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Prediction of Thickening Times of Oil Field Cements Using Artificial Neural Networks and Fourier Transform Infrared Spectroscopy

Philip Fletcher* and Peter Coveney†
*Schlumberger Dowell Europe-Africa Technology Center, Westhill Industrial Estate, Westhill, Skene, Aberdeen, United Kingdom and †Schlumberger Cambridge Research, High Cross, Cambridge, United Kingdom

Nonlinear statistical models based on artificial neural networks have been constructed to predict the thickening times of class G, class H, and class A oil well cement slurries from physicochemical data on cement powders. These data include chemical composition, particle-size distributions, and Fourier transform infrared (FTIR) spectra. Thickening times can be predicted with mean residual errors of less than ±10% from measurements of major oxide composition, loss on ignition, insoluble residue, the concentrations of the minerals gypsum, bassanite, anhydrite, calcium hydroxide, and calcium carbonate, and particle-size distribution. This error rises to ±13% when particle-size distribution is omitted from the input data. Similar conclusions apply to models that predict thickening times of cement slurries retarded with 0.2 weight percent calcium lignosulfonate. Slurry thickening times can also be predicted from cement powder FTIR spectra alone, with errors in predictions similar to those for models using the full chemical composition and particle-size distribution data. This implies that the FTIR spectrum of a cement is a signature of its slurry performance properties. Additionally, neural networks can be trained to predict the particle-size distributions and mean particle diameters from FTIR spectra. The occupancies of all particle-size fractions can be predicted to within an absolute error of ±1%, approximately twice the expected experimental error on the measurement. However, the model is able to predict general trends in particle-size distributions between cements effectively. ADVANCED CEMENT BASED MATERIALS 1995, 2, 21–29

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The thickening time of an oil field cement is defined by the American Petroleum Institute as the time taken for the slurry to reach a specified consistency, as measured in an atmospheric or pressurized consistometer [1]. The consistency is a measure of the stress exerted on a metal vane rotated in the slurry; the thickening time measures the maximum length of time for which the cement is pumpable. Typical values lie in the range from 3 to 10 hours, depending on the physicochemical composition of the slurry, as well as on the temperature and pressure. A slurry formulated for a specific oil well contains cement mixed with a cocktail of additives designed to yield the required thickening time at the specified temperature and pressure.

It has long been recognized that different batches of oil field cements show a marked variability in their thickening times for identical formulations. This variability is observed between cements from different manufacturers, between different cement batches from the same manufacturer, and between samples from the same batch of cement that may have aged differently during storage. Owing to the complexity of cementitious materials, this variability can normally be ascribed to a range of factors, including differences in bulk mineral composition; in particular, the aluminum- and iron-containing minerals, the magnesium content, and the total granular surface area are all recognized as having an influence on cement hydration [2,3]. The particle-size distribution of the cement grains is also expected to be significant [4]. In addition, there are many more subtle effects which may arise due to imperfections in the crystal structures of cement minerals and the natural variability in the elemental composition of these same minerals [2,3].

To date, the complexity of cement hydration has defied comprehensive mathematical description. This is particularly true of the interactions between cement and additives during the hydration process. Indeed, even a generally agreed upon qualitative framework for cement hydration does not exist today [5]. In the work we report here, we have pursued an alternative

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Address correspondence to: Peter Coveney, Schlumberger Cambridge Research, High Cross, Madingley Road, Cambridge, CB3 OHG, United Kingdom.
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approach based on a novel combination of spectroscopic and statistical techniques which enables us to circumvent these difficulties. The objective of this preliminary communication is twofold. First, we demonstrate that the variability of cement thickening times can be described in terms of combinations of carefully selected physicochemical properties of the neat cement prior to hydration. Second, we show that the diffuse reflectance Fourier transform infrared spectrum (DRIFTS) can be used as a quantitative signature for cement variability. DRIFTS was chosen since (1) it is known that quantitative information on the chemical composition of mixtures is encoded in their infrared spectra; and (2) diffuse reflectance spectra of powders are distorted by particle-size effects and other factors related to the refractive indices of the components. It is expected that a combination of these factors may in some way reflect the surface physicochemistry of the cement, which in turn influences its hydration.

The methods of prediction employed herein are based on discovering statistical correlations between selected variables. This approach is free of restrictive assumptions underlying deterministic methods and produces predictions which are either within or very close to experimental error. There are certain similarities between our work and that of Hunt [4] and Bensted and Becker [6]. In the former, a statistical model was developed for the prediction of the thickening times of oil well cements based on the Blaine air permeability measurement, while in the latter certain correlations based on chemical considerations were uncovered between thickening times, temperature, and retarder concentrations.

