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Dynamic Neural Network Modeling for Hydrochloric Acid Recovery Process

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Abstract−This paper describes neural network models for the prediction of the concentration profile of a hydrochloric acid recovery process consisting of double fixed-bed ion exchange columns. The process is used to remove the Fe^{2+} and Fe^{3+} ion from the pickling liquor, resulting in increasing the acid concentration for reusing in the pickling process. Due to the complexity and highly nonlinearity of the process, the modeling of the process based on the first principle is difficult and involve too many unknown parameters. Therefore, an attractive alternative technique, neural network modeling, has been applied to model this system because of its ability to model a complex nonlinear process, even when process understanding is limited. The process data sets are gathered from a real hydrochloric acid recovery pilot plant and used for neural network training and validation. Backpropagation and Lenvenberg-Marquardt techniques are used to train various neural network architectures, and the accuracy of the obtained models have been examined by using test data set. The optimal neural network architectures of this process can be determined by MSE minimization technique. The simulation results have shown that multilayer feedforward neural network models with two hidden layers provide sufficiently accurate prediction of the concentration profile of the process.

Key words: Neural Network Modeling, Pickling Process, Hydrochloric Acid Recovery Process, Ion Exchange Resin

INTRODUCTION

The iron and steel industry is one of the industries that causes numerous pollution problems due to its wastewater released from a steel pickling process containing oil and grease, metal scraps, acid and steel ion. Steel pickling is part of the finishing processes in the production of steel products in which oxides and scale are removed from the surface of strip steel, steel wire, and some other forms of steel, by immersing the steel in acidic solution. A solution of either hydrochloric acid (HCl) or sulphuric acid is generally used to treat steel products.

Almost all the iron and steel pickling processes in ***Thailand*** use hydrochloric acid as a pickling agent. The used acid consisting of ferrous and ferric ions in a pickling bath thus becomes a highly polluted residue. The government has strictly regulated the waste ferrous and ferric solution properly treated before direct discharge to natural water streams [Thailand: Bureau of Industrial Environment Technology, Ministry of Industry]. The steel industry's concerns about this waste acid solution stem from the fact that the ferrous and ferric ions in aqueous solution can be readily separated or removed; then, the used acid with less concentration of the ferrous and ferric ions can be reused in the pickling process. At present, the acid recovery techniques are chemical precipitation - the classical treatment is neutralization with lime, but this has certain disadvantages: the acid cannot be recycled and a high volume of sludge containing the precipitated metal is obtained; and evaporation [Oswald, 1996] - the concept of this technique is to evaporate both acid and water in the pickling liquor into acid vapour and steam using an evaporator. Cooling and condensing these vapours can subsequently recover the acid solution. The residue of the evaporator is the concentrated solution of ferrous chloride that has to be further neutralized. The disadvantage of this technique is that high-energy demand is needed. Alternatively, ion exchange and adsorption have commonly been employed for the removal of steel ions. Among these, adsorption has been thought to be efficient and economically feasible as a waste acid treatment operation. So an ion exchange and adsorption technique becomes a popular technique that has received much attention in recent years. Maranon et al. [1999, 2000] described two ion exchange resins to remove iron and zinc from pickling liquor. Lin et al. [2002] used an ion exchange process for chromic acid recovery from waste acid solution. Rengaraj et al. [2003] used ion exchange resins to remove copper from aqueous solution. Juang et al. [2003] discussed the fixed-bed adsorption to remove metal ions (CO^{2+}, Ni^{2+}, Mn^{2+}, Sr^{2+}) from waste acid solution using strong acid resins.

Over the past decade, ion exchange processes have been increasingly applied in a wide range of diverse fields, most of which use a fixed-bed ion exchange cylinder column. The study of the dynamic behavior of a fixed-bed adsorption column is the history of effluent concentration referred to as the concentration-time profile. Theoretical models are developed for the prediction of the concentration profile of the fixed-bed column. The models consider axial dispersion in the direction of waste acid flow, film diffusion resistance, intra-particle diffusion resistance which may include both pore and surface diffusion, and sorption kinetics at the adsorbent surface. Alternatively, simplified modeling approaches require a numerical method that has been used by a number of investigators. Wong et al. [1982] applied a simplified model to predict the concentration profile. Ruthven et al. [1983] used a method of orthogonal to solve PDE for the prediction of the dynamic behavior of the fixed bed adsorption column.

The ultimate goal of this work is to develop an advanced control technique to control a system consisting of steel pickling baths and

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acid recovery columns. To achieve this, two researches focus on the control of the steel pickling baths and the control of the acid recovery columns by neural network inverse models. In this paper, a hydrochloric acid recovery process consisting of two columns that contain different resins is used to remove Fe^{2+} and Fe^{3+} from the pickling liquor. Due to its highly nonlinear dynamic behavior, experimental data are then used to develop neural network models to predict the concentration profile of the system. In addition, the prediction of the system's concentration profile of the neural network models is compared with that of the numerical solution of its first principle models.

