GEOSOUND

Geosound, 2022, 55 (1) 71-79 ISSN: 1019-1003
Geosound (Yerbilimleri) Dergisi
Araştırma Makalesi / Research Article

Prediction of the Rapid Hardening Property of Calcium Aluminate Cement Based on Mineralogical Composition by Neural Network

Kalsiyum Alüminatlı Çimentonun Hızlı Sertleşme Özelliğinin Sinir Ağı ile Mineralojik Kompozisyona Dayalı Tahmini

SUPHİ URAL[1*] ORCID 0000-0003-4865-011X
MURAT AYDIN[1] ORCID 0000-0002-2719-4998

[1]*Çukurova Üniversitesi, Mühendislik Fakültesi, Maden Mühendisliği Bölümü, Adana, Türkiye*

Geliş (Received): 07/03/2022 Kabul (Accepted): 21/04/2022

ABSTRACT

Quantitative X-ray diffractometry using a Rietveld-based computational method was carried out for a series of Calcium Aluminate Cement (CAC) samples. This indicated that the CA content ranged between 37.7% to 47.7% while Brownmillerite (C_4AF) amount varies between 11.0% to 23.6%. Magnetite was found in all the samples, ranging from 0.7% to 3.9% while Gehlenite amount varies between 0.5% and 6.5%. The amount of spinel varies between 0.5% and 0.1% and its average value is 1.3%.. The amorphous content of CAC is ranged between 12.0% and 32%. The Mayenite and amorphous content could be a good indicator of the Rapid Hardening (RH) property of CAC. Samples with the high Mayenite content showed less RH properties, whereas RH increased as the content of amorphous material increased. The RH properties of CAC based on its mineralogical composition was predicted through various neural network techniques. The R^2 value of the models was 0.39 for Linear Regression analysis model (LR), 0.56 for feed forward neural network (ANN) and 0.78 for Generalized Regression Neural Network (GRNN) approaches. The best prediction approach for RH value of the CAC with an Al_2O_3 content of 40% was GRNN that can be applied to predict RH.

.

Keywords: CAC, GRNN, neural network, rapid hardening, Rietveld

Yazar adı-soyadı suralpl@cu.edu.tr

[1*]*Çukurova Üniversitesi, Mühendislik Fakültesi, Maden Mühendisliği Bölümü, Adana, Türkiye*

ÖZ

Bir dizi Kalsiyum Alüminat Çimentosu (CAC) numunesi Rietveld tabanlı hesaplama yöntemi kullanılarak nicel X-ışını difraktometresi yöntemi ile incelenmiştir. Analiz sonuçları, CAC içeriğinin %37.7 ile %47.7 arasında, Brownmillerit (C_4AF) miktarının ise %11.0 ile %23,6 arasında değiştiğini göstermiştir. Tüm örneklerde %0,7 ile %3,9 arasında değişen manyetit bulunurken, Gehlenit miktarı %0,5 ile %6,5 arasında değişmektedir. Spinel miktarı %0.5 ile %0.1 arasında değişmektedir ve ortalama değeri %1.3 tür.. CAC'nin amorf içeriği %12.0 ile %32 arasında değişmektedir. Mayenit ve amorf içerikleri, CAC'nin Hızlı Sertleştirme (RH) özelliğinin iyi bir göstergesi olabilir. Mayenit içeriği yüksek olan numuneler daha az RH özelliği gösterirken, amorf malzeme içeriği arttıkça RH artmıştır. CAC'nin mineralojik bileşimine dayanan RH özellikleri, çeşitli sinir ağı teknikleri ile tahmin edildi. Modellerin R^2 değeri, Lineer Regresyon analiz modeli (LR) için 0.39, İleri Beslemeli Sinir Ağı (ANN) için 0.56 ve Genelleştirilmiş Regresyon Sinir Ağı (GRNN) yaklaşımları için 0.78'dir. %40 Al_2O_3 içeriğine sahip CAC'nin RH değeri için en iyi tahmin yaklaşımı, RH'yi tahmin etmek için uygulanabilen GRNN yöntemi olmuştur.

Anahtar Kelimeler: *CAC, GRNN, sinir ağı, hızlı sertleştirme, Rietveld*

INTRODUCTION

CAC is well known and used in various applications (Pöllmann, 2001; Pöllmann, 2012). One of the known special characteristics of (CAC) is its rapid hardening (RH) property. Hydraulic hardening of CAC is primarily due to the hydration of CA, but other compounds may also participate in the hardening process especially in long term strength development (Bensted, 2002). A model is proposed to predict the mechanical performance of CAC based on the composition of cement, curing temperature, fineness and water to cement ratio. It is explained that the main reaction scheme of the CA hydration at temperatures less than 20˚C is applied to predict the composition of iron-rich calcium aluminate cement paste (Ukrainczyk et al., 2008). In this study, a model is proposed to explain the relationship between mineralogical content and rapid hardening property of CAC.

