24], and none from two others [22,23], could be used in the data set UCS1A. The remaining 136 data points were retained as a separate data set, UCS1B.

Table 1
Summary of data collected for modelling of unconfined compressive strength of Portland cement containing pure compounds

Reference[a]	Admixtures[b]	Number of curing: Temperatures	Number of curing: Times	Number of UCS measurements
[14]	Na_2HAsO_4, CdO, $CdCl_2$, Cr_2O_3, $CrCl_3$, $Cr(NO_3)_3$, $FeSO_4$, PbO, $Pb(NO_3)_2$, HgO, $HgCl_2$	1	4	32
[15]	$Cd(NO_3)_2$, $Cr(NO_3)_3$, $CuCl_2$, $Pb(NO_3)_2$, K_2SO_4, $NaCl$, $Zn(NO_3)_2$	1	7	82
[16]	$Cd(NO_3)_2$	1	3	6
[17]	Cr_2O_3[c], Fe_2O_3, PbO, ZnO	1	6	53 + 4[c]
[18]	$Cr(NO_3)_3$, $Pb(NO_3)_2$, $Mn(NO_3)_2$, $Zn(NO_3)_2$	1	6	47 + 3[c]
[19]	$Ba(NO_3)_2$, $Cd(NO_3)_2$, $Cr(NO_3)_3$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Pb(NO_3)_2$, $Zn(NO_3)_2$	1	3	9
[20]	$Ba(OH)_2$, $Cd(OH)_2$, $Cr(NO_3)_3$, $Cu(OH)_2$, $Ni(OH)_2$, $Pb(NO_3)_2$, $ZnCl_2$	1	5	79
[21]	$Pb(NO_3)_2$	1	2	8
[22]	K_2CrO_4	1	1	4
[23]	$CsNO_3$	1	1	8
[24]	$CrCl_3$, Cr_2O_3, CrO_3	1	1	13
[25]	$NiCl_2$	1	1	5

[a] Listed by first author.
[b] Not including waters of hydration.
[c] Included in NNAPICS QA/QC programme; one product tested in three laboratories.

Table 2
Summary of data set UCS1A

Variable	Minimum	Maximum	Number of levels/products
Portland cement (% of total dry mass)	80	100	56/66
Water (% of total dry mass)	32	65	60/66
Cations (mg/kg total dry mass)[a]			
Ba	263	9810	5/11
Cd	1330	23,700	7/16
Cr(III)	979	111,000	15/26
Cu	1320	9710	5/12
Ni	1340	59,100	9/14
Pb	588	56,900	14/20
Zn	3130	121,000	8/16
Anions (mg/kg total dry mass)[a]			
Cl^-	1480	115,000	13/25
NO_3^-	815	102,000	23/33
Curing temperature (°C)	22.5	60	2[b]/66
Age (days)	1	90	11/66
Specimen shape (1-of-*n*)	0	1	3/66
Smallest dimension (cm)	2	5	6/66
Unconfined compressive strength (kPa)	80	115,000	210/66

[a] Minima and numbers of levels do not include zero addition controls.
[b] Includes room temperatures reported between 20 and 25 °C, as one level = 22.5 °C.

Table 2 shows the variable ranges for the input and output variables in data set UCS1A. Cement composition would be expected to have an impact on UCS, but compositional information was not available for all the cements; the cement strength class was available for seven references [15,17–20,24,25], but not the others, despite inquiries to the authors. Consideration was given to using the strength of the control specimens as an input variable, or to expressing the target strength of all products relative to the control, but control specimens were not available for all products at comparable ages. The 10 references that contributed data to UCS1A used ordinary Portland cement from eight different sources, so the effect of the cement type, including the strength class, was confounded with the laboratory, which was encoded as a categorical variable with 1-of-*n* encoding.

Numeric values were used for the addition of cement, water and pure toxic metal compounds. The pure toxic metal compounds were separated into their component anions and cations, as listed in Column 1 of Table 2, in order to allow their individual effects to be distinguished in modelling. Oxides were assumed to hydrate to hydroxides in the products, and hydroxide was not included as a separate input variable, as the added concentrations were minor in comparison to the amount of hydroxide released by hydrating cement. All of the contaminants were added individually, as well as in combinations (although not all combinations) with the others, which is potentially useful for identifying nonlinear and interaction effects. The cement and water contents were as dry weight percent of the total dry mass of the product (i.e., before water addition). The contaminants were expressed as milligrams per kilogram total dry product mass for initial analysis, and then converted to milligrams per kilogram dry cement for further analysis.

Curing temperature, specimen age (i.e., curing time) and UCS also had numeric values in the data set. Since specimen size and shape are known to affect the UCS, the specimen shape was included as a 1-of-*n* encoded input variable, and the smallest specimen dimension was included as a numeric input. Specimen height or height-to-diameter ratio was not included separately as it was correlated with the smallest dimension.

Ultimately, UCS1A had 16 input variables, represented by 217 data points. All 26 data points from a single reference [18] were reserved for testing; another six test data were selected at random from data set OPCUCS1A, as were the 32 data points for validation. UCS1B was used as a separate test set.

