Characterization of Construction Materials
Prof. Manu Santhanam
Department of Civil Engineering
Indian Institute of Technology – Madras

Lecture – 56
Spectroscopy Techniques – FTIR and NMR Spectroscopy – Part 1

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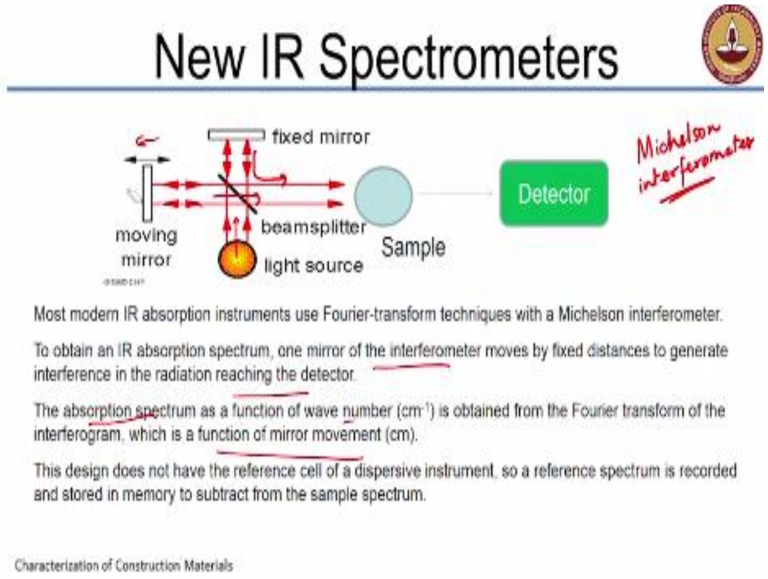

New IR Spectrometers

Most modern IR absorption instruments use Fourier-transform techniques with a Michelson interferometer.

To obtain an IR absorption spectrum, one mirror of the interferometer moves by fixed distances to generate interference in the radiation reaching the detector.

The absorption spectrum as a function of wave number (cm^{-1}) is obtained from the Fourier transform of the interferogram, which is a function of mirror movement (cm).

This design does not have the reference cell of a dispersive instrument, so a reference spectrum is recorded and stored in memory to subtract from the sample spectrum.

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So, we were discussing about how the infrared radiation is made to pass through the sample. In most infrared spectrophotometers, which are labeled as FTIR instruments, the infrared radiation is sent through a source into a beam splitter that transmits the beam partially and reflects the beam partially. The transmitted beam goes to a fixed mirror and the reflected beam goes to a moving mirror. So, the moving mirror is moved in discrete positions. So, there is a fixed position first for the moving mirror. In the second stage, the moving mirror moves by a certain distance. So, as a result what happens is a certain set of wavelengths are generated at a phase difference as compared to the wavelengths that are generated from the fixed mirror. So, when the phase difference is such that there is constructive interference, you produce a certain set of wavelengths that are able to go through the sample. On the other hand, when the destructive interference occurs between the waves that are out of phase with respect to each other coming from the moving mirror and from the fixed mirror, there is cancellation of the signal.

So, what happens is for every position of the moving mirror, only a specific set of wavelengths is transmitted through the sample. In the next stage, the moving mirror is moved by another increment. So, when it is moved by a different increment, now a different set of wavelengths actually ends up passing through the sample because of constructive interference.

So, what we are doing as a result of this experiment or as a result of this instrumentation is that by each position of the moving mirror, we are able to send a different packet of wavelengths of infrared radiation through the sample. So, in other words, we are not really separating the wavelengths through a monochromator or a diffraction grating. We are sending several wavelengths by changing the position of the moving mirror. So, that is the fundamental idea about the use of the Michelson interferometer (Do not get confused with the Michelson-Morley experiment, which is another really well known phenomenon in physics). Here we are talking about interferometer which looks at the interference between the light rays or infrared rays that are generated from the fixed mirror and from different positions of the moving mirror which generates constructive or destructive interferences leading to the passage of certain sets of wavelengths through the sample.