The Statistical Database

The approach reported here required the construction of a database containing the information described in this section on 159 oil well cements, which was collected on a worldwide basis. Approximately 65% of the data are for API class G cements, the remaining being class A and class H. Due care was taken to ensure that the cement samples were protected from the effects of atmospheric aging during storage by rigorously excluding carbon dioxide and moisture.

Elemental and Composition Analysis

The elemental composition was determined for all cements by acid dissolution of the cements, followed by inductively coupled plasma (ICP) emission spectroscopy. Analysis was expressed as weight percent of the following major oxides: SO_3, Al_2O_3, Fe_2O_3, MgO, Na_2O, K_2O, CaO, and SiO_2; a further 10 minor oxides were also determined. The sulfate minerals syngenite, gypsum, and bassanite were estimated from peak height measurements on the DRIFT spectra. Calcium hydroxide and calcium carbonate were determined by thermogravimetric analysis. The experimental procedures and associated uncertainties are discussed in ref 7. Also determined were the acid insoluble residue (IR), loss on ignition (LOI), and free lime, the latter determined by titration. Note that in the study reported here the SO_3 value was not used, since the sulfate minerals already provide this information; indeed, their use gave better results in modeling than the bulk SO_3 content. Furthermore, for modeling purposes no useful information was found within either the minor oxide or the free lime analyses and these are not discussed further here.

TABLE 1. Mean particle diameters

Bin	Diameter Range (μm)
1	0–1
2	1–1.5
3	1.5–2
4	2–3
5	3–4
6	4–6
7	6–8
8	8–12
9	12–16
10	16–24
11	24–32
12	32–48
13	48–64
14	64–96
15	96–128
16	128–192

Particle-Size Distributions

Particle-size distributions and mean particle diameters (micrometers) were measured using a Cilas granulometer. Results were reported in volume fraction occupancies of the 16 particle-size bins shown in Table 1.

Diffuse Reflectance FTIR Spectra

The DRIFTS spectrum of each cement sample in a KBr background was collected at 2 cm^{-1} resolution using a Nicolet 5DX spectrometer, as described in ref 7. Rep-

TABLE 2. Neat cement thickening time data computed using neural networks

Model Inputs	Mean Error (minutes)	2 σ (minutes)	Mean % Error
Oxides/minerals	±22.0	42	±13.1
Oxides/minerals/PSD	±16.8	32	±9.9
DRIFT spectra	±16.0	31	±9.5

TABLE 3. Retarded cement thickening time data computed using neural networks

Model Inputs	Mean Error (minutes)	2σ (minutes)	Mean % Error
Oxides/minerals	±29.7	55	±16.0
Oxides/minerals/PSD	±20.8	39	±11.3
DRIFT spectra	±19.5	37	±10.6

licate spectra were collected for 100 cements from the set of 159.

Thickening Time Curves

Two thickening time profiles were determined for each cement: (1) the profile for a neat cement slurry at 50°C and a solid:water ratio of 0.44, and (2) the profile for a slurry at 85°C with 0.2% by weight calcium lignosulfonate retarder and at the same solid:water ratio as the neat slurry. The objective of adding a retarder in (2) was to enhance the variability of the cement performance in a way that might not be apparent with the low temperature neat slurry. It should be stressed that the lignosulfonate used in all this work came from a single batch, so as to minimize potential problems arising from variations in retarder composition. Such additive variability can itself be a problem in cement slurry formulations.

Modeling Techniques

The primary objective of this study was to construct models to predict the thickening times of neat and retarded cements based on the following input data: (1) the oxide analysis (excluding SO_3) together with the sulfate minerals, calcium hydroxide, and calcium carbonate plus LOI and IR; (2) the oxide and mineral analysis as in (1) together with the particle-size distributions and mean particle diameter; (3) the DRIFT spectra as sole input data. Thus, six models were constructed in total (three for neat cements and three for retarded cements). Chemical composition alone represents the simplest input data set, while the inclusion of particle-size data adds a source of potentially useful information. The models based on FTIR spectra are used to evaluate the previously mentioned signature for cement performance.