3. Results and discussion

The performances of the best neural network models constructed for prediction of UCS with data set UCS1A are summarised in Table 3. The number of "hidden cells" in Column 4 is the number of simple nonlinear multidimensional (sigmoid) functions that have been superimposed by the neural network to create the model.

3.1. General observations

The lower root-mean-square errors of most of the neural network models with respect to the root-mean-square errors of the linear model in Table 3 show that it was possible to construct neural networks whose performances were better than that of the linear model for the same data set. In other words, the neural networks were able to account for nonlinear features that could not be accommodated by a linear model.

The normal probability plot of the residuals for neural network UCS1A-1 in Fig. 1 shows the residuals falling in a straight line with an overall root-mean-square error of 7580 kPa, and no evidence of a systematic trend or pronounced outliers. The results from the NNAPICS quality control programme were used to calculate an interlaboratory standard deviation of 4120 kPa for UCS [4]. Neville [26] reports that the intralaboratory standard deviation for high-strength concrete (i.e., with a UCS greater than about 35000 kPa, which is comparable to the mean target strength for UCS1A of 44000 kPa) lies between about 3500 and 5500 kPa. Comparing with these values, and considering that the straight line appearance of the normal probability plot suggests that the model accounts for all but random error, it is possible that the root-mean-square error of 7580 kPa determined for the best neural network represents the interlaboratory error, given that some of the variables that might be an additional source of interlaboratory error were harmonised in the NNAPICS programme.

Table 3 shows that the root-mean-square errors for the validation set were slightly greater than for the training set for all the neural network models. For a reasonably well-distributed validation set, which this one was [4], this phenomenon indicates that the data set is relatively small to adequately describe the system. Additional training data would help to define the data space such that validation performances would be improved. The performances on the random test data were similar to the training or validation data. However, the performances on some of the new test data [18] were not as good, leading to higher root-mean-square errors and lower correlation coefficients for the test set as a whole. Since the contaminant ranges in the new test data set were within the range of the training data, it is postulated that the less successful predictions are due to the fact that the laboratory for the new test data was unfamiliar. Also, the less successful predictions for the new test data tended to be for low target UCS values, near the minimum of the training range.

Table 3
Summary of neural network models constructed for data set UCS1A

Model ID code	Inputs		Hidden cells	Root-mean-square error			Correlation coefficient		
	Number	Type		Tr	V	Te	Tr	V	Te
Linear	16	(1)	0	12,272	11,970	17,701	.87	.85	.81
UCS1A-1	16	(1)	5	7166	8261	8685	.96	.93	.92
UCS1A-2	3	(2)	5	9227	10,726	15,550	.93	.87	.70
UCS1A-3	13	(3)	7	10,575	13,383	13,249	.90	.79	.84
UCS1A-4	12	(4)	3	6800	8532	10,101	.96	.92	.91
UCS1A-5	12	(4)	3	6692	8625	11,533	.96	.92	.90
UCS1A-6	12	(4)	6	6932	8808	10,893	.96	.91	.87
UCS1A-7	12	(4)	5	7775	8839	10,568	.95	.92	.90
UCS1A-8	12	(4)	2	7218	8911	12,284	.96	.91	.90

Tr = training set; V = validation set; Te = test set.

Input types: (1) All with product components on total dry mass basis; (2) laboratory, water content, age with product components on total dry mass basis; (3) all but laboratory, specimen shape and size with product components on total dry mass basis; (4) all but cement content, curing temperature, specimen shape and size with product components on mass of dry cement basis.