CASE STUDY

1. The Steel Pickling Process

The pickling process is one of most common chemical procedures used to remove oxides and iron contamination during the hot rolling of steel in the air. This oxide has to be removed before subsequent forming or processing operations. The process consists of two major steps: pickling and rinsing [Kittisupakorn and Kaewpradit, 2003]. The pickling step is used to remove surface oxides and other contaminants out of metals by an immersion of the metals into normally an aqueous acid solution containing 5-15 vol% hydrochloric acid (HCl). For alloy steels like stainless steels, scale removal may require the use of acid mixture containing 8-20 vol% nitric acid and 0.5-5 vol% hydrofluoric acid (HF). The pickling process in this work consists of three pickling baths, containing 5%, 10% and 15% by weight of hydrochloric acid (HCl), respectively. The metals move countercurrently to the acid stream. The chemical reactions involved in the pickling process are as follows:

$$FeO+2HCl \Rightarrow FeCl_2+H_2O \qquad (1)$$

$$Fe_2O_3+6HCl \Rightarrow 2FeCl_3+3H_2O \qquad (2)$$

$$Fe+2HCl \Rightarrow FeCl_2+H_2 \qquad (3)$$

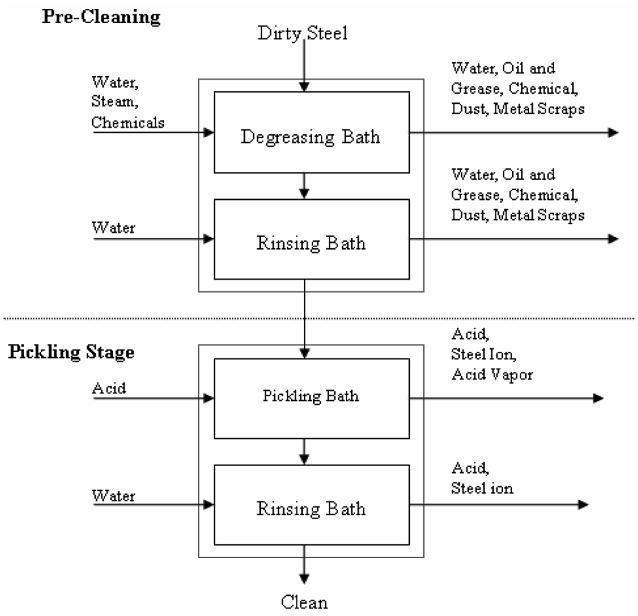

Fig. 1. Process diagram of pickling process.

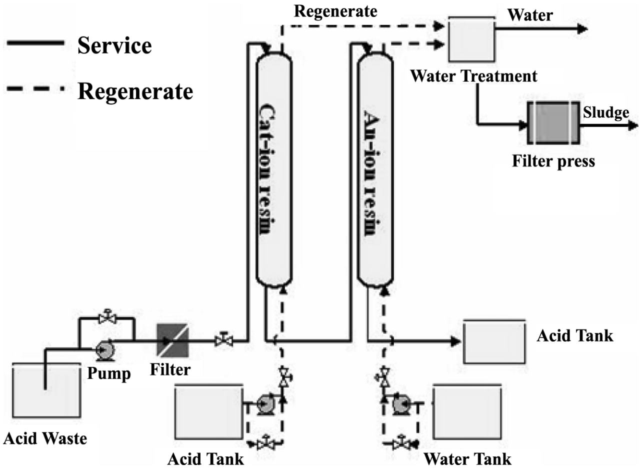

Fig. 2. Double fixed bed ion exchange resin column [Atron, 2002].

$$FeCl_3+½H_2 \Rightarrow FeCl_2+HCl \qquad (4)$$

In the steel pickling process (Fig. 1), most of the wastewater generated from the pickling process contains pickling acids, steel ion (Fe^{2+}/Fe^{3+}) and some of the used chemical in the cleaning baths.

Before the wastewater (pickling liquor) is discharged to a natural water stream, it is fed into a hydrochloric acid recovery process shown in Fig. 2 consisting of ion exchange columns for recovering any unreacted acid [Atron, 2002]. The procedure of the hydrochloric acid recovery process will be described in the next section.

2. Hydrochloric Acid Recovery System by Ion Exchange

The objective of the acid recovery system is to recover as much as possible unreacted acid in the wastewater by separating free acid out of steel (Fe^{2+}/Fe^{3+}) ions. At present, available acid recovery techniques are evaporation, retardation acid adsorption, retardation iron adsorption and pyrohydrolysis with various efficiency [Oswald, 1996]. Details and comparisons of these techniques are given in the Table 1.

For a waste acid treatment operation, adsorption is considered to be more efficient and economically feasible than other techniques.

3. Adsorption Model

Table 1. Comparison of acid recovery systems [Oswald, 1996]

Type	Available for	How its works
Evaporation	HCl	Evaporation of HCl and H_2O from spent pickling acid bath
Retardation acid adsorption	HCl	Adsorption of free acid on ion exchange resin, $FeCl_2$ pass through, adsorbed free acid regenerated with water
Retardation iron adsorption	HCl	Oxidation Fe(II) to Fe(III) with H_2O_2, adsorption of $FeCl_4^-$ anion complex by the ion exchange An-ion resin regenerated with water
Pyrohydrolysis	HCl	Heating, roasting, oxidation Fe(II) to Fe(III), condensation of chlorides as free acid and chemically fixed acid

An adsorption fixed-bed consists of a vertical cylindrical pipe filled or packed with an ion exchange resin. Macroscopic conservation equations of the ion exchange column are complex and highly nonlinear. Concentration profile of the bed can be calculated by several numerical methods with initial and boundary conditions [Duong et al., 2001]. Raghavan and Ruthven [1983] used an orthogonal collocation method to simulate and predict the transient response of an adsorption column. Hand et al. [1996] used this method to predict the performance of fixed bed columns. Alternatively, Brain et al. [1987] used the method of Line to predict the response of the columns. Here, the following assumptions made to set up the model equations are

(i) The system operates under an isothermal condition.

