Investigation of the Use of an Artificial Neural Network Method for the Prediction of Crystal Structures of Zeolites from XRD Data

Melkon Tatlier[1] and H. Kerem Cigizoglu[2]

[1] Department of Chemical Engineering, Istanbul Technical University
Maslak, 34469 Istanbul, Turkey

[2] Department of Civil Engineering, Division of Hydraulics, Istanbul Technical University
Maslak, 34469 Istanbul, Turkey

Abstract. The possibility of using artificial neural network methods for the prediction of zeolite crystal structures, such as pore size and unit cell dimensions, from X-ray diffraction patterns was investigated. The Generalized Regression Neural Network method and X-ray diffraction data obtained from literature were utilized in these investigations. The predictions made by using this neural network method were, in general, more reliable than those performed by regression. The best predictions were achieved for the estimation of the pore size, while the neural network method improved significantly the very poor results obtained by regression for the unit cell dimensions.

1 Introduction

Zeolites are hydrated microporous crystalline aluminosilicates that may be used in diverse applications related to ion exchange, catalysis, adsorption and separation [1-3]. Zeolites have developed into a large industry due to their unique and versatile properties. They may be utilized in the separation of linear and branched hydrocarbons, for catalytic cracking and hydrocracking or as detergent builders, to name a few, while a significant number of potential applications are waiting to emerge. Zeolites may occur naturally or be synthesized in laboratory conditions. The most significant parameters determining the type of the zeolite formed from a certain initial reaction mixture composition are the synthesis time and temperature as well as the molar ratios of the reactants. Suitable reagents that form a clear solution or a gel mixture should be used to obtain different types of zeolites. After carrying out the synthesis procedure with these reagents, the solid material formed in the solution should be separated by filtration, which is then characterized by using various techniques. X-ray diffraction (XRD) is one of the basic and essential techniques to characterize the solid material thus obtained. XRD may be used to determine the crystallographic structure, grain size and orientation of the crystals. It is commonly utilized to identify unknown substances by comparing diffraction data against a database. The relative abundance of crystalline materials in solid mixtures may also be determined by this technique.

Tatlier M. and Cigizoglu H. (2009).
Investigation of the Use of an Artificial Neural Network Method for the Prediction of Crystal Structures of Zeolites from XRD Data.
In *Proceedings of the 5th International Workshop on Artificial Neural Networks and Intelligent Information Processing*, pages 97-105
DOI: 10.5220/0002263700970105

Additionally, when coupled with lattice refinement techniques, it can provide structural information on unknown materials. The achievement of this last deed is not a simple task to perform and requires significant amount of knowledge on the numerous peaks pertaining to the X-ray diffraction patterns of different materials.

Artificial neural networks (ANNs) have the ability to learn from input data and are very useful for the prediction of complex high-dimensional data. ANN methods have a broad range of applications, including research in chemical engineering. Artificial neural networks have been successfully used for dynamic modeling and control of chemical processes and fault diagnosis [4], in the catalytic modeling and design of solid catalysts [5] and for modeling the kinetics of a chemical reaction [6]. The applicability of ANN methods in emulsion liquid membranes [7] and in the prediction/estimation of the vapor-liquid equilibrium data [8] has been investigated. It has also been shown that ANN methods might learn efficiently from available zeolite synthesis data in the literature to predict the complex relationship between the chemical compositions of initial reaction mixtures and the zeolites formed from them [9].

A detailed theoretical investigation of the rather complex and high dimensional relationship between the XRD peaks and the crystallographic properties of various zeolites (as well as other crystalline materials) may be very useful to provide a more common and practical use of the XRD technique in the prediction of the crystal structures of unknown zeolites and other materials. In this study, the Generalized Regression Neural Network (GRNN) method was utilized to perform this investigation. The results obtained were compared to XRD data reported in the literature, as well as to the estimations made by using multilinear regression.