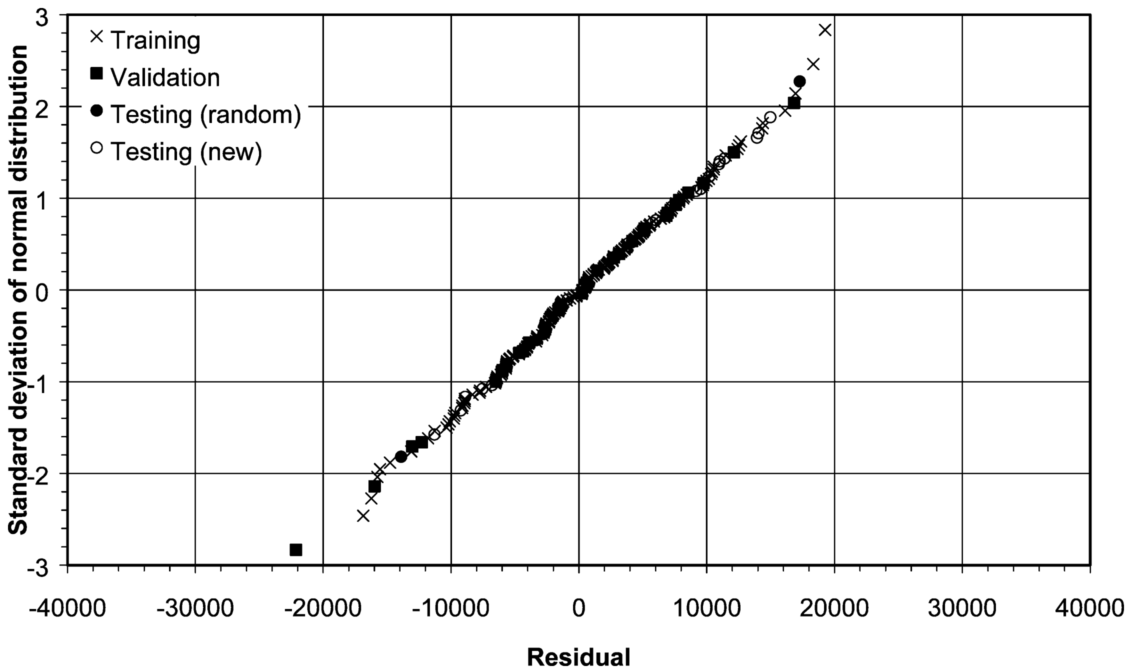

Fig. 1. Normal probability plot of residuals for neural network UCS1A-1, constructed using all the input variables.

3.2. Effects of input variables

Sensitivity analysis of UCS1A-1 and a group of neural networks constructed with the same input variables was conducted by observing the effect of omission of each of the input variables in turn on the root-mean-square error. The results suggested that the laboratory, age and water content were much more important to the models than the other input variables [4]. However, the relatively poor performance of neural network UCS1A-2 (Table 2), constructed without the contaminant additions as inputs, demonstrated that the good performance of neural networks constructed including the contaminant additions as inputs, was due to their ability to account for the effects of the contaminant additions on the UCS.

The laboratory was omitted as an input for neural network UCS1A-3 to determine whether development of a more practically useful model, which would be applicable without prior information about the laboratory, is possible. Since specimen shape and size were correlated with the laboratory as a side effect of the small size of the data set, they were also omitted as input variables. The performance of UCS1A-3 (Table 2) was significantly worse, with similar deterioration in performance across the training, validation and test sets. A normal probability plot of the residuals showed that they did not fall in a straight line [4], suggesting the existence of missing variables. As was mentioned in defining the data, neither cement compositions nor strength classes were available as separate variables for model development. Therefore, the laboratory acted as a surrogate variable for these important variables, as well as other variables that are known to have an effect on UCS, such as the cement-hardening characteristics (e.g., normal or rapid), product mixing and preparation details, laboratory conditions (e.g., curing temperature and humidity) and testing details (e.g., specimen size and shape, capping, loading rate, platen type, operator, etc. [26]).

The reliance of successful neural networks on the laboratory as an input variable limits the practical usefulness of these models because the best predictions cannot be made without prior information about the source of the UCS measurements. However, the fact that the laboratory can be used as an input variable to improve predictions means that there are likely to be additional, more quantitative, variables that could potentially be captured by more detailed reporting of experimental conditions and used in development of future models. Also, it would be feasible, and could be useful in a practical scenario, for a single laboratory to construct predictive models that would predict the outcome of in-house UCS testing.

In order to investigate the individual effects of different concentrations of the input variables on the UCS, response graphs of the predicted UCS as a function of each input variable were created. Because the cement content was negatively correlated with the contaminant additions, and the effect of cement content on its own was thought to be weak [4], the product component additions were converted to a dry mass of cement basis from the total dry product mass basis used in previous models. A series of neural networks was created using the converted data set, with laboratory, age, water content and contaminant concentrations as the input variables. The normal probability plot of the residuals for the best network, UCS1A-4, is seen to be a straight line with a root-mean-square error of 7640 kPa, similar to Fig. 1 for UCS1A-1, in Fig. 2. The five best of

