Characterization of Construction Materials
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Lecture 21
Sample Preparation

In this lecture, we will discuss about sample preparation which is very important step before carrying out any characterization. So, we will look at the most important part of sample preparation which will apply to most of the techniques which we will learn during the course.

In this lecture we will see how to prepare samples for x-ray diffraction, which we discussed in the last lecture.

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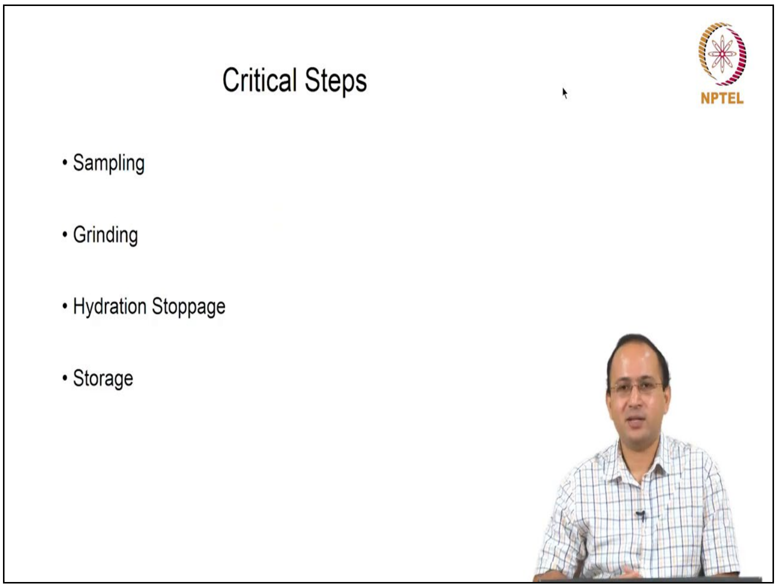

Critical Steps

- Sampling
- Grinding
- Hydration Stoppage
- Storage

Critical steps of sample preparation involve sampling, grinding, hydration stoppage and storage. We will go over these so that we know how to do it.

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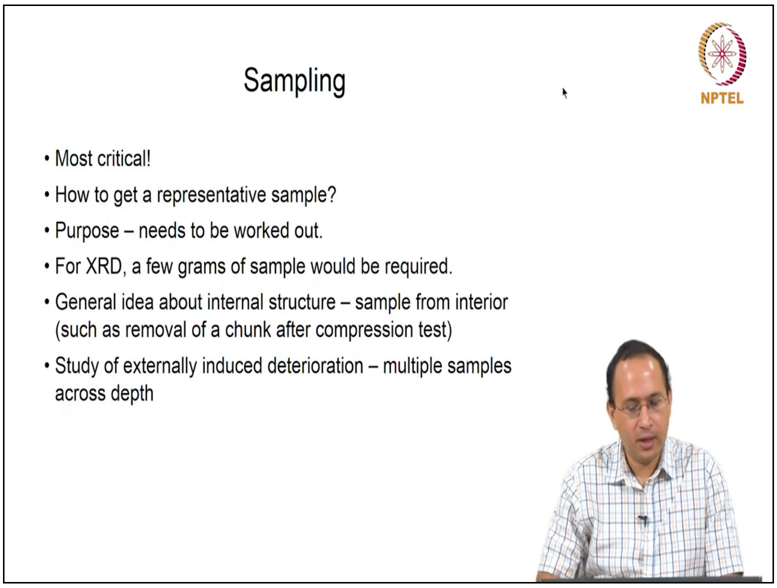

Sampling

- Most critical!
- How to get a representative sample?
- Purpose – needs to be worked out.
- For XRD, a few grams of sample would be required.
- General idea about internal structure – sample from interior (such as removal of a chunk after compression test)
- Study of externally induced deterioration – multiple samples across depth

Sampling is most critical step as it is always a challenge to get a representative sample. If you want to get an idea about the overall behaviour you need to have a representative sample and that is very important. So for that you have to work out the purpose or the aim of the experiment and technique .For an example, for XRD, a few grams of samples would be required, but for strength determination few grams would not be sufficient.

We need to have a general idea about the internal structure too, for sample from interior, for example, if you are doing a compression test right. After compression test, you may have induced micro cracking in the sample. So, you have to be aware of that. So, you want to make sure that the sample you are taking is free of microcracks.

