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Materials Letters 58 (2004) 723–726

MATERIALS LETTERS

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Quantification of $CaCO_3$–$CaSO_3{\cdot}0.5H_2O$–$CaSO_4{\cdot}2H_2O$ mixtures by FTIR analysis and its ANN model

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Received 24 March 2003; received in revised form 1 July 2003; accepted 5 July 2003

Abstract

A new quantitative analysis method for mixtures of calcium carbonate ($CaCO_3$), calcium sulphite hemihydrate ($CaSO_3{\cdot}1/2H_2O$) and gypsum ($CaSO_4{\cdot}2H_2O$) by FTIR spectroscopy is developed. The method involves the FTIR analysis of powder mixtures of several compositions on KBr disc specimens. Intensities of the resulting absorbance peaks for $CaCO_3$, $CaSO_3{\cdot}1/2H_2O$ and $CaSO_4{\cdot}2H_2O$ at 1453, 980, 1146 cm^{-1} were used as input data for an artificial neural network (ANN) model, the output being the weight percent compositions of the mixtures. The training and testing data were randomly separated from the complete original data set. Testing of the model was done with successfully low-average error levels. The utility of the model is in the potential ability to use FTIR spectrum to predict the proportions of the three substances in unknown mixtures.

Keywords: Characterization methods; Computer simulation; Modelling; Artificial neural networks; FTIR; Sulphur dioxide; Calcium carbonate; Gypsum

1. Introduction

Quantitative analysis of mixtures of calcium carbonate ($CaCO_3$), calcium sulphite hemihydrate ($CaSO_3{\cdot}1/2H_2O$) and gypsum ($CaSO_4{\cdot}2H_2O$) has been gaining increased attention in two main areas: flue gas desulfurization (FGD) from power plants and the decay of calcareous stones due to air pollution in historic buildings.

Calcium sulphite hemihydrate and gypsum are the reaction products in the wet FGD process, which mainly uses calcium carbonate [1,2]. The same reaction products are also observed in the decay process of calcareous stones under the effect of air pollution [3]. So the quantitative analysis of mixtures of calcium carbonate, calcium sulphite hemihydrate and gypsum is important in order to understand the reaction mechanisms of calcium carbonate with sulphur dioxide under different conditions and medium [4].

Calcium carbonate, calcium sulphite hemihydrate and gypsum are generally qualitatively determined by X-ray powder diffraction, infrared spectroscopy and scanning electron microscopy. Quantitative analysis is, however, performed by ion chromatography by measuring the concentration of sulphite and sulphate ions. Some difficulty was encountered in measuring sulphites due to their easy oxidation into sulphates and hindering effect of sulphates in the separation of sulphite ions [5,6]. Among these techniques, the FTIR method for inorganic solid mixtures by pellet preparation appeared to be a reasonably fast and accurate quantitative technique for the above analysis.

Factors that affect the quantitative IR analysis are particle size, the polymorphism and orientation. The effects of polymorphism and orientation are negligible for the analysis of inorganic substances (soils, rocks, etc.) [7]. The effect of particle size, on the other hand, is significant. When the particle size is smaller than the wavelength of the incident radiation in the range 2.5–25 μm, the particles will not act as mirrors and thus not decrease the intensity of the transmitted light. Therefore, the samples must be well ground to obtain precise quantitative results [7].

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doi:10.1016/j.matlet.2003.07.008