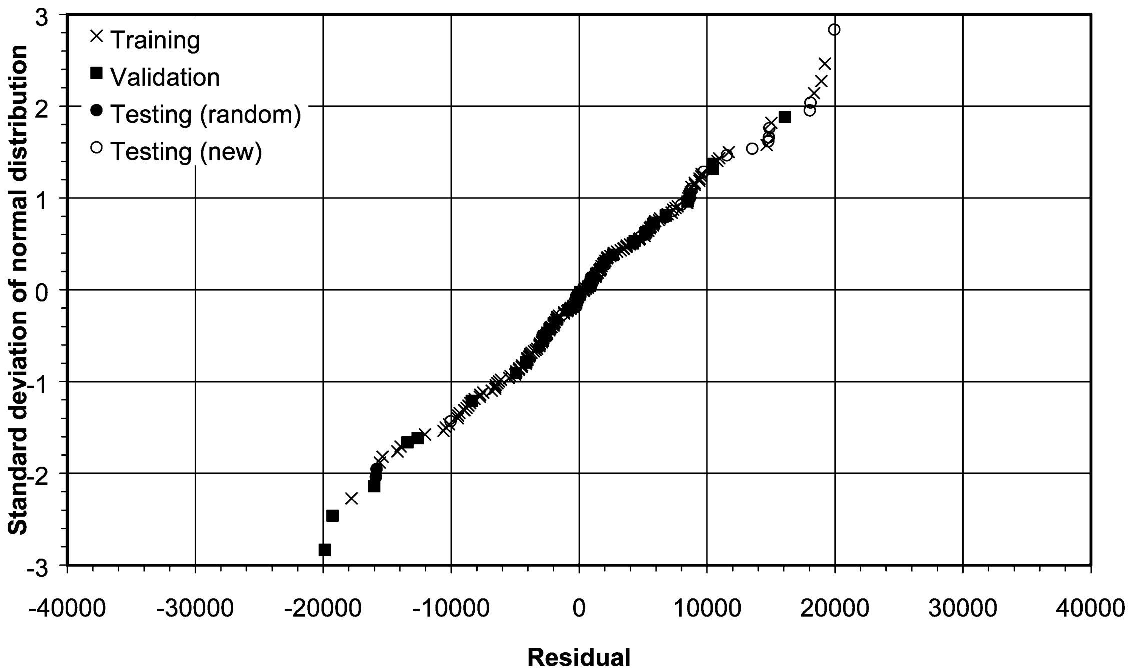

Fig. 2. Normal probability plot of residuals for neural network UCS1A-4, based on laboratory, age, water content and contaminant concentrations.

these models, UCS1A-4–8 in Table 3, performed similarly to UCS1A-1 on the training and validation sets, and slightly worse on the test sets, perhaps because the omitted specimen size and shape were helpful in predicting the new test data that had an unfamiliar laboratory.

Response graphs for UCS1A-4–8 were constructed by varying the value of each input over its range in the data set (in 10 steps) while the levels of the contaminant additions were held at 0, at the average water content of 41.5%. The minimum and maximum predictions by neural networks UCS1A-4–8 over the input variable ranges have been plotted in Figs. 3–5 to gain an impression of the effect of each variable on the response, and the uncertainty associated with the predictions. The range of 7-day predicted strengths

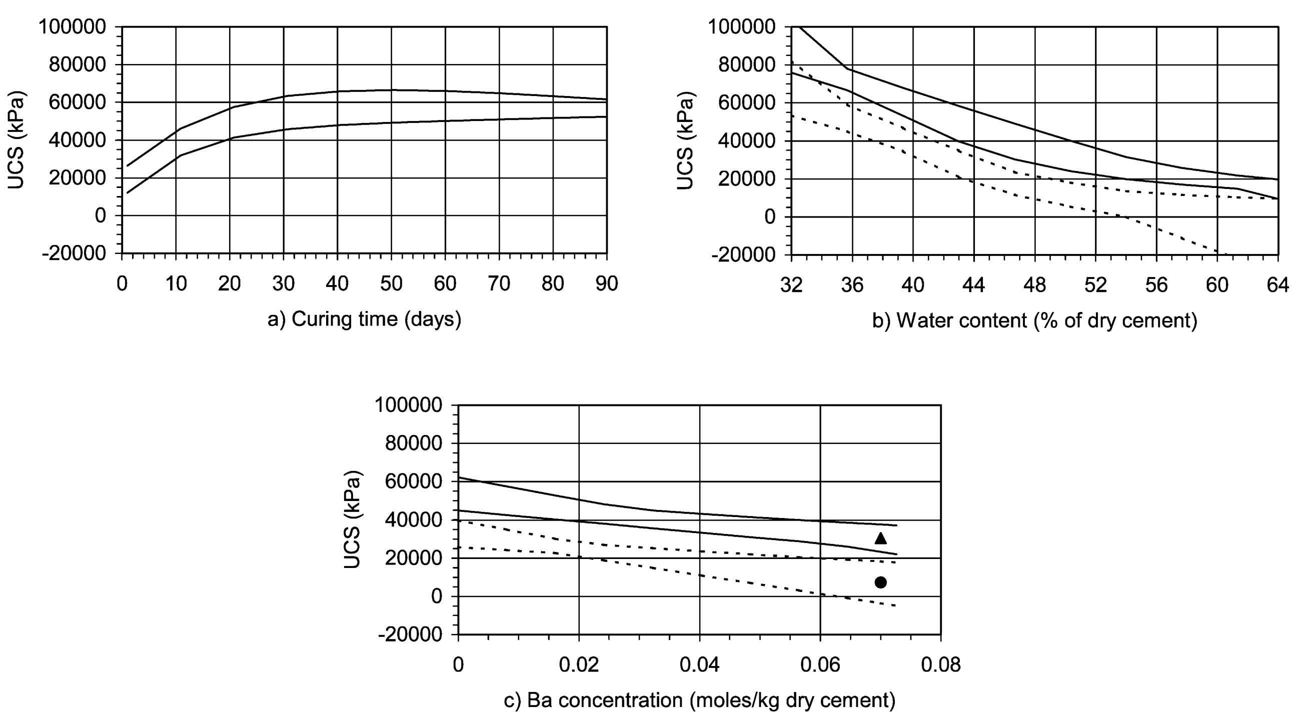

Fig. 3. Plots of predicted UCS at 7 (------) and 28 (—) days as a function of (a) age, (b) water content and (c) Ba concentration for neural networks UCS1A-4–8.

