

Use of Fourier-Transform Infrared Spectroscopy

Subjects: **Engineering, Civil**

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The Fourier-transform infrared (FTIR) spectroscopy method is a method of bond characterization that could be used quantitatively and qualitatively with X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy, and electron energy dispersive spectroscopy (SEM/EDS) to study the chemical composition, compound composition, microstructural morphology, and their elemental compositions in CB applications, respectively.

Fourier-transform infrared spectroscopy

geopolymers

alkaline-activated binder

1. Introduction

The Fourier-transform infrared (FTIR) spectroscopy method is a method of bond characterization that could be used quantitatively and qualitatively with X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy, and electron energy dispersive spectroscopy (SEM/EDS) to study the chemical composition, compound composition, microstructural morphology, and their elemental compositions in CB applications, respectively. Supplementary cementitious materials (SCMs) can be used in OPC to enhance secondary hydration. These SCMs can either be pozzolanic materials or hydraulic materials, such as ground granulated blast furnace slag (GGBFS) or pozzolanic materials, which comprise alumina and/or silica in significant quantities. Pozzolanic materials can also include fly ash (Class F), silica fume, metakaolin, palm oil fuel ash, glass waste, and rice husk ash ^{[1][2]}. Utilizing these materials in mortar and concrete productions reduces the carbon footprint and enhances cost-efficient materials for sustainable environments. These materials can be used as precursors for the synthesis of geopolymer (GP), alkaline-activated slag, or alkaline-activated binders (AABs). These precursors can also be named alkaline-activated materials (AAMs) ^{[3][4]}. Understanding the bond characterization of the binder through the application of the FTIR technique is quite helpful for the technical analysis of the binder with a view to controlling the strength and durability of the products ^{[5][6][7]}.

2. A Brief Background on the Use of FTIR in Material Characterization

Infrared (IR) light belongs to the spectrum whose frequency range lies between 4–140,000 cm⁻¹. It is bounded by microwaves and visible light. Generally, different parts of the electromagnetic spectrum are characterized by radiation velocity as well as the frequency which is inversely related to the wavelength ^[8]. There have been several applications of FTIR in different fields, such as the study of healthy and pathological blood samples and deducing molecular bond differences.

Furthermore, spectrometry has been used to study healthy and pathological blood samples in order to deduce molecular bond differences ^[9], organic chemistry ^[10], biomedical applications ^[11], and building diagnostics ^[12] in order to conserve energy and achieve a sustainable environment. In recent times, this technique is used for nano-particle detection, as reported by Hermann et al. ^[13], through its ability to identify bonds existing within the main compositions such as S-O bonds in gypsum, C-O in carbonates, hydroxyl (H-OH) groups, and aluminosilicates (Si-O-T; T is Si or Al) ^[14]. The purpose of FTIR is to provide additional information on X-ray diffraction (XRD) by relating bond characteristics to mineral characteristics. It remains a

versatile tool for bond characterization of aluminosilicate and hydroxyl-based compounds. It could also be used to differentiate between amorphous and crystalline products with linear or cross-link chain products [12][15].

3. Mechanism of Fourier Infrared Spectroscopy

The mechanism of FTIR spectroscopy involves passing IR or signals of lumped frequencies from a polychromatic light source, such as a globar, an incandescent lamp, a nichrome wire, or a Nernst glower, to obtain mid-range IR radiation [16], whereas tungsten–halogen and mercury lamps can produce near and far IR, respectively [17]. The emitted radiation then travels via a collimator and Michelson interferometer (**Figure 1**), which consists of fixed mirrors, moveable mirrors, beam splitters, and helium–neon (He-Ne) laser beams. The beam splitter could be built of germanium coated with potassium bromide (KBr) and is used to split radiation into fixed and moveable mirrors prior to reflection and indentation on the sample [8]. Connecting the adjustable mirror to the He-Ne laser beam enables precise monitoring of its position, which has a direct correlation with optical path difference (OPD) and radiation amplitude (measured in electron volts) [16][18][19]. The amplitude results from constructive interference (in-phase) of returning waves from both the fixed and moveable mirrors, whereas destructive interference (out-of-phase) produces waves with zero amplitude.