2 Theory

2.1 X-Ray Diffraction Technique

Crystals are regular arrays of atoms, and X-rays can be considered as waves of electromagnetic radiation. Atoms scatter X-ray waves, primarily through their electrons. An X-ray striking an electron produces secondary spherical waves emanating from the electron, which is known as elastic scattering. Although these waves cancel one another out in most directions through destructive interference, they add constructively in a few specific directions, determined by Bragg's law,

$$2d\sin\theta = n\lambda \quad (1)$$

where d is the spacing between diffracting planes in Å, θ is the incident angle in degrees, n is any integer, and λ is the wavelength of the beam in Å. These specific directions appear as spots on the diffraction pattern. It should be mentioned that X-rays have wavelengths on the order of a few angstroms, the same as typical interatomic distances in crystalline solids. This means that X-rays can be diffracted from minerals which, by definition, are crystalline and have regularly repeating atomic structures. In the XRD technique, the X-ray intensity is recorded and reported as a function of the 2θ angle.

2.2 Artificial Neural Networks

Artificial neural networks are black box models that can perform an estimation using limited input and output data patterns. In this study, the Generalized Regression Neural Network (GRNN) method was used to relate the XRD data to the properties of the crystal structures of zeolites.

The basics of the GRNN can be found in the literature [10,11]. The GRNN method does not require an iterative training procedure but instead estimates any arbitrary function between input and output vectors, drawing the function estimate directly from the training data. This method is consistent, that is, as the training set size becomes large, the estimation error approaches zero, with only mild restrictions on the function. The GRNN is used for estimation of continuous variables, as in standard regression techniques. It is based on a standard statistical technique called kernel regression. By definition, the regression of a dependent variable y on an independent x estimates the most probable value for y, given x and a training set. The regression method will produce the estimated value of y, which minimizes the mean-squared error. The GRNN consists of four layers: input layer, pattern layer, summation layer, and output layer. The first layer is fully connected to the second, pattern layer, where each unit represents a training pattern and its output is a measure of the distance of the input from the stored patterns. Each pattern layer unit is connected to the two neurons in the summation layer: S-summation neuron and D-summation neuron. The S-summation neuron computes the sum of the weighted outputs of the pattern layer while the D-summation neuron calculates the unweighted outputs of the pattern neurons. The connection weight between the i^{th} neuron in the pattern layer and the S-summation neuron is y_i, the target output value corresponding to the i^{th} input pattern. For D-summation neuron, the connection weight is unity. The output layer merely divides the output of each S-summation neuron by that of each D-summation neuron. In this method, the spread σ is a smoothing parameter, the optimal value of which is often determined experimentally [12]. When the spread parameter σ is made large, the estimated density is forced to be smooth and in the limit becomes a multivariate Gaussian with covariance $\sigma^2 I$. On the other hand, a smaller value of σ allows the estimated density to assume non-Gaussian shapes, but with the hazard that wild points may have too great an effect on the estimate. In this study, different spreads were tried to find the best one that gave the minimum difference between predicted and experimental values for the utilization of the cross-validation data.

2.3 Method

Zeolites are hydrated microporous crystalline materials. The zeolite framework consists of an assemblage of SiO_4 and AlO_4 tetrahedra, joined together in various regular arrangements through shared oxygen atoms, to form an open crystal lattice. The micropore structure is determined by the crystal lattice, which contains pores of molecular dimensions into which guest molecules can penetrate. The cations (e.g., Na) are placed in special positions near the Al atoms. The pore size varies for different zeolites, depending on the arrangement of the atoms forming the zeolite crystal structure. The crystal structure of a material or the arrangement of atoms in a crystal structure

can be described in terms of its unit cell. The unit cell is a tiny box with one or more spatial arrangements of atoms. The unit cells stacked in three-dimensional space describe the bulk arrangement of atoms of the crystal. The crystal structure has a three dimensional shape. The unit cell may be represented by its lattice parameters, including the length of the cell edges and the angles between them.

