

Estimation of water-to-cement ratio in cementitious materials using electrochemical impedance spectroscopy and artificial neural networks

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ABSTRACT

In this study, electrochemical impedance measurements were investigated to estimate the water-to-cement (w/c) ratio of unhardened cementitious materials. The proposed approach is based on electrochemical impedance spectroscopy (EIS) and artificial neural networks (ANN), where the interpretation of EIS data was significantly improved without subjectively selected equivalent circuit models. The EIS method is sensitive to the changes in the electrochemical properties of a tested material such as the capillary porosity of cement paste, which enables the use of EIS in estimating the w/c ratio of cementitious materials. The EIS data were collected from cement paste samples with a w/c ratio in the range of 0.30–0.45. The following features were considered to train ANNs: raw impedance data (both real and imaginary parts); features extracted by the raw impedance data via the principal component analysis; and circuit parameters extracted from the raw impedance data via analysis of equivalent circuit models suggested from previous studies. Experimental results indicate that the w/c ratio can be predicted from the fresh-state cement composites with a mean absolute error of 0.014 using the ANN trained with principal components. The results demonstrate that the proposed approach significantly improves EIS data interpretation without subjectivity and shows considerable potential for estimating the w/c ratio of cementitious materials in situ.

1. Introduction

The quality control of fresh concrete at construction sites directly influences the durability and mechanical properties of the structure. Therefore, quality control techniques, including slump, air content, and chloride concentration tests, are generally performed in the field. However, methods used for fresh concrete are limited to characterizing the mechanical properties of hardened concrete, such as the initial compressive strength. The initial compressive strength of early-age concrete is one of the most important pieces of information on construction sites. Despite research efforts to estimate the early-age compressive strength of concrete in laboratory setups [1,2], the application of the technology on actual construction sites is still limited.

Recent advances in machine learning algorithms have significantly broadened the scope of the engineering domain, providing a new approach to deal with historical problems. The compressive strength of concrete was predicted using machine learning techniques based on an

experimental database that consisted of mix proportions and curing environment [3–8], Feng et al. predicted the compressive strength from concrete mixture components by using adaptive boosting algorithms, achieving 95 % accuracy [3]. Song et al. predict the compressive strength through algorithms using the Gene expression programming (GEP), Artificial neural networks (ANN), and Decision Tree (DT) on 98 data points consisting of 7 parameters of cement components [4]. Zeng et al. proposed a model using SVM, ANN, and AdaBoost algorithms to predict the compressive strength of concrete, considering both engineering formulation and job-site information as well as predictive performance [5]. Young et al. predicted the compressive strength using more than 10,000 data with four different machine learning algorithms, where each algorithm successively estimated the compressive strength within a 10 % error [6]. Asteris et al. further investigated the prediction of compressive strength using an ensemble model of machine learning algorithms [7]. Ziolkowski and Niedostatkiewicz also predicted the compressive strength using ANN and suggested a new formula of

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mixture proportions to achieve the target strength [8]. Based on the results of previous studies, the water-to-cement (binder) ratio (w/c) is one of the most sensitive parameters affecting the compressive strength of concrete.

Based on the results of several machine learning studies, the prediction of compressive strength in concrete becomes optimistic if sufficient and reliable data such as mixture proportions and curing conditions are available. In particular, the w/c ratio is a major factor in ensuring strength. Several studies have investigated the measurement of w/c ratio in situ, based on the concepts of mechanical and electromagnetic wave propagation [9–12], nuclear [13,14], microwave oven [15–18], and electrical resistivity [19]. Despite several attempts to measure the w/c ratio, each method has limitations for practical issues, such as calibration (wave propagation and electrical resistivity), commercialization (nuclear), and slow progress and inaccuracy (microwave oven). Therefore, the w/c ratio of cementitious composites is not directly measured at a site and is commonly provided by suppliers of ready-mixed concrete.

Electrical impedance spectroscopy (EIS) has been used to analyze the mechanism and composition of subjects in a broad range of applications, including the human body, referred to as bioelectrical impedance analysis [20,21], battery industries [22], and cementitious materials [23–27]. In the case of cementitious materials, Dong et al. studied the carbonation behavior of cementitious materials by using EIS [23]. Ribeiro & Abrantes develop a new method to apply EIS to concrete to solve the interpreting problem caused by the complexity of concrete [24]. Zhu et al. studied hydration behavior, fluidity, and drying shrinkage of cement paste by analyzing EIS parameters, such as R_{ct} , related to these properties [25]. As a nondestructive method, EIS has been recognized as a promising technique for the characterization of cementitious materials in both hardened and fresh states [26,27]. However, this method has limitations, such as data interpretation and electrode and parasitic effects [28]. In particular, the selection of an equivalent circuit model for the interpretation of EIS data is a highly subjective task, considering that no consensus has been made on the selection of an equivalent circuit model for cement-based materials among various available circuit models [29]. In addition, estimating the w/c ratio of a cementitious material is difficult using EIS data, as a direct mapping function between the analyzed equivalent circuit parameters and the w/c is not available.

In this study, we propose a method that estimates the water-to-cement ratio of cement paste using EIS and a machine learning algorithm, ANN. The w/c ratio that a ready-mixed concrete supplier provides can be different from the actual w/c cement ratio. Hence, the estimation of the w/c ratio of cementitious materials is important for the quality control of fresh concrete as well as the safety in construction fields. In our method, an ANN takes features extracted from measured EIS data as an input and gives an output of the water-to-cement ratio of cement paste. We considered various equivalent circuit parameters as an input to the ANN model through literature reviews on equivalent circuit models used to analyze EIS data for cementitious materials. In addition to circuit parameters, purely data-driven features directly extracted from EIS data without an assumed model through the principal component analysis (PCA) were also considered. A series of EIS measurement tests were conducted to configure an EIS dataset that covers various water-to-cement ratios of cement paste. Our method is a unique inverse approach that predicts the water-to-cement ratio from EIS data, whereas most existing studies examine mixture design proportions (e.g. w/c ratio) to understand the characteristics of measured EIS data. Our method provides the following advantages: (1) The water-to-cement ratio can be directly predicted from EIS data without subjective data interpretation (i.e. data-driven direct prediction); (2) It does not require expert knowledge of the equivalent circuit theory to obtain high accuracy in water-to-cement ratio prediction; and (3) The method is a rapid nondestructive material characterization method that instantly predicts water-to-cement ratio from fresh cement paste.

2. Methodology

2.1. Electrochemical impedance spectroscopy (EIS)

EIS is a nondestructive method that measures the opposition to electrical flow through connected nodes between moisture and conductive ions of materials. There are two types of EIS: potentiostat and galvanostat. The potentiostat EIS functions by applying an alternative voltage signal with broadband frequency ranges and measuring the corresponding current signal. Galvanostat EIS measures the voltage signal while an alternating current is applied to the sample. The response per driving frequency is presented in the form of an impedance, which is a set of complex numbers.

2.1.1. Analysis of EIS signatures

The response impedance spectrum contains the information (voltage or current) at each frequency point, which is typically expressed by a Nyquist plot (the real and imaginary portions of the impedance) or a Bode plot (the magnitude and phase of the impedance). The basic way to analyze an impedance spectrum is to draw an EIS curve in complex Cartesian coordinates, fit the equivalent circuit model appropriate for the curve, and explain the impedance spectrum based on the fitted circuit model, considering the realistic possibilities and physical properties of the material. The equivalent circuit is a combination of resistor and capacitor elements connected in series or in parallel. To illustrate a more complex impedance behavior, a constant phase element (CPE) for a depressed arc and Warburg impedance for the diffusion effect can be applied. Therefore, the scattered raw data points were analyzed using visible parameters drawn from the fitted circuit. A schematic of the EIS concept is shown in Fig. 1. Note that actual EIS data are not used to interpret after fitting, but the parameters extracted from the fitted circuit are. In other words, the interpretation of impedance behavior is based on the assumption that the fitted equivalent circuit is appropriate to represent the actual EIS data or at least sufficient to explain them.

The circuit parameter fitting procedure is based on solving an optimization problem, and generally accepted algorithms include the simplex Nelder–Mead [30] and Levenberg–Marquardt [31] algorithms. The Nelder–Mead algorithm (or simplex search algorithm) directly searches for the minimum of an objective function. This algorithm enables finding an optimal solution quickly after satisfying the minimum number of iterations. To obtain the minimum value of a function, a polygon consisting of n vertices, that is, the points of the unimodal function, is assumed in the n -dimensional space. The Levenberg–Marquardt algorithm combines the Gauss–Newton and gradient descent methods to solve nonlinear least squares problems. This algorithm can quickly find a solution, even if the initial value is far from the optimal value, where the objective function is repeatedly updated to find the minima from the initial assumption.