(ii) The flow pattern in the column is axial dispersion; radial dispersion is negligible.

(ii) The macro porous adsorbent particles are spherical and homogeneous in size and density.

The adsorption model is:

$$\frac{\partial c}{\partial t}+\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial q}{\partial t}=-\frac{F_L}{\varepsilon A_c}\frac{\partial c}{\partial z}+D_L\frac{\partial^2 c}{\partial z^2} \tag{5}$$

where, ε is an external void fraction of the bed; F_L is the flow rate; A_c is a circular cross-section area; c is the concentration of solute in solution; q is the concentration of solute in adsorbent; D_L is solution phase dispersion coefficient, m^2/s; t is time; and z is the column height. The first term represents an accumulation of solute in the liquid. The second term is an accumulation of the solute in the solid. The third term represents the amount of solute flowing in and out by convection to the section dz of the bed. The last term represents axial dispersion of solute in the bed.

Mass transfer resistance of adsorbent particles is

$$\frac{\partial q}{\partial t}=\frac{3}{R_p}k_f(c-c_p) \tag{6}$$

where, k_f is a mass transfer rate coefficient; c_p is the pore concentration at the resin surface; R_p is the resin bead radius. Substituting Eq. (6) into Eq. (5) gives:

$$\frac{\partial c}{\partial t}+\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{3}{R_p}k_f(c-c_p)=-\frac{F_L}{\varepsilon A_c}\frac{\partial c}{\partial z}+D_L\frac{\partial^2 c}{\partial z^2} \tag{7}$$

From this equation, the concentration profile of the column can be determined by solving partial differential equations problem using available numerical method.

NEURAL NETWORK MODELING

Neural network is emerging as a promising tool in process identification and control owing to its ability to model processes with accuracy [Hussain and Rahman, 1999; Hussain and Kershenbaum, 2000]. It also offers a cost-effective method in developing useful relationships between variables, when the experimental data of these variables are available. Neural network is a universal function approximator that typically works much better in practical applications than a traditional (polynomial) function approximation method. A typical neuron takes in a set of inputs, sums them together, takes some function of them, and passes the output through a weighted connection to another neuron. The neuron is thus just a predictor variable, or a function of a nonlinear combination of predictor variables. The connection weights serve as adjustable parameters, which are set by a training method, that is, they are estimated from part of the data.

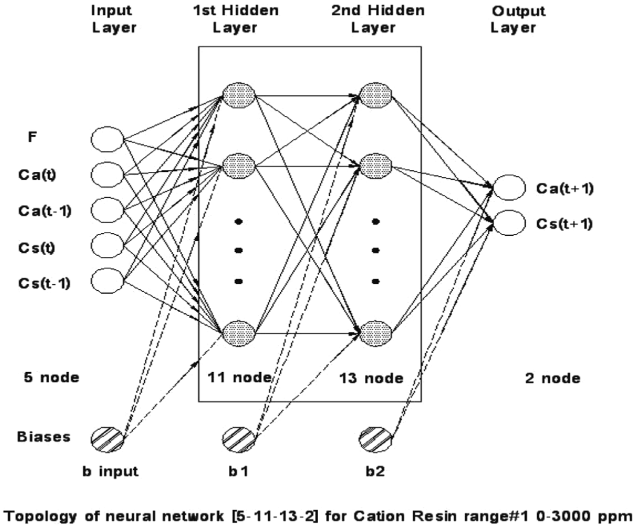

Fig. 3. The multilayer feedforward neural network.

Table 2. The components of neural network models

Training Algorithm	:	Back Propagation Algorithm
Basis Function	:	Linear Basis Function
Transfer Function	:	Sigmoid Function
Input Signals Data	:	Flow Rate Steel Ion Concentration Hydrochloric Concentration
Output Signals Data	:	Steel Ion Concentration Hydrochloric Concentration
To Predict	:	Concentration Profile Hydrochloric Concentration

Neural network builds a class of very flexible models which can be used in various applications. Unfortunately, the neural network is not uniquely defined; it can be configured in many different network types and models. Here, the multilayer feedforward network with backpropagation shown in Fig. 3 is used to model the system. The component of the neural network models of this process is shown in Table 2.

1. Neural Network Inputs and Outputs Data Set

In Fig. 4 the dynamic behavior data of the double fixed-bed ion exchange resin pilot plant (Fig. 2) are gathered from several experiments covering a wide range of scenarios. The flow rates of the waste acid fed into the column are adjusted by a manual diaphragm valve with accurate flow meter. Experimental data used in the neural network data sets are collected with a frequency of 1 minute sampling time.

