Characterization of Construction Materials
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Lecture 22
X Ray Diffraction_ Sample Preparation and Application in study of cements _ Part 2

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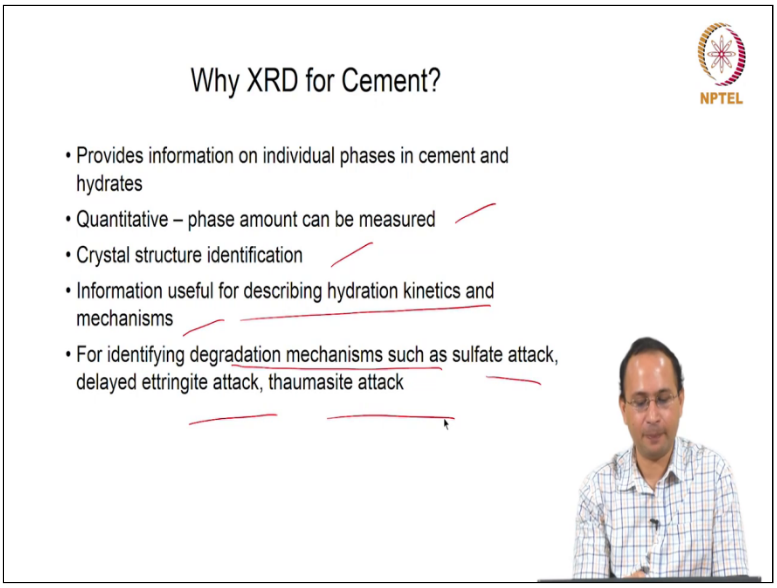

Why XRD for Cement?

- Provides information on individual phases in cement and hydrates
- Quantitative – phase amount can be measured
- Crystal structure identification
- Information useful for describing hydration kinetics and mechanisms
- For identifying degradation mechanisms such as sulfate attack, delayed ettringite attack, thaumasite attack

So now, we will look into the application of XRD in cement-based materials. So, why is XRD used for cement? It provides information on individual phases in cement and hydrates. You can find out what you have in cement, what you have in hydrates. Quantitative phase analysis can be done, we have seen that. This also we have seen crystal structure determination, this all goes back to the principles of X-ray diffraction.

Also we can use that information to describe hydration kinetics. You can monitor the hydration kinetics and mechanism. And also we can use it to identify the degradation mechanisms such as sulphate attack, delayed ettringite attack and thaumasite attacks. These are few examples.

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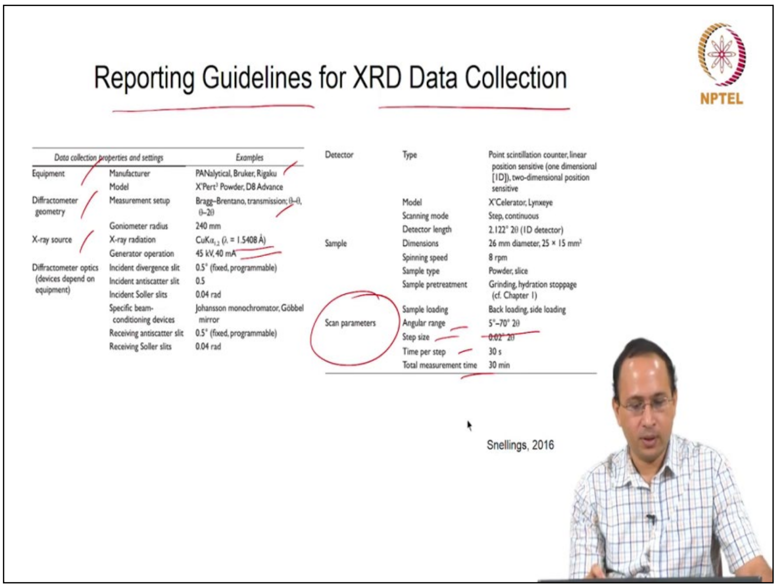

Reporting Guidelines for XRD Data Collection

Data collection properties and settings		*Examples*
Equipment	Manufacturer	PANalytical, Bruker, Rigaku
	Model	X'Pert³ Powder, D8 Advance
Diffractometer geometry	Measurement setup	Bragg–Brentano, transmission; θ–θ, θ–2θ
	Goniometer radius	240 mm
X-ray source	X-ray radiation	CuK$\alpha_{1,2}$ (λ = 1.5408 Å)
	Generator operation	45 kV, 40 mA
Diffractometer optics (devices depend on equipment)	Incident divergence slit	0.5° (fixed, programmable)
	Incident antiscatter slit	0.5
	Incident Soller slits	0.04 rad
	Specific beam-conditioning devices	Johansson monochromator, Göbbel mirror
	Receiving antiscatter slit	0.5° (fixed, programmable)
	Receiving Soller slits	0.04 rad
Detector	Type	Point scintillation counter, linear position sensitive (one dimensional [1D]), two-dimensional position sensitive
	Model	X'Celerator, Lynxeye
	Scanning mode	Step, continuous
	Detector length	2.122° 2θ (1D detector)
Sample	Dimensions	26 mm diameter, 25 × 15 mm²
	Spinning speed	8 rpm
	Sample type	Powder, slice
	Sample pretreatment	Grinding, hydration stoppage (cf. Chapter 1)
Scan parameters	Sample loading	Back loading, side loading
	Angular range	5°–70° 2θ
	Step size	0.02° 2θ
	Time per step	30 s
	Total measurement time	30 min

Snellings, 2016

So, how do you report this X-ray data collection? So you have to get the X-ray diffraction pattern from X-ray diffractometer. So usually what you see when you read any paper or even if you have carried out your work, these are the things you have to report. Either in publication or in a report, you have to report what equipment you used, what was the geometry, what was the X-ray source, what was its wavelength, because that will affect your diffraction pattern if you use different wavelength that will also affect the peak position. We know that it is all related to 'λ'.

So these are the things you have to keep in mind when you report the data, or you see the data you will see that this data was obtained using this instrument, for this geometry, with this wavelength, things like that. Then, scanning parameters are very important. What are the step size, scanning rate, measuring time, 2θ range, in this case you see 2θ range of 5° to 7°. So these are the common things you have to report.

These are the ways you load samples. We did not go in detail, back-loading as I said, you flip your sample and then load it. Side is side again. So there are different ways to load the samples. You obviously have to make a compact sample.

But also you have to make sure that there is no preferred orientation. Depending on the sample, you may not even have preferred orientation but since we are talking about the cement system where you have calcium hydroxide and Ettringite, you tend to see preferred orientation.