Several considerations must be made when fitting an equivalent circuit model to an impedance spectrum. The circuit models should be established based on feasible physical phenomena of the inner system of the materials. Satisfactory circuit models are then repeated to fit the curve from the initial value while satisfying the minimum error within the set iteration. Here, an optimal fit depends on the subjectivity of an operator who determines an appropriate equivalent circuit model and adjusts the degree between graphic matching and physical evidence. For example, to obtain good results, the operator needs to set initial values of circuit elements, appropriately limit the parameter range, and select an appropriate fitting algorithm. Thus, there are no absolute standards for deriving optimal fitting results suitable for each case.

2.1.2. Equivalent circuit models for unhardened cementitious materials

The literature published since 1985 on the EIS method for various cementitious materials was investigated to understand the equivalent circuit models for unhardened cementitious materials. The studies were mainly conducted in two parts: experimental implementation and

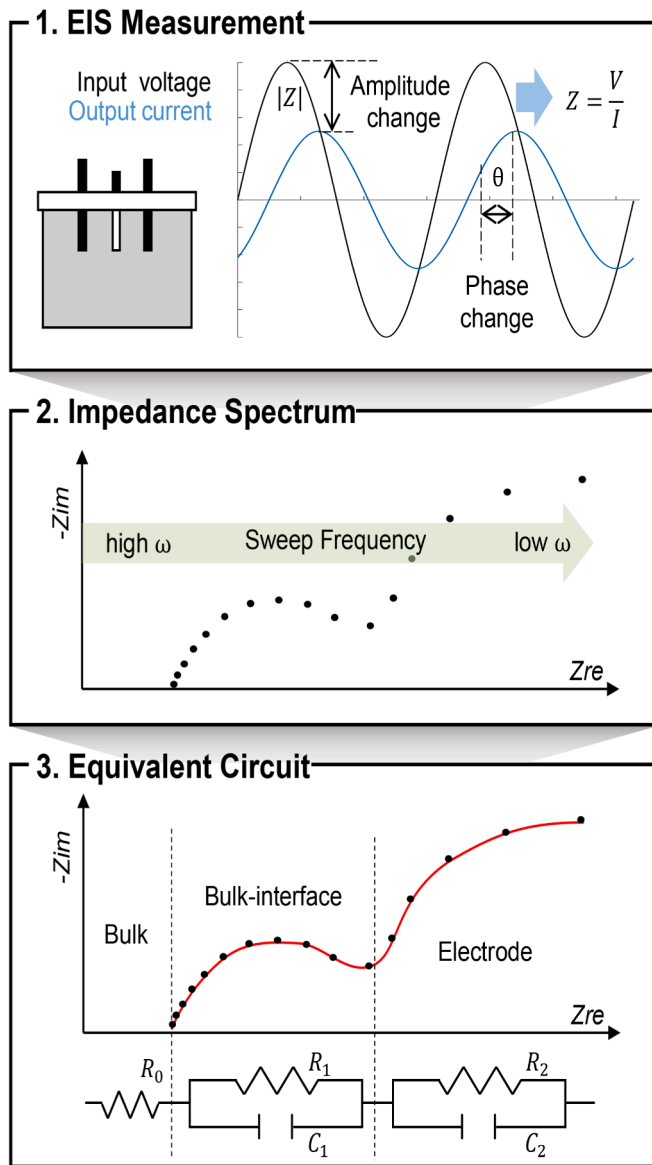


Fig. 1. A schematic illustration of the conventional EIS interpretation process using the measurement data and the assumed equivalent circuit.

theoretical explanation. Various studies have been conducted on the electrochemical responses related to microstructural changes in unhardened cementitious materials. Seven different equivalent circuit models were proposed for unhardened cementitious materials, as presented in Table 1.

Circuit 1 is the simplest, where the circuit parameters R_0 , R_1 , and C_1 correspond to the bulk resistance and the electrode effect, including resistance and capacitance in parallel, respectively. The impedances of resistance, R , and capacitance, C , are expressed in Eq. (1) and Eq. (2), respectively.

$$Z_R = R, \quad (1)$$

$$Z_C = \frac{1}{j\omega C}, \quad (2)$$

where ω is the angular frequency and j is the imaginary number. The circuit explains the EIS response of the cement paste using a serial connection between the bulk resistance of the materials and electrode polarization. McCarter showed an increasing effect of bulk resistance among cement paste, mortar, and concrete, where a low-frequency arc

in the Nyquist plot was dominant in the case of cement paste [32]. This circuit was also applied to a hydrating cement system, which was theoretically modeled as an interfacial reaction between a solid and a liquid [33].

In the case of Circuit 2, the capacitor from Circuit 1 is replaced by a CPE having a depression angle factor [34]. The impedance of a CPE is generally expressed by Eq. (3) [35].

$$Z_{CPE} = \frac{1}{Q_0(j\omega)^n}, \quad (3)$$

where Q_0 is a constant indicating the active area and n is related to the angle of rotation from a pure capacitance plotted on complex Cartesian coordinates. The value of n is between 0 and 1, where $n = 1$ represents an ideal capacitance, and $n = 0$ represents a pure resistance. Thus, in the Nyquist plot, the parallel combination of the resistance and CPE is drawn in an inclined semicircle with a constant phase of $-90n$. The CPE element applied to cementitious materials refers to the pore-size distribution of the conduction path during hydration [36].

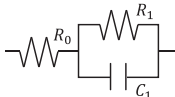
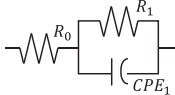
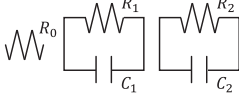
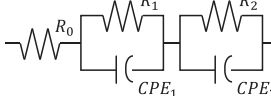
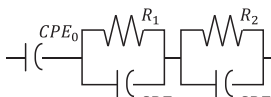
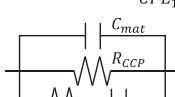
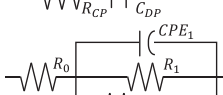
In Circuit 3, the former part of Circuit 1, corresponding to the bulk effect, is divided into two parts: the bulk itself and the bulk-interface effect [37]. This circuit was proposed to explain the physical microstructural elements of the cement paste during hydration, representing two semicircles in the Nyquist plot. In Circuit 4, all the capacitors in Circuit 3 are replaced by CPE elements [38]. Circuit 5 explains EIS behavior with respect to frequency and relaxation. Tsonos et al. suggested this equivalent circuit model associated with the response from capillary pores and C—S—H gel pores [39]. The connected elements of Circuit 5, which are CPE_0 , a parallel set of R_1 and CPE_1 , and a parallel set of R_2 and CPE_2 , sequentially describe the electrode/sample interface response, the relaxation of low frequency, and the relaxation of high frequency.

Circuit 6 uniquely explains the cementitious system by establishing electrical paths based on the conductance of the randomly formed gel and pores in the microstructures [40]. The theoretical model includes four elements: R_{CCP} , R_{CP} , C_{DP} , and C_{mat} . C_{mat} is related to the cement matrix, which is described as the insulation path formed by the hydration products and unhydrated cement. R_{CCP} is the resistance of a continuous conductive path (CCP) composed of micropores and capillary pores. The discontinuous path (DP), which is the conductive path (CP) blocked by some nonconductive pieces, such as cement paste, is described as parallel to R_{CP} and C_{DP} . Notably, C_{mat} is usually neglected because its value is too small compared with that of C_{DP} . Marriaga et al. modified Circuit 6 to analyze the transport and electrical properties of cement, where the additional resistance represents the effect of solution–electrode–sample interfaces, and all the capacitances are replaced by CPEs [41].

Once equivalent circuit parameters are determined by fitting collected EIS data to an assumed circuit model described earlier, they can be used to estimate the w/c ratio of cementitious materials. As the w/c ratio increases, the capillary porosity of cementitious materials increases. The capillary porosity affects the electrical flow within the tested cement paste sample, resulting in changes in the measured EIS signatures. Hence, given an assumed equivalent circuit model, different circuit parameters can be obtained depending on the w/c ratio. Note that a direct relationship or mapping function between circuit parameters and the w/c ratio is not available which complicates the estimation of the w/c ratio using EIS data. In this study, a machine learning approach that directly maps input features (circuit parameters or data-driven features) onto the w/c ratio is proposed. Details can be found in the following sections.

Table 1

Equivalent circuit models for unhardened-state cementitious materials.

