

Characterization of Construction Materials
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Lecture – 57
Spectroscopy Techniques – FTIR and NMR Spectroscopy – Part 2

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NMR Spectroscopy



- Uses radiofrequency radiation (4 – 900 MHz) to induce transitions between different nuclear spin states of samples in a magnetic field
- Most useful for determining the structure of molecules because different atoms in a molecule experience slightly different magnetic fields and therefore transitions at slightly different resonance frequencies in an NMR spectrum.
- Furthermore, splitting of the spectra lines arise due to interactions between different nuclei, which provides information about the proximity of different atoms in a molecule.

Spin quantum number

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So, the final technique that we will talk about in this chapter of spectroscopy techniques is Nuclear Magnetic Resonance Spectroscopy. Now, this is something that some of you may have had an experience of in medical imaging. For instance, when X-ray techniques in medical imaging do not give the intended information, very often the doctors prescribe you to go and get an NMR scan or MRI scan - they call it magnetic resonance imaging. It is nothing but the same as nuclear magnetic resonance.

So, what is done in this case is that we use radiofrequency radiation to induce transitions between nuclear spin states of samples in a magnetic field. Now, you know that in the atomic structure you have nucleus in the center, and if there is an unbalanced number of neutrons and protons, the nucleus will have a spin. The greater the imbalance, the greater will be the spin quantum number. We call it the spin quantum number of different nuclei. I will just show you the examples of different types of elements in just a minute. So when there is an imbalance between neutrons and protons, you get a nuclear spin.

So, what happens is, when you apply radiofrequency radiation, this spin may change as a result of absorption of that radiation. So, the change in spin is characteristic again of a certain energy being absorbed or in other words if the spin wants to come back to its original ground state, it has to re-emit that energy and detecting that re-emitted energy will give you an idea about what kind of element was actually present in your sample. Same sort of analysis as we had in the other means of spectroscopy, all you are doing is introducing radiofrequency waves, which generate a different kind of transition in your species that are present in your sample.

So once again to recap, atomic absorption and ultraviolet-visible light led to promotion of outer shell electrons to higher orbitals. Absorption of that radiation led to outer shell electrons getting promoted to higher orbitals, whereas your IR radiation had energy only capable of introducing vibrations, molecular vibrations.

Now, we are talking about radiofrequency waves that have much longer wavelengths, as a result the energy level is even lower and they are not able to induce all those kinds of transitions that the previous examples had. So, here we are only inducing transitions which are related to spin of the nuclei when you have an electric field applied to the system. So, this is most useful for determining structure of molecules because of different atoms in a molecule which experience slightly different magnetic fields and therefore transitions at different resonance frequencies in an NMR spectrum. So, if you are again able to isolate the frequencies at which the absorption takes place, you can then characterize the type of element that you have in your sample.

So, again, if there are interactions happening between different nuclei, they will be splitting of the spectra lines and that will give you information about how close the atoms are in a molecule. So, I will show you the examples of what happens in all these cases.

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NMR Principle

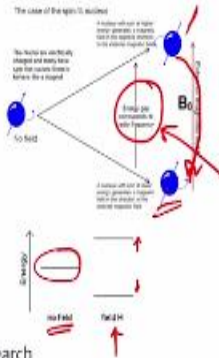


Nuclei with an odd number of protons, neutrons, or both, will have an intrinsic nuclear angular momentum or "nuclear spin".

Spin quantum number for various nuclei

Number of protons	Number of Neutrons	Spin Quantum Number (I)	Examples
Even ✓	Even ✓	0	¹² C, ¹⁶ O, ³² S
Odd ✓	Even ✓	1/2	¹ H, ¹⁹ F, ³¹ P
Even ✓	Odd ✓	1/2	¹³ C, ¹⁵ N, ¹⁷ O, ³³ S
Odd ✓	Odd ✓	1	² H, ¹⁴ N

When a nucleus with a non zero spin is placed in a magnetic field, the nuclear spin can align in either the same direction or in the opposite direction as the external magnetic field. A nucleus that has its spin aligned with the external field will have a lower energy than when it has its spin aligned in the opposite direction to the field. Thus, these two nuclear spin alignments have different energies and application of a magnetic field results in an energy level diagram shown here to the right.