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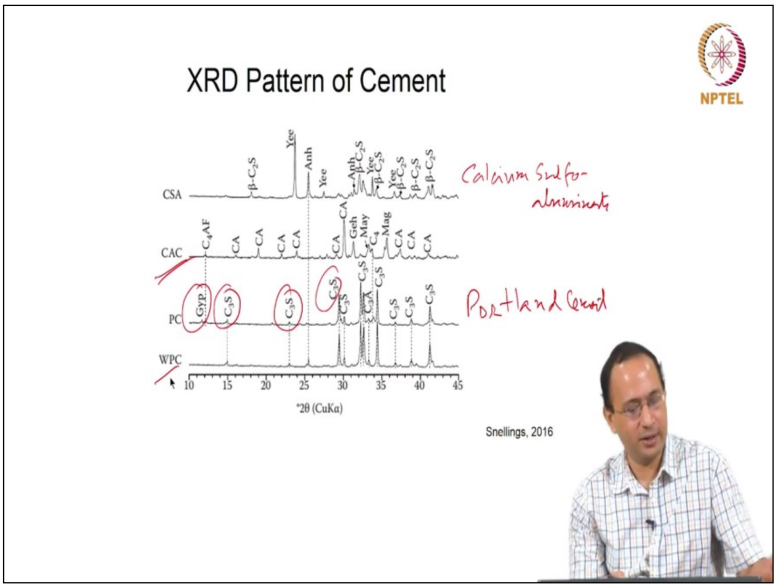

XRD Pattern of Cement

Snellings, 2016

So, what does a typical X-ray pattern of cement look like? So obviously we have plotted here different types of cement (Diagram in slide). So let us look at the PC. You are familiar with the Portland cement. This is the PC - Portland cement. You see different peaks that tell you what kind of phases are present in your cement. Gypsum, C3S, this is Alite, C3S, you have C2S. So these are the major peaks.

We are seeing in different cements. So, this is CSA cement, calcium sulfoaluminate cement. The idea is you can get an idea about the phases present in your cements. If you resolve all the peaks, you will be able to tell what the phases are and depending on the system you will have different phases.

This is CAC - Calcium aluminate cement, and this is WPC - White Portland cement. So, you can get an idea about the phases present in your cement by looking at X-ray diffraction pattern.

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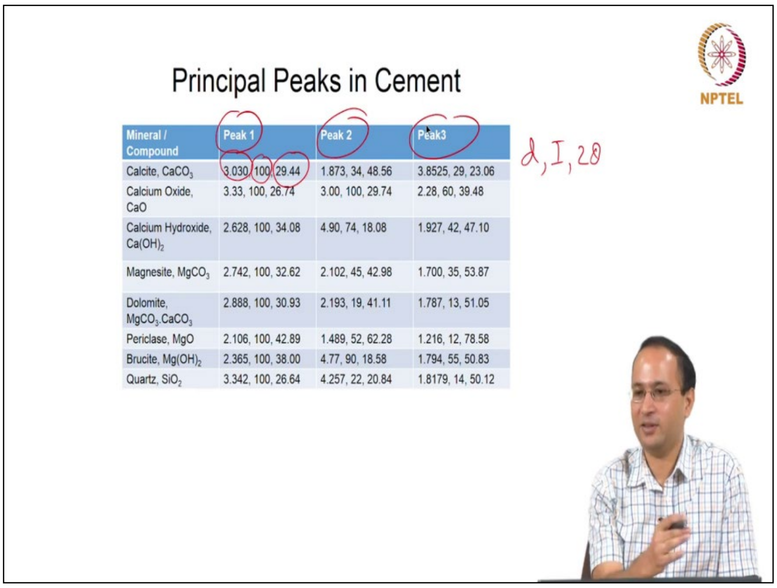

Principal Peaks in Cement

Mineral / Compound	Peak 1	Peak 2	Peak3
Calcite, $CaCO_3$	3.030, 100, 29.44	1.873, 34, 48.56	3.8525, 29, 23.06
Calcium Oxide, CaO	3.33, 100, 26.74	3.00, 100, 29.74	2.28, 60, 39.48
Calcium Hydroxide, $Ca(OH)_2$	2.628, 100, 34.08	4.90, 74, 18.08	1.927, 42, 47.10
Magnesite, $MgCO_3$	2.742, 100, 32.62	2.102, 45, 42.98	1.700, 35, 53.87
Dolomite, $MgCO_3.CaCO_3$	2.888, 100, 30.93	2.193, 19, 41.11	1.787, 13, 51.05
Periclase, MgO	2.106, 100, 42.89	1.489, 52, 62.28	1.216, 12, 78.58
Brucite, $Mg(OH)_2$	2.365, 100, 38.00	4.77, 90, 18.58	1.794, 55, 50.83
Quartz, SiO_2	3.342, 100, 26.64	4.257, 22, 20.84	1.8179, 14, 50.12

d, I, 2θ

What are the principal peaks? So this is a table, and you can see often these kinds of phases, like Calcite ($CaCO_3$) for an example, calcium carbonate. So, first is the‘d’ value, second is intensity, and then 2θ. Basically, it is in the order d, I, 2θ. So you have a pattern, this is the X-ray diffraction pattern of calcite and this is the strongest peak (peak 1), second strongest (Peak 2), and the third strongest (Peak 3).

This gives you an idea what are the possible phases, principal peaks in the cements. Three peaks, you should always check for at least three peaks when you want to make sure a particular phase is there.

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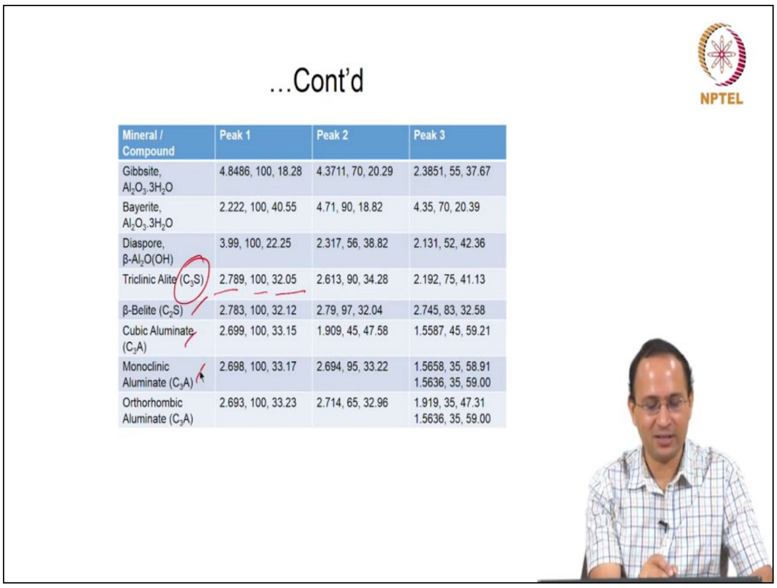

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Mineral / Compound	Peak 1	Peak 2	Peak 3
Gibbsite, $Al_2O_3.3H_2O$	4.8486, 100, 18.28	4.3711, 70, 20.29	2.3851, 55, 37.67
Bayerite, $Al_2O_3.3H_2O$	2.222, 100, 40.55	4.71, 90, 18.82	4.35, 70, 20.39
Diaspore, β-$Al_2O(OH)$	3.99, 100, 22.25	2.317, 56, 38.82	2.131, 52, 42.36
Triclinic Alite (C_3S)	2.789, 100, 32.05	2.613, 90, 34.28	2.192, 75, 41.13
β-Belite (C_2S)	2.783, 100, 32.12	2.79, 97, 32.04	2.745, 83, 32.58
Cubic Aluminate (C_3A)	2.699, 100, 33.15	1.909, 45, 47.58	1.5587, 45, 59.21
Monoclinic Aluminate (C_3A)	2.698, 100, 33.17	2.694, 95, 33.22	1.5658, 35, 58.91 1.5636, 35, 59.00
Orthorhombic Aluminate (C_3A)	2.693, 100, 33.23	2.714, 65, 32.96	1.919, 35, 47.31 1.5636, 35, 59.00

So you can go over this list. You see C3S (tricalcium silicate). So, the primary peak is, the strongest peak is at 32° (2θ), you see Belite C2S. C3A has three forms - cubic, monoclinic, orthorhombic crystal structures.