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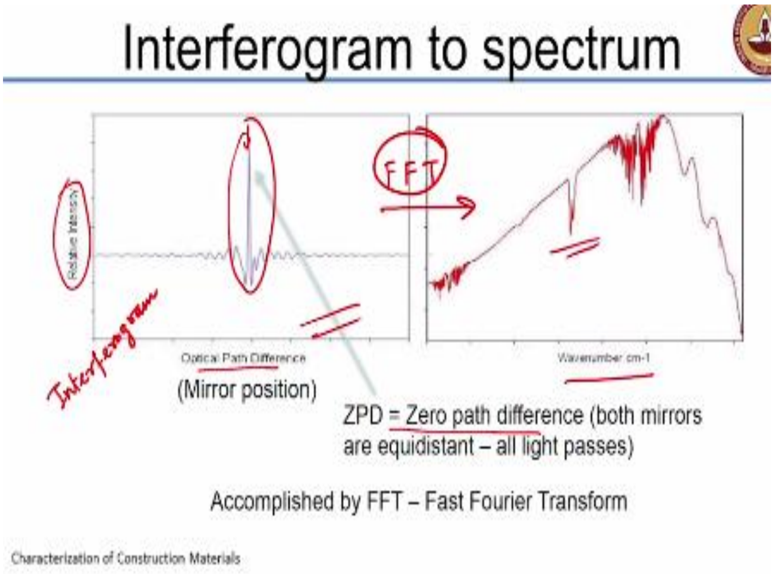

Interferogram to spectrum

ZPD = Zero path difference (both mirrors are equidistant – all light passes)

Accomplished by FFT – Fast Fourier Transform

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So, what is produced as a result of this movement of the mirror is what is called an interferogram. So on the left what you see is an interferogram. So, interferogram plots the relative intensity of the light that is coming into the sample and the path difference. The path difference is created because of different positions of the moving mirror, and in the center you get a peak, which is nothing but zero path difference, that means both mirrors are equidistant, all the light that is converging from 2 mirrors is passing through the sample.

So, at this particular location of the mirror, you are actually transmitting the entire light. So, once again when you move the mirror to a certain distance, you will be generating another set of wavelengths which pass through the sample. Now, what you need to do is convert this optical interferogram into the Fourier transform spectrum or rather infrared spectrum. This infrared spectrum is obtained from the interferogram by using the Fast Fourier Transform - FFT, that is why we call this as Fourier Transform Infrared Spectroscopy. Now, why is Fourier transform done? What we do is we convert the signal into something that is a mixture of signals at different frequencies. Now, here of course, we know that frequency is represented by the wave number (wave number = 1/λ). So, frequency is equivalent to wave number and so here we are trying to represent the interferogram as the interference pattern or absorption pattern, conversely, transmission pattern of the infrared radiation which is passing through the sample, which is expressed now as a function of the wave number. So the conversion from this to this happens through a Fast Fourier Transform.

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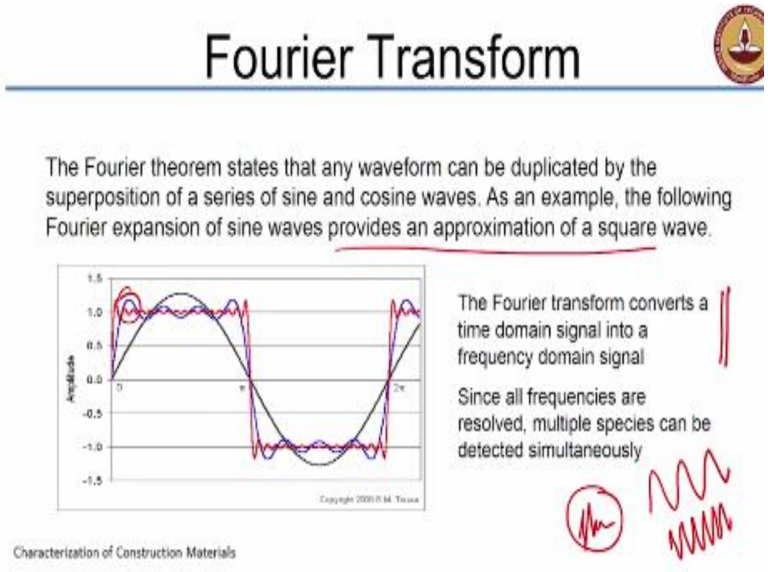

Fourier Transform

The Fourier theorem states that any waveform can be duplicated by the superposition of a series of sine and cosine waves. As an example, the following Fourier expansion of sine waves provides an approximation of a square wave.

The Fourier transform converts a time domain signal into a frequency domain signal

Since all frequencies are resolved, multiple species can be detected simultaneously

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So, what is Fourier transform? This is something you have learned in mathematics earlier. What we do in a Fourier transform is we are able to represent any function as a summation of sine and cosine waves. So, for example here the Fourier expansion of sine wave provides an approximation of a square wave. So, this is the wave (as shown in figure), the red is indicating a square wave and the black is a sine wave, which is approximately following the same pattern, but then what you do is you add a set of cosine and sine terms in the series to provide a wave that is able to more closely resemble the actual waveform that you have.