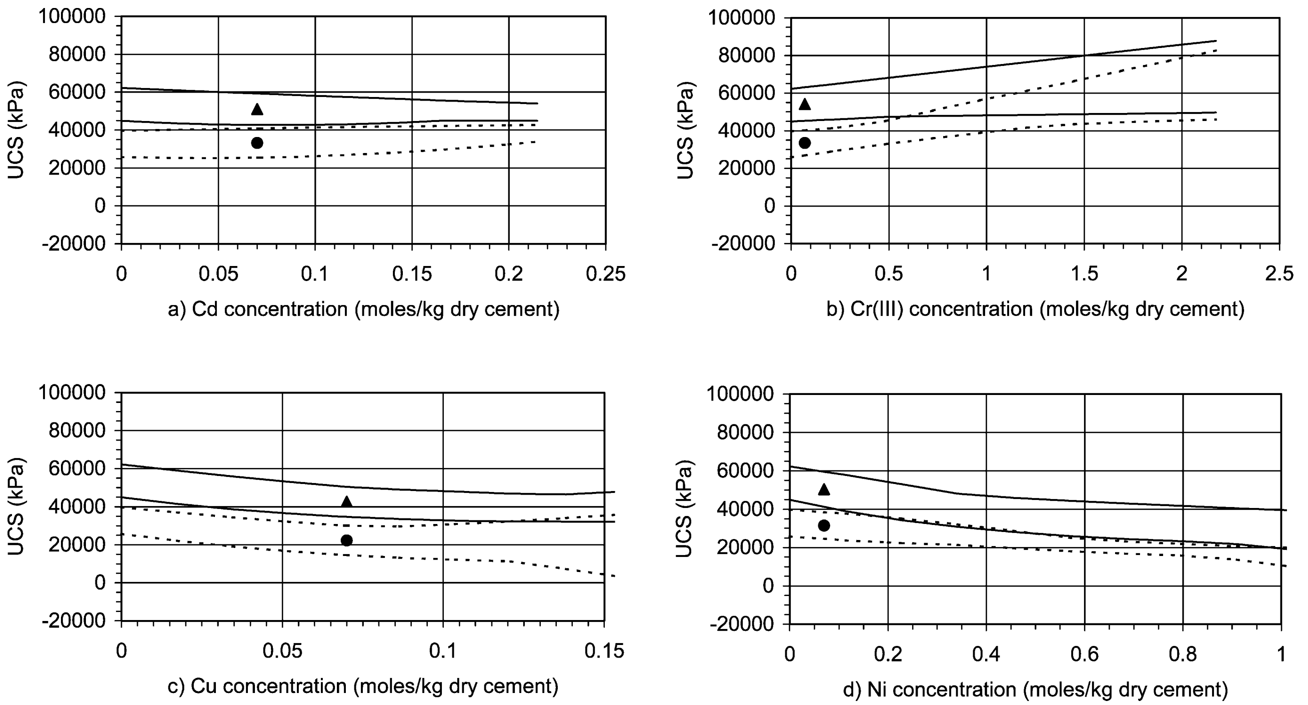

Fig. 4. Plots of predicted UCS at 7 (------) and 28 (—) days as a function of (a) Cd, (b) Cr, (c) Cu and (d) Ni concentration for neural networks UCS1A-4–8.

is indicated with dashed lines, while the range of 28-day predicted strengths is indicated with solid lines. The midpoint of the prediction range at a concentration of 0.07 mol/kg dry cement for each contaminant has been marked with a solid triangle for the 28-day UCS; a solid circle was used to mark the 7-day UCS. The position of the triangles and circles with respect to the *x*-axis emphasizes the different concentration ranges for the different contaminants.

In general, the difference between the maximum and minimum predictions by the five networks was about twice