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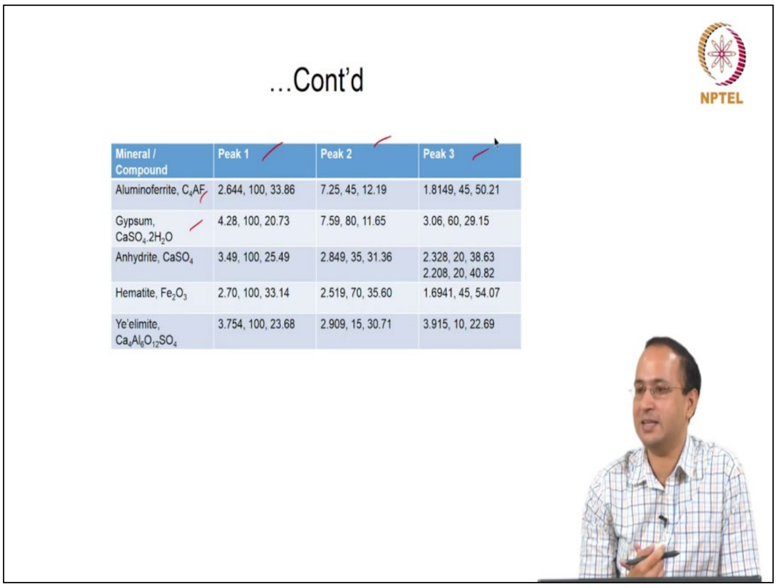

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Mineral / Compound	Peak 1	Peak 2	Peak 3
Aluminoferrite, C_4AF	2.644, 100, 33.86	7.25, 45, 12.19	1.8149, 45, 50.21
Gypsum, $CaSO_4.2H_2O$	4.28, 100, 20.73	7.59, 80, 11.65	3.06, 60, 29.15
Anhydrite, $CaSO_4$	3.49, 100, 25.49	2.849, 35, 31.36	2.328, 20, 38.63 2.208, 20, 40.82
Hematite, Fe_2O_3	2.70, 100, 33.14	2.519, 70, 35.60	1.6941, 45, 54.07
Ye'elimite, $Ca_4Al_6O_{12}SO_4$	3.754, 100, 23.68	2.909, 15, 30.71	3.915, 10, 22.69

C4AF, gypsum. So, these are the common phases you encounter in your cement. You can identify your phases based on the peak positions. Also you can see how the intensity is varying.

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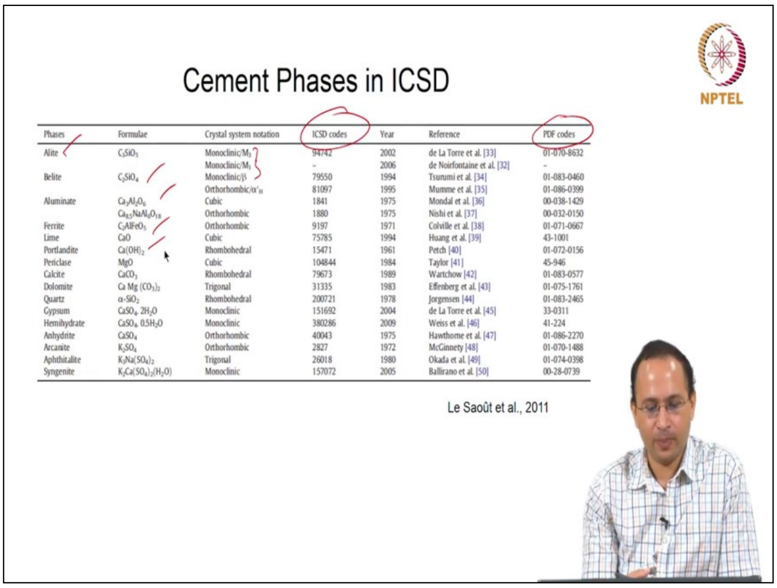

Cement Phases in ICSD

Phases	Formulae	Crystal system notation	ICSD codes	Year	Reference	PDF codes
Alite	C_3SiO_5	Monoclinic/M_3	94742	2002	de La Torre et al. [33]	01-070-8632
		Monoclinic/M_1	-	2006	de Noirfontaine et al. [32]	-
Belite	C_2SiO_4	Monoclinic/β	79550	1994	Tsurumi et al. [34]	01-083-0460
		Orthorhombic/α'_H	81097	1995	Mumme et al. [35]	01-086-0399
Aluminate	$Ca_3Al_2O_6$	Cubic	1841	1975	Mondal et al. [36]	00-038-1429
	$Ca_{8.5}NaAl_6O_{18}$	Orthorhombic	1880	1975	Nishi et al. [37]	00-032-0150
Ferrite	C_2AlFeO_5	Orthorhombic	9197	1971	Colville et al. [38]	01-071-0667
Lime	CaO	Cubic	75785	1994	Huang et al. [39]	43-1001
Portlandite	$Ca(OH)_2$	Rhombohedral	15471	1961	Petch [40]	01-072-0156
Periclase	MgO	Cubic	104844	1984	Taylor [41]	45-946
Calcite	$CaCO_3$	Rhombohedral	79673	1989	Wartchow [42]	01-083-0577
Dolomite	$Ca\,Mg\,(CO_3)_2$	Trigonal	31335	1983	Effenberg et al. [43]	01-075-1761
Quartz	α-SiO_2	Rhombohedral	200721	1978	Jorgensen [44]	01-083-2465
Gypsum	$CaSO_4.\,2H_2O$	Monoclinic	151692	2004	de La Torre et al. [45]	33-0311
Hemihydrate	$CaSO_4.\,0.5H_2O$	Monoclinic	380286	2009	Weiss et al. [46]	41-224
Anhydrite	$CaSO_4$	Orthorhombic	40043	1975	Hawthorne et al. [47]	01-086-2270
Arcanite	K_2SO_4	Orthorhombic	2827	1972	McGinnety [48]	01-070-1488
Aphthitalite	$K_3Na(SO_4)_2$	Trigonal	26018	1980	Okada et al. [49]	01-074-0398
Syngenite	$K_2Ca(SO_4)_2(H_2O)$	Monoclinic	157072	2005	Ballirano et al. [50]	00-28-0739

Le Saoût et al., 2011

Again, if you are doing quantitative analysis you want to get the appropriate PDFs – Powder diffraction file. These are some common PDF codes. Also you see ICSD codes for the phases present in the cement - depending on its crystal systems you have different files. Alite (C3S), Belite, Aluminate , Ferrite, Portlandite. So, these are the common phases present.