Process inputs and outputs are chosen as:

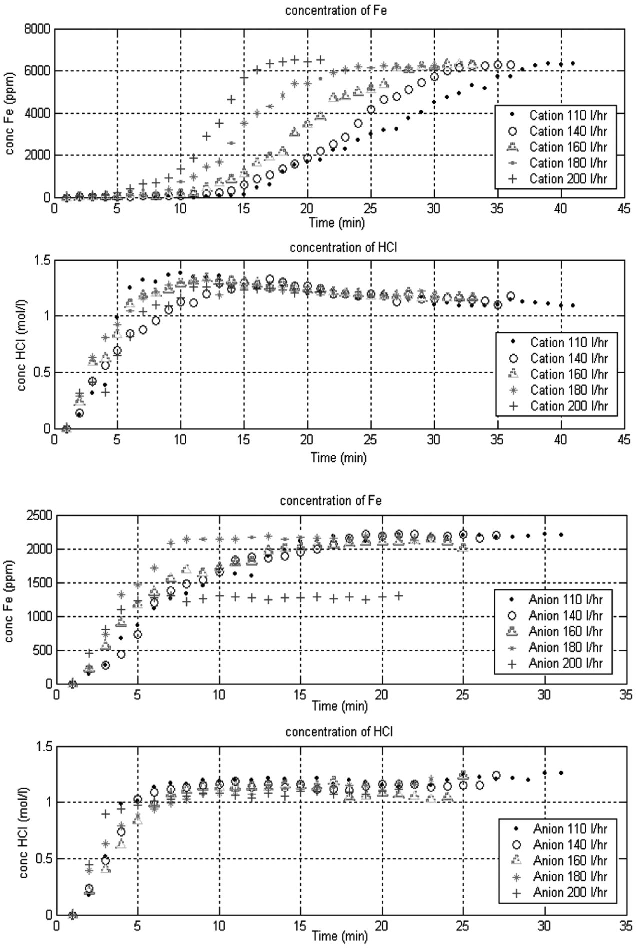

Fig. 4. Raw data from ion exchange Cation and Anion resin process.

$$x=\begin{bmatrix} F \\ C_a(t) \\ C_s(t) \\ C_a(t-1) \\ C_s(t-1) \end{bmatrix},\ y=\begin{bmatrix} C_a(t+1) \\ C_s(t+1) \end{bmatrix} \tag{8}$$

where F, C_a and D_s denote the flow rate of the pickling liquors, the concentration of hydrochloric acid and the concentration of steel ions, respectively.

A data set of 215 patterns for Cation resin and of 140 patterns for Anion resin are collected after the wide range of experiments. 60% of patterns are used to train the models and 40% of patterns are used to validate the optimal models as shown in Fig. 5.

2. Procedure for Obtaining Neural Network Models

The procedures for obtaining reliable neural network models are summarized in Fig. 6. Training and validation data sets are obtained by varying inputs of the columns covering several scenarios in experiments. The data sets need to be scaled in order to overcome the significant minimum and maximum values used in the training process. In this work, a sigmoid function is used as an activated function of the network and the networks are trained with Levenberg-Marquardt method, where the common objective is to reduce the error between the neural network predicted value and the actual targeted value. The training will stop when the desired mean squared

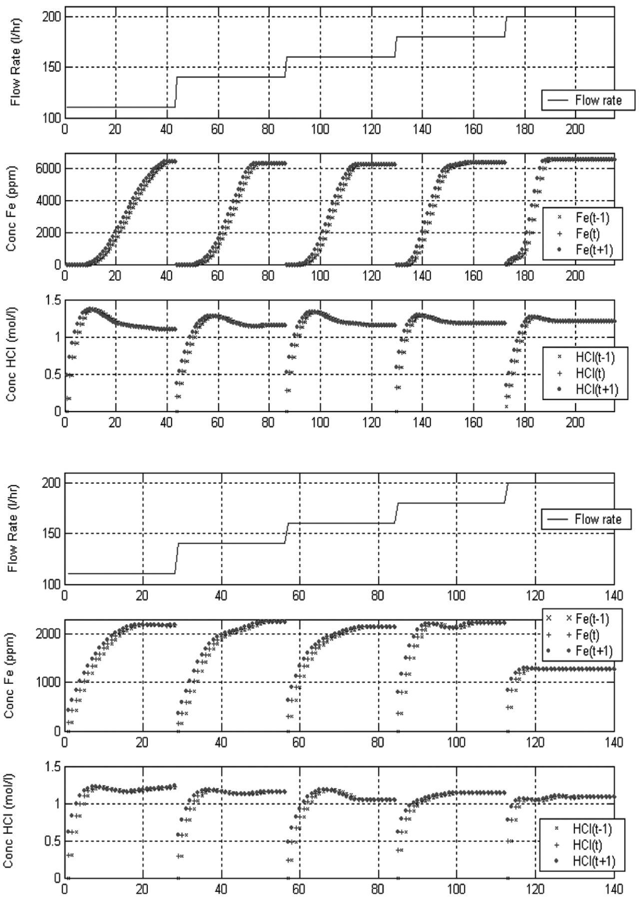

Fig. 5. Data set patterns for ion exchange Cation and Anion resins.