²⁹Si, ²⁷Al common in cement-based materials research

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So, again, as I said nuclei with odd number of protons or neutrons or both will have an intrinsic nuclear angular momentum or "nuclear spin". So for example, if the number of protons is even, number of neutrons is even, the spin quantum number is 0, such as what you have for carbon, oxygen, or sulphur. If the number of protons is odd and neutrons is even, then the quantum number is (1/2) in certain cases like in the hydrogen atom, fluorine or phosphorus. Now, if there is a greater imbalance, again with odd and even combinations, you can have a higher spin quantum number (3/2), for example, the case of boron, chlorine, bromine, iodine, etc. You can also have even number of protons and odd number of neutrons generating similar spin quantum numbers and in some cases you have odd number of protons and neutrons and you get a spin quantum number of 1 in that case like in the hydrogen molecule or in the nitrogen molecule.

So, when a nucleus with a spin that is not 0, that means any nucleus which does not satisfy this even number of protons and neutrons condition, when such a nucleus is placed in a magnetic field, the nuclear spin can either align in the same direction of the magnetic field or reverse its direction when the external magnetic field is applied. So, where is this system placed? Now, the system is placed in a magnetic field where the nucleus can have either alignment in the spin along the magnetic field direction or reversal in the spin as compared to the magnetic field. A nucleus that has been aligned with the external field will have lower energy than when it has been aligned in opposite direction to the field. So, when you are applying the electric field and nucleus gets a spin in the same direction, it is present at a

lower energy level as opposed to the other case, which is obviously the opposite, where the nuclear spin is opposite to the external magnetic field.

So, these 2 alignments have different energies and application of magnetic field results in an energy level diagram which is shown in this case. For example, when you have no field, you have a certain energy level for your nucleus. When you apply a certain magnetic field of strength 'H', you could have two states - one is the lower state which happens when the nuclear spin is in same direction as the field and a higher state when you have nucleus which is spinning in the opposite direction of the aligned magnetic field. So, now this gap that happens exists between the low energy state and the high energy state, it corresponds to radiofrequency. So, if you want to actually bridge that gap, it can happen either by absorption of radiofrequency radiation which will bring this up to that level (lower energy nucleus to higher energy level) or it can happen because of emission of radiofrequency radiation, which will bring the higher energy nucleus back to the lower energy level. So, this gap is in the radiofrequency range and based on the different types of elements that are present in your sample, each gap between the high and low energy states will be having a very discrete value and that discrete value will obviously have a very single set radiofrequency. So with the use of radiofrequency radiation of nuclei that are subjected to magnetic field, you can then analyze what types of nuclei are generating those transitions.

So, in medical imaging what happens? You have, for instance, if you want to do an imaging of your knee, what they do is they envelope your knee in a very sophisticated, anyone has got an MRI scan done? Yeah, it is a very scary experience because they send you into this room where there is absolutely no sound coming in. It is a soundproof room and then they make you lie on this bed and send you inside this instrument and they actually envelop the location which is being scanned or totally encase it, I had my knee scanned, so I have that experience, and then what happens is the instrument then applies a very high magnetic field or specific ranges of magnetic fields to your location which is getting imaged. So, what is that in our system is we have water and we have calcium carbonate in our bones. So, there are very specific species inside, for example if you want to do bone analysis, you are basically looking at calcium or maybe you are looking at different states of your carbon and oxygen that are present in the system. So, based on that, the radiofrequencies that are generated in the magnetic field or absorbed in the magnetic field are then analyzed to detect the presence of the elemental species, and in our case, in the medical imaging case, the spectrograph is then

converted into an image. For example, if your bone density is low or if you have had a fracture in your bone or a tear in your muscle, even that can be actually imaged quite easily with an MRI scan. In the case of X-rays, your muscular tissue cannot be easily imaged. You can image bones because bones are fairly significant in terms of density as opposed to your flesh, but in MRI you can actually make distinctions of your flesh also. You can actually look at muscular orientations, muscular tears and things like that also. So, in the MRI scans, what we are simply doing is converting this entire exercise into an image which is representative of the phenomena that is being observed inside your system.

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Nuclear spin

spinning proton loop of current bar magnet

- A nucleus with an odd atomic number or an odd mass number has a nuclear spin.
- The spinning charged nucleus generates a magnetic field.

When placed in an external field, spinning protons act like bar magnets.

For more information,
https://www.nanocem.org/uploads/Modules/MCMedias/1409057876894/thesis_valor_final.pdf

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So again, a nuclear spin. So for example, if you have a spinning proton, the spinning of this charged particle, there will be some sort of a nucleus with an odd atomic number or an odd mass number has a nuclear spin. The spinning charged nucleus generates a magnetic field. So any charged particle, when it has a spin, it will generate a magnetic field. So when you place this charged particle inside a magnetic field, they can be either alignment with the external field or opposition to the external field.