No.	Circuit expressions	Impedance equations	Circuit diagrams	Ref.
1	$R_0 - (R_1 : C_1)$	$Z = R_0 + \frac{1}{\frac{1}{R_1} + j\omega C_1}$		[31,32]
2	$R_0 - (R_1 : CPE_1)$	$Z = R_0 + \frac{1}{\frac{1}{R_1} + Q_{0.1}(j\omega)^{n_1}}$		[34]
3	$R_0 - (R_1 : C_1) - (R_2 : C_2)$	$Z = R_0 + \frac{1}{\frac{1}{R_1} + j\omega C_1} + \frac{1}{\frac{1}{R_2} + j\omega C_2}$		[37]
4	$R_0 - (R_1 : CPE_1) - (R_2 : CPE_2)$	$Z = R_0 + \frac{1}{\frac{1}{R_1} + Q_{0.1}(j\omega)^{n_1}} + \frac{1}{\frac{1}{R_2} + Q_{0.2}(j\omega)^{n_2}}$		[38]
5	$CPE_0 - (R_1 : CPE_1) - (R_2 : CPE_2)$	$Z = Q_{0.0}(j\omega)^{n_0} + \frac{1}{\frac{1}{R_1} + Q_{0.1}(j\omega)^{n_1}} + \frac{1}{\frac{1}{R_2} + Q_{0.2}(j\omega)^{n_2}}$		[39]
6	$C_{mat} : R_{CCP} : (R_{CP} - C_{DP})$	$Z = \frac{1}{j\omega C_{mat} + \frac{1}{R_{CCP}} + \frac{1}{R_{CP} + \frac{1}{j\omega C_{DP}}}}$		[40]
7	$R_0 - (CPE_1 : R_1 : (R_2 - CPE_2))$	$Z = R_0 + \frac{1}{Q_{0.1}(j\omega)^{n_1} + \frac{1}{R_1} + \frac{1}{R_2 + \frac{1}{Q_{0.2}(j\omega)^{n_2}}}}$		[41]

3. Experimental and data processing methods

3.1. Experimental data acquisition

3.1.1. Specimen preparation

Cement paste is the most fundamental cementitious material and is prepared by simply combining cement and water. The test specimens were made of Type I ordinary Portland cement and tap water. The cement paste specimens had the water-to-cement ratio ranging from 0.30 to 0.45 with intervals of 0.01, and 20 specimens were prepared per each water-to-cement ratio. Considering the volume of the mold, the mix proportion was designed by increasing the weight of the water by 2 g. The details of the cement composition and mix proportions are listed in Tables 2 and 3, respectively. After water began to be poured into the cement, hand mixing was performed for 3 min. The mixed cement paste was poured into a PET cylinder mold of volume 300 mL with a diameter and height of 70 and 90 mm, respectively. Compactions were also conducted. The specimens were then left at room temperature ($25 \pm 2^\circ\text{C}$) for 10 min to stabilize the mixture.

Table 2

Chemical composition of cement.

Components	Mass %
CaO	61.09
SiO ₂	21.26
Fe ₂ O ₃	3.25
Al ₂ O ₃	5.38
SO ₃	2.55
MgO	2.27
Na ₂ O	0.15
K ₂ O	1.18
Loss in ignition	2.87

Table 3

Mixing information.

No	w/c by weight	w/c by volume	Water (kg/m ³)	Cement (kg/m ³)
1	0.30	0.942	483	1610
2	0.31	0.973	490	1581
3	0.32	1.005	497	1553
4	0.33	1.036	504	1527
5	0.34	1.068	511	1503
6	0.35	1.099	518	1480
7	0.36	1.130	525	1458
8	0.37	1.162	532	1438
9	0.38	1.193	539	1418
10	0.39	1.225	546	1400
11	0.40	1.256	553	1383
12	0.41	1.287	560	1366
13	0.42	1.319	567	1350
14	0.43	1.350	574	1335
15	0.44	1.382	581	1320
16	0.45	1.413	588	1307

3.1.2. EIS measurements

The experimental setup used in this study is illustrated in Fig. 2. Potentiostat EIS was performed on the specimens by using a PCI4/300 Gamry instrument. Alternative voltage signals with the amplitude of 10 mV (RMS) and frequencies ranging from 100 kHz to 0.2 Hz with 10 points per decade were applied to the specimens: 58 data points were recorded for each EIS measurement. A three-electrode configuration was applied, consisting of two graphite rods operating as the working and counter electrodes and a saturated calomel electrode operating as a reference. Graphite rods of diameter 6 mm were inserted into the specimen at approximately 40 mm and positioned at intervals of 10 mm apart from each other. The electrodes were connected to the equipment using a cable.

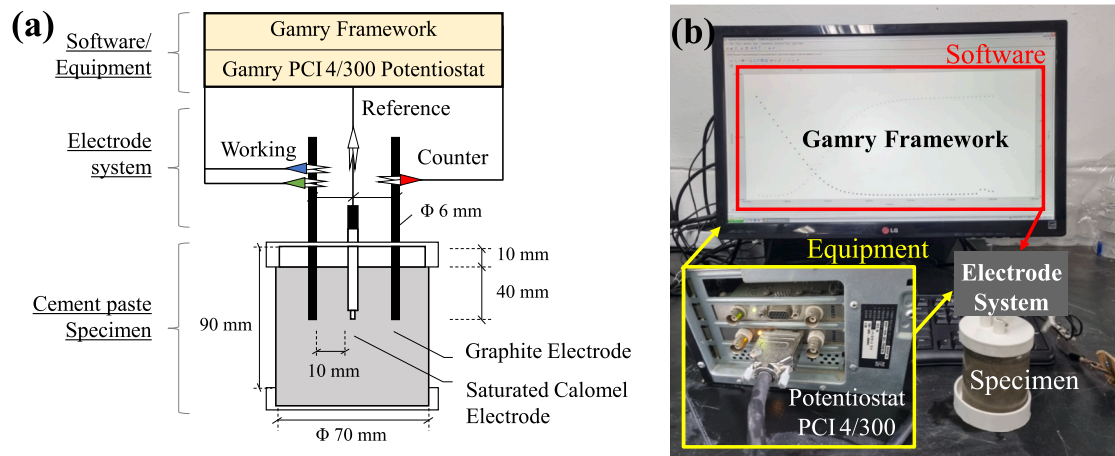


Fig. 2. The EIS experiment setup for cement pastes with various w/c ratios: (a) diagram of specimen-electrode system and (b) photo of measurement system and specimen.

Note that the open circuit potential (OCP) was measured to evaluate the electrochemical potential state of the cement paste before the EIS measurements. The variation in OCP represents the unstable state of the materials, which possibly affects the results of the EIS response. After mixing, the specimens were stabilized for about 10 min. Then, EIS was measured in which was automatically set to begin if the general stability condition within ± 0.05 mV/s was satisfied. The minimal change in OCP per second was verified to check the stability of the electrochemical state. As an example, the change in the OCP from the set of cement paste specimens is shown in Fig. 3. The difference rate changed sharply, and the condition was satisfied less than 50 s. The duration of EIS measurement itself was about 3 min. Within the stable condition, the electrochemical potential state of the cement paste specimens was stable, indicating that the hydration was in a dormant period and that the hydration reaction minimally influenced the EIS measurements.

3.2. Machine learning algorithms

3.2.1. Artificial neural network (ANN)

In this study, we estimated the water-to-cement ratio from electrochemical impedance data using an ANN, which is one of the most widely

used machine learning algorithms. An ANN is inspired by the information processing of the human brain, and it mimics the way biological neurons signal to one another. An example of the ANN used in this study is shown in Fig. 4a. An ANN is composed of input and output layers, with one or more hidden layers between them. Each layer includes neurons connected to the neurons of the adjacent layers, as shown in Fig. 4a. In this study, an ANN with two hidden layers having 64 neurons each was used for the backbone model architecture. The number of neurons for the input layer is chosen based on the dimension of the input data (e.g., three circuit parameters extracted from impedance data), and that of the output layer is chosen based on the dimension of the desired output information (i.e., w/c).

Mathematical computations performed between two adjacent layers of an ANN are illustrated in Fig. 4b. For visualization purposes, the dimensions of each layer are limited to three, as shown in the figure. Vector z_1 , which is the input to the first hidden layer, is computed as.

$$z_1 = W_1 x + b_1, \quad (4)$$

where x is the input vector from the input layer, W_1 is the weight matrix of the first hidden layer, and b_1 is the bias vector. Here, the elements of W_1 and b_1 are trainable parameters, and their optimal values are

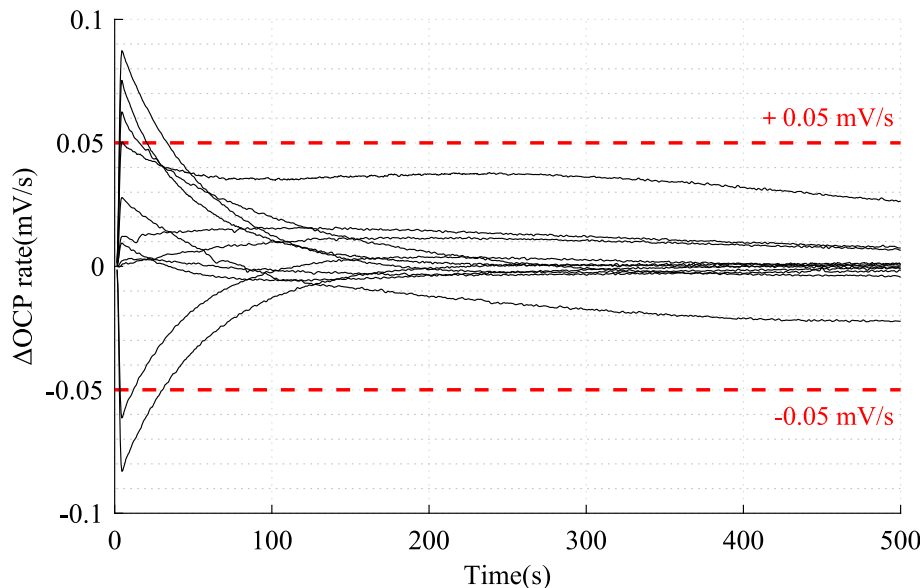


Fig. 3. Example of OCP rate obtained from specimens.