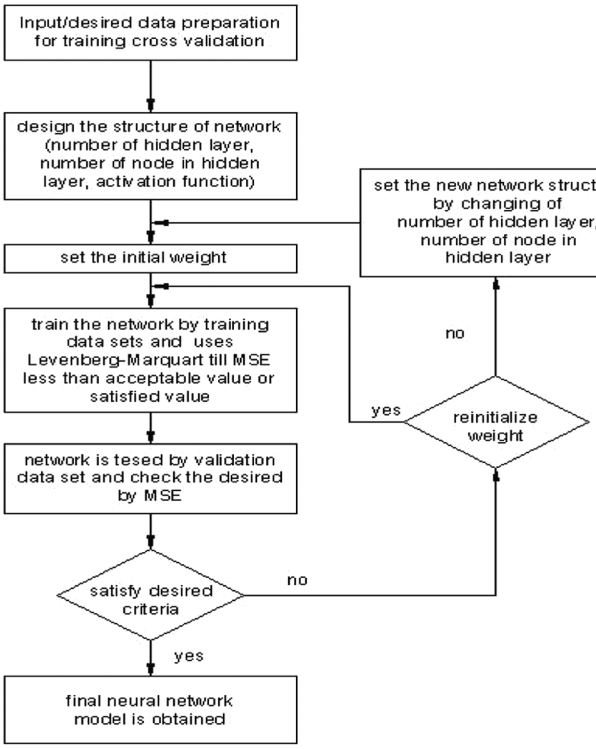

Fig. 6. Procedure for obtaining neural network models.

Table 3. Characteristic properties of the resins

Purolite C-150 Cation Resin	
Matrix	Polystyrene divinylbenzene
Appearance	Spherical beads
Functional groups	$R-SO_3^-$
Ionic form as ship	Sodium - Na^+
Total exchange capacity	1.8 eq/*l* minimum
Moisture Retention	48-53%
Screen Size Range	16-50 US Standard Mesh
Max reversible swelling	$Na^+ \Rightarrow H^+$ 5%
pH Limitations	None
Purolite A-500 Anion Resin	
Matrix	Polystyrene divinylbenzene
Appearance	Opaque, spherical beads
Functional groups	$R-N(CH_3)_3^+$
Ionic form as ship	Chloride - Cl^-
Total exchange capacity	1.15 eq./*l* minimum
Moisture Retention	53-58%
Screen Size Range	16-50 US Standard Mesh
Max reversible swelling	$Cl^- \Rightarrow OH^-$ 15%
pH Limitations	0-14

error (MSE) reaches the specified value of 0.001.

The optimum structures varying hidden nodes are selected by the MSE minimization method. The hidden node that corresponds to the minimum MSE value is selected.

EXPERIMENTAL STUDY

This section describes the experimental study of the ion exchange column pilot plant. The experimental data are collected every 1 minute sampling time. The data are then used for neural network training and validation.

1. Ion Exchange Resin

The resin of this process can be divided into two types, which are Purolite C-150 (cationic resin) and Purolite A-500 (anionic resin) with their characteristic properties given in Table 3. The first type, the Purolite C-150 in Sodium form (Na^+), is a polystyrene macroporous strong acid cation exchange crosslinked with divinybenzene. The C-150 resin is firstly washed with deionized water to eliminate impurities remaining after a manufacturing process. After that it is regenerated by 10% HCl to obtain hydrogen from (H^+) [Maranon, 1999]. The reactions of these steps are shown as follows:

Cation exchange loading: $R-H+Fe^{2+} \Rightarrow R_2Fe+2H^+$

Regeneration: $R_2Fe+HCl \Rightarrow 2R-H+Fe^{2+}$ (9)

The second type, Purolite A-500 in Chlorine form (Cl^-), is a polystyrene macroporous strong base anion exchange crosslinked with divinybenzene. The A-500 resin is firstly washed with deionized water to eliminate impurities remaining after a production process. After that it is regenerated by 9% NaCl to obtain (Cl^-) from [Maranon, 1999]. The reactions of these steps are:

Cation exchange loading: $R-Cl+FeCl_4^- \Rightarrow R-FeCl_4+Cl^-$

Regeneration: $R-FeCl_4^-+H_2O \Rightarrow FeCl_3+R-Cl$ (10)

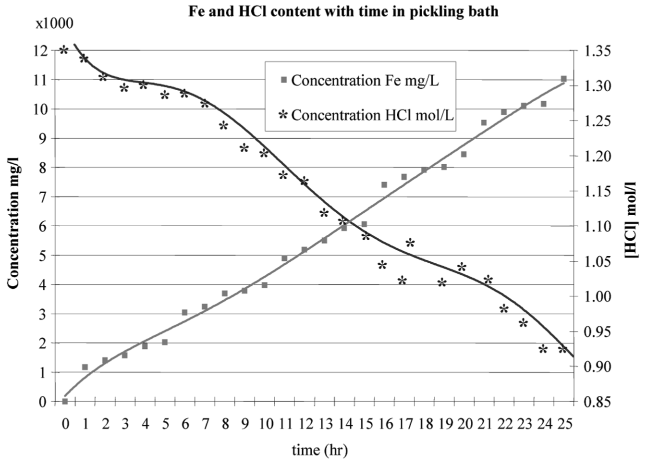

Fig. 7. The saturated steel concentration in acid concentration.

2. Double Fixed-bed Ion Exchange Resin Columns

The double fixed-bed ion exchange resin column pilot plant consists of two PVC columns (80 cm height×24 cm internal diameter). The first column contains 13 liter Cation C-150 and the other contains 13 liter Anion A-500. The flow rate of the waste acid is controlled by a manual diaphragm valve with accurate flow meter.