So, spinning protons when they are placed in an external field start acting like magnets, you have all used horseshoe magnets, so you will understand what this is. So, for instance, if this spinning proton is placed inside this horseshoe magnet, your twisting motion may actually happen because of the external field being different compared to the internal field or you can get an alignment in this configuration where the north pole of your proton magnet, the small bar magnet, is aligned with the south pole of your external field and south pole of your proton is aligned with the north pole - that is a stable configuration or lower

energy configuration. But if this twisting leads to the other configuration that is the north-north and south-south, you know that like charges will repel as a result of which this configuration will be less stable. In other words, it will be the higher energy configuration. To make this stable, what needs to happen now? Radiation needs to be emitted, some energy needs to be lost to the surroundings to bring it back to the stable state, and that emission is in the radiofrequency range.

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Energy states and shielding

- The magnetic fields of the spinning nuclei will align either *with* the external field, or *against* the field.
- A photon with the right amount of energy can be absorbed and cause the spinning proton to flip.

Circulating electrons create an induced magnetic field that opposes the external magnetic field
Magnetic field strength must be increased for a shielded proton to flip at the same frequency.

The diagram illustrates the energy states of a proton in an external magnetic field B_0 . It shows two energy levels: the α state (lower energy) and the β state (higher energy). A transition between these states is labeled $h\nu = \Delta E$. Below this, three scenarios are shown: 1) A 'naked proton' with an effective field of 14,092.0 Gauss, absorbing a photon at 60 MHz. 2) A 'shielded proton' where circulating electrons create an induced field that opposes B_0 , resulting in a lower effective field of 14,072.0 Gauss and a lower absorption frequency of 40 MHz. 3) A 'shielded proton' where the external field is increased to 14,192.0 Gauss to compensate for the shielding, restoring the absorption frequency to 60 MHz.

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So again, magnetic fields with spinning nuclei align either with the field or against the field. A photon with the right amount of energy can be absorbed and cause the spinning proton to flip. So, the proton is spinning either with the magnetic field or opposite to that. So, if you send in a radiofrequency photon, that means a light particle into this system, it can get absorbed by the system and cause the spin to change directions. So, these absorptions are generated at specific frequencies for specific elements that you have in your sample. So, carbon will have a specific frequency, aluminum may have a specific frequency, silicon may have a specific frequency and so on.

So, these circulating electrons create an induced magnetic field. So, we know that it is not just the nucleus in the atom? We have electrons also which are orbiting the nucleus. So, when you have this magnetic field which is causing this nuclear spin to change, it has some sort of an effect of shielding by the externally present electrons that are present in the system. So, the electrons can create an induced magnetic field that opposes the external field. So, magnetic field strength must be increased for the shielded proton to flip at the same frequency. So, because of the effect of the electrons, you have to increase the strength of your

magnetic field to cause the spin transition of your element to happen at the same frequency level.

So, again, this is an example where you have just a proton which absorbs at a frequency of 60 MHz. A shielded proton does not feel the effect of the same magnetic field. So, here the magnetic field applied is 14,092 gauss, but a shielded proton because of the effect of the electrons around it does not feel the same level of magnetic field being applied around it. So, because of that, it does not really absorb this radiation coming in at 60 MHz frequency. Now, in the other case, if you increase the magnetic field by the amount that the electrons actually reverse that field, then it will start absorbing at that frequency. So, what you need to understand is, what is the influence of the electronic clouds that are over this sample? So, now what will happen if I go with samples that have much bigger atomic structures? The interference by the electronic cloud will be more, so I need to actually make adjustments in my external magnetic field to cause my proton to absorb the radiofrequency radiation.

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NMR Principle (contd.)

The energy (and thus frequency) of an NMR transition depends on the magnetic-field strength and a proportionality factor for each nucleus called the gyromagnetic ratio, γ . The frequency of a transition is given by:

$$\nu = \frac{\gamma H}{2\pi}$$

where ν is the frequency of the resonant radiation and H is the strength of the magnetic field.