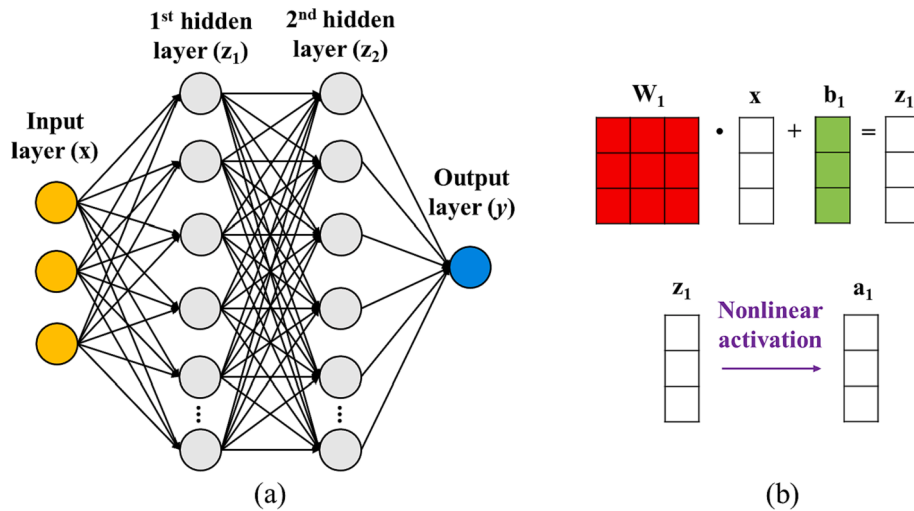


Fig. 4. Schematic of the ANN used in this study: (a) example model architecture and (b) example illustration of computation between two adjacent layers.

determined in the training process for the neural network. Once z_1 is computed, nonlinear activation is applied to obtain.

$$\mathbf{a}_1 = f(\mathbf{z}_1), \quad (5)$$

where $\mathbf{a}_1$ is the output vector of the first hidden layer and $f()$ is the nonlinear activation function. Among various activation functions, the rectified linear unit (ReLU) function is used in this study. The ReLU function is given by

$$f(x) = \max(0, x). \quad (6)$$

In the same computation, Eqs. (4)–(6) were applied throughout the layers of the neural network, except for the final output layer. In the output layer, Eq. (4) was applied in the same manner, but linear activation ($f(x) = x$) was applied instead of the ReLU function, as the w/c estimation problem is a regression problem.

To train and test an ANN model, an impedance dataset including 280 raw impedance data with w/c ranging from 0.32 to 0.45 was configured. In addition to the raw impedance dataset, we considered eight additional features extracted from it: a direct data-driven feature extraction case using principal component analysis (PCA), and seven feature cases based on equivalent circuit models. The configured dataset for each feature case was divided into 196 training data (70 %) and 84 test data (30 %). For all nine feature cases, including the raw impedance data case, network training was performed 10 times to analyze the obtained w/c prediction results statistically.

ANN training is performed by solving an optimization problem to minimize the mean absolute error (MAE) loss function, given by.

$$L_{MAE} = |Y_{pred} - Y_{true}|, \quad (7)$$

where Y_{pred} and Y_{true} are the w/c values predicted by the ANN and corresponding ground-truth w/c value, respectively. An L_{MAE} value closer to zero represents a more accurate w/c prediction performance. The hyperparameters used to train the ANN models with nine different input feature cases are summarized in Table 4. More details about hyperparameters and their effects on the performance of a machine

learning algorithm can be found elsewhere [42,43].

3.2.2. Principal component analysis (PCA)

PCA is a widely accepted technique to reduce the dimensionality of datasets [44]. PCA increases the interpretability of a dataset (particularly one with high dimensions) by reducing its dimensions; however, it also minimizes information loss [45]. In this study, we employed PCA for feature extraction to make the training and testing of an ANN model more efficient compared with doing so with raw impedance data. The procedure for applying PCA to data matrix $\mathbf{X}$ is as follows:

- (1) A dataset is organized into an $n \times p$ data matrix $\mathbf{X}$, where n is the total number of individual data and p is the number of variables (dimension) of each data. In this study, each row vector $\mathbf{x}_j^T$ ($j = 1, 2, \dots, n$) within $\mathbf{X}$ represents the individual raw impedance data with p elements. Here, superscript T represents the transpose operation.
- (2) An $n \times p$ mean matrix $\bar{\mathbf{X}}$ is computed. By computing the mean along each column of $\mathbf{X}$, the mean row vector $\bar{\mathbf{x}}$ is computed as follows:

$$\bar{\mathbf{x}} = \frac{1}{n} \sum_{j=1}^n \mathbf{x}_j. \quad (8)$$

Then, the $n \times p$ mean matrix $\bar{\mathbf{X}}$ is computed as follows:

$$\bar{\mathbf{X}} = \mathbf{h}\bar{\mathbf{x}}^T, \quad (9)$$

where $\mathbf{h}$ is an $n \times 1$ column vector with all the elements of value one.

- (3) The deviation matrix $\mathbf{B}$ is then computed by subtracting $\bar{\mathbf{X}}$ from $\mathbf{X}$:

$$\mathbf{B} = \mathbf{X} - \bar{\mathbf{X}}. \quad (10)$$

- (4) The $p \times p$ covariance matrix $\mathbf{C}$ is computed using $\mathbf{B}$:

$$\mathbf{C} = \mathbf{B}^T \mathbf{B} \quad (11)$$

- (5) The eigenvectors and eigenvalues of $\mathbf{C}$ are computed by solving the following eigenvalue problem:

$$\mathbf{C}\mathbf{v} = \lambda\mathbf{v} \quad (12)$$

Table 4
Hyperparameters used to train ANN models.

Hyperparameters	
Optimizer	Adam
Learning rate	0.001
Mini-batch size	16
Number of epochs	5000

where $\mathbf{v}$ and λ are the eigenvector and eigenvalue, respectively. Eq. (12) can also be represented in the following form:

$$\mathbf{CV} = \mathbf{VD} \quad (13)$$

where $\mathbf{V}$ is the matrix of eigenvectors and $\mathbf{D}$ is the diagonal matrix of the eigenvalues of $\mathbf{C}$. The columns of the eigenvector matrix $\mathbf{V}$ and their corresponding eigenvalues are sorted in the order of decreasing eigenvalues.

- (6) A subset of the eigenvectors, $\mathbf{V}_r$, is selected as the basis vector, considering the cumulative energy E_r . E_r is computed as.

$$E_r = \frac{\sum_{k=1}^r \lambda_k}{\sum_{k=1}^p \lambda_k} \quad (1 \leq r \leq p) \quad (14)$$

where λ_k is the k^{th} eigenvalue of $\mathbf{C}$. For dimensionality reduction, r must be as small as possible while maintaining a high value of E_r to minimize information loss. In this study, a value of 3 was chosen as an appropriate r value, as it provides an E_r close to one. Once an appropriate r value is selected, a subset of eigenvectors $\mathbf{V}_r$ is obtained by taking the first r columns of $\mathbf{V}$.

- (7) The dimension of the original data is reduced from p to r by projecting the data onto the new basis (i.e., $\mathbf{V}_r$). Dimensionality reduction (feature extraction) can be achieved by multiplying the mean-subtracted data matrix ($\mathbf{B}$) by $\mathbf{V}_r$:

$$\mathbf{T}_r = \mathbf{BV}_r \quad (15)$$

Note that the size of the $n \times p$ original dataset is reduced to $n \times r$ ($r \leq p$), indicating that r -dimensional features are extracted from p -dimensional original data. The projection of the original data onto $\mathbf{V}_r$ is conceptually illustrated in Fig. 5, where the two-dimensional original data ($p = 2$) are reduced to a one-dimensional feature ($r = 1$).

In this study, we suggest PCA as a data-driven feature extraction method, and its performance for ANN training and testing is compared with that using raw impedance data (no feature extraction) and several equivalent circuit-based feature extraction methods. The original dimension of impedance data used in this study is 116 ($p = 116$), and the reduced dimension (the dimension of extracted features) is three ($r = 3$).