If you are looking at microstructure for an instance internal cracking will affect the observations and you will not be able to determine lot of characteristics. These are the things that you have to keep in mind. If you are looking at externally induced deterioration like salt attack or sulphate attack, you need to get multiple samples across as the sample is exposed.

In real life structures which are exposed to salt attack show different characteristics across the section depending on the extent of diffusion of that aggressive salt or solution. So, you need to have sample across the depth. These are the few basic things to keep in mind.

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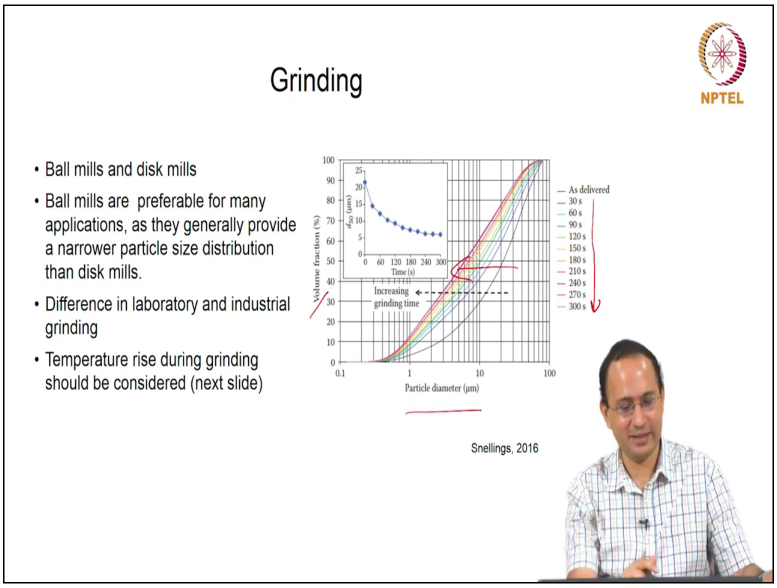

Grinding

- Ball mills and disk mills
- Ball mills are preferable for many applications, as they generally provide a narrower particle size distribution than disk mills.
- Difference in laboratory and industrial grinding
- Temperature rise during grinding should be considered (next slide)

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After sampling we need to grind the sample. For grinding we use ball mills, disk mills and other different types of mills available. Ball Mills are preferable for many applications as they generally provide narrower particle size distribution than disk mills. Important point to note is that there is difference in laboratory and industrial grinding. Industrial grinding is harsher than laboratory grinding. You can see plot volume fraction versus particle diameter. The plot shows the effect of grinding time i.e. 30 seconds to 300 seconds. If you are grinding for 300 seconds the curves shifts and shows that you are making the powder finer. Suppose, you adopt different types of grinding times for your samples so it will certainly affect the properties.

Also we need to keep in mind the temperature rise which occurs during grinding. As you are grinding for few minutes there will be an increase in temperature and the same will have effect on your sample.

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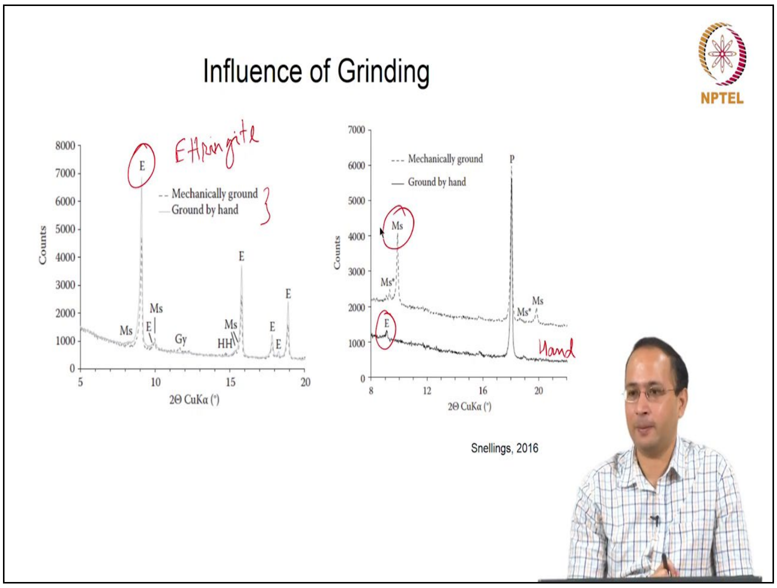

Influence of Grinding

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For example we take cement paste sample. X-ray diffraction plot for the cement paste sample is shown. So here the comparison is drawn between mechanical grounding and grinding by hand. E in the plot is basically Ettringite which is one of the phase in hydrated cement paste.