And when you do quantitative analysis, you have to get these files from the database. This will be useful when you have to look for the phases; you can just get these PDFs then see if it matches with what you have in your sample.

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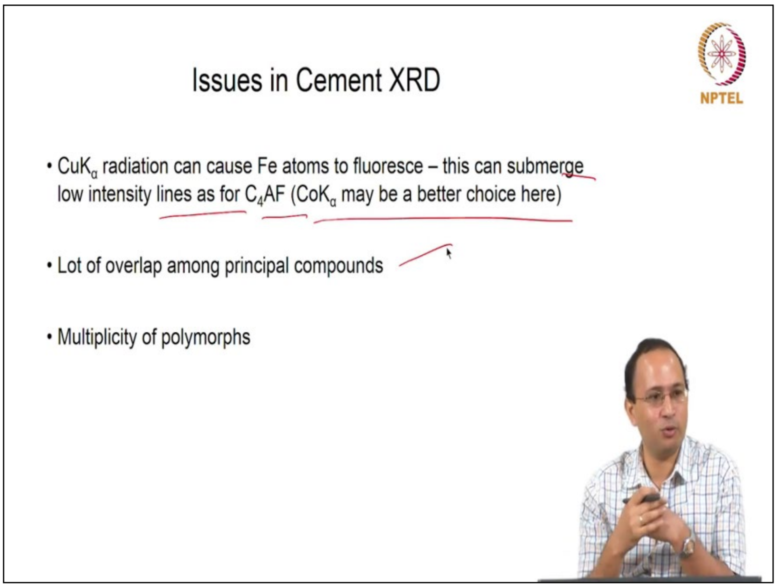

Issues in Cement XRD

- CuK_α radiation can cause Fe atoms to fluoresce – this can submerge low intensity lines as for C_4AF (CoK_α may be a better choice here)
- Lot of overlap among principal compounds
- Multiplicity of polymorphs

So, what are the issues in cement XRD? See, Copper K alpha radiation (CuK_α) can cause iron (Fe) atoms to fluoresce. So, this can submerge low intensity lines as for C_4AF. So, Cobalt K_α is another example; CoK_α may be a better choice here. There is a lot of overlap among principal compounds, when you actually look at your X-ray diffraction pattern you will see lot of overlap. Also you have a multiplicity of polymorphs.

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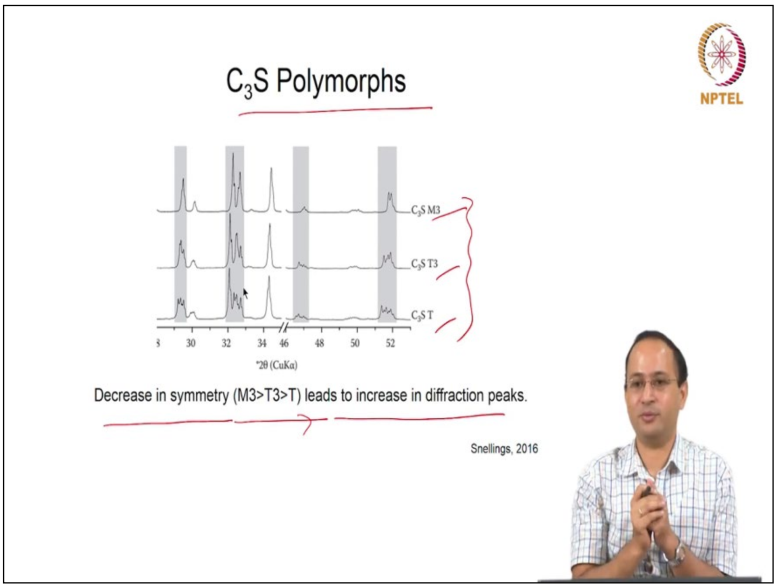

C_3S Polymorphs

Decrease in symmetry (M3>T3>T) leads to increase in diffraction peaks.

Snellings, 2016

What do you mean by, so C_3S for an example right has three - monoclinic M3, T3, T, depending on the temperature, you have these polymorphs and through XRD you can detect that. See the X-ray diffraction pattern, what are the changes? T means Triclinic, M is Monoclinic. So, decrease in the symmetry (M3>T3>T) usually leads to increase in diffraction peaks.

So, if you look at the triclinic, you see more peaks compared to monoclinic. So, idea is you can use this X-ray diffraction pattern to identify these polymorphs.

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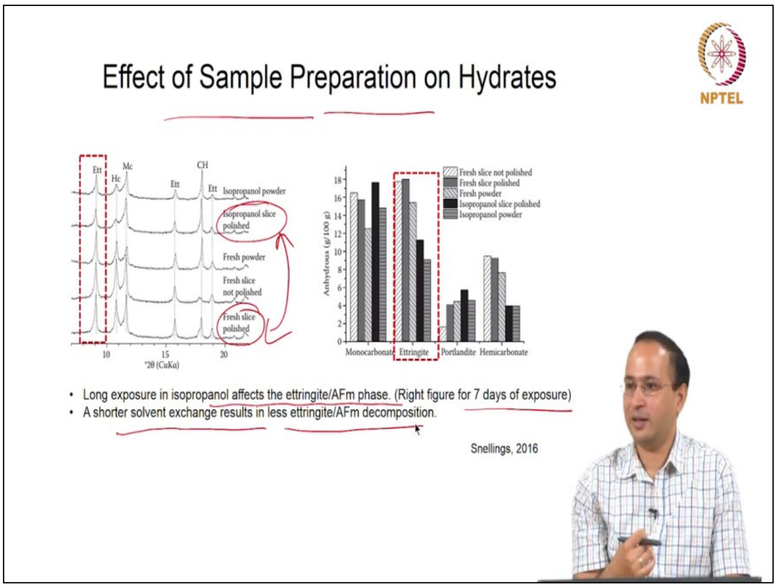

Effect of Sample Preparation on Hydrates

- Long exposure in isopropanol affects the ettringite/AFm phase. (Right figure for 7 days of exposure)
- A shorter solvent exchange results in less ettringite/AFm decomposition.

Snellings, 2016

We are looking at now application. So, one thing is X-ray diffraction can be used for phase identification. X-ray diffraction can be used to identify the polymorphs. Also you can study or you can use X-ray diffraction to examine effect of sample preparation. If you want to compare different techniques you want to see which one is better, which one is worse you can use the X-ray diffraction.

So, here you see an example where we have compared you see on the left plot X-ray diffraction, fresh slice polished, so, the way you treat your sample. When you use solvent exchange, for an example, isopropanol slice polished. So, the only difference between these two samples is: one is treated with isopropanol, and one is not. So, what do you see? If you look at the Ettringite peak, the intensity has reduced significantly.