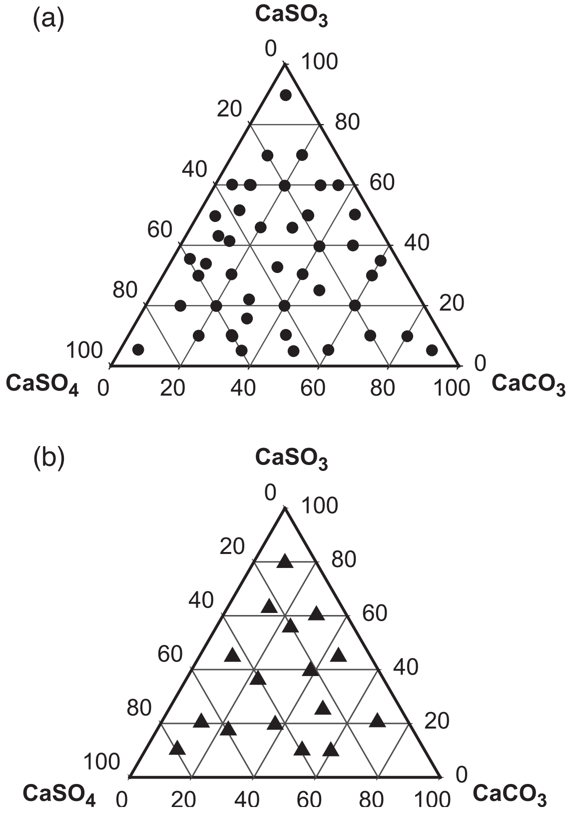

Fig. 1. Powder mixture compositions used in this study: (a) training data, (b) testing data.

In the present study, quantitative analysis by FTIR spectrometry of mixtures of known compositions of calcium carbonate, calcium sulphite hemihydrate and gypsum are reported. The purpose was to develop a technique that can be used to determine the relative amounts of reaction products of calcite and SO_2. The absorbance peak height data collected from the above analysis were used as feed to an ANN model to predict the compositions of unknown mixtures.

2. Experimental and data collection

Powder mixtures of known concentrations of calcium carbonate (Merck), gypsum (Merck) and calcium sulphite hemihydrate were used for sample preparation. Calcium sulphite hemihydrate used in these experiments was prepared in-house by mixing 0.1 N calcium chloride and 0.1 N sodium sulphide solutions by producing a precipitate free from basic salt and then checking its purity by XRD and FTIR.

Sixty-two different mixtures of the three components were prepared (Fig. 1). The amount of each component was varied from 5 to 90 wt.%. Each mixture was thoroughly mixed and finely ground on an agate mortar. 0.3–0.5 mg of these mixtures were then dispersed and further ground in about 80 mg of spectral grade KBr and pressed into pellets under about 10 tons/cm^2 pressure.

Spectral measurements were carried out on an FTIR spectrometer (Nicolet Model 510) that was operated in the absorbance mode. Spectra were normally acquired with the use of 4 cm^{-1} resolution yielding IR traces over the range of 400–4000 cm^{-1}. All data were corrected for background spectrum.

The FTIR spectrum of pure calcium carbonate shows the presence of a strong band centered around 1453 cm^{-1}, characteristics of the C–O stretching mode of carbonate together with a narrow band around 873 cm^{-1} of the bending mode (Fig. 2). The observed bands at around 980 and 652 cm^{-1} are characteristic of those reported in the literature for sulphite ion [8]. The broad absorption at 980 cm^{-1} is assigned to the symmetric and asymmetric S–O stretching modes. The narrow peak at 652 cm^{-1} is characteristic of the symmetric bending mode (Fig. 2). The strong band centered around 1140 cm^{-1} which splits into two components at around 1146 and 1116 cm^{-1} and the small peaks at 669 and 602 cm^{-1} are assigned to the stretching and bending modes of sulphate as seen in the pure gypsum spectrum (Fig. 2). The stretching vibrations of the H_2O

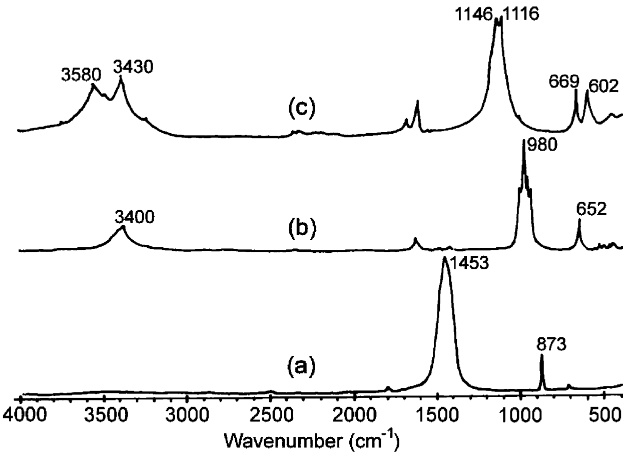

Fig. 2. IR spectra of: (a) pure calcium carbonate; (b) pure calcium sulphite hemihydrate; (c) pure gypsum.