4. Results

4.1. EIS response

A total of 320 data were obtained, corresponding to cement pastes of various w/c ratios ranging from 0.3 to 0.45. Examples of the measured responses are shown in Fig. 6 in which the three sets of data including the maximum, median, and minimum of water-to-cement ratios were presented. Noted that the lines indicate the averaged values of 20 specimens while the shaded area presents the range of individual

measurements. In the Nyquist plot, the straight lines were dominant, similar to the results from previous studies [32,46,47], representing a diffusion region at a low frequency. The straight lines indicate a small part of the arc, which is usually analyzed as the effect of the interfacial response between the bulk and the electrode [48]. Owing to the relatively high conductivity of the unhardened cement paste during the dormant period, the EIS response was controlled by mass transfer instead of kinetic control. Therefore, the pre-positioned semicircle in the high-frequency region was not well developed because of the relatively low resistance of the bulk in the fresh cement paste.

As the w/c ratio decreased, the slopes of the diffusion lines were generally inclined, which indicates a higher contribution of resistance compared with the capacitance reaction. The trend of a lower phase angle at low frequency was identified for specimens with lower w/c ratios, whereas the magnitudes of the impedance were not different among the specimens. It is known that the phase angle (the slope of the line) is dependent on ion diffusion into pores in electrolytes, and the unit slope represents a very narrow pore size distribution with perfectly cylindrical pores plateaus [49,50]. In the case of unhardened cement paste, the shape and size of pores in the microstructure are irregular [51]. Therefore, the effect of the pore distribution at different w/c ratios may have influenced the phase angle of the EIS response. The general trend of the phase angle was determined from the experimental data; however, the variation in the impedance obtained for the same w/c ratio was comparably high. Therefore, a quantitative analysis is required to understand the relationship between the EIS response and the w/c ratio in cement paste.

4.2. Feature extraction

To quantify the contribution of bulk and interfacial effects as a feature in the ANN, the seven equivalent circuits shown in Table 1 were fitted to each experimental data using the Nelder–Mead simplex algorithm. The Nelder–Mead simplex algorithm iteratively modifies a simplex to find a minimum of the object function, where the repeated steps include three parts: reflection, expansion, and contraction. The objective function goodness (GN) applied to the fitting process is given by:

$$GN = \sum_{i=1}^n \frac{[(Zre_{meas}(i) - Zre_{fit}(i))^2 + (Zim_{meas}(i) - Zim_{fit}(i))^2]}{Zre_{meas}(i)^2 + Zim_{meas}(i)^2}, \quad (16)$$

where Zre_{meas} and Zim_{meas} are the real and imaginary components of the impedance measured in the n^{th} EIS experiment, respectively, and Zre_{fit} and Zim_{fit} are the impedance elements from the assigned equivalent circuits. The optimal value of goodness was obtained using the MATLAB function “fminsearch.” An average goodness value computed over the impedance dataset for each equivalent circuit model case is shown in Table 5. Here, the lower the goodness value indicates the higher the confidence of circuit parameter fitting. The circuit parameters obtained from the fitted equivalent circuit were used as features input to ANNs to

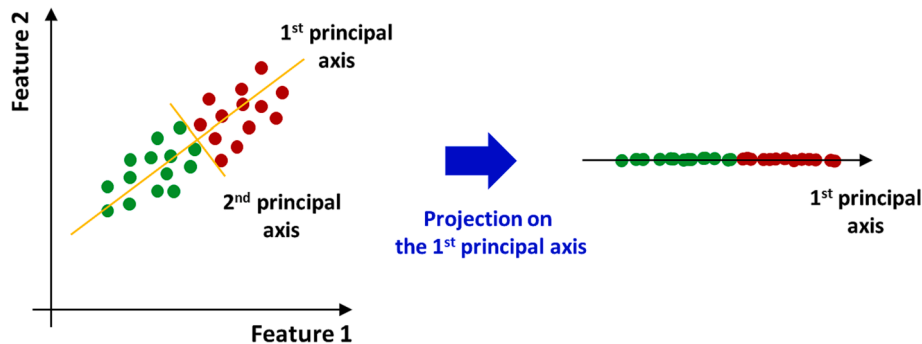


Fig. 5. Schematic of dimensionality reduction (feature extraction) of a dataset via PCA.

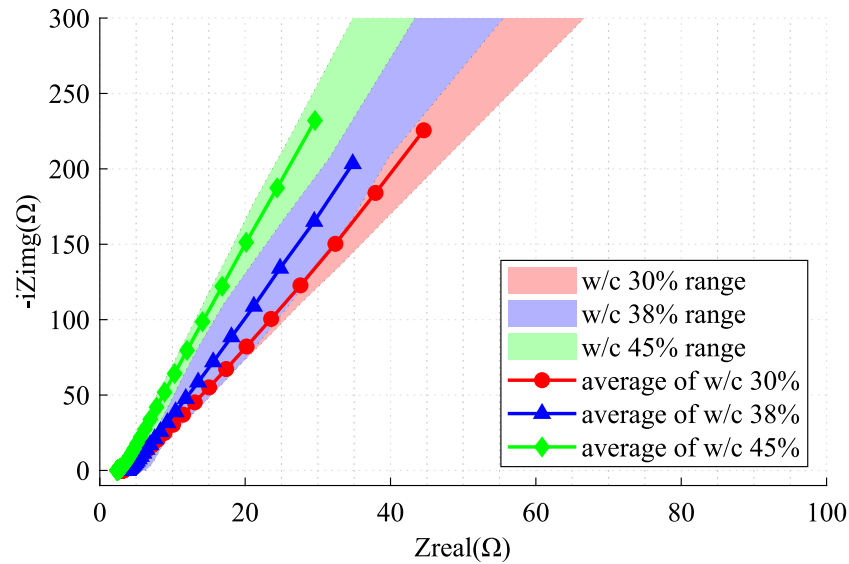


Fig. 6. Results of impedance spectra in a Nyquist plot (hydration time is about 15 min.), presenting the averaged values from specimens with different w/c ratios (dotted lines) and the range of impedance from specimens with the same w/c ratio (shaded area).

Table 5

Average goodness of circuit parameter fitting for each equivalent circuit model case. Circuit parameters that represent each model can be seen in Table 1.

Equivalent circuit model	Goodness of fitting
Circuit 1	1.035
Circuit 2	0.052
Circuit 3	0.177
Circuit 4	0.143
Circuit 5	0.940
Circuit 6	N/A
Circuit 7	0.249

predict the w/c ratio of cement pastes.

We performed PCA as a direct feature extraction step to determine the number of principal components (PCs) to be extracted from the raw impedance data. Fig. 7 shows the cumulative energy E_r (computed by Eq. (14)) as a function of the number of PCs (r) extracted from the collected impedance data. The E_r curve illustrates how much information (variance) can be explained for the collected impedance dataset using a particular number of PCs. For example, E_r of 0.9 indicates that 90 % of the total variance in the dataset can be explained with the chosen r . Fig. 7 indicates that the first three PCs ($r = 3$) explain nearly 100 % of the total variance. Thus, we chose three PCs to be extracted from the impedance data. Note that extracting PCs is a purely data-driven feature extraction from impedance data that does not require the knowledge of equivalent circuit modeling. In addition to PCA, the

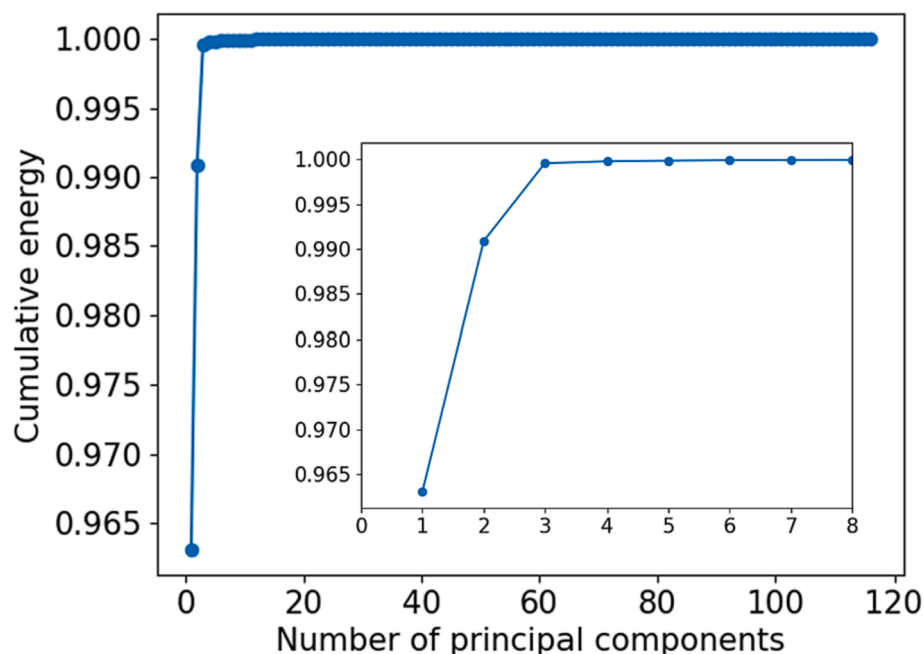


Fig. 7. Cumulative energy E_r as a function of the number of principal components (PCs).

circuit parameters for the equivalent circuit models described earlier were used as the model-based features.