EXPERIMENTAL

Mechanical properties and mineralogical content of the CAC samples produced according to TS EN 14647 standard were examined. Elemental analyses of CAC samples were carried out by X-ray fluorescence (XRF) spectrometry technique. X-ray diffraction (XRD) data of the CAC samples were obtained using a Rigaku diffractometer system with CuKα radiation at the laboratories of the Cimsa Cement Plant, Adana, Turkey. Samples were run from 2˚ to 70˚ 2θ, with a step of increment of 0.02˚ and counting time of 2 s/step, and the relevant data were stored in a digital form. Diffractograms obtained from the CAC samples were evaluated using an interactive data processing system based on Rietveld interpretation methods (Rietveld, 1969). This approach provides a definitive appraisal of the minerals actually present in crystalline form, which is more germane to the applications in the present study. The amorphous content was estimated by "spiking" the sample with a known weight of an internal standard, e.g. corundum, which were not already present in the sample. RH tests are carried out at the laboratories of the Cimsa Cement Plant, Adana, Turkey according to TS EN 196-3. The statistical characteristics of the CAC samples are summarized in Table 1.

Table 1. Range of the analyses of CAC samples studied.

Çizelge 1. İncelenen CAC numunelerine ilişkin analiz sonuçları

Variable	**Min. (%)**	**Max. (%)**	**Mean (%)**	**Std. Dev. (%)**
Calcium Dialuminum Oxide (CA_2)	37.7	47.6	43.8	2.0
Mayenite ($C_{12}A_7$)	0.5	2.4	1.4	0.4
Brownmillerite (C_4AF)	11.0	23.6	15.6	2.6
Gehlenite (C_2AS)	0.5	6.5	2.5	1.2
Spinel ($MgAl_2O_4$)	0.0	1.3	0.5	0.3
Perovskite ($CaTiO_3$)	1.8	3.9	2.7	0.5
Hematite (Fe_2O_3)	0.1	1.0	0.6	0.1
Calcium Aluminium Magnesium Silicate $(Na, Ca)_{0.33}(Al, Mg)_2(Si_4O_{10})$	0.0	6.2	1.4	1.0
Magnetite (Fe_3O_4)	0.7	3.9	2.6	0.6
Tricalcium Titanium Oxide (C_3FT)	0.6	1.3	1.0	0.1
Dicalcium Silicate-Alfa (C_2S)	1.0	4.5	2.6	0.5
Dicalcium Silicate-Beta (C_2S)	0.0	3.9	2.0	0.6
Wuestite (FeO)	0.0	0.4	0.0	0.1
Amorphous Content	12.0	32.9	23.3	3.6

Ninety-seven CAC samples were studied. 67 samples from them were selected randomly for training prediction approach, and remaining 30 samples were utilized as test data set. In this random selection procedure, k-fold cross validation method was applied. Linear Regression (LR), Feedforward Neural Networks (ANN) and Generalized Regression Neural Networks (GRNN) artificial intelligence approaches were built to predict the RH values of CAC using the experimental data obtained at the laboratory. All of these methods were trained and tested by the same random divided train and test datasets in order to make a fair comparison.

The artificial neural network structure that was used in the study is given in Figure 1. The feed forward neural network approach is selected for modelling the system. In this approach the neural network consists of neurons which are arranged into three or more layers which are input, hidden and output layers. In this study, there are fourteen inputs which are given in Table 1. The number of hidden neurons in the hidden layer is set to three after some experiments with different numbers of neurons. The number of outputs is one which is the initial set value of the CAC sample. In this ANN approach each neuron is connected between a weight coefficient and it is aimed at determining the best weight values which reflects the degree of importance of the given connection (Svozil et al., 1997). An iterative training procedure, which is aimed to minimize errors between predictions and actual data samples, is applied for determining best weight coefficient values. In this study, Levenberg-Marquadt learning algorithm (Hagan et al., 1999) is used for this aim.

GRNN is one of the variations of radial basis neural networks which provide one pass training algorithm (Specht, 1991). In this algorithm, the spread value affects the performance of the algorithm. In this study, it is set 0.96 after some experimental calculations.

RESULTS

The main crystalline phases of CAC with an Al_2O_3 content in the region of 40% are Monocalciumaluminate (CA) and Brownmillerite (C_4AF), whereas the minor phases are Mayenite ($C_{12}A_7$), Gehlenite (C_2AS), Spinel, Magnetite and Calcium Aluminum Magnesium Silicate. The CAC also significantly contains an amorphous phase.