Frequency is represented generally in terms of the 'Chemical Shift' in ppm, which is written as:

$$\delta = \left(\frac{\nu_{\text{sample}} - \nu_{\text{ref}}}{\nu_{\text{ref}}} \right) \times 10^6$$

The reference is usually taken as TMS (Tetramethyl silane) – unreactive with other organic compounds, volatile, and gives absorption which is mostly shielded

So, the energy of the NMR transition depends on the magnetic field and the proportionality factor for each nucleus which is called the gyromagnetic ratio (γ). So, frequency (ν) of a transition is given by:

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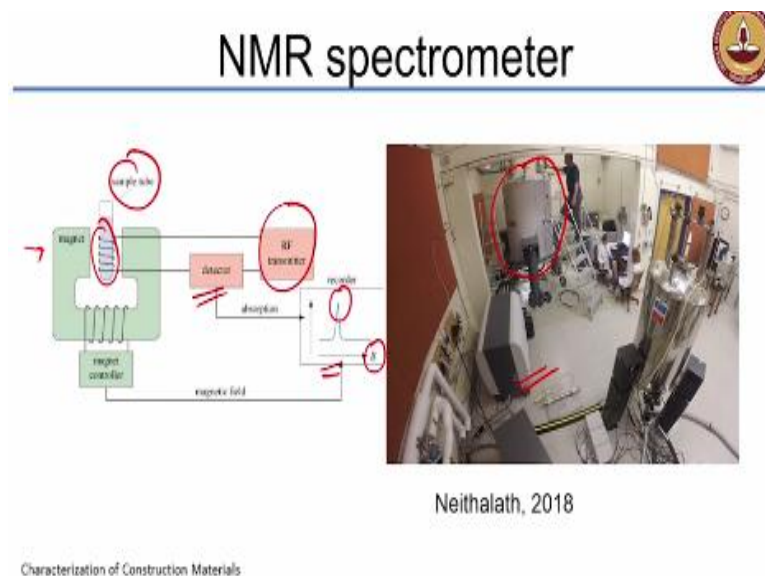
where γ is the gyromagnetic ratio; H is the applied magnetic field .

Now, what happens is as a result of the absorption or emission of the radiation, your frequency can undergo a shift. So, frequency is generally represented in terms of ‘chemical shift’, which is given as frequency of the sample expressed as a difference with the frequency of a reference.

$$\delta = \left(\frac{\nu_{sample} - \nu_{ref}}{\nu_{ref}} \right) 1 * 10^6$$

The reference typically is taken as a tetramethyl silane or TMS which is unreactive with other organic compounds and gives absorption which is mostly shielded. So, this is a typical reference frequency that is taken in your NMR systems and you represent the frequencies of the sample as a function of this frequency of the reference that is tetramethyl silane.

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So, this is your NMR spectrometer. So, this is a sample tube which is encased inside a very powerful magnet. So, what happens is you apply the magnetic field and then you have the radiofrequency transmitter, that is transmitting the specific radiofrequency radiation and the absorption of that radiation is then detected by the detector and you get the absorption spectra; you get absorbance as a function of the applied magnetic field.

So, this is again the instrument that is there. So, you see here, this is the overall system in which you have the magnet as well as the introduction the sample inside and the remaining are basically generators of the kind of magnetic field that you have. If you go again inside an MRI lab of a hospital or of a big laboratory, you will see that the instrument is fairly large , and each instrument is capable of producing different levels of magnetic fields.

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NMR experiment



- Keep external magnetic field strength constant and vary the frequency of radiation to see an absorption
- Keep the radio frequency constant and vary the field strength until splitting of spin states corresponds to energy of radio wave
- New instruments use intense RF pulse to excite all nuclei simultaneously and then FT is done

So, in the experiment what we do is we keep the external magnetic field constant and vary the frequency of radiation to see absorption. It is as simple as that. So, for constant applied external field, we vary the radiofrequency radiation that is sent into the sample to look at specific locations at which absorption takes place and this is detected by the detector.

So, the other way is to keep the radiofrequency constant and vary the field until splitting of the spin states corresponds to the energy of radio wave. What does it mean? Splitting of spin states means there is a low energy state and a high energy state, and that corresponds to the energy of a radio wave. So, incoming energy of a radio wave is equal to the energy difference between the low energy state and the high energy state. So, that is the other way of actually doing the experiment.

In new instruments, you get an intense radiofrequency pulse to excite all the nuclei simultaneously, and then we do a Fourier transform to extract all the information together. In the old instruments, again, you had to send in one radiofrequency at one time and analyze each element separately. In this case, in the new instruments, what you are doing is sending in a strong radiofrequency pulse that is a combination of several different frequencies, and you are then doing a Fourier transform of your detected signal to separate out all the elemental compositions that may be there in the system.