Now, what is the advantage here? When you convert an unknown waveform into a summation of sine and cosine waves, you can then pick out specific wavelengths which are involved in that wave. This is similar to ultrasonic techniques, where we actually send in an impulse through a specimen. Now, what happens is this impulse is actually a summation of several waves having different wavelengths. When you send an impulse through an object and you actually analyze the sound that is coming out of the object, it is a combination of several different wavelengths. Now, separation of these wavelengths into their individual characteristics is accomplished by Fast Fourier transform or FFT. Fourier transform converts basically a time domain signal into a frequency domain signal. So, what you are doing is getting a complex wave that is composed of several different frequencies and converting that into a wave where each frequency can be specifically separated. So, when you separate out the frequencies, you then get information, in this case of course, in the IR spectroscopy, about the specific wave number at which that transformation is actually happening and that wave number is corresponding to a certain set of molecular or atomic vibrations that are taking place between the bonds in the species. We talked about several types of vibrations; you can have stretching, bending, rotational vibrations and all those kinds of things.

So, the advantage of the Fast Fourier transform is it is a mathematical technique, which allows you to resolve multiple frequencies simultaneously. So you are not spending time on sending separate packets of wavelengths through the sample, with the selection of a wavelength through the monochromator. You are sending a set of wavelengths which are representative of the entire species that may be present in a sample and then collecting all the wavelengths together, detecting everything together and then converting that into a frequency domain signal that isolates each individual wave number that you would like to analyze.

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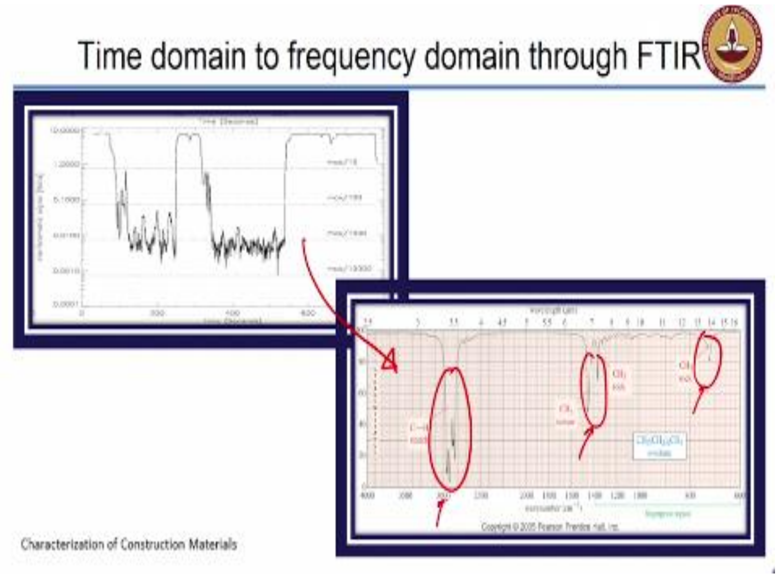

Time domain to frequency domain through FTIR

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So this is a time domain signal, which is transformed into a frequency domain signal and you are able to get very specific frequencies or wave numbers for different types of molecular vibrations that may happen in the system. So, that is the principle of Fourier Transform Infrared Spectroscopy. Of course, what we are concerned with is the end result and we have to understand how to analyze the end result. For example, when we look at these patterns, we need to now understand what is responsible for causing these specific peaks. There are bonds present in your system, the molecular vibrations or inter-atomic vibrations that take place in the system lead to the generation of these peaks and those are standardized for different types of molecular combinations or atomic combinations, for instance, carbon-oxygen, silicon-oxygen, aluminum-oxygen, each one of them will have a very specific sort of location or energy at which these vibrational frequencies actually occur. So, that way you can actually isolate these transitions and get an estimate of the elemental composition or the types of bonding present in your sample.

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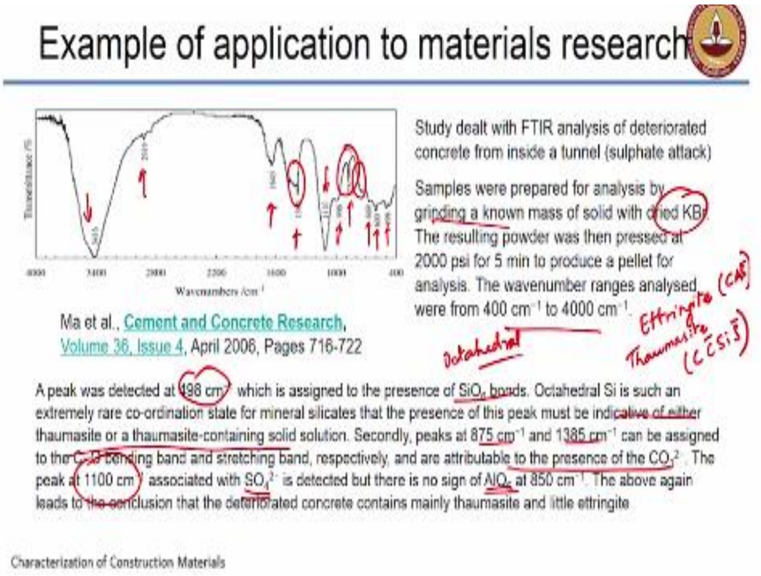