Data obtained from the literature [13], describing the XRD patterns of different zeolites were used in the estimations carried out by using the ANN method. Preliminary estimations indicated that the GRNN method was more successful in the prediction of the zeolite crystal structure from XRD data when compared to the Radial Basis Function-Based Neural Networks (RBF) and Feed Forward Back Propagation (FFBP) methods, which were also examined. Thus, the GRNN method was used for the estimations performed in detail. The components of the input vector were the 2θ angles of eight XRD peaks with the highest intensity pertaining to different zeolites, while the components of the output vector were the pore sizes (r) and lengths of the unit cell edges (a,b,c) of these zeolites. The pore sizes and unit cell dimensions of zeolites generally vary between a few angstroms and a few nanometers. Since the pores of some zeolites are not uniform and some others may have pore channels of different lengths, the largest dimensions of the pores were taken into consideration in this study.

The application of the ANN to data consisted of two steps. The first step was the training of the neural networks, which comprised the presentation of training data (data set 1) describing the input and output to the network and obtaining the interconnection weights. The components of the input vector were eight different 2θ angles of the XRD peaks, while the components of the output vector were the pore sizes and the three different lengths of the unit cell edges of corresponding zeolites. The input and output data were normalized between 0 and 1 prior to the training. Once the training stage was completed, the ANNs were applied to the cross-validation data (data set 2). Determining an appropriate architecture of a neural network for a particular problem is an important issue, since the network topology directly affects its computational complexity and its generalization capability. The number of hidden layers and the number of nodes in the hidden layers were determined after trying various network structures. The network structure providing the best result was determined according to the success of the predictions performed by using the cross-validation data set. The ANN method was used to predict only one component of the output vector at a time.

The number of data used for training was 55 while that used for cross-validation was 7. The zeolites consisting of silicon, aluminum, oxygen, water and different cations were taken into consideration in the investigations carried out in this study.

The results obtained by using the GRNN method were compared to the actual values [13] as well as to those values estimated by using multilinear regression. In regression, the relationships between the 2θ angles of eight XRD peaks and the pore sizes and lengths of the unit cell edges of zeolites were determined by using data set 1. The information obtained was used in the estimation of the pore sizes and lengths of the unit cell edges of the zeolites investigated in data set 2. Since, to our knowledge, a similar theoretical attempt, for determining such a relationship has not been performed before, the comparison of the results obtained from ANN methods to those determined by multilinear regression may be a reasonable first approach. The regres-

sion model tested in this study was of simple linear form, as given below. R represents either the pore size or the lengths of the unit cell edges of zeolites

$$R = a_0 + a_1(2\theta_1) + a_2(2\theta_2) + a_3(2\theta_3) + a_4(2\theta_4) + a_5(2\theta_5) + a_6(2\theta_6) + a_7(2\theta_7) + a_8(2\theta_8)\ a_8(2\theta_8) \quad (2)$$

The relative error (d) was used to monitor the success of the ANN method and regression used in the prediction of zeolite crystal properties from the 2θ angles of the X-ray diffraction patterns. d was determined by taking into consideration the deviation (%) of the pore sizes or lengths of the unit cell edges of zeolites, calculated by using the ANN method (c_{calc}), from the corresponding actual values (c_{act}).

$$d = | c_{act} - c_{calc} | / c_{act} \ \text{x}\ 100 \quad (3)$$

d_m was defined as the arithmetic mean of the relative errors obtained for the different data used in prediction.

3 Results and Discussion

3.1 Criteria assuring Best Performance for the GRNN Method

The predictions of the pore sizes and lengths of the unit cell edges of zeolites investigated in data set 2 were performed by using GRNN method mentioned above, and data set 1 for training. As mentioned before, the network structure providing the best result was determined according to the success of the predictions performed by using the cross-validation data. It was also established that the conditions providing the best results in the testing stage could allow the ANN method to exhibit quite high performances in the training stage.