So, you can just using X-ray diffraction you can tell that your Ettringite phase may have gotten affected through this treatment. So, you can quantify it also, on the right plot, you see here we have anhydrous amounts. So, you can see how the sample preparation affects your amount. But again, this long exposure of isopropanol affects the ettringite/AFm phases.

You see here, this was for seven days of exposure, when you expose your sample for long time, which tells you that maybe that is not good if you want to study the phases like ettringite. So a shorter solvent exchange results in less ettringite and AFm decomposition. So, basic idea is you can use this simple X-ray diffraction technique to understand the effect of sample preparation.

You can compare different techniques and then find out which one will be best for your research or your work.

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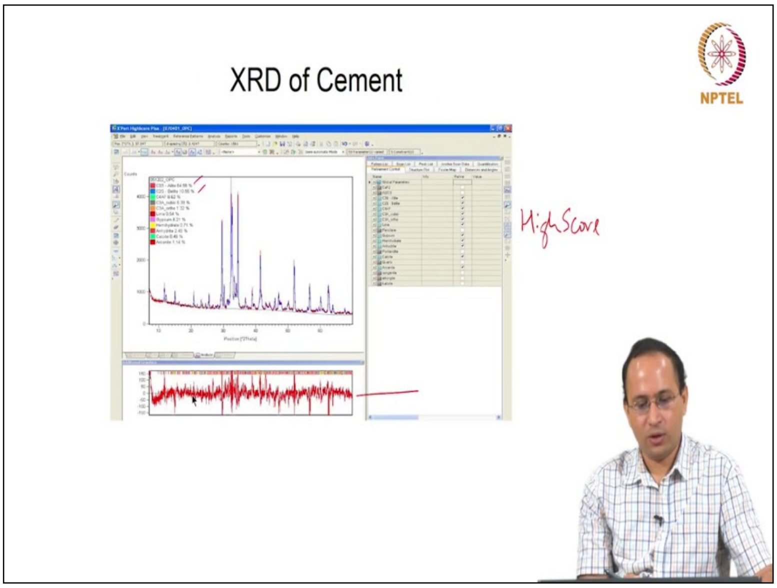

XRD of Cement

This is again X-ray diffraction of cement. You see here this is HighScore Plus software which was used here. Then, you can see different phases, when you do quantitative analysis, it can give you the different phases like C_3S, C_2S, C_4AF. How much of these phases are present. This is again Rietveld analysis. You can identify all the phases. This is the difference plot, I mean idea in Rietveld refinement is you are minimizing the error between observed and calculated intensity.

If it is very small within the error, how do we judge is, Goodness-of-Fit. You want to reduce that.

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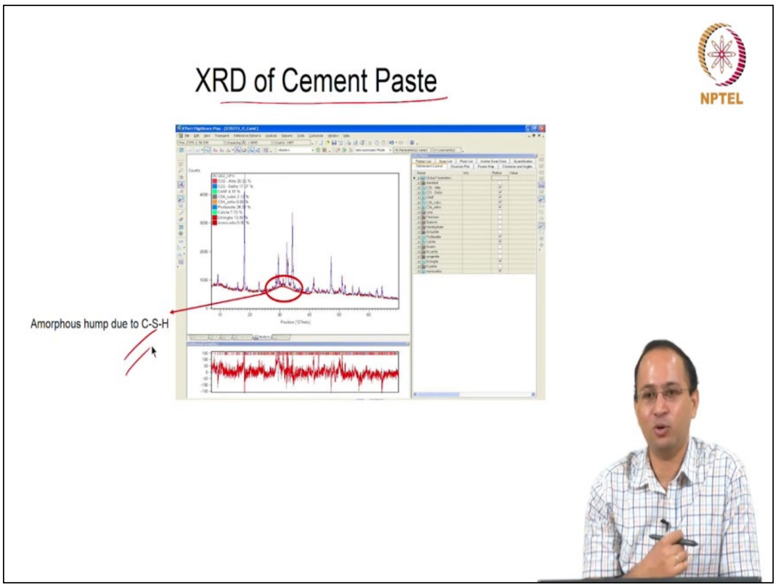
XRD of Cement Paste

Amorphous hump due to C-S-H

So, what happens when you carry out X-ray diffraction of cement paste, you start seeing this hump at around 29°. This is amorphous hump primarily because of the calcium silicate hydrate, because calcium silicate hydrate is the main phase you get during the hydration of cement. But unfortunately it is not perfectly crystalline, it's a nano crystalline phase. You do not get a sharp peak. That poses a challenge in quantification.

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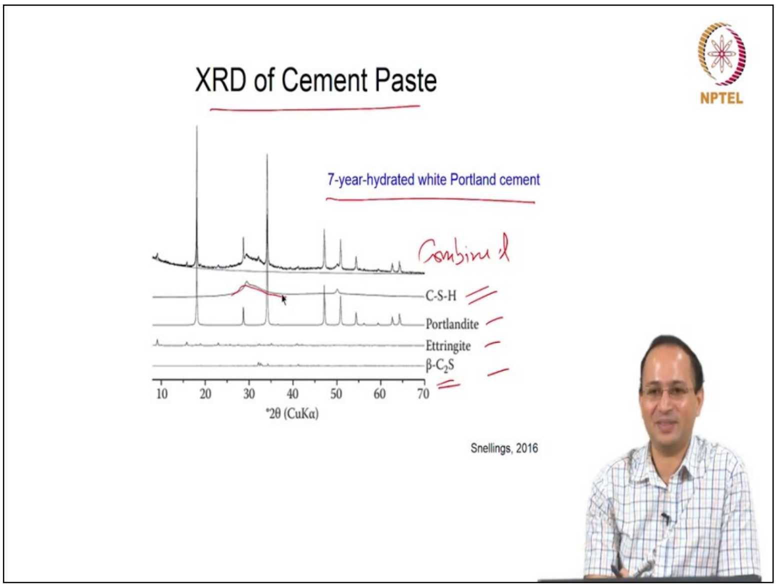
XRD of Cement Paste

7-year-hydrated white Portland cement

Snellings, 2016

Also here, if you look at the X-ray diffraction, this is the X-ray diffraction of 7-year hydrated white Portland cement. So, what is white Portland cement? How do you get white Portland cement? Without iron. Everyone knows what white cement, white Portland cement is. So, obviously it has white colour. So yes, it does not have iron. So in this test, what they did is to let it hydrate for 7 years.

It is 7-year hydrated white Portland cement. So, obviously you will see most of your phases like C_3S have hydrated. So, you have a C-S-H so, these are different phases - pure phases. So you have the combined pattern - the topmost is the combined. This is the combination of these phases. You see some C_2S, because C_2S is anyway slow in reacting. So, you have some Ettringite, Portlandite and you see the C-S-H, you see this kind of not sharp peak. Again it shows you that the complex nature of the hydrates.