The change in type of grinding method affects the intensity. In mechanical ground sample the intensity is lower. The reason is the temperature rise for mechanically ground sample which leads to the decomposition of the ettringite decomposed. Here also you see that in this case on the right plot for hand ground sample,you have Ettringite.

But when you do Mechanical grounding you see a formation of Mono-sulphate. Basically, some of the phases which are present in your sample may get affected by the temperature rise during grinding.

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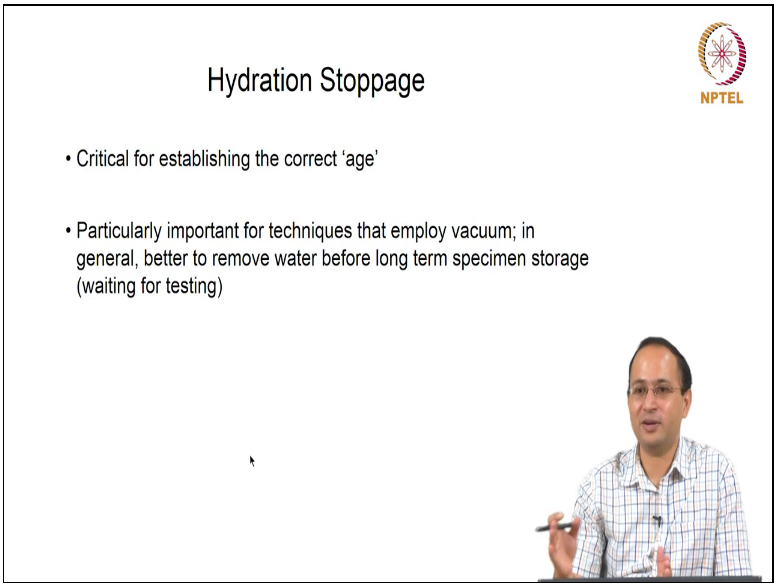

Hydration Stoppage

- Critical for establishing the correct 'age'
- Particularly important for techniques that employ vacuum; in general, better to remove water before long term specimen storage (waiting for testing)

One of the most critical steps in sample preparation is hydration stoppage. We need to know the reason for stopping hydration. We mix cement and water and let it hydrate and during the hydration there is formation of calcium silicate hydrate and other cement hydrates, which continues and contributes in gaining strength. It is critical for stabilizing the correct age.

If you want to understand the effect of degree of hydration and compare different samples, let us say 1 day, 7 days or 28 days old sample. We need to stop the further hydration from taking place. This is most important for techniques employing vacuum or basically for techniques requiring sample without moisture content.

It is generally better to remove water before long term specimen storage. Usually we collect the sample, grind it and stop the hydration and then, store it for some time if we cannot test immediately. Then the analysis is done depending on the availability of instrument. Suppose you want to test it after 7 days, you go to the field after 7 days, but you cannot carry out all the techniques on the same day, ideally.

So what we do is we easily collect the sample then treat it, stop the hydration and store it. Then, depending on the availability, we do the test. But there are lot of other techniques which will learn like this case, X-ray diffraction, Scanning electron microscope, you have other characterization techniques. For many of the techniques such as X-ray diffraction, Scanning electron microscope we need to make sure that there is no hydration as these techniques are sensitive to water.

Assume you cannot carry out on the hydrated sample like without treatment XRD may not get affected XRD you can still do but since we are you know, you are not following different sample preparation processes for Different techniques usually we want to follow the same sample preparation technique then get the sample and use techniques.

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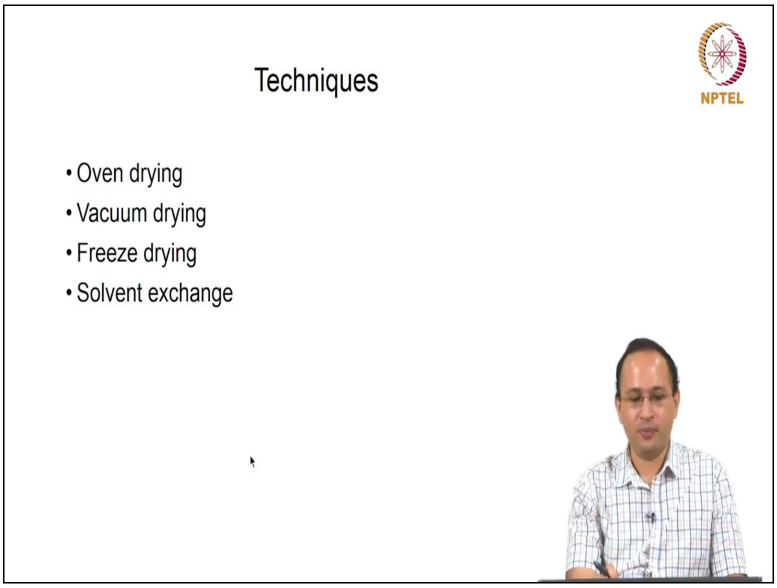