For the GRNN method, spread factors in the range 0.02-0.2 were the conditions determined to give the best results. The spread factor was determined to be equal to 0.15, 0.075, 0.2 and 0.02 for r (pore size of zeolites), a, b and c (lengths of unit cell edges of zeolites), respectively, by using the cross-validation data for the optimization. When the optimization was performed by using training data (data set 1), without taking into consideration data set 2, the d_m values, representing the deviation of the predicted values of data set 1 from experimental values, were less than 10% for all the cases investigated. When the spread factor was optimized by using data set 2, the predictive power of the GRNN method was not reduced significantly. The predictions made by using the GRNN method for the pore size and lengths of the unit cell edges of zeolites are detailed below.

3.2 Evaluation of the Predictions made by the GRNN Method

The results obtained by the GRNN method are depicted in Figures 1-4 for r (pore size), a, b, and c (lengths of the unit cell edges) of zeolites, respectively. The deviations of the results obtained by using the ANN method from the actual values may be observed more clearly from Table 1. The performance exhibited by multilinear re-

gression may also be seen in the table. It may be observed from Figures 1-4 and Table 1 that the GRNN method provided fairly good fits to the actual results for most of the data, though there were some discrepancies. The average deviation from actual results was smaller for the pore size predictions while the largest deviation was observed for length, a, of the unit cell edge.

Table 1. Relative errors obtained for the predictions.

Method	d_m (%)			
	r	a	b	c
GRNN	12.0	30.9	17.5	22.2
regression	14.7	149.4	169.2	160.7

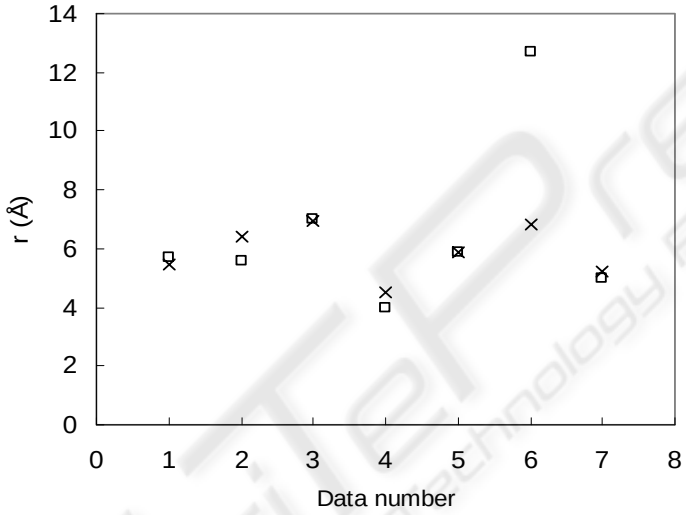

Fig. 1. Zeolite pore size predictions by (x) GRNN in comparison to (_) actual values.

The results obtained for regression given in Table 1 should also be taken into consideration before arriving at a conclusion about the success of the ANN method in the prediction of the zeolite crystal structure properties. When multilinear regression was utilized, the average deviation from the actual values was slightly higher than that of the GRNN method for the prediction of the pore size. However, the predictions of the lengths of the unit cell edges were very poor with multilinear regression. The average deviation was equal to about 150-170% for the estimation of all the three edges of the unit cell. When this information is taken into consideration, the average deviations between 17% and 31% provided by the GRNN method may be regarded to be quite promising. For further improvement, additional XRD data, for example, those pertaining to zeolite-like materials may also be included for the training of the neural networks. Furthermore, the height and width of the XRD peaks may also be taken into consideration as components of the input vector. Different ANN methods may also be tested for possible improvements in the prediction of crystal structures from XRD data.