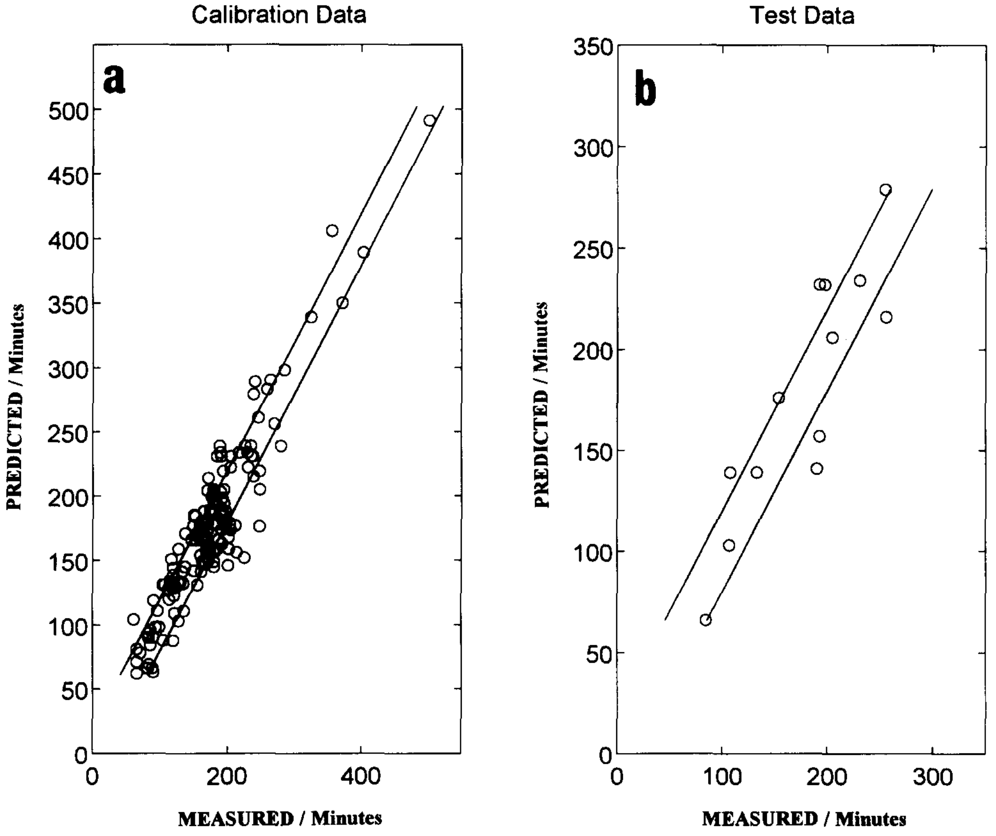

FIGURE 1. The predictions of thickening times of neat cements for (a) training (calibration) data and (b) independent test data from chemical composition data plus loss on ignition and insoluble residue. The solid lines in Figures 1 through 6 indicate the ±20-minute limits.

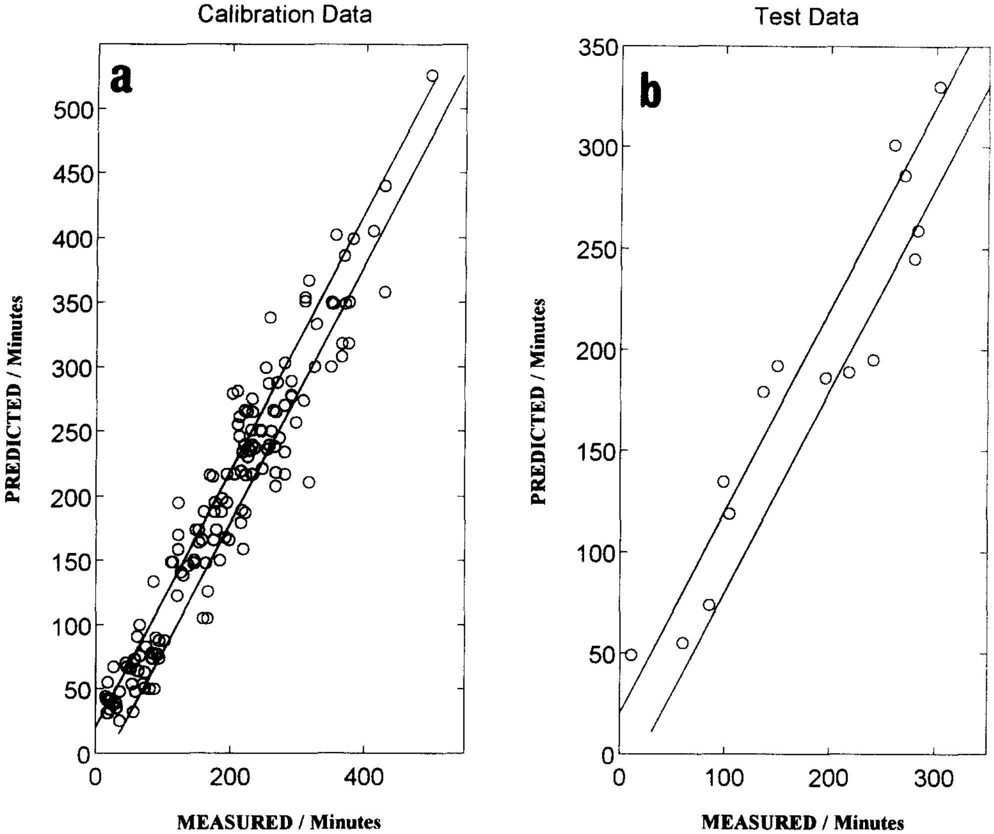

FIGURE 2. The predictions of thickening times of retarded cements for (a) training (calibration) data and (b) independent test data from chemical composition data plus loss on ignition and insoluble residue.

