Near infrared emission spectroscopy for rapid compositional analysis of Portland cements

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HIGHLIGHTS

- Near infrared emission spectroscopy was used for cement samples analysis.
- The six main oxides have been estimated in Portland cement samples.
- An emission spectrometer was specially assembled for the method development.
- Emission spectra were correlated with reference analysis using chemometric models.
- No sample preparation is required and analysis takes only 6 min per sample.

GRAPHICAL ABSTRACT
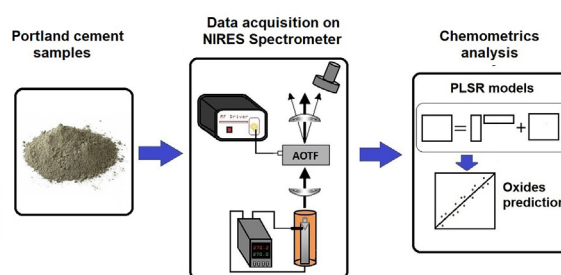
ABSTRACT

Near infrared emission spectroscopy (NIRES) has been investigated to yield a new analytical method for determination of CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, and SO_3 in Portland cement samples. The analyses were accomplished by correlation of the second derivative NIRES spectra with reference elemental analyses made by X-ray Fluorescence (XRF), using Partial Least Square (PLS) regression models. Four different types of cements (type II, III, IV and V) were included in the models. The results show RMSEP from 0.18 to 1.67% (m/m) (which represents 8.6 to 2.8% of the mean value parameters, respectively) and precision (repeatability) from 0.12 to 1.49% (m/m). The worse performance of prediction [RMSEP = 0.18% (m/m), $r^2 = 0.63$] was found for Fe_2O_3 determination due its low variability in the samples employed in the calibration and validation set, usual low content in cements, and high correlation with the weak emitting C_4AF phase. However, the paired *t*-test at 95% confidence level demonstrated that the analytical results obtained by NIRES multivariate models are equivalent to measurements performed by XRF for all oxides analyzed. The cost, speed and safety aspects are improved in comparison with the XRF method. The method based on NIRES requires no sample preparation and speed up the cement analysis (6 min) about 5 times when compared with the method based on XRF presently employed by cement industries.

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1. Introduction

The main components of Portland cements are tricalcium silicate (C_3S),[1] dicalcium silicate (C_2S), tricalcium aluminate (C_3A), tetracalcium aluminoferrite (C_4AF) and a sulfate phase, usually gypsum [1]. Cements are variable in composition due to variability in raw materials and to different recipes designed for specific applications. Additionally, during the manufacturing process, unwanted compounds are also produced and must be controlled at certain levels. Therefore, rapid, accurate and low-cost methods are desirable for quality and process control. Chemical quality control is based on elemental analysis of the bulk composition which is normally expressed in terms of equivalent oxides [2] (using, e.g., wet chemical methods [3], FAAS [4,5], ICP [6,7], and X-ray fluorescence (XRF) [8,9]) or minerals constituent determination with, e.g., X-ray diffraction [10], and optical and electron microscopy [11]. These methods usually require laborious sample preparation, several of them require the use of chemicals and drastic dissolution procedures, and/or are timing consuming.

Current analytical requirements for hydraulic cements follows ASTM C114-15 [3], which states that any test method of demonstrated accepted precision and bias, according the criteria of ASTM C114, may be used. Classical chemical test methods are described as reference methods and XRF is cited as an alternative instrumental rapid test method. The criteria found in ASTM C114 are based upon the reference methods, however none of the qualification requirements for rapid test methods has supporting data available yet. A new XRF standard test method is now under development. For the moment, the performance criteria available for XRF is that provided by an ASTM interlaboratorial study [9]. Although faster than classical wet methods, the XRF test method requires sample preparation, sample analysis takes about 28 min per sample, presents a relative high cost and safety issues due to the use of radioactive source.

Therefore, there is room yet for the development of new analytical methods which can perform faster, safer (no radioactive issue), at lower cost and meet the requirements for routine quality control of cements.