Example of application to materials research

Study dealt with FTIR analysis of deteriorated concrete from inside a tunnel (sulphate attack)

Samples were prepared for analysis by grinding a known mass of solid with dried KBr. The resulting powder was then pressed at 2000 psi for 5 min to produce a pellet for analysis. The wavenumber ranges analysed were from 400 cm^{-1} to 4000 cm^{-1}.

Ma et al., Cement and Concrete Research, Volume 36, Issue 4, April 2006, Pages 716-722

Octahedral

Ettringite (CA$\bar{S}$)

Thaumasite (C$\bar{C}$Si$\bar{S}$)

A peak was detected at 498 cm^{-1} which is assigned to the presence of SiO_6 bonds. Octahedral Si is such an extremely rare co-ordination state for mineral silicates that the presence of this peak must be indicative of either thaumasite or a thaumasite-containing solid solution. Secondly, peaks at 875 cm^{-1} and 1385 cm^{-1} can be assigned to the C-O bending band and stretching band, respectively, and are attributable to the presence of the CO_3^{2-}. The peak at 1100 cm^{-1} associated with SO_4^{2-} is detected but there is no sign of AlO_6 at 850 cm^{-1}. The above again leads to the conclusion that the deteriorated concrete contains mainly thaumasite and little ettringite

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So, just to give you an example of application of FTIR to materials research, so here there was an investigation of concrete that was taken from inside a tunnel. Now, this tunnel was in a mountainous region which had a soil which was rich in sulfate and a lot of the sulfate was penetrating into the concrete and creating a lot of damage at the surface of the concrete. So, the investigators wanted to analyze what was the damage because of, what kind of products are actually forming in the system.

Now, if you do an X-ray diffraction analysis, what happens is there are two compounds which can almost give similar locations of the peaks in X-ray diffraction analysis, which is ettringite which we know is calcium aluminium sulfate (CA$\bar{S}$). The other compound which can give similar peaks is called thaumasite. Thaumasite is calcium carbonate silicate sulphate (C$\bar{C}$Si$\bar{S}$). It is a very complicated product, which usually forms whenever there is a source of carbonates in your system and it is also specifically formed when you have low temperatures prevailing in your system.

So here, there was a case where sulphate attack was happening, not necessarily at low temperatures in this case. So the investigators were actually looking for ettringite. Indeed, they found specific peaks in the X-ray diffraction pattern, which seemed to indicate it was ettringite, but then they resorted to FTIR analysis to see whether you had ettringite or thaumasite in the system. So what happens here is, the samples first need to be prepared. So in this case, samples were prepared by grinding with dried potassium bromide (KBr).

Now, you will see in FTIR spectroscopy that KBr is often used for FTIR analysis. What happens is when your infrared light passes through your sample, as I said earlier, there is a lot of interference from background radiation also. So when you have very small amount of sample, you can actually immerse that or mix that with potassium bromide, which does not produce any interference in the range of wave numbers that we want to investigate 4000 to 400 cm^{-1}. In that range, we do not really get any interference from KBr. So for viewing solid particles or for viewing solid systems, use KBr as a dispersant to ensure that your sample is well distributed in the matrix. It is a very well known and very popular idea to actually use KBr because it does not create any interference in that range.

So, here wave number ranges analyzed were 400 to 4000 cm^{-1}. Now, what are the different peaks here? You have this peak here at 3416 cm^{-1} and you have one at 2919 cm^{-1}, you have 1643 cm^{-1}, 1383 cm^{-1} and all these different peaks are there. So, each one of these can be separately distinguished from your FTIR pattern. Now this peak at 498 cm^{-1} is assigned to the presence of SiO_6 bonds, which means silica in what state, is it tetrahedral or octahedral? SiO_6 is octahedral state. So, octahedral Si is a rare coordination state, because we know that most stable silica exists in the tetrahedral state, SiO_4, but here in an octahedral state, it is quite rare.

So, again, this peak must be indicative of either thaumasite or thaumasite containing solid solution. So, in thaumasite, the structure is such that the silica exists in an octahedral state. Now, again for reconfirmation, peaks at 875 cm^{-1} and 1385 cm^{-1}, this peak here and this peak here can be assigned to the carbon-oxygen bending band and stretching band. So at 875 cm^{-1}, you have carbon-oxygen bending happening and at 1385 cm^{-1} you have stretching of the carbon-oxygen bond. These are attributed with presence of carbonate (CO_3^{2-}). So, we know now that there is some carbonate present in your system. So, if you have a system which has calcite formation in it or calcium carbonate formation it, you will obviously get some carbonate signals also in the Fourier transform spectrograph.