There is little evidence in the literature to suggest that thickening times can be determined accurately from linear correlations with composition or other data. Indeed, elementary kinetic theories of inorganic reactions indicate that the evolution of cement hydration will be nonlinear with time, a fact which has been exploited in a recent simple clock reaction model of the process [5]. In addition, cement is in reality a highly multivariate reaction mixture, and this adds additional complexity to the nonlinearity. Since the relationship between the measurable properties of a cement powder and its slurry performance is not known, it is best to choose a technique for finding such correlations which makes as few assumptions as possible regarding their nature. Artificial neural networks offer the possibility of finding input/output correlations of essentially arbitrary complexity, and consequently form the basis for the statistical methods we used in this work.

The primary feature of neural network methodology is that input/output information is correlated via a system of interconnected nodes [8–10]. Signals are transmitted between nodes connected to one another in a specified manner according to the architecture of the network. The strength of the signal received by any one node is a weighted sum of inputs sent by all the nodes to which it is connected. The strength of an output signal from any node is given by a nonlinear function of the input signal. In the commonly used, supervised, feedforward, layered networks, nodes in an input layer first receive signals equal to the values of the external input data. This information is passed on in a nonlinearly convolved fashion to nodes in an output layer representing target data (output data). The nonlinear expressions are modified using a supervised training procedure such that input data are correlated with target data. In some networks there may be one or more hidden layers of neurons connecting the input and output layers. These layers add mathematical features to networks necessary to model complex relationships. A fully trained artificial neural network is effectively a nonlinear map between specified variables which is capable of filtering noise in the input data and has a predictive capacity; that is, it is capable of making predictions for situations not previously encountered. In the work reported here the input data are cement powder property data whose precise nature depends on which of the models (1, 2, or 3) is being studied. The output layer is a single node representing the slurry thickening time for all models.

The procedures for optimizing artificial neural networks are described elsewhere [11]. There are many different types of neural networks which can be implemented to solve a wide range of complex nonlinear problems. The network type we found to be the most suitable for predicting cement properties employed radial basis functions [12,13]. In all cases the networks were trained using a subset of the full database and their predictive capabilities evaluated using a completely independent test set (that is, one containing data which had not been previously used by the network during training) selected randomly from the database. More details of the data analysis will be provided in a later publication. It should be noted, however, that statistical models such as the ones reported here can be relied upon when used for predictions based on interpolation, but they may break down when extrapolated.

Computation times for optimizing neural networks increase dramatically with the number of variables in the input data. A typical mid infrared DRIFT spectrum measured at 2 cm^{-1} resolution of the kind used here has approximately 2000 digitized points. Thus, to use FTIR spectra as input data for neural networks, it was found necessary to reduce the number of variables representing any spectrum. This was performed using the principal component method based on spectral eigenvector analysis and led to the useful information content in each spectrum being reduced to approximately 35 orthogonal variables [14]. These orthogonal variables were correlated with thickening times.

Results and Discussion

Tables 2 and 3 show statistical data for the prediction errors on the thickening times in the independent test sets for both neat and retarded cements and for each model input 1, 2, and 3 described above. The data presented for each model include a mean error (in minutes), the value of two standard deviations in error (an indication of the maximum errors likely to be encountered), and a mean percentage error. Inspection of Tables 2 and 3 shows that the trends in both retarded and neat thickening times can be predicted using oxide and mineral compositions only. All three measures of error are greater for retarded cements than neat cements.

Tables 2 and 3 reveal that the incorporation of particle-size distributions into the input data significantly improves the predictions of thickening times for both neat and retarded cements. Thus, on the basis of the