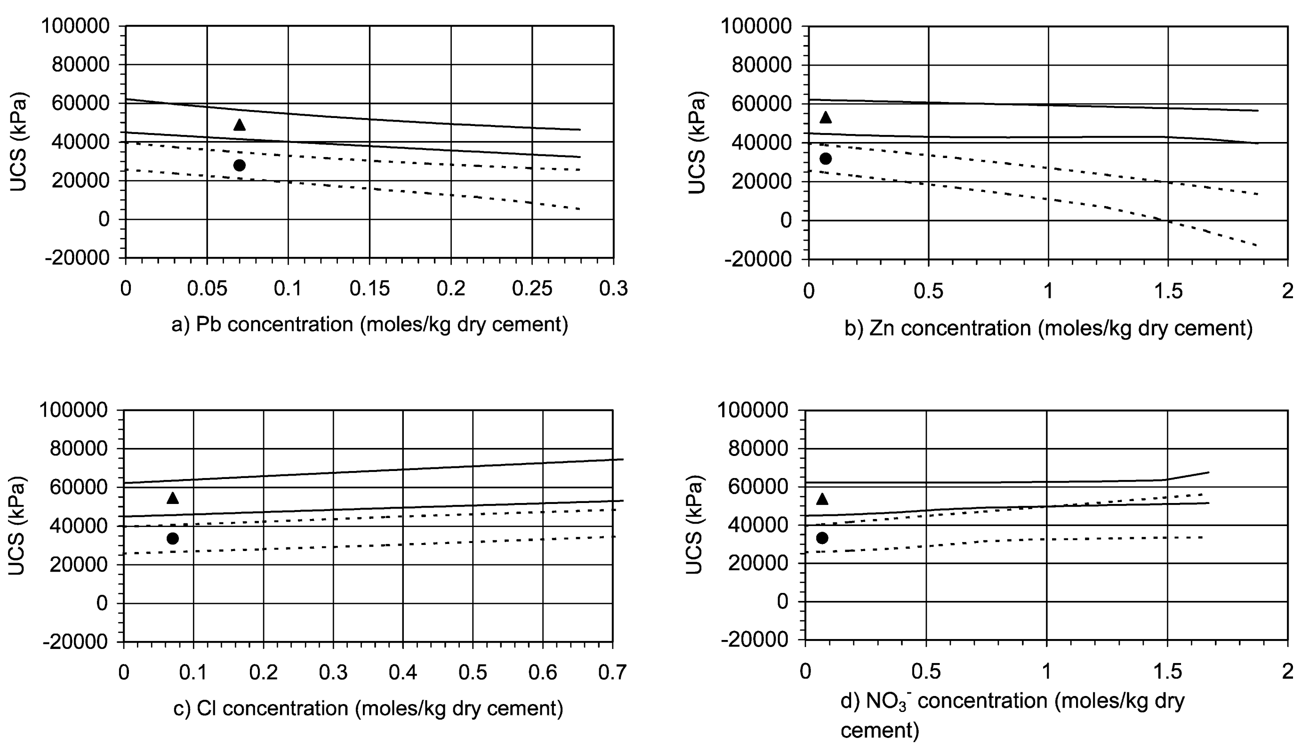

Fig. 5. Plots of predicted UCS at 7 (------) and 28 (—) days as a function of (a) Pb, (b) Zn, (c) Cl^- and (d) NO_3^- concentration for neural networks UCS1A-4–8.

Table 4
Summary of literature conclusions for contaminants used in modelling (0 = no effect; A = accelerator; R = retarder)

	Ba	Cd	Cr(III)	Cu	Ni	Pb	Zn	Most
Cl^-	A [1]	0, R, A [32]	A [32]	ND	A (1–3%) [24]	ND	ND	A [2,35]
NO_3^-	ND	0 [2], R [33]	A [32]	A, R [30]	ND	R (< 2%) [30], A (5–8%) [30]	R (>2%) [2]	0, A, R [2]
Most	A [2], R [34]	A [28], R [35]	A [2]	R [2]	ND	R [2,28,35]	R [2,28,35]	

ND = no data.

the root-mean-square error on the validation set, which ranged from 8500 to 8900 kPa for these networks, over all parts of the concentration range. Greater uncertainty was observed for UCS predictions on the basis of Cr(III), and for 7-day UCS at the upper extreme of water content and Ba, Cu and Zn content, with some predictions of negative UCS values for water content, Ba and Zn. The regions of higher uncertainty and the obviously false negative predictions are a consequence of a lack of training data to define these regions of the data space.

3.2.1. Effect of age

Specimen age was clearly an important predictive parameter for UCS from the outset because cement paste hardens over time. Indeed, the curves of the minimum and maximum strength predictions plotted in Fig. 3a look like the strength development curves typical of hydraulic cements (e.g., Ref. [26]). As they are nonlinear, this is undoubtedly one of the nonlinear system features that could not be accounted for by the linear model.

3.2.2. Effect of water content

It is also well known that strength decreases as matrix porosity increases, and that porosity increases as the water-to-cement ratio increases above an optimal value (e.g., Ref. [26]). Fig. 3b illustrates that this known effect of water content holds true for Portland cement products containing contaminants at both 7- and 28-day curing. The shape of these plots is typical for cement paste and concrete [26]. Again, although the curvature of the plots is not high, they are nonlinear, and could therefore not be addressed by the linear model.

3.2.3. Effects of contaminant additions used in modelling

Comparing the position of the solid triangles indicating the average predicted UCS for a concentration of 0.07 mol/kg dry cement, which was common to the ranges for all contaminants, and their corresponding maximum and minimum UCS values, in Figs. 3–5, it appears that Ba has a strong effect on UCS, yet the predicted UCS values for the other contaminants are difficult to distinguish from that of the control at this concentration, particularly when the uncertainty of the predictions is taken into account. However, at 7-day curing, a generally negative slope for Ba, Cu, Ni, Pb and Zn suggests that addition of these contaminants results in a decrease in UCS, and a positive slope for Cd, Cr(III), Cl^- and NO_3^- suggests that these contaminants increase UCS. For Cl^-, Ni, Pb, Cu and Ba, the trends were the same at 28-day curing, but Cr(III) and NO_3^- increased 7-day UCS more than 28-day UCS; Cd increased 7-day UCS, but possibly decreased 28-day UCS; and Zn decreased 7-day UCS appreciably, but did not affect 28-day UCS.