Techniques

- Oven drying
- Vacuum drying
- Freeze drying
- Solvent exchange

There are different techniques for hydration stoppage including oven drying, vacuum drying, freeze drying, and solvent exchange. In oven drying, you are simply putting sample at some high temperature remove the capillary water so as to stop hydration.

You know when cement is mixed with water, we have formation of hydration products like calcium hydroxide, calcium silicate hydrate, ettringite, we also have some capillary water left in the pores. So in oven drying we put it in oven, vacuum drying you put it in vacuum. Freeze drying, you freeze the water then let it sublimate.

Solvent exchange is you are heating some solvent which is miscible with water then let it evaporate.

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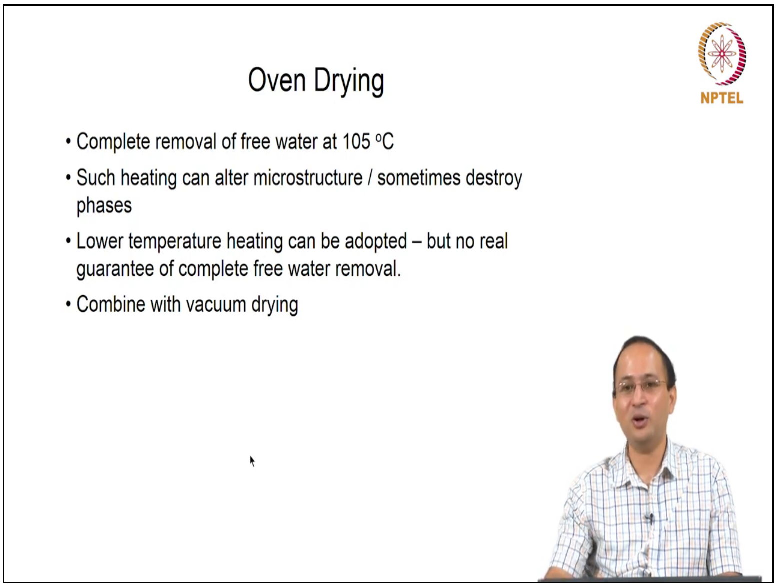

Oven Drying

- Complete removal of free water at 105 °C
- Such heating can alter microstructure / sometimes destroy phases
- Lower temperature heating can be adopted – but no real guarantee of complete free water removal.
- Combine with vacuum drying

Oven drying is complete removal of free water at 105 degree Celsius. If you treat your sample i.e. cement paste or concrete at 105 degree Celsius then you will remove the capillary water. But the key issue with this method is heating at this high temperature can alter the microstructure and sometimes destroy phases.

For an example ettringite gets affected when the sample is heated above 60 to 70 degrees. Even on CSH you will see some effect of the harsh heating. We are talking 105 degree Celsius although you are removing water but you are affecting other phases. So to address this issue lower temperature heating can be adopted but there is no guarantee of complete free water removal.

You can use 50 degrees or 40 degrees but then it will take a long time to remove completely. Usually it is combined with vacuum drying.

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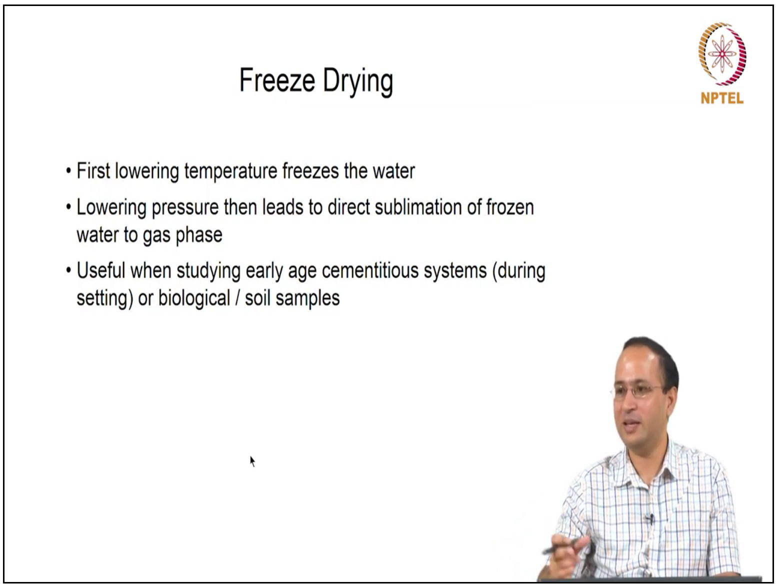