The peak at 1100 cm^{-1} which is typically associated with sulfur-oxygen (SO_4^{2-}) is detected, but there is no sign of octahedral alumina (AlO_6) at 850 cm^{-1}. So if ettringite was present, you would have sulfate and you would also have the octahedral alumina (AlO_6). But in this case at 850 cm^{-1}, you do not really have any signature of octahedral alumina, which means there is no ettringite in the system. What you are looking at primarily is thaumasite.

So, again using X-ray diffraction in this case would have proven to be a difficult proposition because most of the peaks of ettringite and thaumasite are almost at the same location. So, you have to choose your techniques carefully to understand the kind of detections that you want to do and then what you really want to prove as a result.

No, EDX will give you elemental composition, that elemental composition can be converted to an oxide composition. Now EDX, you would have to do on a number of points to really understand that your microstructure is rich in thaumasite and not in ettringite. However, here all you are doing is preparing a powder and running one analysis and showing very clearly that there is thaumasite and not ettringite. And please remember EDX is usually done with backscattered electron microscopy where you have to polish the sample properly. So again, the amount of work involved in backscattered SEM and EDX is far greater than what you actually do for FTIR, and all this you do in a matter of minutes. All you need to do is grind your sample, preparation of pellet takes a few minutes, you will see that when you actually visit the lab, and then doing the experiment takes you hardly a few minutes. So, all this information can be gained in a matter of minutes. Whereas for backscattered electron imaging, the specimen preparation itself takes nearly totally about 24 hours including epoxy impregnation and then polishing to different levels, coating, all those kinds of things need to be done. So, that is not easy at all.

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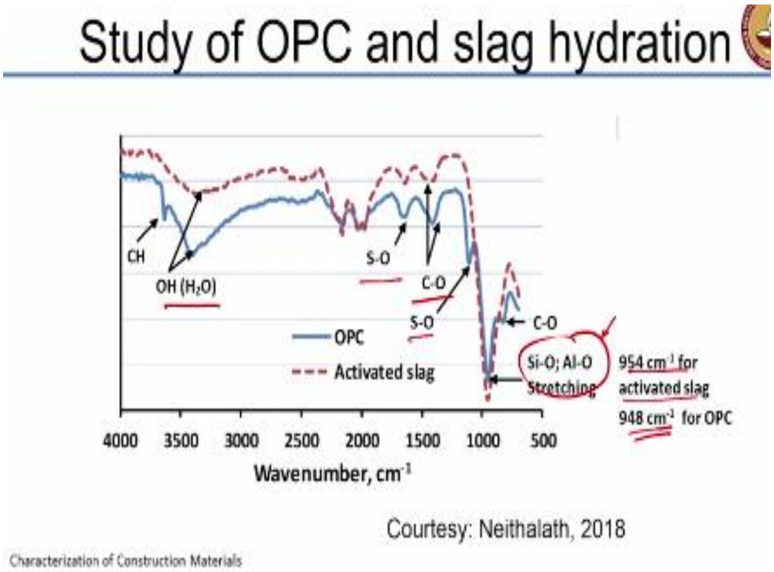

Study of OPC and slag hydration

Courtesy: Neithalath, 2018

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So again, this is an example of OPC and slag hydration that was performed by Professor Neithalath at Arizona State University. So again, what this shows you is the transmittance spectra for different wave numbers and what you are able to observe in both these cases in

OPC and slag hydration are common locations, for example, of oxygen-hydrogen stretching, silica-oxygen, carbon-oxygen, sulphur-oxygen, Si-O is silica-oxygen and Al-O is aluminum-oxygen stretching.

So, what happens here is there is very little to actually distinguish between these 2 systems. Why is that? Because when slag hydrates, the typical hydration products that form are similar to the formation of hydration products in Portland cement. Only minor changes are observed for activated slag, your primary silicon-oxygen and aluminum-oxygen stretching happens at a slightly different wave number as compared to what happens for OPC. So, there is only a minor difference in this case.