The waste acid is prepared by the immersion of steel pieces in pickling bath (5% by weight HCl) to obtain the concentration of steel ions in the range of 3-6 g/*l*. The condition in the pickling bath, the acid concentration in the bath, is decreased from 5% by weight HCl (1.4 mol/*l*) to 2% by weight HCl (0.8 mol/*l*). The relation between saturated steel and acid ions concentration is shown as Fig. 3. The waste acid or pickling liquor is then fed into the first column where Fe(II) ion in the pickling liquor is adsorbed by the Cation C-150 resin. Next, Fe(II) ion is oxidized by hydrogen peroxide (H_2O_2) to be Fe(III) ion form. After that the liquor is fed into the second column where Fe(III) ion is adsorbed by the Anion A-500 resin.

3. Chemicals and Analysis Methods

The concentration of steel ions (g/*l*) in the acid solution is determined by an atomic absorption spectrophotometer using a Varian Spectro model AA-300 spectrometer. The concentration of hydrochloric acid (mol/*l*) is determined by basic titration with NaOH 0.5 mol/L.

RESULTS AND DISCUSSION

In this work, neural network models are developed to predict the concentrations of the Fe and HCl acid in each column of the ion exchange process. To develop neural network models for the prediction of the concentrations, five inputs and two outputs are used in one or two hidden layer(s) network structure of each resin column. The numbers of neural nodes of each hidden layer are varied to 3, 5, 7, 8, 9, 11, 13, 15, 17 and 19, respectively. Each defined neural network is trained with Levenberg-Marquardt method using two data sets. The common objective is to reduce the error between the neural network predicted value and the actual targeted value. The concentration of Fe ions in pickling liquor is about 6,000 ppm. There-

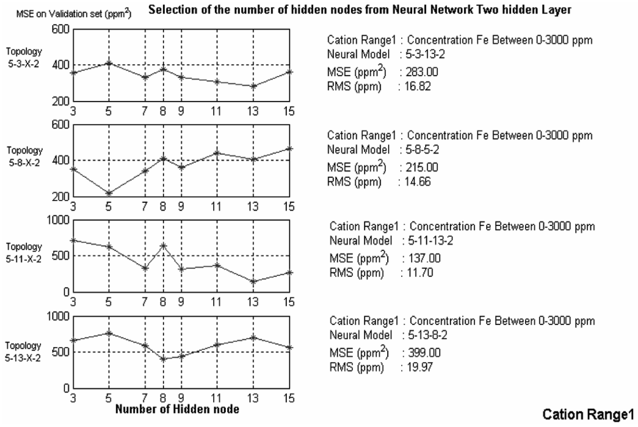

Fig. 8. Two hidden layer for cation Range#1.

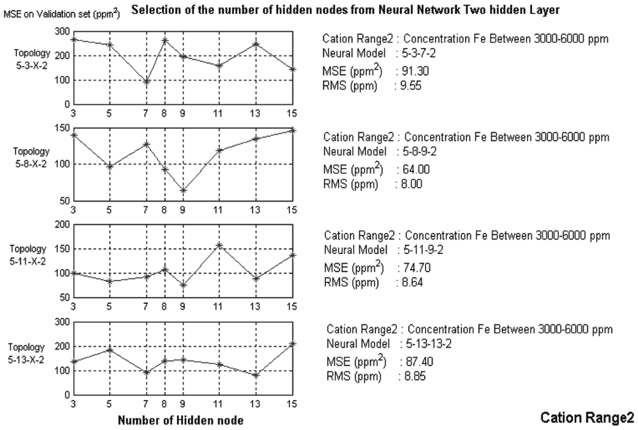

Fig. 9. Two hidden layer for cation Range#2.

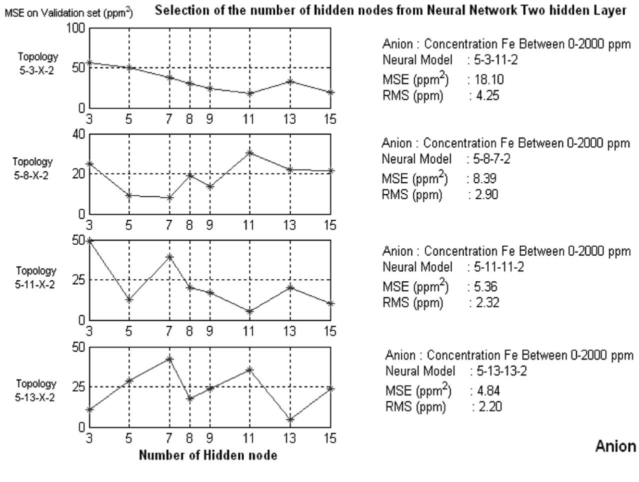

Fig. 10. Two hidden layer for anion.

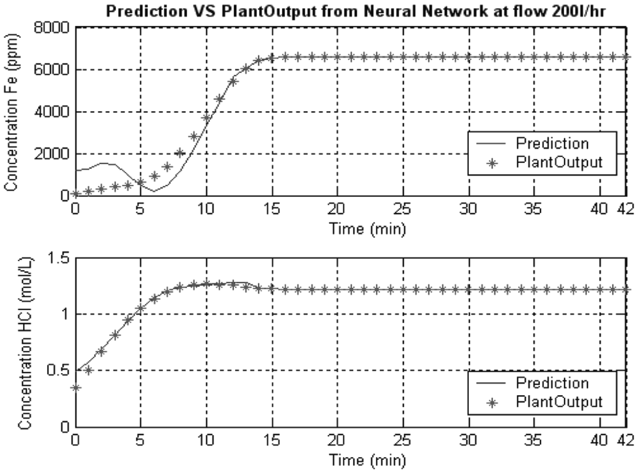

Fig. 11. The prediction of Fe and HCl concentration profile in the cation resin column using [5-11-13-2] and [5-8-9-2] NN models at the flow rate of pickling liquor 200 *l*/hr.