Thus, the trends shown in the response graphs indicate the following ranking of predicted UCS values, on an equimolar basis:

at 7 days, $Cl^- \approx$ Cr(III) > NO_3^- $\approx$ Cd > control > Zn $\geq$ Ni > Pb > Cu >> Ba;
at 28 days, Cl^- > Cr(III) > NO_3^- $\approx$ control $\geq$ Zn $\geq$ Cd > Ni > Pb > Cu >> Ba.

Since the contaminants are necessarily added as a cation/anion combination, Table 5 summarises the effects to be expected for the metal salts, based on these trends.

For comparison, a summary of conclusions drawn from the literature for these contaminants is shown in Table 4. It should be noted that a large proportion of the conclusions from the literature are not from the studies that were used in modelling. The literature conclusions tended to be either generalisations from literature reviews, taken from studies for products composed of materials other than just Portland cement and pure compounds, or anecdotal. Also, it should be noted that the literature does not necessarily distinguish between effects on set and hardening. Thus, the acceleration and retardation effects summarised in Table 4 are a mixture of both.

Notwithstanding the greater diversity of sources for the conclusions from the literature, comparing the last row and column of Table 5 with the last row and column of Table 4, it appears that the overall effects found by the model are consistent with the general effects for individual contaminants concluded by the literature sources. However, there seem to be some discrepancies between the literature sources, and also with the results from neural network analysis, for some of the salts.

Table 5
Predicted effects of salts on 7- and 28-day UCS of Portland cement (+ = strength gain; − = strength loss; 0 = no effect)

	Ba	Cd	Cr(III)	Cu	Ni	Pb	Zn	Overall
Cl^-	−/−	+/0	+/+	−/−	0/0	−/−	+/+	+/+
NO_3^-	−/−	+/0	+/+	−/−	0/−	−/−	+/0	+/0
Overall	−/−	+/−	+/+	−/−	−/−	−/−	−/0	

The strongest effect found by the neural network analysis was for Ba, yet the literature does not report particularly strong retardation by Ba. In fact, the general literature does not report any actual UCS results for Ba, and the modelling results are based on data generated for the NNAPICS project [3,4,19,20]. While Stegemann et al. [20] did not separately identify any marked effects for the very low concentration of $Ba(OH)_2$ that was studied, supporting data for Hills and Ouki [19] did show a strong effect for a higher concentration of $Ba(NO_3)_2$ on UCS, upon which the neural network prediction is based. Cocke and Mollah [27] report that Ba forms a very insoluble $BaSO_4$, which could act as a hydration barrier and cause severe retardation. It is also conceivable that Ba affects hydration by competing with Ca, in either dissolution or hydration reactions. Nevertheless, the model conclusions are based on only a small amount of data and should be treated with caution. Because of the important role of SO_4^{2-} in moderating the hydration of tricalcium aluminate, it is conceivable that small changes in hydration chemistry could cause Ba to act as an accelerator.

The literature reports a variety of effects for Cd. According to Trussell and Spence [28], precipitation of Cd hydroxide forms nucleation sites for other hydration products. This would account for the acceleration observed in some cases and the enhanced 7-day strength predicted by the neural networks, with less effect as hydration proceeds normally over time.

For Cr(III), the results from the literature and neural network analysis all confirm that it acts as an accelerator, with decreasing effect as hardening continues over time. There seems to be agreement in the literature that Cr(III) substitutes for Si(IV) in calcium silicate hydrate [2]. Tashiro [29] showed initial acceleration of tricalcium aluminate hydration by Cr_2O_3.

The fact, that Cr(III) enhances strength, whereas the remaining metals (with the possible exception of Cd) decrease it, indicates that its mechanism for interaction with cement must be different than that of the other metals. A mechanism of Ca-aided preferential sorption of metal species at high pH to form mixed Ca/metal precipitates on cement grains has been proposed [27]. Several literature sources agree that Zn and Pb interfere with cement hydration by precipitating as hydroxides on cement grains and acting as a hydration barrier [2]. Unfortunately, such a mechanism does not explain the differing effects observed for different metals. For example, Cocke and Mollah [27] observed the precipitation of a Ca–Cd hydroxide, yet most literature studies have not found Cd to be a retarder, and neural network analysis did not show it to decrease UCS. In another example [30], an increase in 28-day UCS for addition of $Pb(NO_3)_2$ and $Cu(NO_3)_2$, but a decrease for other binder systems, was found. Then, while the results from neural network analysis found that Zn decreased 7-day strength but had no effect on 28-day strength, as was individually found in the studies that provided the data for modelling [17,20], other workers have shown a decrease in 28-day UCS as a result of addition of several percent of Zn [29–31]. The latter results could not be used in model development because their products contained materials other than ordinary Portland cement and pure compounds. It is not known whether their results disagree with those from modelling because of this, or some other factor. It appears probable that there are factors affecting the kinetics of the hydration barrier formation and rupture, which may account for the different behaviours observed for different metals in different matrices.