The superiority of the ANNs over conventional methods for the prediction of complex and high dimensional relationships, such as the one investigated in this study, can be attributed to the capability of the ANNs to capture the nonlinear features and generalize the structure of the whole data set. ANN methods are flexible alternatives and standard ANN software can be used to construct intricate multipurpose nonlinear solutions. The method has no limitations in the form of fixed assumptions or formal constraints. The neural network has a distributed processing structure. Each individual processing unit or the weighted connection between two units is responsible for one small part of the input–output mapping system.

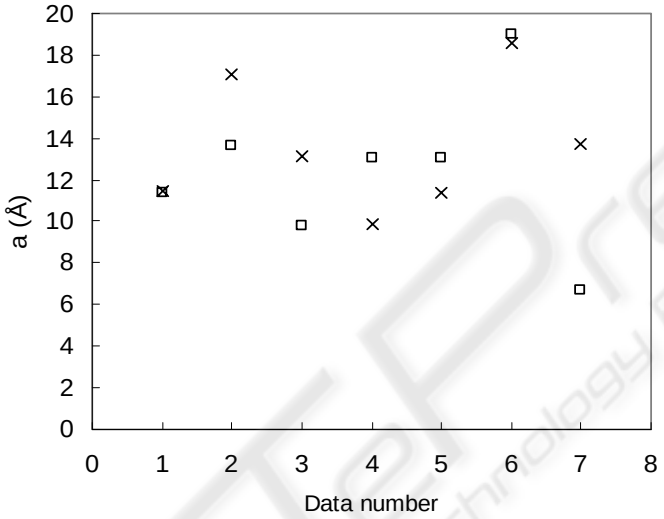

Fig. 2. Unit cell length, a, predictions by (x) GRNN in comparison to (_) actual values.

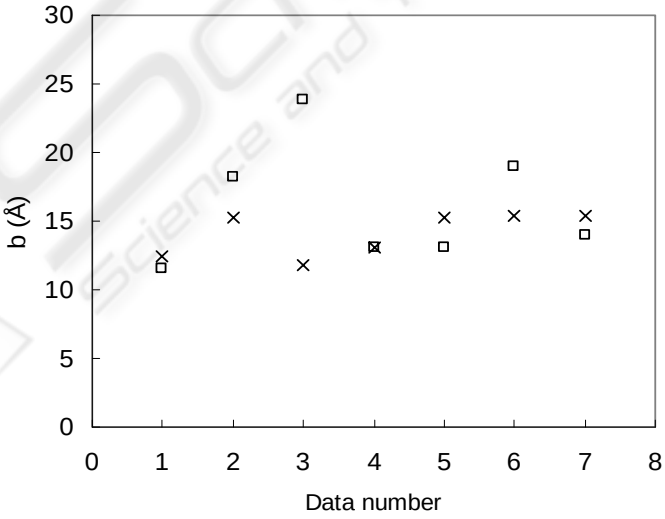

Fig. 3. Unit cell length, b, predictions by (x) GRNN in comparison to (_) actual values.

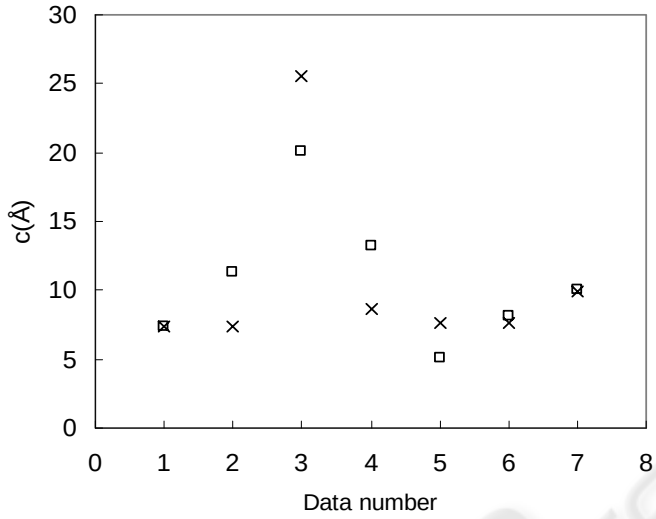

Fig. 4. Unit cell length, c, predictions by (x) GRNN in comparison to (_) actual values.