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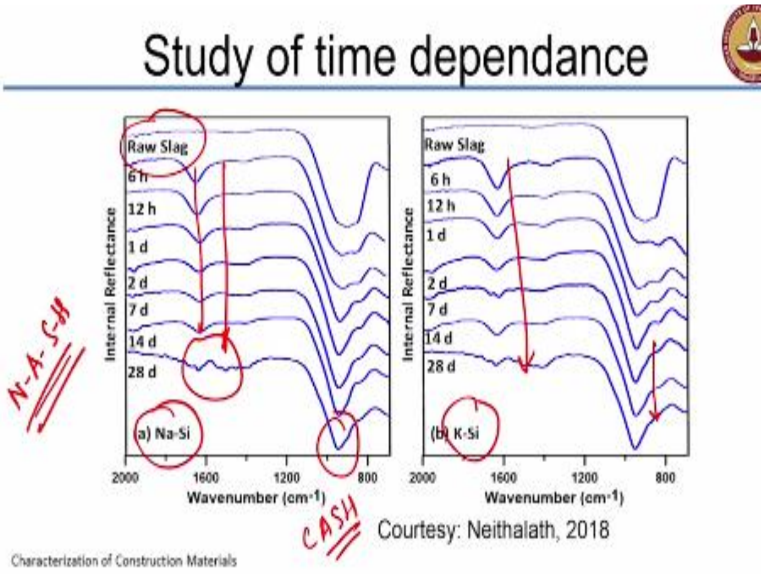

Study of time dependance

Courtesy: Neithalath, 2018

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Even time dependent hydration can be actually studied by FTIR quite easily because again all you need to do is at different time intervals, prepare these powders and then prepare your sample or pellet for the analysis, and what is shown here is raw slag and how the hydration evolves as the slag hydrates more and more. So you see that primarily, the peak for the silica-oxygen and aluminum-oxygen bond is becoming more and more prominent. That is what we are actually observing in this case. There are certain peaks, which are getting removed in the system. So there was a strong peak for the raw slag and then after a certain period of time, you do not get any peak.

This is actually alkali activated slag. So, what you are actually looking at is the sodium-silica (Na-Si) peak, which typically forms in the type of a gel which we call as N-A-S-H gel, sodium aluminum silicate gel. So, that typically happens in geopolymeric systems.

So, in this case what is happening is your system is evolving with respect to time from raw slag up to this location at 28 days where you do not actually see this peak occurring in the system at all. Similarly, potassium-silicon (K-Si) is also seen in this to be completely getting obliterated by the time you reach the 28 days hydration of the slag. So, what this goes to show is when you have these alkalis, sodium or potassium, they are trying to actually increase the rates of dissolution of the slag. But they do not really form major complexes such as N-A-S-H in the species, because what happens overall is that your system actually ends up forming calcium alumino-silicate hydrate (C-A-S-H), unlike in the case of fly ash or calcined clay, where your alkalis actually geopolymerize the system and produce compounds such as sodium aluminosilicate hydrate (N-A-S-H). So, in this case, your sodium aluminosilicates and potassium aluminosilicates are not really stable in the long run and the reaction shifts towards the formation of calcium aluminosilicate hydrate, which is indicated by this peak. Once again if you look at the location of this peak (previous slide) close to 900 cm^{-1}, that is where this transition is also happening. That is the same peak which we saw in the previous picture.

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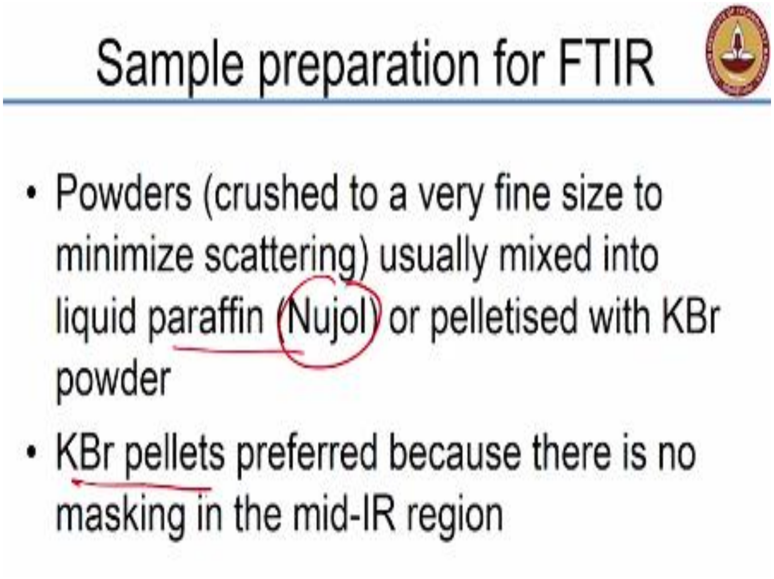

Sample preparation for FTIR

- Powders (crushed to a very fine size to minimize scattering) usually mixed into liquid paraffin (Nujol) or pelletised with KBr powder
- KBr pellets preferred because there is no masking in the mid-IR region

Now, typical sample preparation, as I said, where powders are crushed to a very fine size to minimize the scattering. Usually, it is mixed into liquid paraffin, which is otherwise known as Nujol, or pelletised with potassium bromide (KBr). So, you create these pellets which are almost like small biscuits and this is actually put into your instrument to do the FTIR transmission analysis. So KBr pellets are preferred because there is no masking in the mid-infrared region. There is no interference by the presence of KBr in this mid-infrared region that you are trying to analyze in the system.