4.3. W/C prediction using ANN

4.3.1. Correlation matrix

Heat maps of the correlation matrix were computed to investigate the dependency between the extracted features (inputs) and w/c (output). Fig. 8a shows the correlation matrix for the case of three PCs as input variables, and Fig. 8b to h show those for the cases of circuit parameters for Circuits 1 to 7. In these figures, correlation coefficients closer to 1 or -1 indicate a high correlation between the two variables. For example, in Fig. 8a, the first and third PCs (PC1 and PC3) are highly correlated with the coefficient of -0.77 , whereas the other pairs of PCs

(PC1–PC2 and PC2–PC3) are weakly correlated with the correlation coefficients of 0.13 and 0.0082, respectively. In terms of the correlation between input variables and the output variable (w/c), the cases of PCs and Circuits 1, 2, 3, and 6 shown in Fig. 8a, b, c, d, and g indicate that all the extracted features show a significant correlation with w/c, revealing correlation coefficients not close to zero. However, the cases of Circuits 4, 5, and 7 (Fig. 8e, f, and h) reveal that the extracted features show less correlation with w/c, with correlation coefficients close to zero. The performance of the w/c estimation for all feature extraction cases is shown in the following section.

4.3.2. W/C prediction using trained ANNs

Fig. 9a and b show the w/c estimation results using the ANN trained with the raw impedance data and those trained with the extracted PC

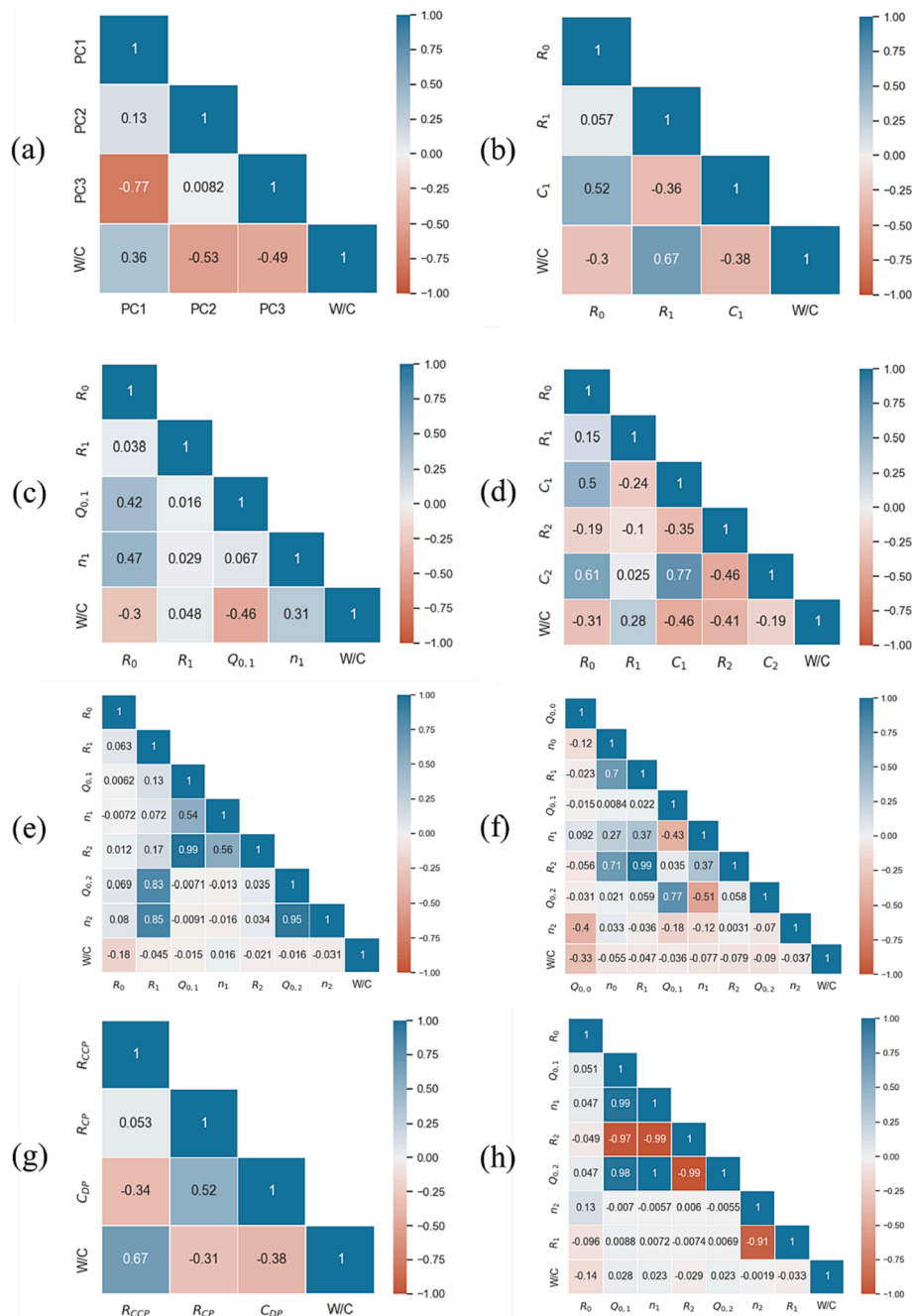


Fig. 8. Heat maps of the correlation matrix of input and output variables for ANNs: (a) principal components, circuit parameters for (b) Circuit 1, (c) Circuit 2, (d) Circuit 3, (e) Circuit 4, (f) Circuit 5, (g) Circuit 6, and (h) Circuit 7.

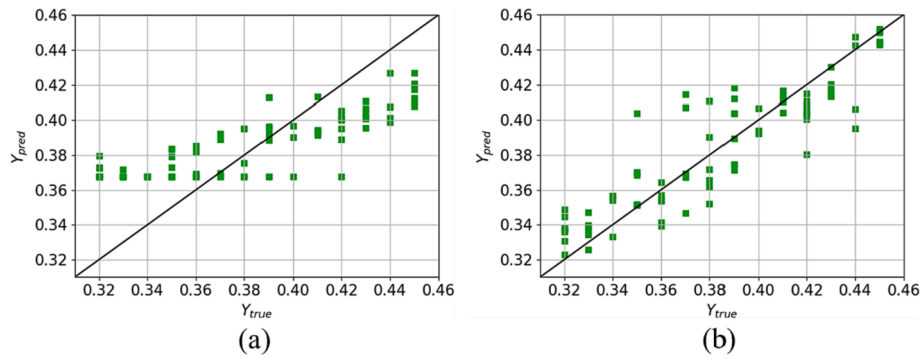


Fig. 9. Water-to-cement ratio estimation results obtained by an ANN: (a) ANN trained with raw impedance data as inputs and (b) ANN trained with three PCs extracted using PCA. In each plot, the x-axis represents true w/c and the y-axis represents the w/c predicted by each trained ANN. Each plot represents the best w/c prediction performance for each ANN model trained for 10 times.

data, respectively. All the w/c prediction results shown hereafter were obtained by applying trained ANN models to the test dataset (not the training dataset). Each plot represents the best w/c prediction performance for each ANN model trained for 10 times. In the plots, the unit lines ($Y_{pred} = Y_{true}$) are indicated to visualize the accuracy of the predicted w/c values. The closer the scattered dots are to the unit line, the better are the w/c estimation results. The w/c prediction results for the raw impedance data case (Fig. 9a) reveal the poor w/c prediction performance of the ANN trained with raw impedance data, showing that predicted w/c data points (particularly w/c below 0.35 and above 0.42) significantly deviate from the unit line. However, the results shown in Fig. 9b indicate that the ANN trained with the extracted PC data provides good w/c prediction results, where the overall predicted w/c data points are reasonably aligned with the unit line. The comparison between the two input cases demonstrates the effectiveness of feature extraction, which provides better w/c prediction results and less computational load during the ANN training process. Quantitative measures of the w/c estimation accuracy, MAE, and coefficient of determination (R^2) were further computed and compared with those of other ANNs in the later part of this section.

Fig. 10 shows the w/c estimation results obtained from the trained ANNs for the equivalent circuit parameter cases. Overall, Circuits 1, 2, 3, and 6, shown in Fig. 10a, b, c, and f, respectively, show reasonable w/c estimation results, comparable to the results shown in Fig. 9b (the PCA case). In particular, Circuit 3 exhibits the best estimation results, with the predicted w/c points being closer to the unit line than in the other circuit cases. The other three circuit models shown in Fig. 10d–f (Circuits 4, 5, and 7) failed to provide reasonable w/c estimations, where the predicted w/c data points do not align with the unit line.