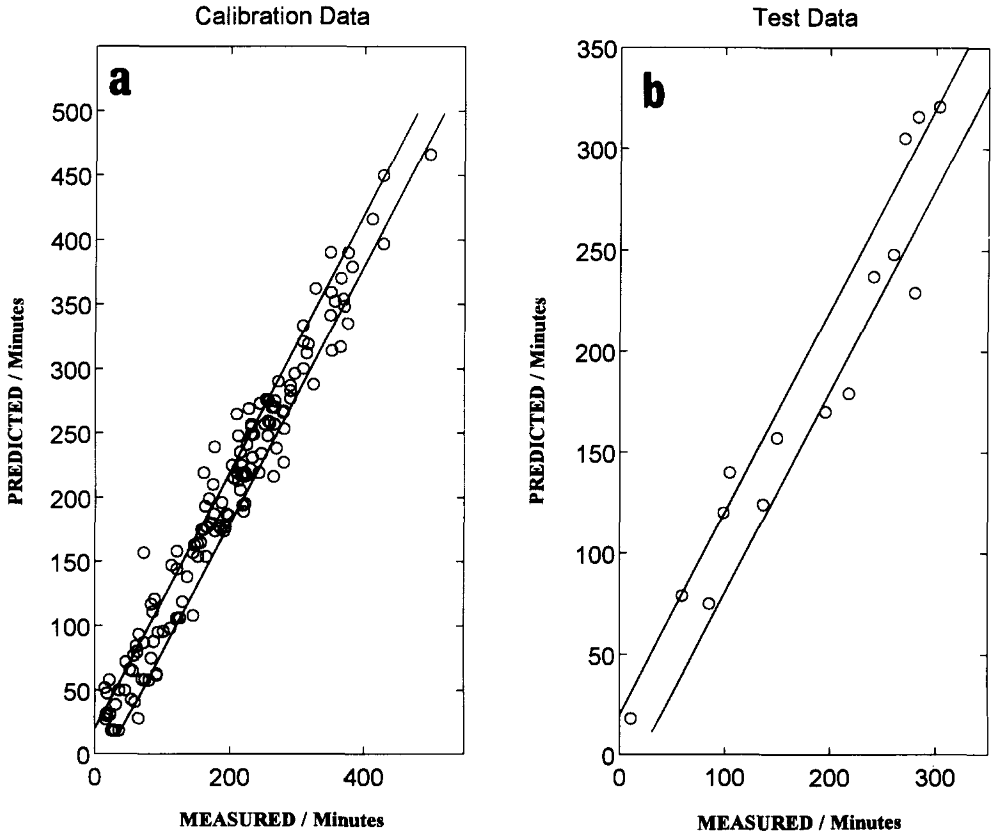

FIGURE 3. The predictions of thickening times of neat cements for (a) training (calibration) data and (b) independent test data from chemical composition data plus loss on ignition, insoluble residue, and particle-size distribution.

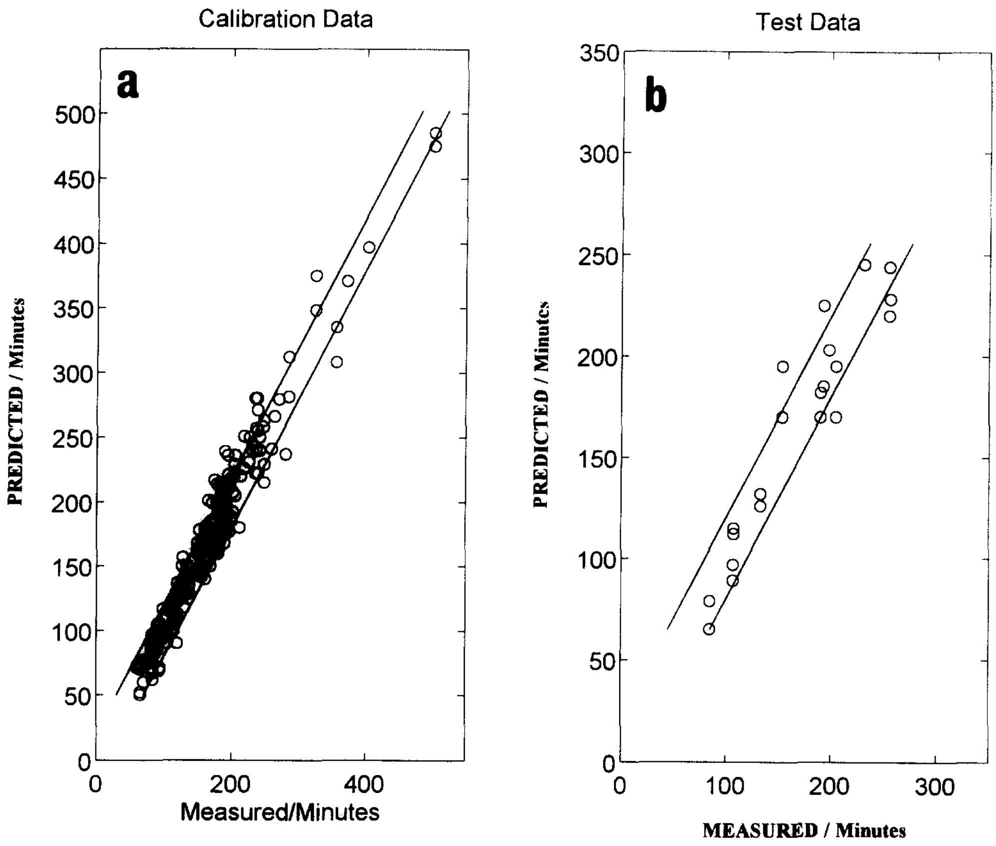

FIGURE 4. The predictions of thickening times of retarded cements for (a) training (calibration) data and (b) independent test data from chemical composition data plus loss on ignition, insoluble residue, and particle-size distribution.