4 Conclusions

It was determined that neural networks might learn from XRD data to predict some properties of the crystal structures of zeolites. The predictions made were, in general, much more reliable than those performed by the multilinear regression. The best prediction was made for the pore sizes of zeolites, which also represented the case where the difference between the success of the predictions made by regression and neural networks was the smallest. The improvement provided by the use of the GRNN method, when compared to regression, was quite significant for the predictions of the lengths of the unit cells of zeolites.

The use of artificial neural network methods may allow a better understanding of the relationship between the X-ray diffraction patterns and the crystallographic properties of zeolites as well as other materials. This will ease and support the discovery of novel crystal materials since a short and practical characterization by using available XRD data will become possible. It should also be remembered that in case training and cross-validation data other than those adopted in this study, (e.g., those pertaining to different types of materials) could be used with GRNN as well as other ANN models to make the predictions, the relative success of prediction might still improve. Recurrent neural networks and optimization of neural network architecture by using genetic programming are methods that may be tested for providing further developments.

References

1. Weitkamp, J.: Zeolites and Catalysis. Solid State Ionics 131 (2000) 175-188.

2. Caro, J., Noack, M., Kolsch, P., Schafer, R.: Zeolite Membranes-State of Their Development and Perspective. Microporous Mesoporous Mater. 38 (2000) 3-24.
3. Ruthven, D.M.: Zeolites as Selective Adsorbents. Chem. Eng. Progr. 84 (1988) 42-50.
4. Hussain, M.A.: Review of the Applications of Neural Networks in Chemical Process Control- Simulation and Online Implementation. Artif. Int. Eng. 13 (1999) 55-68.
5. Huang, K., Chen, F., Lu, D.: Artificial Neural Network-Aided Design of a Multicomponent Catalyst for Methane Oxidative Coupling. Appl. Catal. A 219 (2001) 61-68.
6. Serra, J.M., Corma, A., Chica, A., Argente, E., Botti, V.: Can Artificial Neural Networks Help the Experimentation in Catalysis? Cat. Today. 81 (2003) 393-403.
7. Chakraborty, M., Bhattacharya, C., Dutta, S.: Studies on the Applicability of Artificial Neural Network (ANN) in Emulsion Liquid Membranes. J. Membrane Sci. 220 (2003) 155-164.
8. Sharma, R., Singhal, D., Ghosh, R., Dwivedi, A.: Potential Applications of Artificial Neural Networks to Thermodynamics: Vapor-Liquid Equilibrium Predictions. Comp. Chem. Eng. 23 (1999) 385-390.
9. Tatlier, M., Cigizoglu, H.K., Erdem-Şenatalar, A.: Artificial Neural Network Methods for the Estimation of Zeolite Molar Compositions That Form from Different Reaction Mixtures. Comp. Chem. Eng. 30 (2005) 137-146.
10. Tatlier, M., Cigizoglu, K.B, Cigizoglu, H.K., Erdem-Şenatalar, A.: Low-Silica Zeolite Coatings Prepared by Using Predictions from an Artificial Neural Network Method. J. Porous Mater. 15 (2008) 389-395.
11. Specht, D.F.: A General Regression Neural Network. IEEE Trans. Neural Networks 2 (1991) 568-576.
12. Tsoukalas, L. H., Uhrig, R. E.: Fuzzy and Neural Approaches in Engineering. Wiley, New York (1997).
13. Kim, B., Kim, S., Kim, K.: Modeling of Plasma Etching Using a Generalized Regression Neural Network. Vacuum 71 (2003) 497-503.
14. Treacy, M.M.J., Higgins, J.B.: Collection of Simulated XRD Powder Patterns for Zeolites. Elsevier, Amsterdam (2001).