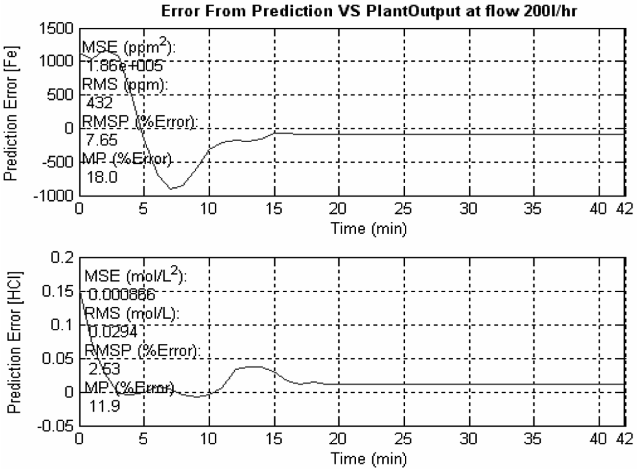

Fig. 12. The error of prediction of Fe and HCl concentration profile in the cation resin column using [5-11-13-2] and [5-8-9-2] NN model at the flow rate of pickling liquor 200 *l*/hr.

fore, three neural network models for 0-3,000 ppm of Fe ions concentration (Range#1), 3,000-6,000 ppm of Fe ions concentration (Range#2) in the cation resin column and 0-2,000 ppm of Fe ions concentration in the anion resin column are developed.

1. Training and Validation Neural Network Models

The values of MSE and RMS for various neural network structures are shown graphically in Figs. 8-10. The minimum MSE criterion is considered for neural network selection. From the figures it is indicated that [5-11-13-2] NN structure, [5-8-9-2] NN structure and [5-13-13-2] NN structure are the optimal structures for Range#1, Range#2 of Fe ions concentration in the cation resin column and 0-2,000 ppm of Fe ions concentration in the anion resin column. respectively; these structures give the least MSE values after validation.

2. Neural Network Prediction

Fig. 11 shows the results of concentration profile prediction with a flow rate of 200 liters per hour of the pickling liquor in the cation column. It was found that in the range of 0-3,000 ppm of Fe ions concentration, the [5-11-13-2] NN model gives good prediction for HCl concentration but with less accurate prediction in Fe concentration. For 3,000-6,000 ppm of Fe ions concentration, the [5-8-9-2] NN model gives good prediction for the both of concentrations. In the range of 0-3,000 ppm of Fe ions concentration, the neural network model gives less accurate prediction of the concentrations

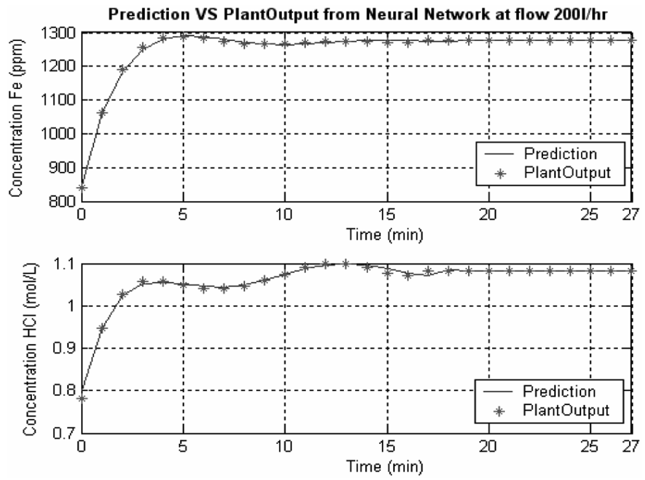

Fig. 13. The prediction of Fe and HCl concentration profile in the anion resin column using [5-13-13-2] NN model at the flow rate of pickling liquor 200 *l*/hr.

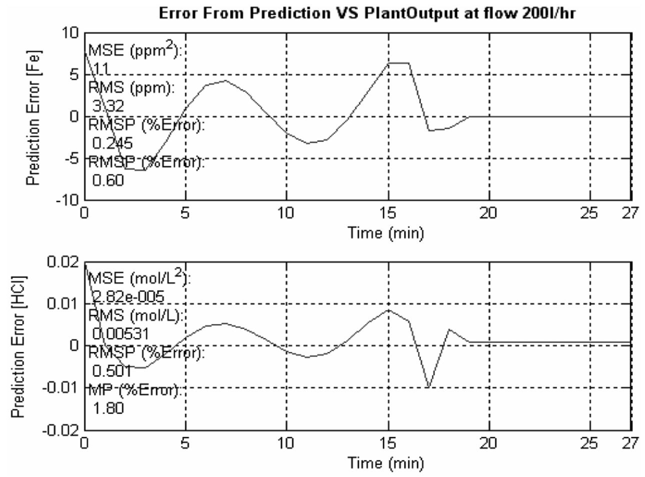

Fig. 14. The error of the prediction of Fe and HCl concentration profile in the anion resin column using [5-13-13-2] NN model at the flow rate of pickling liquor 200 *l*/hr.

because it was developed based on the training input-output data. However, the experiments were carried out with the limitations such as the range of flow rate, sampling time, resolution of instruments etc. Therefore, in the cases where the trained data set are not available, the neural network model cannot provide good prediction in these cases.