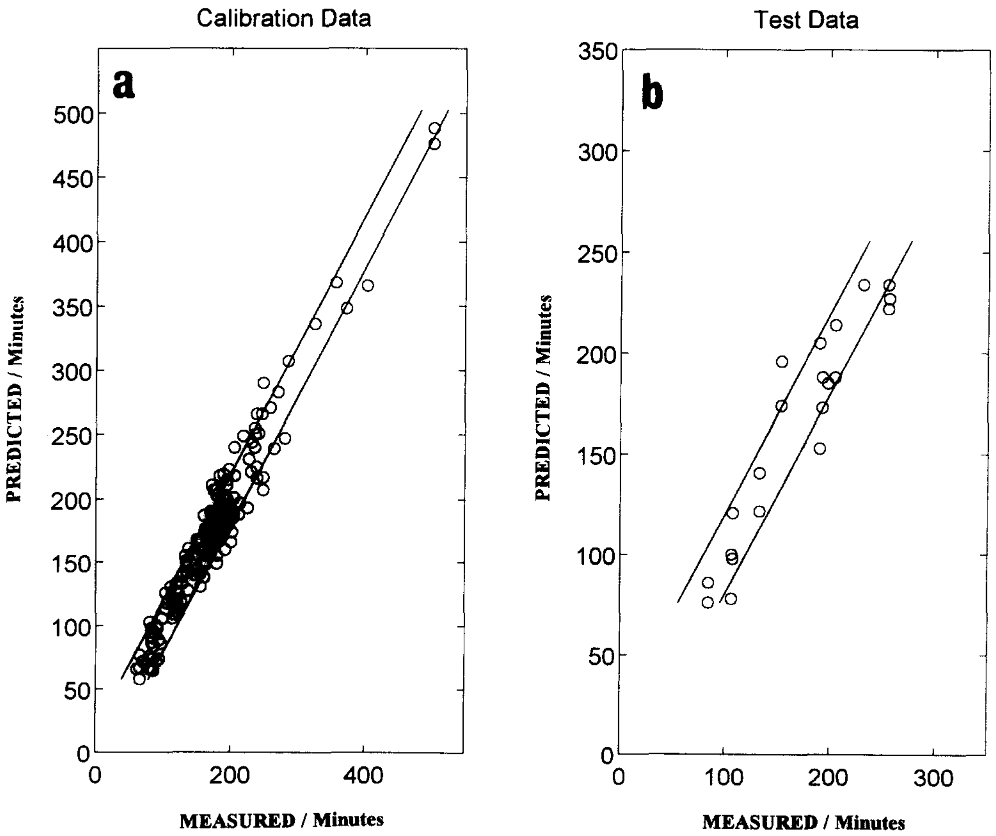

FIGURE 5. The predictions of (a) calibration data and (b) independent test data for neat slurry thickening times as predicted from DRIFT spectra.