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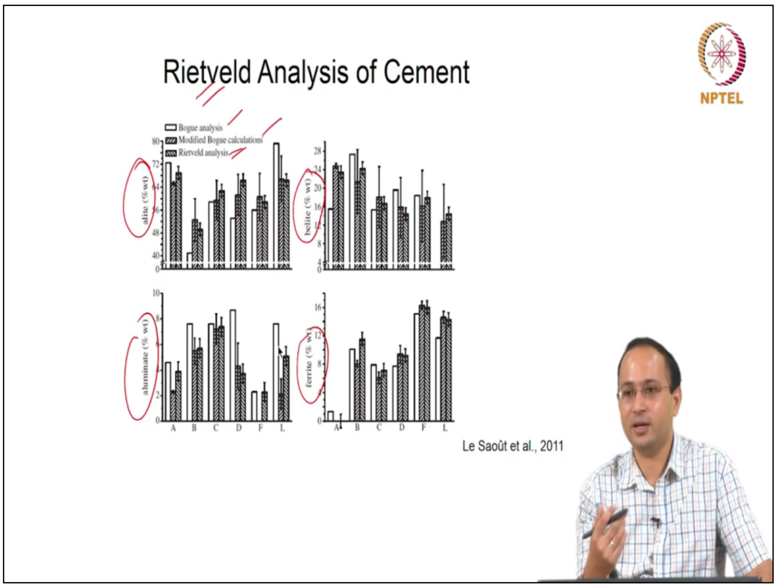

Rietveld Analysis of Cement

Le Saoût et al., 2011

Using quantitative X-ray diffraction, for an example, Rietveld, you can determine the various phases. In this case, you have different cements where you have compared the Bogue analysis. You know that you can also get the phase assemblage using Bogue formulation. This is a modified Bogue formulation. This is a Rietveld analysis. So, there is a very close agreement between modified Bogue calculation and Rietveld analysis.

You can identify all major phases Alite, Belite, Aluminate and Ferrite. That is the application of X-ray diffraction; you can quantify your phases.

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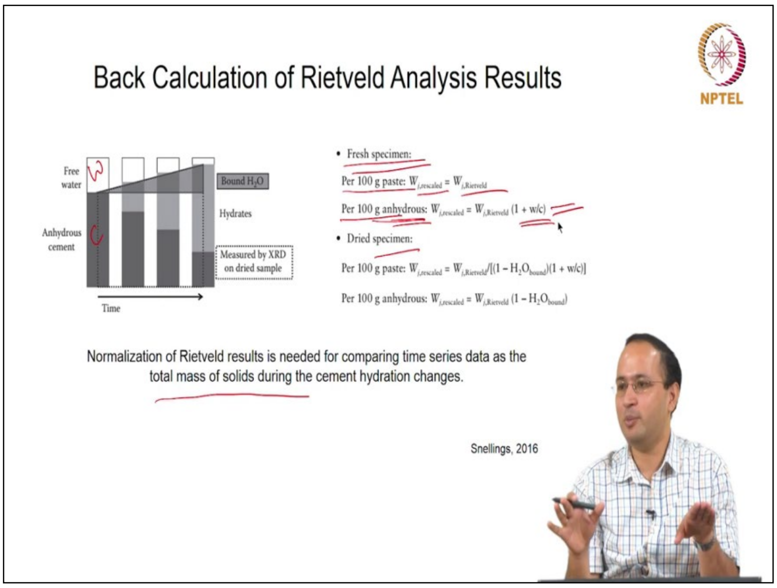

Back Calculation of Rietveld Analysis Results

- Fresh specimen:

Per 100 g paste: $W_{j,\text{rescaled}} = W_{j,\text{Rietveld}}$

Per 100 g anhydrous: $W_{j,\text{rescaled}} = W_{j,\text{Rietveld}}\,(1 + w/c)$

- Dried specimen:

Per 100 g paste: $W_{j,\text{rescaled}} = W_{j,\text{Rietveld}}/[(1 - H_2O_{\text{bound}})(1 + w/c)]$

Per 100 g anhydrous: $W_{j,\text{rescaled}} = W_{j,\text{Rietveld}}\,(1 - H_2O_{\text{bound}})$

Normalization of Rietveld results is needed for comparing time series data as the total mass of solids during the cement hydration changes.

Snellings, 2016

What one important thing to keep in mind, when you are looking at the cement it is fine, no problem. But when you are looking at the paste when you are comparing 7 days old paste versus 28 days old paste or 7 days old concrete versus 28 days old concrete, what is the difference? The difference is the degree of hydration. So, what essentially happens, you know, you start with your cement here, this is water (White portion marked in diagram), you are adding some water.

Then, cement will hydrate. The amount of the solids will change; your part of cement will convert to C-S-H, calcium silicate hydrate. So your solids will change here. So, when you are comparing, you have to normalize it. So, normalization of Rietveld results is needed for comparing time series data. If you are comparing 3 day versus, 7 day versus, 28 day, then you have to make sure you have a proper normalization.

You cannot just take values from Rietveld analysis. So, you have to back calculate. So this gives you some formulas you can use. If you have a fresh sample, you can normalize it by paste or by anhydrous amount and rescale. Rescale means the rescaled values. So, obviously fresh sample, fresh samples and per paste, your rescale value is close to Rietveld value. But when you take into account anhydrous, when you normalize it by anhydrous, your water-cement ratio plays a role.

Dried sample - these are the formulas you can use. The idea is your degree of hydration is changing, your mass of solids is changing, so you have to take that into account using these relationships you can normalize it. And then, you will be able to compare.

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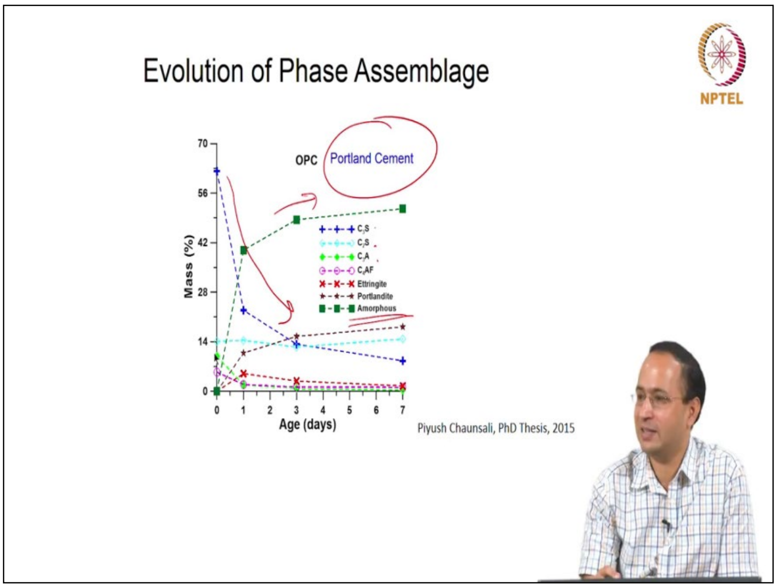

Evolution of Phase Assemblage

Piyush Chaunsali, PhD Thesis, 2015

We can use X-ray diffraction to monitor the hydration progress. So, in this case you see hydration of Portland cement, what do we expect? The C_3S will decrease in the amount, C-S-H will increase or amorphous phase will increase. In this case you have plotted various phases like C_3S, C_2S, C_3S, and C4AF, what happens to these phases? So, phases which are reacting, they will decrease, and phases which are forming, they will increase. So, you can monitor the hydration using X-ray diffraction.