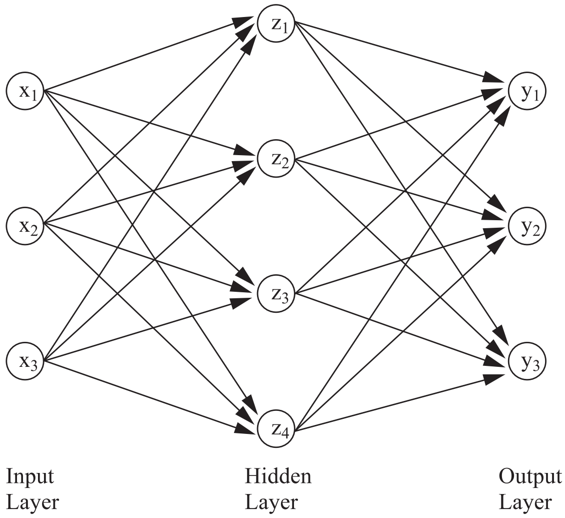

Fig. 3. ANN architecture used in model building in this study.

Table 1
The input quantities used in model building

Variable no.	Input/output parameter	Data used in training of the model		
		Minimum	Average	Maximum
x_1	Absorbance $CaCO_3$	0.04	0.63	1.68
x_2	Absorbance $CaSO_3 \cdot 1/2H_2O$	0.06	0.59	1.77
x_3	Absorbance $CaSO_4 \cdot 2H_2O$	0.05	0.45	1.55
y_1	Weight % $CaCO_3$	4.8	30.9	89.7
y_2	Weight % $CaSO_3 \cdot 1/2H_2O$	4.9	34.4	89.7
y_3	Weight % $CaSO_4 \cdot 2H_2O$	4.7	34.7	89.4

molecules in the gypsum and calcium sulphite hemihydrate occur at 3580 and 3430 cm^{-1} for the former, and at 3400 cm^{-1} for the latter compound. In this work, among those bands described, the strong absorption band of carbonate at 1453 cm^{-1}, the band centered around 1146 cm^{-1} of sulphate and the characteristic band of sulphite at 980 cm^{-1} were used as analyte peaks for the analysis of the related components. The FTIR spectrum of the mixture of these three components showed that there is no significant interference to any of the analyte peak of a component from the other two components present in the matrix, thus the analyte peaks chosen can be safely used for analysis of the individual components in their mixture.

Above collected data for quantification of the mixtures were used to create an ANN model that can be further used to predict the compositions of unknown mixtures based on their absorbance peak height data.

3. Model development

3.1. Artificial neural networks (ANN)

ANN are recently adapted to many different areas owing to their utility in building computational models [9–11]. There are layers of processing elements in ANN, as shown in Fig. 3. The input data are fed into input layer neurons, which, in turn, pass them on to the hidden layer neurons after multiplying by a weight. A hidden layer neuron sums up the weighted input received from each input neuron, and passes the result on through a nonlinear transfer function. The output neurons do the same operation as that of a hidden neuron.

The network is first trained by feeding physically measured data. Learning is done by a back-propagation algorithm details of which is widely documented in the literature [12].

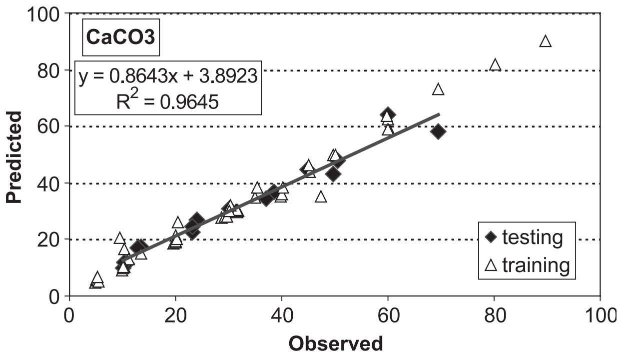

Fig. 4. The observed and predicted values for weight percent of $CaCO_3$ in the mixture for both training and testing data.

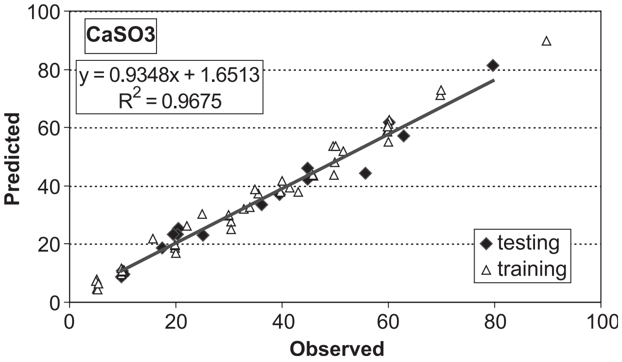

Fig. 5. The observed and predicted values for weight percent of $CaSO_3 \cdot 1/2H_2O$ in the mixture.