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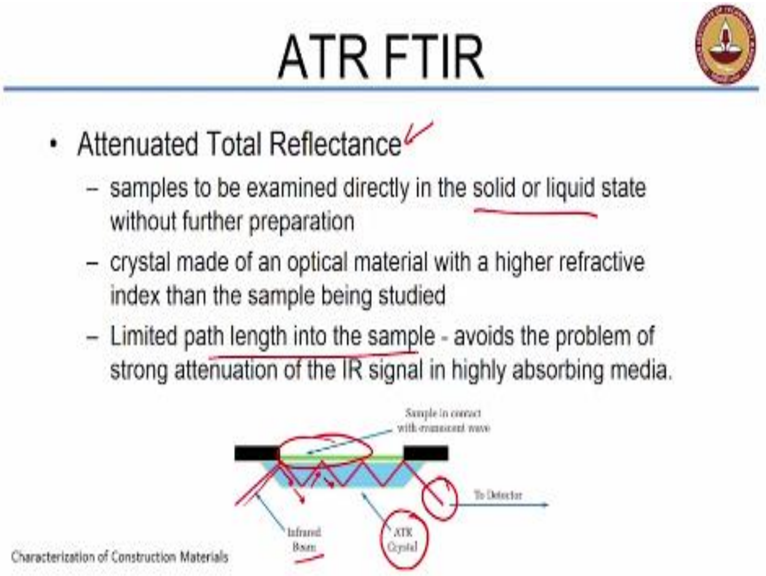

ATR FTIR

- Attenuated Total Reflectance
  - samples to be examined directly in the solid or liquid state without further preparation
  - crystal made of an optical material with a higher refractive index than the sample being studied
  - Limited path length into the sample - avoids the problem of strong attenuation of the IR signal in highly absorbing media.

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There is another type of system available in most modern FTIR spectrometers that is called ATR or Attenuated Total Reflectance. So, here the advantage is that you can actually directly use samples which are either solid or liquid without further preparation. You do not need to actually mix it anymore with potassium bromide. So, what happens is you have a crystal made of an optical material with a high refractive index than the sample being studied.

So for example, if this is your infrared beam (shown in figure in slide), it enters this ATR crystal which is marked in blue. So this beam enters here and your sample is right on top of the crystal. So, what is now happening is this IR beam actually comes and gets reflected from your sample and because of the refractive index that you have chosen for your ATR crystal, there is no transmission of this beam out of the crystal, whereas you get total internal reflection. Again, a concept that you have learned before, at certain angles of incidence, light can be totally internally reflected. For example, in an optical fiber cable, the principle of data transfer is by total internal reflection of the light, which is what is happening in the case of ATR also. So here, your sample is actually reflecting the IR, which is then transmitted to the other side by total internal reflection through the ATR crystal.

So now how is the sample getting detected? Because now you are getting the reflectance signals, that means some amount of the energy IR that is going into the sample is getting absorbed, some wavelengths are getting absorbed while others are getting reflected. So, when you analyze the outgoing IR wave, you can pick out the wavelengths that have been transmitted in the system and the wavelengths that have been absorbed by the sample. So, that helps you actually to study the sample without doing any further sample preparation. So, this is an ATR technique which is not available in older FTIR instruments, but today you can actually get combined FTIR instruments which have both ATR and regular transmission techniques.

So, there is limited path length into the sample which avoids the problem of strong attenuation in highly absorbing media. What do I mean by that is, if you have a very highly absorbing material, which is going to completely weaken your IR signal and not transmit enough, that is going to be a problem for conventional IR spectroscopy. But in this case, since you are only reflecting there is only a small amount of interaction that the IR beam is actually having with the sample. So, the intensity of the IR beam is not getting lost easily. So that is the advantage of using Attenuated Total Reflectance (ATR) spectroscopy. But analysis is same, once you get the signal out, you need to do a Fourier transform and convert the signal into your Fourier transmittance pattern, measure the transmittance as a function of the wave number or frequency.