In this field of application, Infrared spectroscopy (IR) has been more frequently used for identification of minerals constituents, structure studies and hydration rate [12—16]. On the other hand, few works have applied IR for quantitative analysis of similar matrices. Zaine et al. [17] applied shortwave infrared (SWIR) spectroscopy using reflectance measurements in the range of 2100—2400 nm for quality control of carbonate and clay mineral chemistries in carbonate rock samples, which are used as cement raw material. The authors correlated the wavelength position and depth of CO_3 and Al-OH absorption features associated with carbonate and phyllosilicate minerals (Al_2O_3) with measurements of CaO and Al_2O_3 performed by portable X-ray fluorescence (XRF). Separated models were developed for each type of carbonate rock sample with coefficient of determination for CaO and Al_2O_3 of 0.774 and 0.842 (dark gray limestone samples), 0.787 and 0.723 (light gray limestone samples) and 0.695 and 0.934 (dolomitic limestone samples), respectively.

Nasrazadani and Springfield [18] used Fourier Transform Infrared (FTIR) for quantify alkali concentration in cement samples. Analysis was based on the linear correlation between FTIR absorption band area ratio at 750/923 cm^{-1} and equivalent Alkali Na_2O_e ($Na_2Oe = \% Na_2O + 0.658 \times \% K_2O$) measured by XRF (coefficient of determination of 0.97). Sample preparation included dilution with KBr (2 mg of cement and 98 mg of KBr), milling and pellet making. The authors emphasized that extreme care must be taken for controlling pellet making in order to ensure spectral and results reproducibility.

Hughes et al. [19] used diffuse reflectance mid-infrared Fourier transform spectroscopy (DRIFTS) for both qualitative and quantitative analysis. They analyzed a large number of cement samples to construct PLS regression calibration models that relates FTIR spectra to cement composition of nine minerals and five minor oxides. The mineral composition was estimated using API Bogue calculation based on elemental analysis of metals performed by inductively coupled plasma and measurements of free lime, ignition loss, and acid insoluble residue. 13 to 36 latent variables were used in PLS models. Accuracy of independent test sample varied from 0.01 to 3.10% (m/m) and coefficient of determination of validation varied from 0.623 to 0.959. Once again, authors emphasized that for quantitation results special care in steps of sample preparation (milling, dilution and spectral acquisition) must be taken in order to achieve high quality spectra.

To the best of our knowledge, no published work has so far employed infrared emission for quantitative analysis of cement samples. In our research group, we have previously investigated the near infrared emission spectroscopy using an Acousto-Optical Tunable Filter based instrument (NIRES-AOTF) as an alternative technique for characterization and determination of solid materials [20,21]. In this technique, the sample is heated at a selected temperature (usually above 150 °C), its emission spectrum is registered and then can be converted to a linear intensity scale, named emissivity. The spectral features of the near infrared region can reflect the structure of the material as well its physico-chemical characteristics.

In the present work, we describe a new method for rapid Portland cement analysis using NIRES-AOTF for determination of the six major oxides (CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO and SO_3) that usually comprises more than 98% of cement composition. The NIRES-AOTF spectrometer was specially assembled for this method development since there is no commercial instrument presently available. Analyses were accomplished by means of chemometric models, which were calibrated by reference elemental analyses. Water elimination, as a result of sample heating process in the NIRES instrument, represents a remarkable advantage since the signal from water would certainly interfere in the analytes infrared signals. No sample preparation is required what makes the procedure quite simple and fast.

2. Experimental procedures

2.1. Instrumentation

Near infrared emission analysis were performed with a NIRES spectrometer. Fig. 1 shows a diagram of the instrument based on the first equipment previously described in Ref. [20], but improved by reassembling with higher quality devices. The instrument consists of, from bottom to top, a heater connected to an emission cell where sample is located, CaF_2 lens for radiation collimation, an acousto-optical tunable filter (AOTF) as wavelength selector, CaF_2 lens for diffracted beam focusing and a PbS detector. Both, the heater and the emission cell are made of aluminum rod. The heater rod contains a 60 W electric heater and has a conic format on the top to improve heat transfer to the sample cell. The sample cell has 1.2 cm height and an external diameter of 1.4 cm, where a shallow circular roove was machined with 0.6 cm diameter and 0.65 cm depth. The heater system is described in detail in an earlier work [22]. The AOTF, made of TeO_2 crystal (Brimrose EAF5- 1.5-3.0 EH), operates in the spectral region from 1500 to 3000 nm with nominal spectral resolution varying from 6 to 22 nm as the wavelength

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[1] When expressing chemical formulae, C = CaO; S = SiO_2; A = Al_2O_3; F = Fe_2O_3.