Freeze Drying

- First lowering temperature freezes the water
- Lowering pressure then leads to direct sublimation of frozen water to gas phase
- Useful when studying early age cementitious systems (during setting) or biological / soil samples

In freeze drying, you first lower the temperature so that the water freezes. Now, lowering pressures can be used to direct sublimation of freeze water to gas phase. That is how we are removing the water. So it is useful for studying early age cementitious system during setting. Suppose, you are interested in hydrated cement behavior in the early hours of setting you use this method. Freeze drying is also used for biological /soil samples

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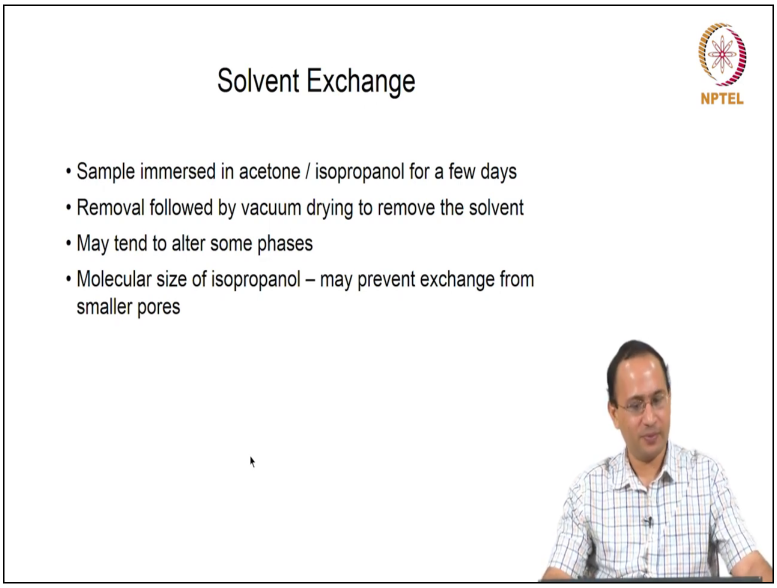

Solvent Exchange

- Sample immersed in acetone / isopropanol for a few days
- Removal followed by vacuum drying to remove the solvent
- May tend to alter some phases
- Molecular size of isopropanol – may prevent exchange from smaller pores

Most commonly used technique is solvent exchange. In this technique, sample is immersed in acetone or isopropanol for a few days. The main idea is alcohol will mix with water as it is immiscible liquid and then we remove it by vacuum drying. So vacuum drying is used to remove the solvent. It may tend to alter some phases.

There are some challenges including the molecular size of isopropanol which may prevent exchange from smaller pores. Then you will not be able to remove the water from the smaller pores.

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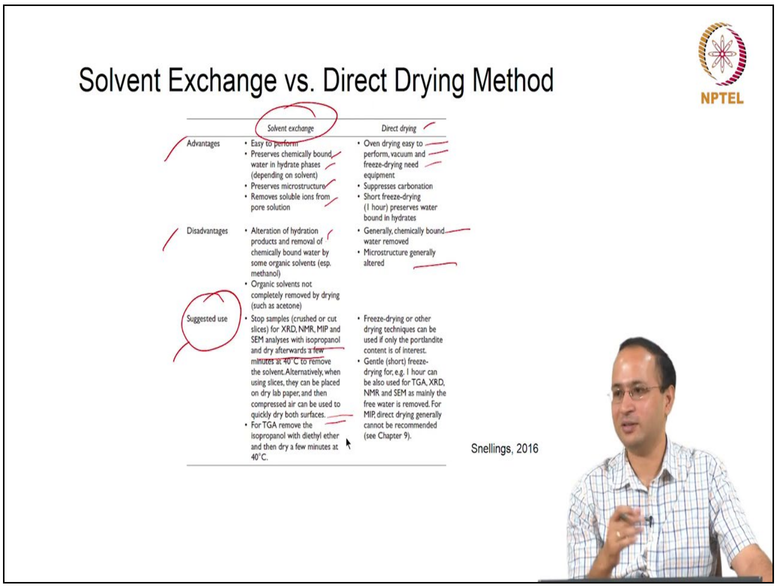