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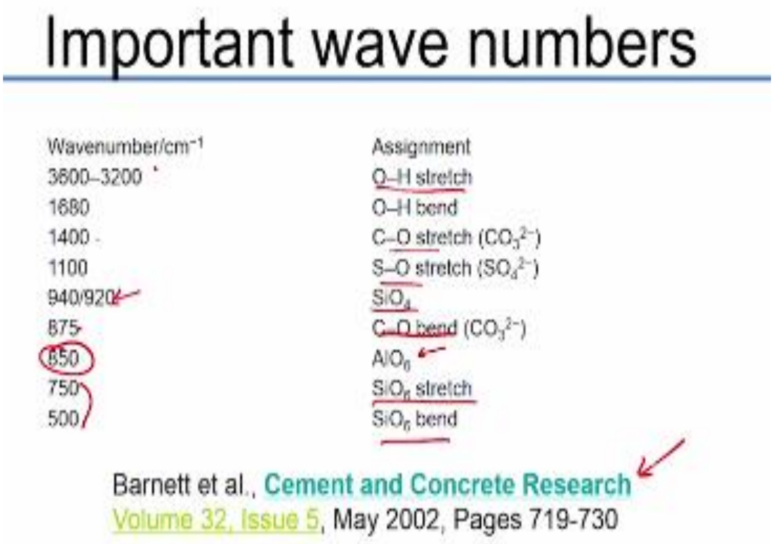

Important wave numbers

Wavenumber/cm^{-1}	Assignment
3600–3200	O–H stretch
1680	O–H bend
1400	C–O stretch (CO_3^{2-})
1100	S–O stretch (SO_4^{2-})
940/920	SiO_4
875	C–O bend (CO_3^{2-})
850	AlO_6
750	SiO_6 stretch
500	SiO_6 bend

Barnett et al., Cement and Concrete Research Volume 32, Issue 5, May 2002, Pages 719-730

So, just to give you an idea about what these different wave numbers mean and how to actually interpret your patterns, there are several papers that have explored different types of cementitious systems and outlined the specific locations of these peaks. For instance, the oxygen-hydrogen stretch happens at 3600-3200 cm^{-1} wave number. O-H bend happens at 1680 cm^{-1}. Carbon-Oxygen stretch is at 1400 cm^{-1} or more precisely as we saw on the other example from the sulphate attacked tunnel lining, it was about 1385 cm^{-1}. Sulphur-Oxygen stretch happens at about 1100 cm^{-1}. SiO_4 that means tetrahedral silicate state is observed at

940 to 920 cm^{-1}. So, if you observe most conventional cement paste systems, you will actually see silicon-oxygen locations at about 940-920 cm^{-1} because silica, even in C-S-H, the silica is pretty much in a tetrahedral state. Carbon-Oxygen bend happens at 875 cm^{-1}. The octahedral alumina which is typical of ettringite is close to about 850 cm^{-1} wave number. The octahedral silica stretching and bending which may be observed when you have thaumasite present is around 750 to 500 cm^{-1}wave number.

So, this is taken from a particular paper published in Cement and Concrete Research. There are several other papers which look at FTIR as a valid means to study cement hydration and you can actually look at several other signals that are getting studied from the same type of analysis.

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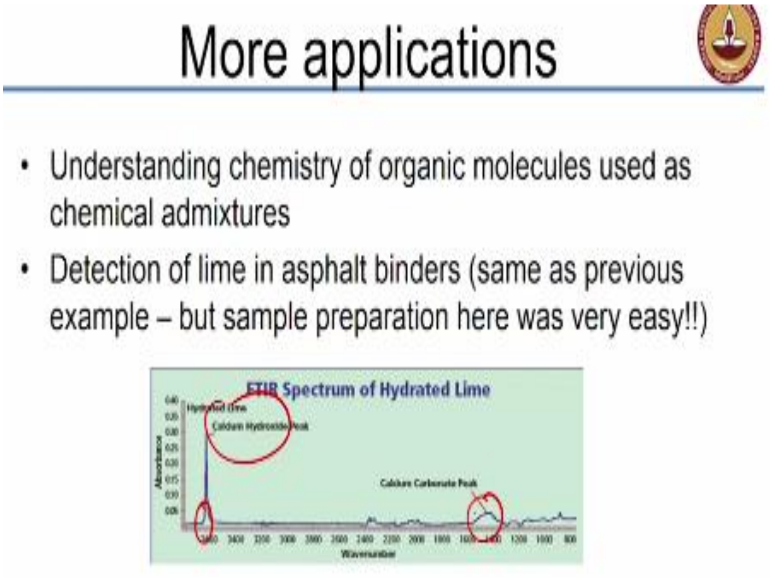

More applications

- Understanding chemistry of organic molecules used as chemical admixtures
- Detection of lime in asphalt binders (same as previous example – but sample preparation here was very easy!!)

So, again, there are more applications obviously in materials research. For example here, similar to the previous case of atomic absorption spectroscopy, the idea was to detect the presence of hydrated lime inside asphalt binders and here the determination is quite easy that calcium hydroxide or O-H stretching location was actually identified and the carbonate peak was also identified, which identified the presence of the hydrated lime and calcite in the asphalt systems.