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NMR Signals



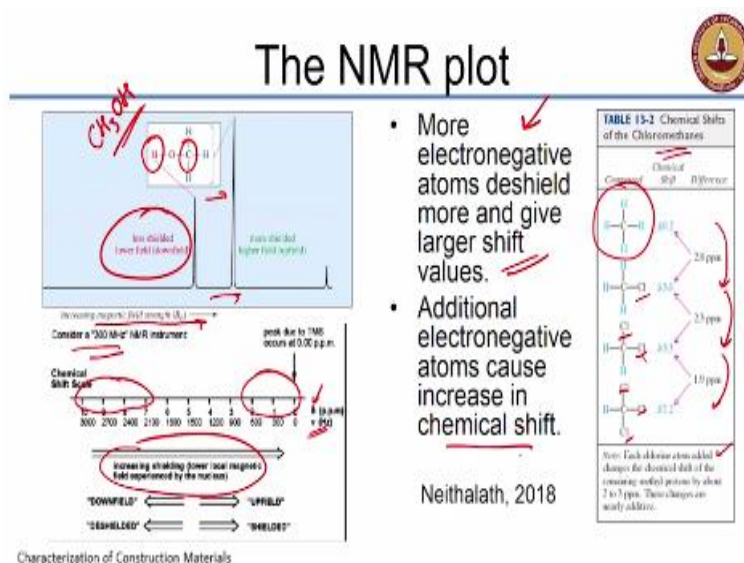
- The **number** of signals shows how many different kinds of protons are present.
- The **location** of the signals shows how shielded or deshielded the proton is.
- The **intensity** of the signal shows the number of protons of that type.
- Signal **splitting** shows the number of protons on adjacent atoms.

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Now, the signals can be interpreted in several ways.

- The number of signals shows how many different types of protons are present.
- The location of the signals can indicate how shielded or deshielded the proton is. So, location implies position with respect to the magnetic field. So, the higher the shielding, the greater will be the applied magnetic field; lower the shielding, the lesser will be the magnetic field.
- The intensity of the signal shows the number of protons of that type. If there are more number of protons of a specific element, then you get higher intensities shown by the spectra that you see from NMR.
- Signal splitting shows the number of protons on adjacent atoms. Again, I will show you some examples of signals that will make it clearer.

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So, this is the NMR plot. What is plotted here is in terms of increasing magnetic field strength. As I said, when you have less shielding, you get a peak earlier, when you have more shielding, you get a peak later. That means at higher magnetic fields, you are producing the peaks when there is more shielding in your system. So, here a very simple structure is chosen, that is CH₃OH, what is this? Methyl alcohol or methanol, CH₃OH or it is otherwise known in newspapers as hooch. This is a major killer in our country. A lot of people consume this thinking that it is ethyl alcohol, but this is poisonous, it can actually effect death in very fast time.

So this is CH₃OH or methanol, and you can see here that the carbon is better shielded in this case because there are several hydrogen atoms around it. In this case, your hydrogen is exposed and not really getting shielded very well. So, what happens is the peak shows upward or up field, higher strength of the magnetic field to show the same location of the atom. So, if you consider a specific frequency in the NMR instrument like 300 MHz, what we are trying to see is how increased shielding gets represented in the typical NMR spectrum. As I said earlier NMR spectra is typically represented in terms of the peak shift δ which is represented as the difference of the frequency of this proton minus the frequency of the reference sample.

So, here for instance, the frequency in Hz is also given and the shift δ is also given. So, when you have more shielding, you show lesser shift, and when you have lesser shielding, you show a higher shift in your NMR spectra. So, for instance, in chloromethanes,

so here this is just methane, now you have single chlorine replacing the hydrogen atom, here you have 2 chlorines with the hydrogen atom, you have 3 chlorines here. So, all you are doing is increasing the level of substitution of hydrogen with chlorine, so you are forming different types of chloromethanes. So, each chlorine atom added changes the chemical shift of the remaining methyl protons by about 2 to 3 parts per million (ppm) because more and more electronegative atoms are shielding more and giving larger shift values. So again, your shift is changing from 0.2 to 3, to 5.3, and finally to 7.2 as you replace your hydrogen with chloride atoms in the case of chloromethanes. So, what will happen is when you try to detect chloromethane with NMR spectroscopy, you will be able to detect the extent of chlorine present in the system by looking at the positions of the shift. So, there is an increase in chemical shift when you have additional electronegative atoms here. In this case, chlorine obviously is an electronegative atom and you are tending to shift more and more and that helps you to actually understand where to detect different states of chlorine, which are substituted in the methane structure.