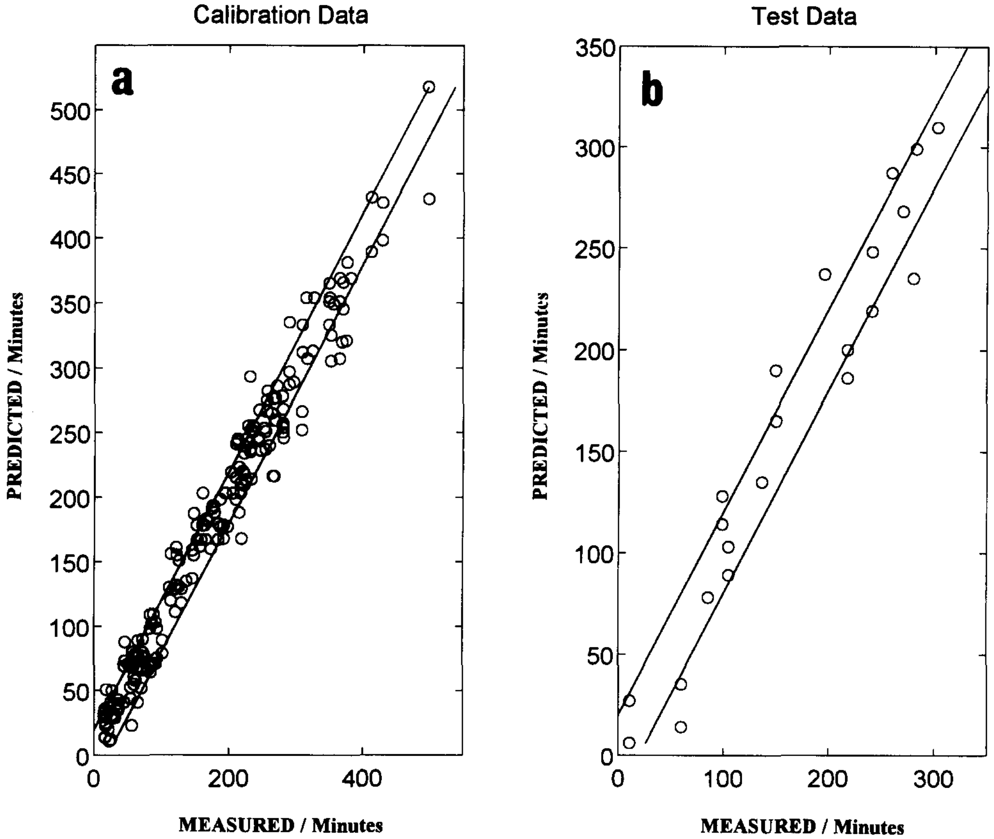

FIGURE 6. The predictions of (a) calibration data and (b) independent test data for retarded slurry thickening times as predicted from DRIFT spectra.

mean percentage error it appears that up to 90% of the variance in thickening time can be explained in terms of bulk composition and particle-size distribution. These general observations do not imply that subtleties such as isomorphic substitution, the surface compositions of minerals, or crystal defects do not play a role in determining performance properties. Rather, these effects may be represented implicitly in the combined composition and particle-size data or contribute to the 10% of thickening time variance that cannot be accounted for in the present models.

Figures 1 and 2 show the predictions of neat and retarded slurry thickening times for training (calibration) data and independent test data made from model 1 using chemical composition data with LOI and IR, while Figures 3 and 4 show similar predictions made from model 2, which includes particle-size distribution data. These figures confirm that the inclusion of particle-size distributions improves both training and independent testing of the models. In particular, there are improvements in the predictions for cements that have thickening times close to the mode of the thickening times for both neat and retarded cements, which correspond to regions where there is a great deal of data available. Thus, the particle-size distribution enhances the discrimination of cements which cannot be discriminated by composition alone. This is most noticeable in plots of the calibration data for retarded cements predicted from chemical composition data only (Figure 2a). Here the thickening time predictions appear to be clustered rather than being fully discriminated, as is the case when particle-size data are included (Figure 3a).

These conclusions confirm the assertion made by Bensted and Becker [6] that improved chemical models of cement hydration may be developed by incorporating cement physical properties as input data. Additionally, the neural network models we have developed can themselves be used to investigate the sensitivity of thickening times to changes in the values of the individual input variables. A discussion of this application is, however, beyond the scope of the present communication.

The models based on DRIFT spectra alone show errors similar to those of the models based on oxides, minerals, and particle-size distribution (Tables 2 and 3). The implication is that the DRIFT spectrum is an appropriate quantitative signature for cement variability and that such spectra contain similar information to the combined particle-size distribution and composition data. That the FTIR results are marginally better is due to the fact that less assumptions and approximations are made in obtaining models in this case. Again, this does not imply that subtleties in surface chemistry or crystal imperfections do not play a role. Rather, these effects may be represented implicitly in the spectra. Figures 5 and 6 show the predictions of calibration data and independent test data for neat and retarded thickening times as predicted from DRIFT spectra alone.

On the basis of established molecular theories of spectroscopy, it is expected that FTIR spectra such as those furnished by DRIFTS can be correlated with the chemical composition of mixtures such as cements. This is confirmed in ref 7. Less obvious is the implication from the foregoing results that features of the DRIFT spectra can be correlated with the particle-size distribution, although it is known that spectral intensity and bandwidth do depend on particle size in diffuse reflectance measurements [15]. To test this hypothesis, a neural network was trained to predict the full 16 bin particle-size distribution occupancies together with the mean particle diameter. Independent testing of the model showed that the occupancies of all particle-size bins can be predicted to within an absolute error of ±1%, which is approximately twice the expected experimental error on the measurement. However, the ability of the model to predict general trends is demonstrated in Figure 7, which shows, by way of examples, predictions of the mean particle size and the percentage occupancy of the 0 to 1 μm size fraction. It is apparent, therefore, that the DRIFT spectra of cement powders do indeed contain information on the particle-size distribution.