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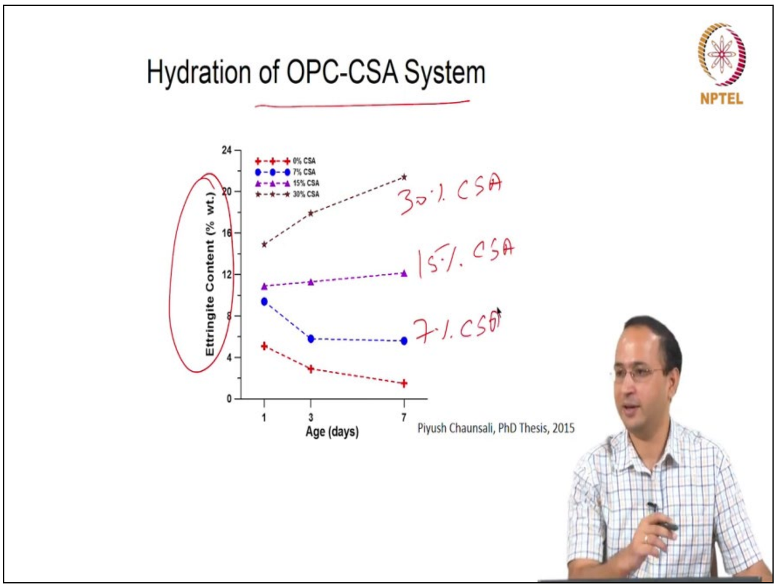

Hydration of OPC-CSA System

Piyush Chaunsali, PhD Thesis, 2015

This is again application of XRD to understand the hydration of OPC-CSA system. OPC-CSA is Portland cement, calcium sulfoaluminate system. So, you can monitor the amount of, in this case, ettringite with the time so you see when you have 30% CSA, ettringite is much more than other (15%, 7%, 0%). So you can compare different systems, here you see the example of quantification of ettringite.

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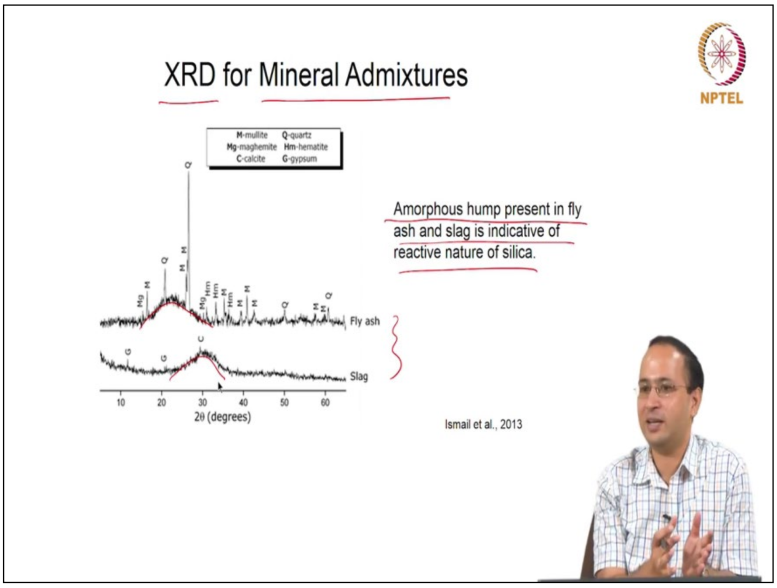

XRD for Mineral Admixtures

Amorphous hump present in fly ash and slag is indicative of reactive nature of silica.

Ismail et al., 2013

Now, you know that we use mineral admixtures, in our concrete. So, we can also study mineral admixtures. In this case you see comparison between fly ash and slag. So, amorphous hump present in fly ash and slag is indicative of reactive nature of silica. So, in fly ash you see that this amorphous hump usually is between 20°-30°. So, when you see this kind of hump, first thing which should come to your mind is amorphous nature which we can use.

That is the reason we use fly ash, because then fly ash dissolves, it releases silica, reacts with calcium hydroxide and forms calcium silicate hydrate. So, this XRD can give you insight about that.

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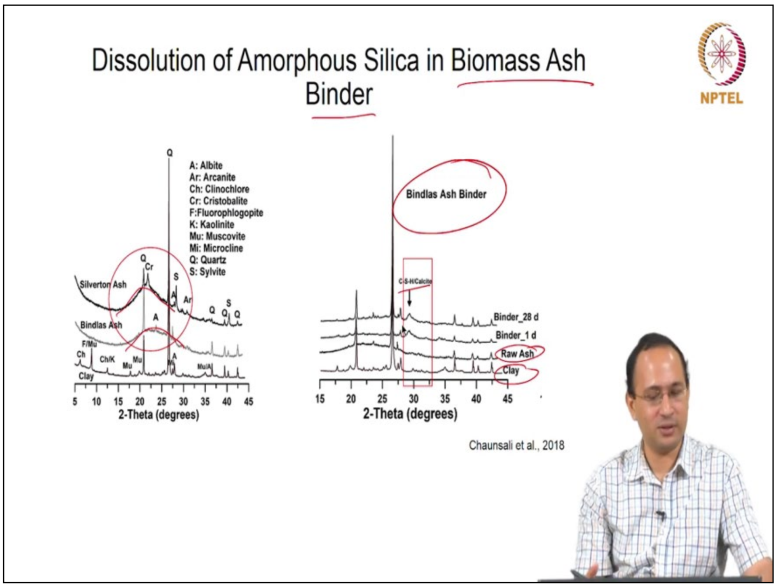

Dissolution of Amorphous Silica in Biomass Ash Binder

Chaunsali et al., 2018

See in this case, here is a biomass ash, not exactly fly ash, but it has also amorphous silica, you see a hump, which is indicative of your amorphous silica. This is the X-ray diffraction of raw powders; here you have clay also, which does not seem to have any amorphous hump, so crystalline, in this case.

Now, this is a binder (Diagram on right) when you mix this biomass ash with lime, you see formation of C-S-H. See in raw ash and clay you do not have any peak at around 29°. But binder, as soon as you add calcium hydroxide, you see the reaction between amorphous silica and calcium hydroxide. You see the formation of calcium silicate hydrate. So, you can get an idea about the dissolution of the amorphous phase by tracking the hydration. So, this is also application of X-ray diffraction.