The results of Rietveld analyses indicated that The CA content ranges between 37.7% to 47.7% with an average of 43.8% while C_4AF amount varies between 11.0% to 23.6% with an average of 15.6%. The Magnetite is found in all the samples, ranging from 0.7% to 3.9% while Gehlenite amounts vary between 0.5% and 6.5%. The Spinel amount stands between 0.1% to 1.3% with an average of 0.5%. The amorphous content of CAC is ranged between 12.0% and 32%.

The obtained formula of the linear regression analysis (LR) shows that Constant term, Wuestite, CA_2, C_4AF and Amorphous Content terms are most influenced parameters on the RH value. Other parameters have lower coefficient values or not significantly affect the model (p values greater than 0.05). The regression model seems significant (p=0.001) it means that the results obtained from the model can be used.

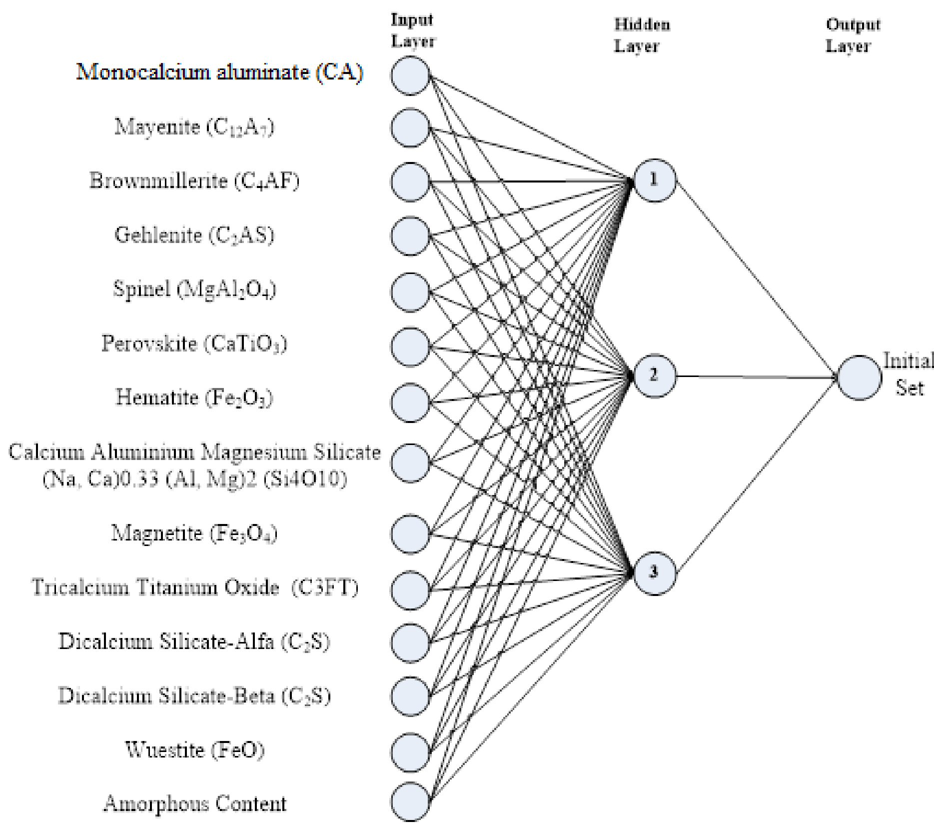

Figure 1. ANN Structure

Şekil 1. ANN yapısı

$$
\begin{aligned}
RH = & -2943.666 + 37.258\ x\ [Calcium\ Dialuminum\ Oxide\ (CA2)] - 3.979\ x\ [Mayenite\ (C12A7)] \\
& + 33.121\ x\ [Brownmillerite\ (C4AF)] + 17.304\ x\ [Gehlenite\ (C2AS)] \\
& + 31.160\ x\ [Spinel\ (MgAl2O4)] + 34.098\ x\ [Perovskite\ (CaTiO3)] \\
& + 27.538\ x\ [Hematite\ (Fe2O3)] \\
& + 32.942\ x\ [Calcium\ Aluminium\ Magnesium\ Silicate\ (Na, Ca)0.33\ (Al, Mg)2\ (Si4O10)] \\
& + 27.332\ x\ [Magnetite\ (Fe3O4)] + 9.93\ x\ [Tricalcium\ Titanium\ Oxide\ (C3FT)] \\
& + 5.237\ x\ [Dicalcium\ Silicate - Alfa\ (C2S)] - 11.28\ x\ [Dicalcium\ Silicate - Beta\ (C2S)] \\
& - 67.593\ x\ [Wuestite\ (FeO)] + 34.663\ x\ [Amorphous\ Content] \qquad (1)
\end{aligned}
$$

Figure 2 shows the actual and prediction values of all prediction methods. It seems that GRNN has more convergence on the changings in actual RH values. Especially all the methods have worse predictions in the samples between 88 and 97.