Solvent Exchange vs. Direct Drying Method

	Solvent exchange	Direct drying
Advantages	• Easy to perform • Preserves chemically bound water in hydrate phases (depending on solvent) • Preserves microstructure • Removes soluble ions from pore solution	• Oven drying easy to perform, vacuum and freeze-drying need equipment • Suppresses carbonation • Short freeze-drying (1 hour) preserves water bound in hydrates
Disadvantages	• Alteration of hydration products and removal of chemically bound water by some organic solvents (esp. methanol) • Organic solvents not completely removed by drying (such as acetone)	• Generally, chemically bound water removed • Microstructure generally altered
Suggested use	• Stop samples (crushed or cut slices) for XRD, NMR, MIP and SEM analyses with isopropanol and dry afterwards a few minutes at 40°C to remove the solvent. Alternatively, when using slices, they can be placed on dry lab paper, and then compressed air can be used to quickly dry both surfaces. • For TGA remove the isopropanol with diethyl ether and then dry a few minutes at 40°C.	• Freeze-drying or other drying techniques can be used if only the portlandite content is of interest. • Gentle (short) freeze-drying for, e.g. 1 hour can be also used for TGA, XRD, NMR and SEM as mainly the free water is removed. For MIP, direct drying generally cannot be recommended (see Chapter 9).

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Here we have listed out some of the advantages and disadvantages of Solvent exchange method in comparison to direct drying method. Considering solvent exchange, it is easy to perform as we just need to submerge sample in isopropanol or acetone. These days most commonly used is isopropanol as acetone is harsher. Solvent exchange preserves chemically bound water and also the microstructure, it removes soluble ions from pore solution.

Direct drying is also easy to perform but in terms of disadvantages it will affect the chemically bound water. Direct drying generally alters the microstructure as we are using high temperatures. You can go through the list of advantages and disadvantages and preferably check the suggested use.

These are some of the processes that you can adopt when you are characterizing. But you have to make sure that you are following the same process because slight difference cause also difference in your properties.

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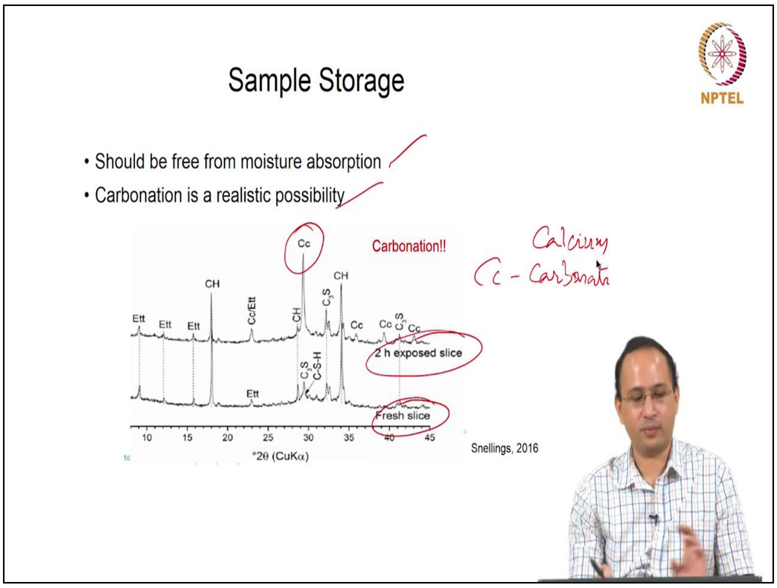

Sample Storage

- Should be free from moisture absorption
- Carbonation is a realistic possibility

Carbonation!!

Cc - Calcium Carbonate

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Sample storage is a very important stage. You want to store the sample so that nothing is altered. In storage we check that sample is free from moisture absorption. You know if there is any moisture then cement will react and hydration will take place which you do not want to occur. Carbonation is a realistic possibility in the system as calcium hydroxide tends to form Calcium Carbonate.