Fig. 12 shows the error in MSE, RMS, RMSP and MP indices of the concentration profile prediction with a flow rate of 200 liters per hour of pickling liquor in the cation column.

Fig. 13 shows the results of concentration profile prediction with a flow rate of 200 liters per hour of pickling liquor in the anion column. From the figure, it was found that the [5-13-13-2] NN model gives good prediction for the both of concentrations. The errors of the prediction are shown in Fig. 14.

Figs. 15 and 16 show a comparison of Fe ion concentration profile in the cation and anion resin columns obtained from numerical solution (Eq. (7)), experiments and neural network models. These figures show that the concentration profile predictions by the NN models are better than those obtained from numerical solution in both columns.

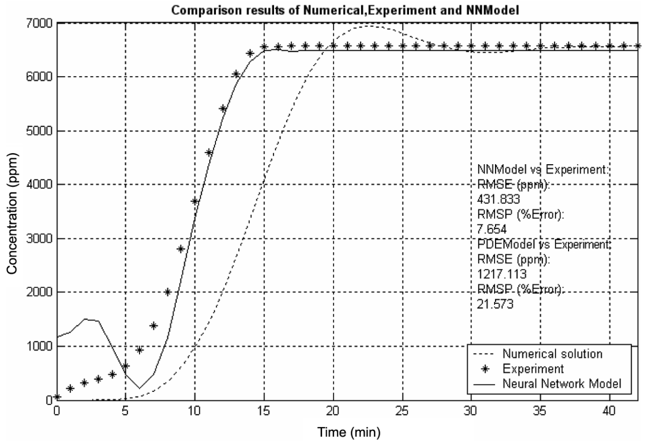

Fig. 15. The comparison of Fe ions concentration profile in the cation resin column obtained from numerical solution, experiments and neural network models.

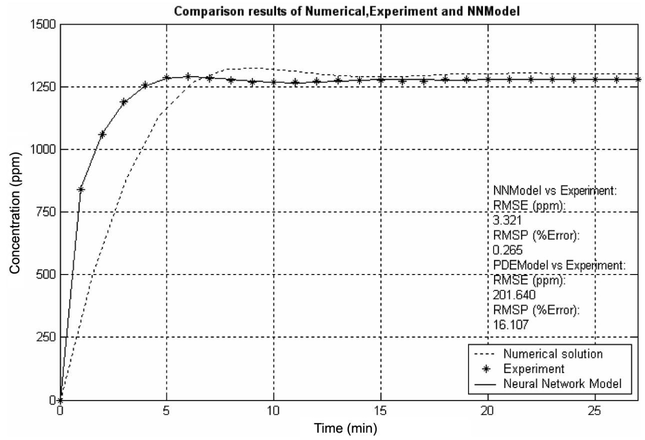

Fig. 16. The comparison of Fe ions concentration profile in the anion resin column obtained from numerical solution, experiments and neural network models.

CONCLUSIONS

A hydrochloric acid recovery process is a complex and highly nonlinear system, which makes it difficult to identify by the first principle approach. Alternatively, modeling of the process can be carried out via neural network configuration. In this work, a neural network has been used to provide the prediction of HCl acid and Fe ions concentration profiles in the hydrochloric acid recovery process. It was observed that the obtained optimal structure neural networks can be successfully used to predict the effluent concentration profile of HCl acid and Fe ions as long as the neural network models have been trained covering such scenarios. The simulation results have shown that the dynamic behavior of concentration profile of HCl acid and Fe ions can be well-predicted in all ranges of operating conditions. The further work will be the control of the acid recovery columns by neural network inverse models. Then the control of the system by neural network inverse models approach will be studied. The ultimate goal of this work is to develop an advanced control technique to control a system consisting of steel pickling baths and acid recovery columns. This whole work will show the applicability of the neural network inverse models approach in the control of the system reducing the use of the pickling liquor and removing Fe ions in the pickling liquor and then reusing of the pickling liquor in the pickling baths.

NOMENCLATURE

ε : external void fraction of the bed
σ_x : standard deviation of the training inputs
σ_y : standard deviation of the training outputs
σ_p : standard deviation of process outputs data
A_c : circular cross-section area [m^2]
C_a : the concentration of hydrochloric acid [mol/l]
C_s : the concentration of steel ion [mol/l]
c : the concentration of solution phase [mol/l]
c_p : the pore concentration at the resin surface [mol/l]
D_L : solution phase dispersion coefficient [m^2/s]
F_L : flow rate [m^3/min]
k_f : mass transfer rate coefficient [mm/s]
p : process outputs
p_{nor} : process outputs (normalized)
$\bar{p}$: mean of process outputs data
q : resin phase solution [mol/g]
R_p : the resin bead radius [mm]
t : time [min]
w : network weight
x : network inputs to a neuron
x_{nor} : network inputs (normalized)
$\bar{x}$: mean of the network inputs
y : network outputs from neuron
y_{nor} : network outputs (normalized)
$\bar{y}$: mean of network outputs
z : column distance [mm]
MSE : Mean Square Error
RMS : Root Mean Square Error
RMSP : Root Mean Square Percent Error Index
MP : Maximum Percent Error Index

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