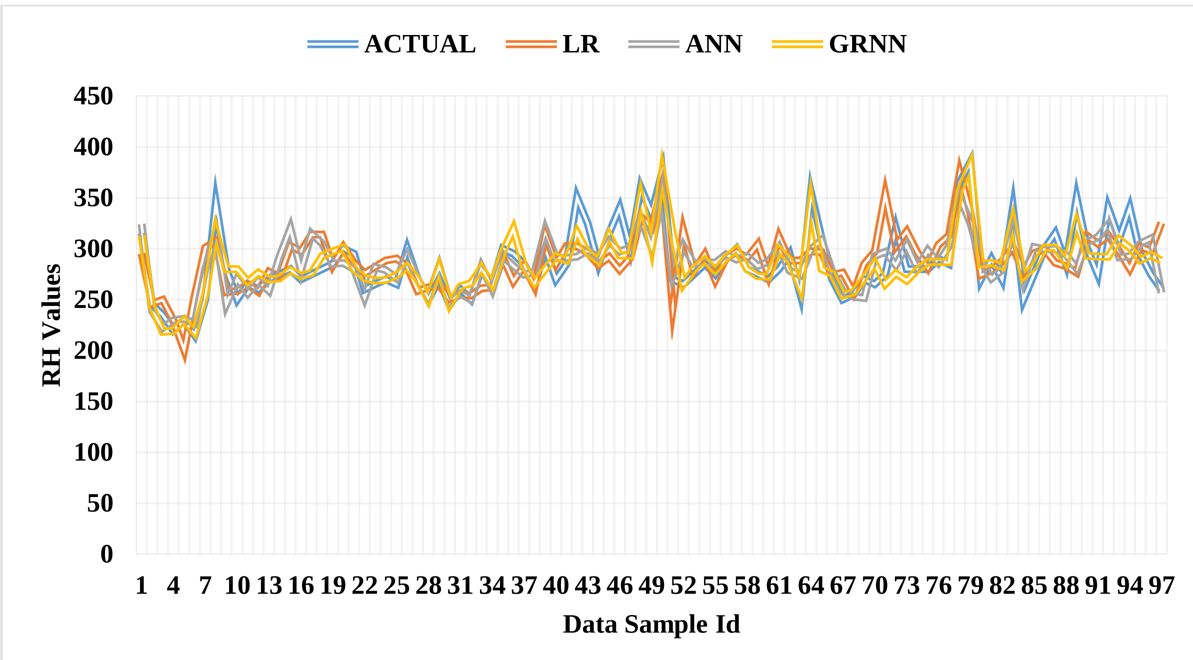

Figure 2. Comparison of the methods

Şekil 2. Farklı kestirim yöntemlerinin karşılaştırılması

Figure 3 shows the performance of methods on the test samples. It is important to predict test samples accurately because, the test samples are not used in the training phase. The figure shows us that the GRNN has a good prediction of RH values in almost all cases.