The detector can be made of deuterium triglycine sulfate (pyroelectric detector) or mercury cadmium telluride (photon detector) [17]. The interferogram is then decoded into specific frequencies (wavenumber) using Fourier mathematical transformation [20]. The ratio of the intensity of the sample with blank spectrum (P/P_0) and sample thickness (w) gives the transmittance (T).

As demonstrated in Equations (1)–(3) [21], the transmittance (T) can be represented as a function of the absorption coefficient (α_{abs}), and if inverted and transformed to logarithmic values, it becomes the absorbance (A):

$$T = \frac{I}{I_0} = e^{-\alpha_{\text{abs}} \cdot w} \quad (1)$$

$$\alpha_{\text{abs}} = \log I - \log T \quad (2)$$

where I is the incident light intensity and I_0 is the transmitted light beam. For weakly absorbing homogeneous samples with known molar absorptivity (γ) and concentration (c), absorbance (A) can be stated as follows:

$$A = -\log T = \gamma \cdot c \cdot w \quad (3)$$

4. Molecular Bond Vibrations

During the vibration of the molecule, the net change in dipole moment in a molecule occurs, thereby resulting in IR absorption [22]. In other words, the vibration of molecules initiates a fluctuation in its dipole moment and causes an interaction in the electric field that associates with radiation [8]. Depending on the degree of freedom, function energy falls into two principal

categories (symmetry and asymmetry) and bending (rocking, scissoring, wagging, and twisting) [21]. It requires more energy to stretch than to bend molecular bonds while slightly more energy is required to asymmetrically move atoms than symmetrically [10][23]. Therefore, bonds vibrate asymmetrically at a higher frequency than their bending. Additionally, the bond between hydrogen and oxygen atoms has been reported to have a higher frequency than heavier atoms. Similarly, the double bond atom has a heavier vibration than a single bond [23].

5. Sampling Methods in FTIR

FTIR spectroscopy can be conducted through different mechanisms of sampling methods, namely the transmission or reflection method, which can be attenuated total reflectance (ATR) and the diffusive reflectance IR transmittance spectroscopy technique (DRIFTS) [24], and the specular aperture grazing angle (SAGA) methods [14][25].

5.1. Transmission Method

This method is convenient and simple and relied on the idea of light passing through a surface through a process of passing IR radiation through a thin, free-standing film with a thickness of fewer than 50 microns, thereby making it suitable for liquid, solid, and gas applications. The sample preparation by direct transmission could be difficult as it requires mixing the sample with a reference substance for quantitative analysis. To create a pellet, mull, or film, the sample would be combined with KBr in a volume ratio of 1 to 10 [15]. The method was utilized by Brown et al. [26] in 1958 to create a translucent disk before conducting the test. Likewise, Yu et al. [27] also added a sample to KBr blank ratio in one hundredth (weight). Yusuf et al. [28][29][30][31] studied bond characteristics in alkaline-activated palm oil fuel ash and also employed the KBr to sample ratio of 1:9 (by volume). Atta et al. [32] made use of kaolin and rice husk ash as precursors but reduced the sample/KBr volume ratio to 1:5. The prepared sample is then compressed using a hydraulic press (10 MPa) into a thin clear pellet before being placed into the radiation absorption device. After absorbing some energy, the sample delivers the remaining energy to the detector. The sample surface area, which can be increased by grinding the sample to a fineness below 2–5 microns, determines the increase in transmittance and resolution of the absorption bands [15][33]. To prevent cracking or shattering of the translucent disc, the sample must be gently inserted into the holder.

For cementitious material application, the transmission method is commonly used as the samples are well-prepared into a paste and then properly cured for a specific period. The sample should be adequately dried and then ground into a finely divided powder through a mortar and pestle before being pressed into a pellet by using a mold at a pressure of about 10 MPa to make it translucent. Grinding the sample into a finely divided powder reduces distortion of the absorption band and scattering losses, while a wet sample that is not properly dried will produce a broad peak with poor resolution. KBr should be well covered to prevent attracting moisture because it is a hygroscopic substance.