Also you have instances of carbonation of Calcium Silicate Hydrate. In this case shown you see there is a fresh slice and the other is a two hour exposed slice. For 2 hour exposed slice, you see the occurrence of the Calcium Carbonate. So, when you are exposing it to atmosphere; you are seeing the formation of calcium carbonate. So, you do not want that because that is altering the phase assembly. So usually you store samples after solvent exchange and store it in low vacuum continuously.

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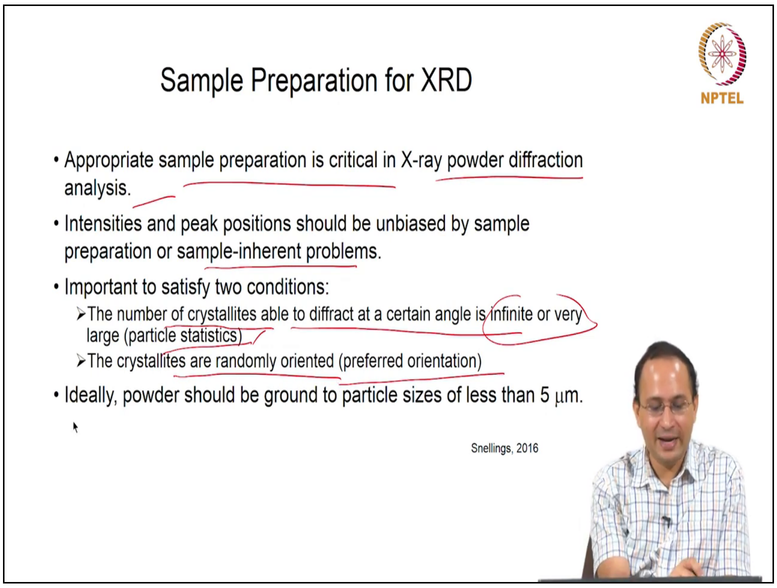

Sample Preparation for XRD

- Appropriate sample preparation is critical in X-ray powder diffraction analysis.
- Intensities and peak positions should be unbiased by sample preparation or sample-inherent problems.
- Important to satisfy two conditions:
  - The number of crystallites able to diffract at a certain angle is infinite or very large (particle statistics)
  - The crystallites are randomly oriented (preferred orientation)
- Ideally, powder should be ground to particle sizes of less than 5 µm.

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So, appropriate sample preparation is critical for x-ray powder diffraction analysis. Intensities and peak position should be unbiased by sample preparation or sample-inherent problems. You do not want to adopt a sample preparation which affects your sample.

So it should be unbiased by sample preparation and sample inherent problems. Basically, you have to take care of two things: one is particle statistics and the other is preferred orientation. In particle statistics, you want to make sure enough number of crystallites are able to diffract at a certain angle which is infinite or very large.

Also you want to make sure that the crystals are randomly oriented because you have lot a plate like structures, needle like structures in your cement paste. So you want to take your preferred orientation. These are the two things you have to take care of. Ideally, powder should be ground to particle size of less than 5 micro metre as we can resolve many of issues using a finer powder.

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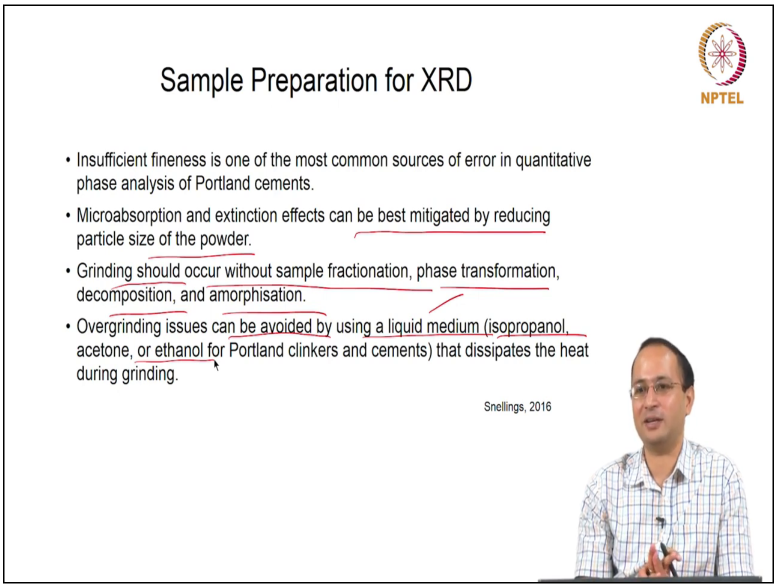

Sample Preparation for XRD

- Insufficient fineness is one of the most common sources of error in quantitative phase analysis of Portland cements.
- Microabsorption and extinction effects can be best mitigated by reducing particle size of the powder.
- Grinding should occur without sample fractionation, phase transformation, decomposition, and amorphisation.
- Overgrinding issues can be avoided by using a liquid medium (isopropanol, acetone, or ethanol for Portland clinkers and cements) that dissipates the heat during grinding.