The w/c prediction performance was quantitatively evaluated for all input parameter cases (raw impedance, PCA, and the seven circuit parameter cases) using two metrics: (1) MAE and (2) R^2 . The MAE measures the inaccuracy of the w/c prediction for an ANN model, where MAE values closer to zero represent w/c predictions with higher accuracy. R^2 measures how well the predicted w/c data points align with the unit line ($Y_{pred} = Y_{true}$) and is computed by

$$R^2 = 1 - \frac{SS_{res}}{SS_{total}} = 1 - \frac{\sum_{i=1}^n (Y_{pred}^i - Y_{true}^i)^2}{\sum_{i=1}^n (Y_{pred}^i - \bar{Y}_{true})^2}, \quad (17)$$

where n is the total number of predicted w/c data; Y_{pred}^i and Y_{true}^i are the i^{th} predicted and its corresponding ground-truth w/c data, respectively; and $\bar{Y}_{true}$ is the mean of the ground-truth w/c data. The MAE computed for all the input parameter cases is shown in Fig. 11a. For each case, the bar height and width of the error bar indicate the mean MAE value (μ_{MAE}) and doubled standard deviations ($2\sigma_{MAE}$), respectively, from 10 trained ANN model outputs on the test dataset. In Fig. 11a, the cases of

PCA and Circuits 1, 3, and 6 show low MAE values with little variation. In particular, Circuit 3 provides the lowest MAE value, indicating the best w/c prediction accuracy among all cases.

The quantitative w/c performance evaluation results using the metric R^2 are shown in Fig. 11b. The cases of raw impedance (raw Z) and Circuits 4 and 7 fail to provide reasonable R^2 values that typically range from 0 to 1. Note that negative R^2 values are caused by large w/c prediction errors (large SS_{res}), along with the similarity of the predicted w/c values with $\bar{Y}_{true}$ (small SS_{total}). Other cases shown in the magnified view (Fig. 11b (right)) show a reasonable R^2 value range (0 to 1). In particular, the cases of PCA, Circuits 1, 3, and 6 show high R^2 values close to 0.7 to 0.8 and little variation, which corresponds to their low MAE values in Fig. 11a. Again, Circuit 3 provided the best w/c prediction performance with the highest R^2 . Fig. 11 demonstrates that the two quantitative metrics, MAE and R^2 , well explain the w/c performance of a trained ANN model, showing good agreement with the qualitative analysis shown in Figs. 9 and 10.

5. Discussion

5.1. Comparison of feature extraction types on w/c prediction accuracy

The w/c prediction results presented in Section 3.2.3 demonstrate that a trained ANN model can predict w/c reasonably once appropriate features extracted from raw impedance data are used to train the ANN model. We consider two types of features: (1) equivalent circuit parameters and (2) PCs. Equivalent circuit parameters have a well-established theoretical basis (i.e., EIS and equivalent circuit models) and are widely accepted to represent the properties of an electrochemical system. Appropriately selected equivalent circuit parameters can provide high w/c prediction accuracy (for example, the case of Circuit 3 providing an R^2 of 0.79). However, choosing an equivalent circuit model can be subjective, and it necessitates the knowledge of EIS, technique, and electrical circuit theory. An inappropriate selection of a circuit model can fail to provide w/c prediction accuracy (see Figs. 9 and 10). Extracting equivalent circuit parameters requires an optimization-based model-fitting process that adds computational loads.

PCA is a purely data-driven feature extraction method that does not require knowledge of the circuit theory or model selection. It is relatively simple and does not require an optimization process for model fitting. Hence, PCA provides easier feature extraction from raw impedance data than from equivalent circuit parameters. PCA is an objective process for extracting features, as it does not require the selection of an appropriate model. Despite its simplicity, the case of PCA showed good w/c prediction performance with an R^2 of 0.74, which is comparable to the best results obtained by the equivalent circuit parameters (R^2 of 0.79, Circuit 2). Considering its simplicity and good performance, we suggest PCA as an alternative feature extraction method when it is

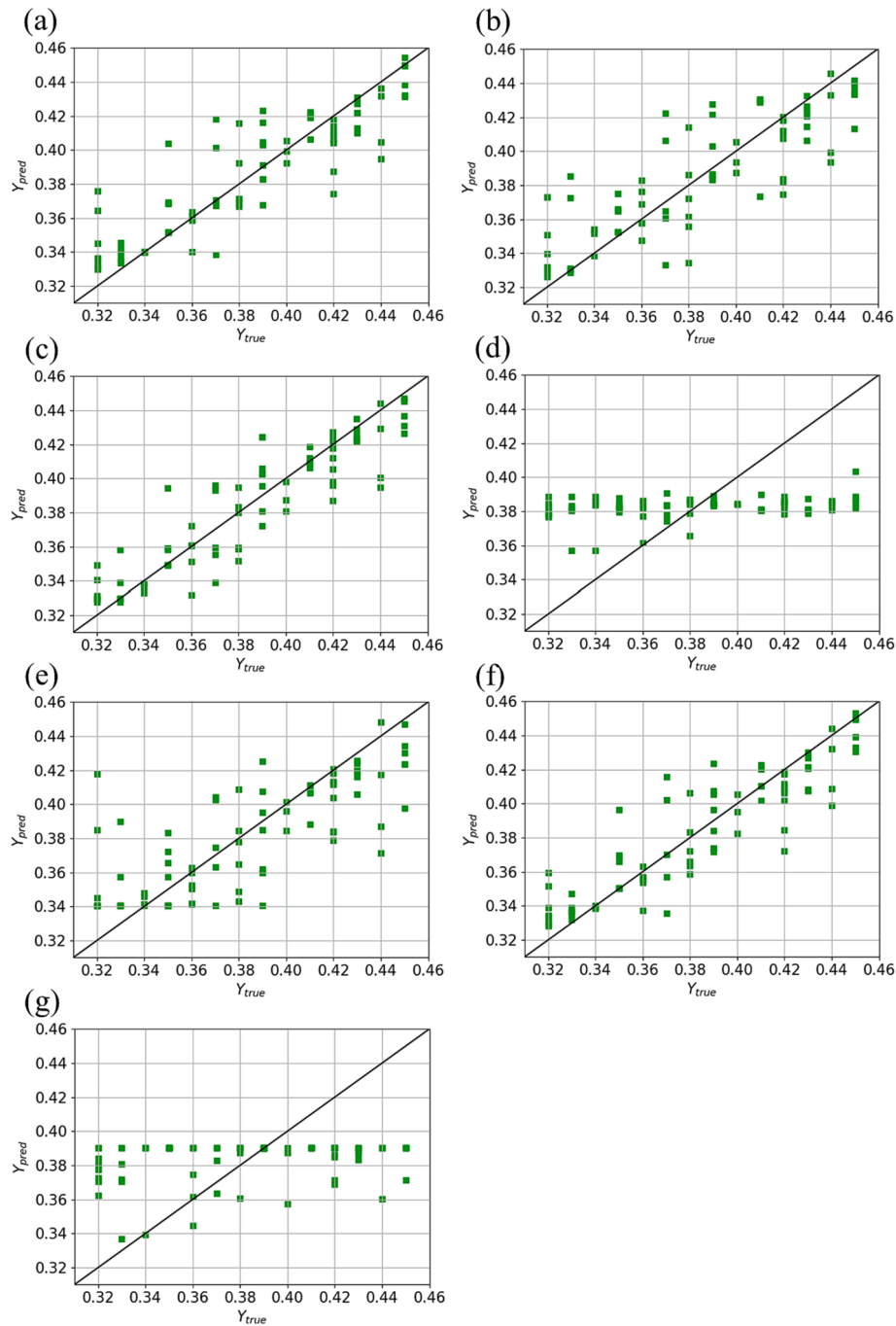


Fig. 10. Water-to-cement ratio estimation results obtained by an ANN trained with equivalent circuit parameters: cases for (a) Circuit 1, (b) Circuit 2, (c) Circuit 3, (d) Circuit 4, (e), Circuit 5, (f) Circuit 6, and (g) Circuit 7. In each plot, the x-axis represents true W/C and the y-axis represents the w/c predicted by an ANN trained with each circuit parameter case.

difficult to select an appropriate equivalent circuit model.

5.2. Influential circuit parameters to estimate w/c for each circuit model

In this study, we considered seven equivalent circuit models to extract circuit parameters from the raw electrochemical impedance data. Each circuit model represents the electrochemical system of a cement paste sample. However, not all circuit parameters provide a “good” representation that provides good w/c prediction results, as shown in Figs. 9, 10, and 11. For example, the circuit parameters for Circuit 3 (R_0 , R_1 , C_1 , R_2 , and C_2) resulted in good w/c prediction results with an average R^2 of 0.8, whereas those for Circuit 5 resulted in poor w/

c prediction results with an average R^2 of 0.2. These results indicate that the selection of an equivalent circuit is an important issue in the interpretation of the EIS response, which is highly dependent on subjective matter.