5.2. Reflection Methods

All samples can be processed through transmission technique in which light waves is directly sent through the sample. Reflection methods, however, requires simple sample preparation and it can be either through internal reflection spectroscopy (attenuated transmission technique, ATR) or external reflection spectroscopy (specular reflection) for smooth and reflective surfaces. It can also be the combination of both internal and external reflections such as in diffusion reflection IR spectroscopy (DRIFTS) for rough surfaces [34].

a. The Attenuate transmission reflection (ATR) technique:

ATR was introduced in the 1960's but now being popular used due to its easier sample preparation. It can be used for qualitative and quantitative analyses of both liquid and solid gel coating samples in accordance with ASTM C494 Section 18.1.2 [35]. Its principle is based on internal reflection of light wave through air/sample, solid/sample or liquid/sample interfaces [36]. It was recently shown that attenuated total reflectance FTIR (ATR-FTIR) spectroscopy could be used for the detailed analysis of hardened fly ash GP [36] or to study pore characteristics or carbonation effect. On this premise, Nedeljkovi et al. [37] use this method to investigate the effect of natural carbonation on the pore structure and elastic modulus of the alkali-activated fly ash and slag pastes. The tested sample is placed in a reflective medium composed of a crystal (such as a diamond) with a high refractive index (usually greater than 2) [24]. Information is collected in internal reflection from the surface or thin layer by external reflection.

Other materials could also be zinc selenide (ZnSe), germanium (Ge), and silicon (Si), with a higher refractive index and varying hardness and depth of penetration. ZnSe is not recommended for strong acid or base samples due to the possibility of surface erosion by the formation of zinc complexes. Rather, water insoluble AMTIR crystals made from germanium, arsenic, and selenium with similar refractive indices are preferred [38]. The crystal generates an exponentially decaying wave (evanescent wave) that projects orthogonally onto the sample [22]. IR is directed into a crystal or an internally reflected element (IRE) of a relatively higher refractive index and then absorbs a portion of the energy of an evanescent wave and transmits the rest to reach the detector [39]. The greater the depth of penetration (path length) onto the sample, the greater the wavelength of IR [38]. The advantage of this technique is that a spectrum can be generated with easy sample preparation by just placing the core sample on the holder and screwing it tightly to receive the radiation.

b. Specular reflectance technique

This requires the sample to be reflective or be on a reflective surface while the required information is collected through a thin layer as it involves externally reflection of incident light waves.

c. Diffuse reflectance IR transmittance spectroscopy (DRIFTS) method

The method has the advantage of higher resolution with no rigorous sample preparation, like the transmission method [24]. The sampling technique is through powder samples without any prior preparation. The sample is added to the sample holder and information is collected in internal reflection from the bulk of the matrix. The reflection of the light depends on the transmitted and reflected quantities by the sample and that also depends on the material bulk properties. The reflected rays are collected with an ellipsoid or paraboloid mirror, while KBR could be used to dilute any absorbent materials. The parameters being analyzed include compactness, shapes, reflectivity, refractive index, and absorption of the particles. The sample should be well-ground and fine to ensure that the wavelength of incident light is bigger than its particles. This is necessary to minimize Mie scattering [40]. They [40] reported that both transmission and ATR are closer in accuracy but at a disparity with the DRIFTS method [24]. The best and appropriate technique depends on the type of application, the nature of the material, and its surface roughness.

For civil engineering applications involving bond characteristics, both transmission and ATR methods are commonly used due to their close accuracy [24]. It should be noted that the sample must be properly dried to enhance the sharpness of the spectra, as the presence of water will affect the accuracy of the data by blinding other signals due to water molecule strong bands [41]. To conduct this test, it is best practice to separate the binders from siliceous aggregates to avoid misinterpreting the Si-O bands in aluminosilicate or CSH binders. However, siliceous aggregate compositions could be studied separately if that is the research focus. Generally, paste samples should be dried without containing free (unbound) water to avoid blinding the relevant peaks of interest in the FTIR spectra. There have been several efforts by different researchers to solve the

problem of the effect of moisture fluctuation on the spectra peaks. The problem is the presence of moisture that causes the fluctuation of temperature on the laser (He Ne), and of transient concentration of moisture along the spectrometer's light path. In recent time, Zhang et al. developed an approach to resolving the problem by using a comprehensive 2D-COS method [42]. Giordanengo et al. [43] proposed a holistic calibration and external parameter orthogonalization (EPO) among the effective approaches to remove additive and multiplicative effects of water on the vibration of -OH chemical bonds.

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