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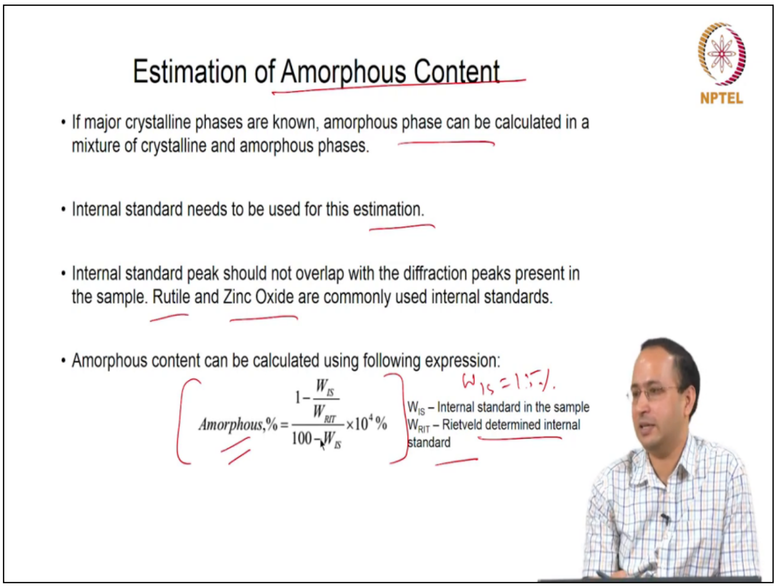

Estimation of Amorphous Content

- If major crystalline phases are known, amorphous phase can be calculated in a mixture of crystalline and amorphous phases.
- Internal standard needs to be used for this estimation.
- Internal standard peak should not overlap with the diffraction peaks present in the sample. Rutile and Zinc Oxide are commonly used internal standards.
- Amorphous content can be calculated using following expression:

$$Amorphous,\% = \frac{1-\frac{W_{IS}}{W_{RIT}}}{100-W_{IS}} \times 10^4\%$$

W_{IS} – Internal standard in the sample
W_{RIT} – Rietveld determined internal standard

$W_{IS} = 1.5\%$

We know that in cement, we do not have any amorphous content, but when you let it hydrate you form calcium silicate hydrate. And then you see, just by nature of the amorphous nature of calcium silicate hydrate which is not fully crystalline, you have amorphous content. We want to quantify it so you can use X-ray diffraction to estimate amorphous content also.

For that you have to use internal standards. How do you do it? So, commonly used internal stands are Rutile and Zinc Oxide. And this is the formula given you can use, Amorphous content can be written as this:

$$Amorphous,\% = \frac{1-\frac{W_{IS}}{W_{RIT}}}{100-W_{IS}} * \ 10^4\%$$

Where, W_{IS} is the internal standard in the sample. So, you are using internal standard, you know how much you have added. Suppose you are using 15% of internal standard, so you know W_{IS} is 15%.

Now, you analyze your sample, W_{RIT} is the Rietveld determined internal standard, when you perform Rietveld, it will give you some number, which will not be 15% because it does not take into account the amorphous content. It assumes everything is crystalline. So, the W_{RIT} will be, Rietveld determined internal standard amount. So, when you know these numbers you can calculate the amorphous content of your sample.

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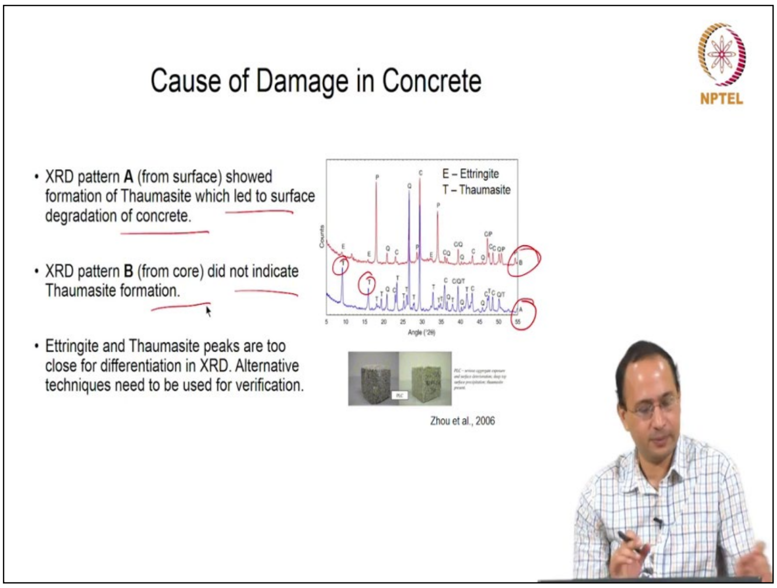

Cause of Damage in Concrete

- XRD pattern **A** (from surface) showed formation of Thaumasite which led to surface degradation of concrete.
- XRD pattern **B** (from core) did not indicate Thaumasite formation.
- Ettringite and Thaumasite peaks are too close for differentiation in XRD. Alternative techniques need to be used for verification.

Zhou et al., 2006

It can also be used to examine the damage in concrete. Here is an example of Thaumasite attack. So, in X-ray diffraction pattern of A, you see presence of Thaumasite 'T'. It is kind of an attack. XRD pattern 'A' showed formation of Thaumasite which led to surface degradation of concrete. B, on the other hand, did not have Thaumasite. It had Ettringite, so it did not have that much damage in this case.

This was a case study. But you see, these are few things you can identify using X-ray diffraction. But the challenge also is Ettringite and Thaumasite peaks are too close for differentiation. So, if you want to make sure that you have a formation of Thaumasite, you may need alternative techniques. So, it is always good to use alternative technique to verify.

In some cases you will be sure, but when you are not sure, then you can use alternative techniques to verify your finding.

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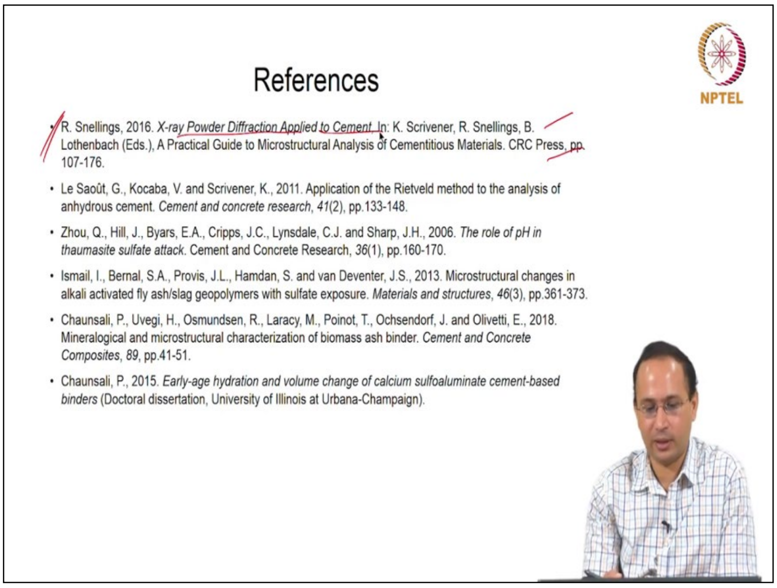

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So these are the references which were used. Reference 1 is very nice, we have recommended this book. So, there is a chapter on X-ray powder diffraction applied to cements. You will get more insights like how do we use X-ray diffraction and these are some papers which were used for this particular lecture.

So that concludes X-ray diffraction. So, we learnt about the technique we have learned how it can be applied to understand the cement based systems.