For anions, suggested mechanisms are uncommon in the literature, and it is beyond the scope of an empirical modelling study such as this to propose one, but it is possible that Cl^- and NO_3^- act in a similar way to each other, given that their effects are similar. In retrospect, use of oxide and hydroxide as separate input variables for neural network analysis might have been useful, not because they are likely to have distinguishable effects at low concentrations, but because the reactivity of the cation may depend on the form in which it is added.

Overall, the response graphs of the predicted UCS as a function of the contaminant concentrations do not show a high degree of nonlinearity. This would be expected from models with a relatively small number of hidden cells (i.e., composed of a small number of sigmoid functions). As such, higher-level interaction effects are also unlikely. Given that interaction effects were found in separate analysis of results from a factorial design experiment that provided data to the models [20], it is possible that development of models with larger and more detailed data sets could change this picture. Nevertheless, it is possible that at least some of the discrepancies in the literature reports regarding the effects of different contaminants, which are suggestive of more complex nonlinear effects, can be attributed to three causes:

1. the reporting of acceleration or retardation on the basis of effects on a variety of different properties, including initial and final setting times, and strengths at a range of different ages;
2. the existence of laboratory-specific factors; and
3. the combined effects of the anion and cation components of salts.

3.2.4. Effects of other pure compounds

Data set UCS1B, which contained 136 data points for compounds that were represented by an insufficient number of data points to use in model development [Na_2HAsO_4, CrO_3, K_2CrO_4, $CsNO_3$, Fe_2O_3, $FeSO_4$, HgO, $HgCl_2$, K_2CrO_4, K_2SO_4, $Mn(NO_3)_2$ and NaCl], was entered into neural network UCS1A-1 to attempt to determine whether any of these contaminants has significant effects on UCS [4]. The probability of the chance occurrence of the difference between the measured and predicted values was calculated based on a normal distribution with 0 mean and a standard deviation of 7580 kPa.

Overpredictions with a low probability of chance occurrence were found for addition of FeO [17], and improbable underpredictions were found for Fe and As additions [14]. These data points are examples of the mistaken impression that can be gained when variables are confounded. In both cases, the contaminant additions coincide with cement contents that lie outside the training range, and the water content for the Bhatty data [14] was also outside the training range. These out-of-range formulations are sufficient to account for the mispredictions, and it is not possible to assess the independent effects of the Fe and As additions.

For the remaining data in UCS1B, the UCS of products containing Cs tended to be overestimated, suggesting that it is a retarder, and the UCS of products containing Cr(VI) was well predicted. For Hg, K, Mn, Na and SO_4^{2-}, no trends were apparent, except that particularly low UCS values tended to be overestimated, as was also found to be the case for some test data [18] above.

4. Conclusions

Neural network analysis of data from the literature concerning the effects of pure metal compound additions on UCS of Portland cement pastes resulted in the following findings.

• The neural networks were able to account for nonlinear features that could not be accommodated by a linear model.

• It was possible to model the known nonlinear effects of curing time and water content on UCS.

• The laboratory was found to be an important predictive variable for UCS, and acts as a surrogate for information regarding laboratory-specific variables that were not adequately reported in the literature, such as cement composition, strength and hardening class, product mixing and preparation details, laboratory conditions and testing details.

• The addition of contaminants was demonstrated to affect UCS by the improved performance of models including the compound additions as input variables, as compared with the performance of models constructed without them.

• The following ranking of predicted UCS values for the added contaminants, on an equimolar basis, was found:

at 7 days, Cl $\approx$ Cr(III) > NO_3^- $\approx$ Cd > control > Zn $\geq$ Ni > Pb > Cu >> Ba;
at 28 days, Cl > Cr(III) > NO_3^- $\approx$ control $\geq$ Zn $\geq$ Cd > Ni > Pb > Cu >> Ba.

• The residuals from application of the best neural network to test data for products containing other contaminants suggested that Cs is a retarder and Cr(VI) has no effect. No trends could be discerned for Hg, K, Mn, Na and SO_4^{2-}.

• The normal distribution of model residuals, and comparison with the reproducibility found in other studies, suggest that the root-mean-square error of 7580 kPa determined for the best neural network is an estimate of the interlaboratory standard deviation for UCS.

Use of happenstance data can result in problems with limited data ranges, correlated variables and missing information, as was experienced in this work. However, while the findings from such modelling may be partly qualitative and inconclusive, the object is to try to maximise the utility of existing data, rather than generate more at great expense. In this particular case, comparison of the model training, validation and testing errors indicated that the data set was sparse, and the certainty associated with neural network predictions is correspondingly low; yet response graphs of predicted UCS as a function of curing time and water content, which emulate known relationships, demonstrate that the neural network modelling approach was generally successful. The trends for contaminant additions are newly identified and cannot, therefore, be verified, but they are plausible based on existing information in the literature.

It was disappointing that the literature data did not consistently include laboratory-specific variables. Nevertheless, the success in using the laboratory as a surrogate categorical input variable for these factors showed that constructing good predictive models on this basis is feasible, and more detailed models could undoubtedly be developed if more detailed quantitative information about the laboratory-specific variables were available.

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