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Magic Angle Spinning (MAS)

- By spinning the sample (usually at a frequency of 1 to 130 kHz) at the magic angle θ_m (ca. 54.74^\circ, where $\cos^2\theta_m = 1/3$) with respect to the direction of the magnetic field, the normally broad lines become narrower, increasing the resolution for better identification and analysis of the spectrum
- Used in solid state NMR

MAS-NMR

Wikipedia

Now, in some cases, you may come across NMR instruments that are characterized as MAS or Magic Angle Spinning NMRs. So what we do here is this we spin the sample usually at a frequency of 1 to 130 kHz at the magic angle θ_m , which is approximately about 54.74° , with respect to the direction of the magnetic field. So, we have the sample kept at a specific angle with respect to the magnetic field direction. What happens here is the normally broad lines become narrower and we increase the resolution of the spectrum. So in many cases, you will actually see MAS-NMR being done. So, all we are trying to do is we are making these

frequency transitions more precise instead of having a broad signal, we are getting a more precise signal in MAS-NMR. We use this significantly in solid state NMR spectroscopy.

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C-S-H's NMR Spectra



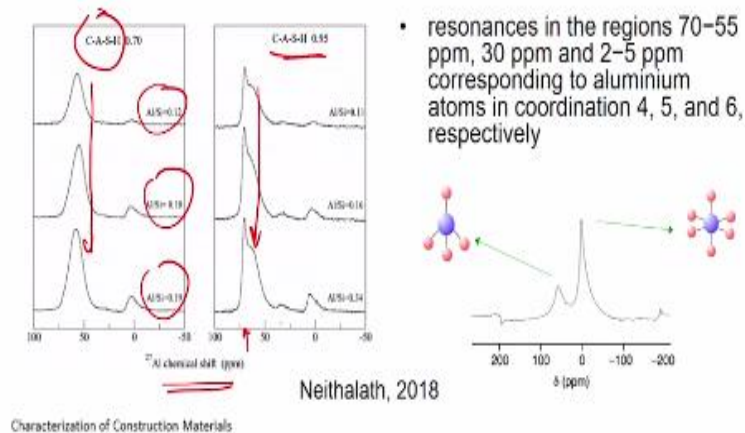
- Frequency of 59.59 MHz for ²⁹Si (magnetic field of 11.72 T) and a frequency of 130.4 MHz for ²⁷Al
- Software enables several NMR spectra to be decomposed simultaneously using the same spectral parameters for each individual component across the collected data.
- Relative intensity of some components can be fixed to agree with the proportion of the corresponding sites in the structural model of the material.
- For ²⁹Si spectra, choosing each component as a mixture of a Gaussian (bell curve) and a Lorentzian (sharp peak) function is an acceptable method

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So, again just to give you an example, let us say we want to analyze calcium silicate hydrate. So, what we have with respect to calcium silicate hydrate are different types of states. As the hydration progresses, there is an increased degree of chain linking in the C-S-H structure. Many of you would have understood the C-S-H structure is actually composed of sheets of silicates. The greater lengths of the sheets are created by progressive states of hydration. So, a frequency of 59 MHz for silica is chosen and a frequency 130 MHz is chosen for alumina. So, we can either do silicon NMR or aluminum NMR at different frequencies to try and understand the state of the C-S-H in the system. So, what happens is the software can actually help us to deconvolute the NMR spectra and analyze each individual component separately.

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^{27}Al NMR Spectra



So, just to give you an example of how aluminum NMR (^{27}Al NMR) spectra is used to actually understand the structure of calcium aluminosilicate hydrate. So, there are 3 different systems which are given here and what is represented in the X-axis is the aluminum chemical shift. So, at different aluminium to silica (Al/Si) ratios, you see that the chemical shift is actually changing or the peak intensity is actually changing as you increase the Al/Si ratio from 0.12 to 0.19. This is for a measurement on calcium aluminosilicate hydrate at a water-cement ratio of 0.7. This is again at $w/c = 0.95$ and again you are seeing an increase in the intensity of the peak that is located at the specific chemical shift that corresponds to the state of the aluminum present inside the calcium aluminosilicate hydrate. We will continue from here in the next lecture.