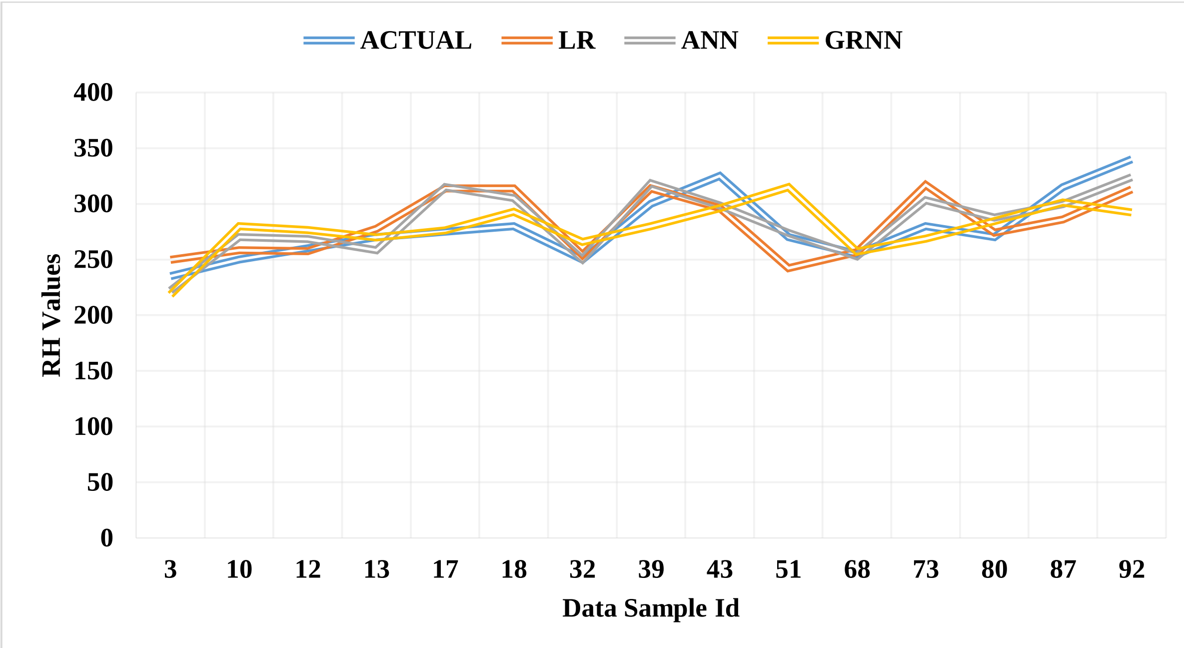

Figure 3. The performance of methods

Şekil 2. Yöntemlerin performansı

The performance of the methods is summarized in Table 2. The results show us that the GRNN method has better performance on the training data, however ANN has better performance on the test dataset for all performance criteria. Mean absolute percentage error values (MAPE) is less than 7% for all methods it means that the predictions are deviated at most 7 percent average from the actual value. According to mean absolute errors (MAE), the method deviates actual RH values at most 19 on average. According to the overall dataset, GRNN seems to have better results for all performance criteria.

Table 2. Performance of the prediction methods

Çizelge 2. Kestirim yöntemlerinin performansı

Performance Criteria	Train Dataset			Test Dataset			Overall Dataset		
	LR	ANN	GRNN	LR	ANN	GRNN	LR	ANN	GRNN
R^2	0.474	0.584	0.913	0.451	0.630	0.377	0.389	0.561	0.775
MAE	18.359	16.000	6.504	18.620	16.090	18.468	19.960	16.673	10.419
MAPE	0.0633	0.053	0.021	0.065	0.057	0.065	0.069	0.056	0.035

RESULTS AND DISCUSSIONS

One of the known special characteristics of CAC is its RH property. There is a strong relationship between mineralogical composition and the hardening property of CAC.

All the estimation methods used have worse prediction in the samples between 88 and 97 may be due to the presence of minor elements, such as Rare Earth Elements (REE) in the bauxite ores used as raw material and not included in the estimation models. It is proposed to investigate the REE contents of CAC.

ACKNOWLEDGEMENT

Financial support from the Cukurova University Scientific Research Project Unit (Under Project No: (FYL-2018-9911) is gratefully acknowledged. The support of the Cimsa Cement Plant, Mersin, Turkey is also acknowledged.

REFERENCES

Bensted, J., 2002. Calcium aluminate cements, Structure and Performance of Cements, 2nd ed., (Eds. Bensted J, Barnes P), London.

Hagan, M.T., and Menhaj, M., 1999. Training feed-forward networks with the Marquardt algorithm. IEEE Transactions on Neural Networks, 5 (6), 989–993.

Pöllmann, H., 2001. Mineralogy and crystal chemistry of calcium aluminate cement. Calcium Aluminate Cements. Proceedings of International Conference, Edinburgh, Mangabhai R J and Glasser F P (Eds). London, IOM Communications, 79-119.

Pöllmann, H., 2012. Calcium aluminate cements - raw materials, differences, properties and hydration. Reviews in Mineralogy & Geochemistry, 74 (1), 1-82.

Rietveld, H.M., 1969. A profile refinement method for nuclear and magnetic structures. J. Appl. Cryst. 2, 65-71.

Specht, D.F., 1991. A general regression neural network. IEEE transactions on neural networks, 2 (6), 568-576.

Svozil, D., Kvasnicka, V., and Pospichal, J., 1997. Introduction to multi-layer feed-forward neural networks. Chemometrics and intelligent laboratory systems, 39 (1), 43-62.

Ukrainczyk, N., Šipušić, J., Dabić, P., and Matusinović, T., 2008 Microcalorimetric Study on Calcium Aluminate Cement Hydration. 13. International conference on Materials, Processes, Friction and Wear - MATRIB'08, Vela Luka, Croatia, pp 382-388.