3.2. Model construction and the results

The network architecture shown in Fig. 3 was chosen in this paper. The input and the output layers had three neurons each while the hidden layer had four neurons. The input variables are listed in Table 1.

There were 62 data sets each with six components (x_1, x_2, x_3; y_1, y_2, y_3), three of which were the input variables while the remainder were the output variables (Fig. 3 and Table 1). Forty-six of the data sets were used for training and the rest for testing of the model (Fig. 1). The program was run on a PC for 20000 iterations and the optimal weights were

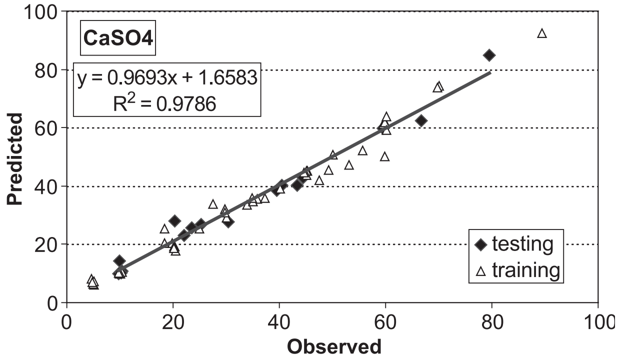

Fig. 6. The observed and predicted values for weight percent of $CaSO_4 \cdot 2H_2O$ in the mixture.

computed with an average percentage training error of 9.9%, 9.7% and 9.7% for calcium carbonate, calcium sulphite hemihydrate and gypsum, respectively. The model was successfully trained with low error levels and a weight matrix was obtained.

Once a trained model was obtained, it needed to be tested with actual measured data. A set of 16 data sets was used for testing of the model. Figs. 4–6 show the results of both training and testing of the model for all three output parameters. The linear least square fit line, its equation and the r^2 values are shown in these figures for the 16 testing data. The coefficient of determination, r^2 for the three output parameters were 0.96, 0.97 and 0.98, respectively. Average testing errors were 10.2%, 9.6% and 9.1% for calcium carbonate, calcium sulphite hemihydrate and gypsum, respectively. The range for testing data was carefully selected to be within the testing data range to avoid extrapolation outside of the limits of the model.

3.3. Limitations of the model

The powders used in this study were analytical grade. Therefore, the effects of potential impurities in the mixture have not been considered. The model was constructed by considering the summation of the three components to be 100%. Any impurity that does not influence the measured peak intensities is not expected to jeopardise the model. Provided that the concentrations of impurities are determined by other analytical techniques, the model results obtained in this study can always be normalized through multiplication by (100 − %impurities)/100.

3.4. Comparison with standard chemical and XRD methods

Mixtures of $CaCO_3$, $CaSO_3 \cdot 1/2H_2O$ and $CaSO_4 \cdot 2H_2O$ cannot be chemically determined by traditional wet analytical techniques owing to the rapid oxidation of sulphite ion [6]. Generally, all sulphite ions are allowed to oxidize to sulphate, and the total sulphate is analyzed by a turbidimetric method using UV visible spectroscopy [13] or ion chromatography [14,15].

Quantification of sulphate and sulphite is important in studies aimed at understanding calcareous stone deterioration due to air pollution [4]. According to Gauri et al. [16,17], XRD cannot be effectively used to quantify these compounds because of the inability to reproduce peak intensities as a result of preferred orientation of analysed crystals. The FTIR method proposed in this work, on the other hand, is immune to such problems.

4. Conclusions

A new quantitative chemical analysis method was developed to accurately determine the compositions of powder mixtures of $CaCO_3$, $CaSO_3 \cdot 1/2H_2O$ and $CaSO_4 \cdot 2H_2O$ from FTIR absorbance peak height measurements. Data collected from the study were used to create an ANN model for prediction of the weight percentages. The testing results showed that the model was successfully created and could be used to predict unknown compositions.

Acknowledgements

The authors thank Dr. Durmuş Özdemir and Dr. Gökmen Tayfur for their valuable comments and discussions during this work.

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