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Insufficient fineness is one of the most common sources of error in quantitative phase analysis of Portland cements. Microabsorption and extinction effects can be best mitigated by reducing particle size of the powder. So you have to make sure of using fine powder.

Grinding should occur without sample fractionation, phase transformation, decomposition, and amorphisation. You have to make sure that there should be no phase transformation and decomposition of phase taking place after grinding.

When you grind too much or adopt mechanical grinding, depending on the temperature you may affect the phase composition. So those things you have to keep in mind that will change your phase assemblies. So over grinding issue can be avoided by using a liquid medium that dissipates the heat during grinding.

But for liquid medium we cannot use water as it will react. We can use the isopropanol, acetone or ethanol as liquid medium. These are commonly used for Portland clinkers and cement.

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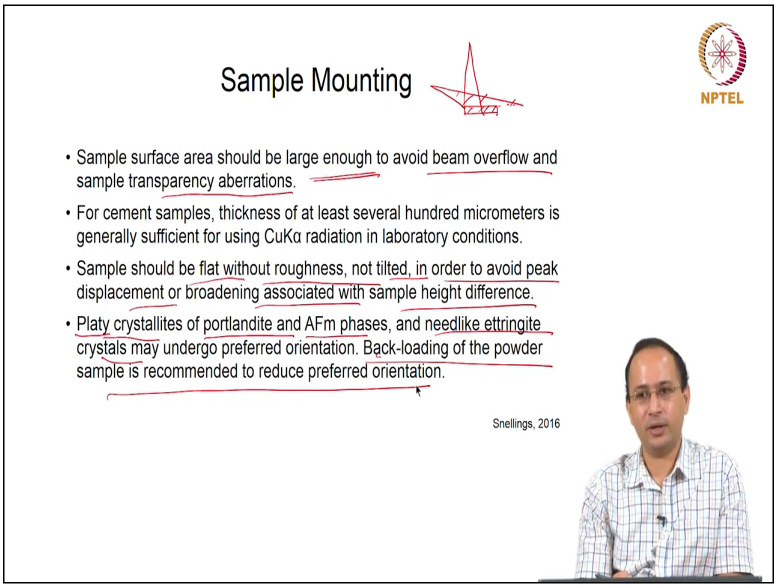

Sample Mounting

- Sample surface area should be large enough to avoid beam overflow and sample transparency aberrations.
- For cement samples, thickness of at least several hundred micrometers is generally sufficient for using CuKα radiation in laboratory conditions.
- Sample should be flat without roughness, not tilted, in order to avoid peak displacement or broadening associated with sample height difference.
- Platy crystallites of portlandite and AFm phases, and needlelike ettringite crystals may undergo preferred orientation. Back-loading of the powder sample is recommended to reduce preferred orientation.

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Now we discuss about sample mounting for X-ray diffraction. Sample surface area should be large enough to avoid beam overflow and sample transparency aberrations. You have to make sure that you have enough thickness of the sample so it is easy to visualise. Your sample should be too small so that there is beam overflow at larger angles as we are moving along the circle theta from 2 theta from small angles to larger angles. These are the issues. You have to make sure that you have enough surface area.

So that is why your sample surface area should be large enough to avoid beam overflow and sample transparency means it should you have some thickness. Few millimetres of sample thickness is good enough for x-ray diffraction of cement. Sample should be flat without roughness not tilted in order to avoid peak displacement or broadening associated with sample height difference.

Platy crystallites of portlandite and AFm phases and needlelike crystals of ettringite may undergo preferred orientation. They tend to orient in the preferred direction just because of the nature of their shape. Backloading of the powder sample is recommended to reduce preferred orientation. Backloading means when you do powder diffraction you have a sample holder and you put powder and press the sample from top while pressing it may lead to preferred orientation.

Backloading means flipping the sample and then analysing it so that can help with the preferred orientation, if you want to see preferred orientation in your sample.