However, the advantage of the assigned equivalent circuit is its utility to understand the physical behavior of materials based on the EIS response. Changing the w/c ratio of the cement paste mainly affects the capillary porosity. In detail, the capillary porosity P_c is represented by the volume ratio between the capillary pore V_c and paste V_p as.

$$P_c = \frac{V_c}{V_p} = \frac{w/c - 0.36\alpha}{w/c + v_c}, \quad (18)$$

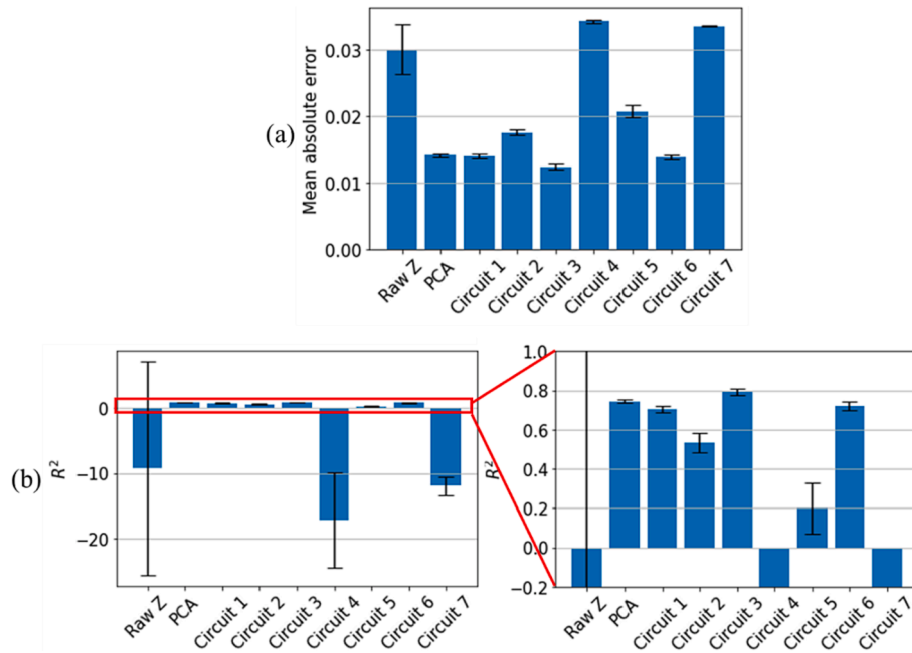


Fig. 11. W/C estimation performance evaluation for ANN models using quantitative metrics: (a) mean absolute error (MAE) and (b) R^2 .

where α is the degree of hydration, and v_c is the reciprocal of the specific gravity of the cement. The capillary porosity assigned to the mix proportion in this study is presented in Fig. 12, where the porosity proportionally increased as the w/c ratio increased.

This phenomenon is well explained by the theoretical model, Circuit 6, in which the porosity of the cement paste is considered a CCP. The circuit parameter R_{CCP} directly represents the total impedance of the CCP that occurs via ion migration. With this concept, a meaningful relationship between R_{CCP} and the w/c ratio in cement paste was identified from the correlation matrix in Fig. 8. Among all the circuit parameters from the seven different equivalent circuit models, the parameters R_{CCP} in Circuit 6 and R_1 in Circuit 1 showed the most significant correlation (0.67) with w/c. By an equivalent comparison of the total impedances from Circuits 1 and 6, the following relation can be addressed:

$$R_0 = R_{CP}R_{CCP}/(R_{CP} + R_{CCP})$$

$$R_1 = R_{CCP}^2/(R_{CP} + R_{CCP})$$

$$C_1 = \frac{1}{2\left(1 + \frac{R_{CP}}{R_{CCP}}\right)^2 C_{DP}} + C_{DP}. \quad (19)$$

From this relationship, R_{CCP} plays a significant role in R_1 in Circuit 1 (square in the numerator), and a significant correlation between R_1 and w/c is also identified, similar to R_{CCP} .

5.3. Limitations

The experimental results demonstrated the potential of w/c estimation from unhardened-state cement pastes; however, several issues should be discussed to enhance the suggested technique. First, experimental validation was only performed during the dormant period in hydration in a controlled environment. As the ion concentration and chemical reaction during hydration are highly dependent on time, the

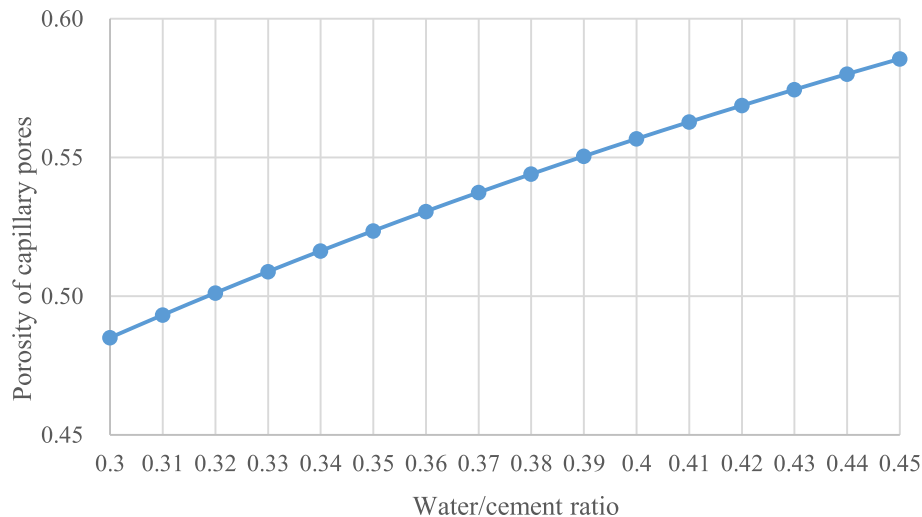


Fig. 12. Theoretical capillary porosity variation with w/c ratio in cement paste ($\alpha = 0$ and $v_c = 0.32$ were used in Eq. (18)).

suggested technique should be further evaluated with different hydration ages. In particular, very limited information on impedance has been provided with regard to the optimization of equivalent circuits. The increase in the duration of the hydration process provided more information about the impedance spectrum, such as the trace of the semi-circle in the Nyquist plot. Thus, a better understanding of the physical behavior through the circuit parameters can be obtained.

The scope of this study is to estimate the w/c ratio of cement paste under a controlled laboratory environment. Hence, it can be assumed that the variations in EIS data are mainly due to the different w/c ratios of the tested cement paste. However, EIS data of cement-based materials can be affected by various variables including temperature, cement type, and the use of mineral admixtures. To improve the practicality of the proposed approach, additional EIS data obtained with the above-mentioned variables need to be considered for future research.

Moreover, an improvement in the testing configuration is required. In this study, a three-electrode system including a reference electrode was applied, which possibly affected the variance of the data in repeated experiments. In particular, rod-type electrodes may cause experimental variations with respect to the applied electrical field surrounding the material thickness and cross-sectional area. Instead, two plate-type electrodes may provide better control of the one-way electric field extending in the outer direction of the electrode.

6. Conclusions

This paper proposed a method for predicting the w/c ratio from unhardened cement paste based on EIS measurements and its interpretation using an ANN. EIS has the benefit of immediate measurement of the electrochemical response from materials, whereas the ANN quantitatively evaluates the relationship between the w/c ratio and EIS response without subjective matter. An alternative voltage with a frequency range of 100 kHz to 0.2 Hz using a three-electrode system was applied to the unhardened cement paste specimens having w/c ratios ranging from 0.32 to 0.45. Nine types of features were extracted from the obtained impedance data, including raw data (a complex number format), PCs, and seven different equivalent circuit parameters. The following conclusions were drawn.

- (1) The impedance responses of cement pastes were obtained during the dormant period of hydration, where only the diffusion lines in the low-frequency arc were dominant owing to the relatively low bulk resistance at this stage. The general trends of increasing phase angle were observed with a higher w/c ratio; however, the variation in the experimental data was comparably high.
- (2) Qualitative analysis using the ANN was performed to establish the relationship between the w/c ratio and EIS response. The w/c ratio can be predicted with circuit parameters from Circuits 1, 3, and 6, in which high R^2 values close to 0.7 to 0.8 were obtained. Moreover, the results of PCA presented a comparably good w/c prediction performance with an R^2 of 0.74, which has the considerable benefit of purely data-driven features instead of a subjective selection of equivalent circuit models.
- (3) The correlation matrix provides a meaningful relationship between the EIS responses of the cement paste and the w/c ratio. The most significant correlation was identified from the circuit parameter R_{CCP} representing CCPs, which was governed by the porosity of the cement paste.

CRediT authorship contribution statement

Joohye Park: Writing – original draft. **Homin Song:** Software, Validation, Supervision. **Hajin Choi:** Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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