In conclusion, we have demonstrated through the use of artificial neural network techniques that the DRIFT infrared spectrum of a cement powder can be used as a quantitative measurement for the prediction of both cement physicochemical parameters and slurry performance properties. Since the DRIFTS measurement is easily performed within the space of a few minutes [7], it compares favorably with methods cur-

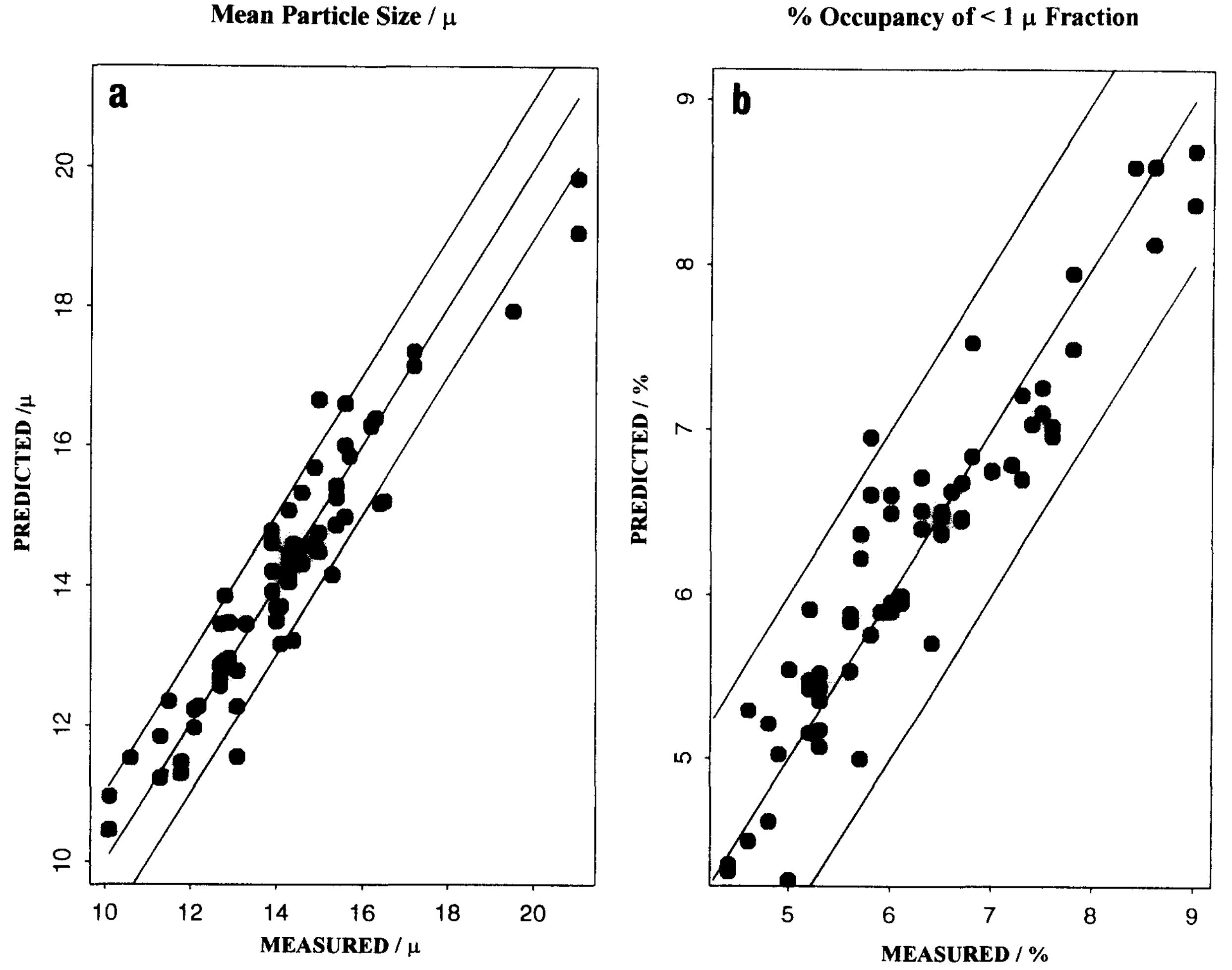

FIGURE 7. The DRIFT spectral predictions of (a) the mean particle size and (b) the percentage occupancy of the 0 to 1 μm size fraction. The outer solid lines indicate the ±1 μ and ±1 wt % bands, respectively.

rently in routine use for the determination of slurry properties. Thus it is clear that we have here the basis for a very rapid quality control method for cements.

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