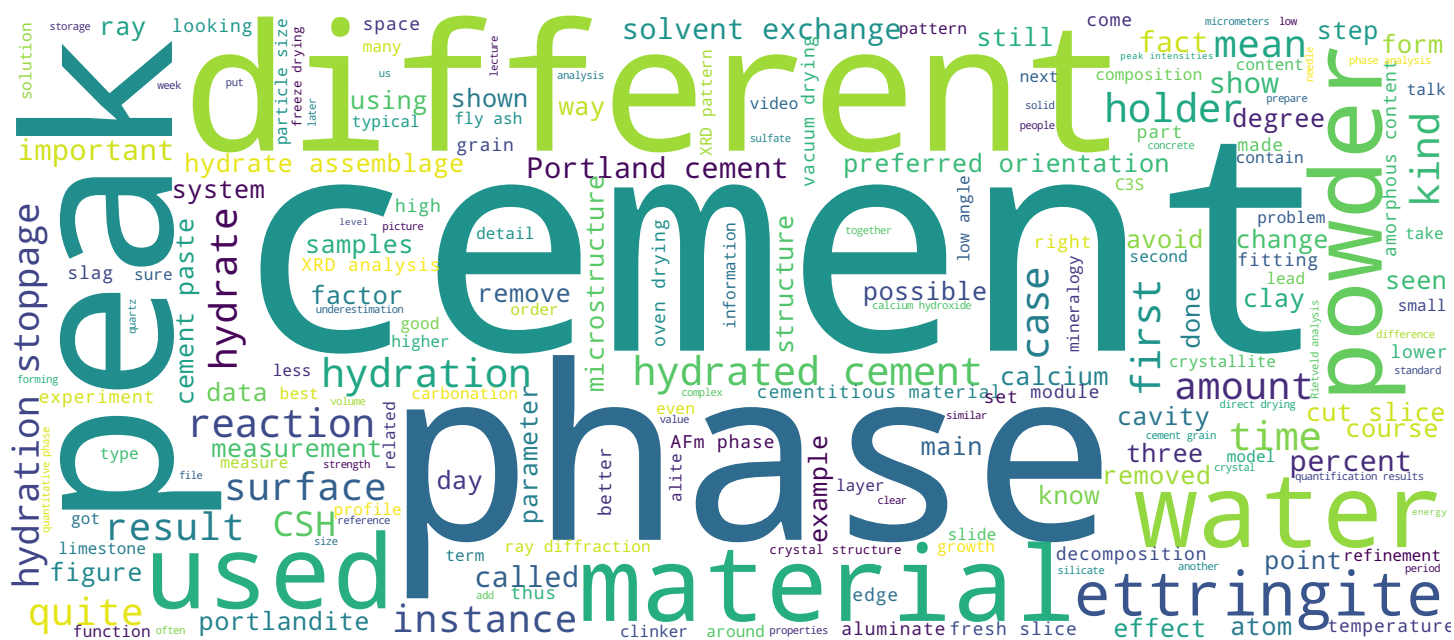


## Cement Chemistry and Sustainable Cementitious Materials

Dr. Ruben Snellings



## Search MOOC



## Video





- **The Rule of Three**

1. Powder fineness (particle statistics)
2. Sample mounting (preferred orientation)
3. Sample preservation (hydration stoppage)

Once you have set up the X-ray diffractometer for your experiment, selected the appropriate optics and chosen the suitable measurement program for your experiment, it is time to prepare your sample for measurements. This lecture will talk about the preparation of samples for XRD analysis and emphasize key factors that may influence your results. In order to obtain accurate and precise results from XRD analysis, one needs to correctly prepare the materials. X-ray powder diffraction is based on two basic assumptions, namely first that the sample consists of an infinite number of crystallites and second that those crystallites are randomly oriented. For cementitious samples we need to add a third important point. This is that the sample mineralogy should be preserved. Altogether this can be summarized as the “rule of three”. First, the powder should be sufficiently fine to have a large number of crystallites able to diffract at any angle, second, the sample should be mounted so that any artifact are avoided such as preferred orientation and third, the sample mineralogy should be preserved as much as possible. To do this it is often necessary to stop the hydration of hydrated samples. Let's have a closer look at these three rules.

Notes

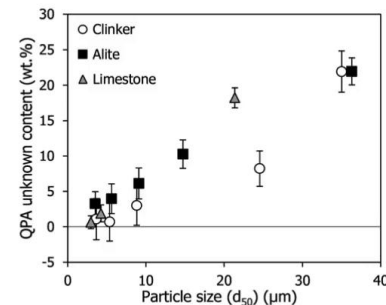
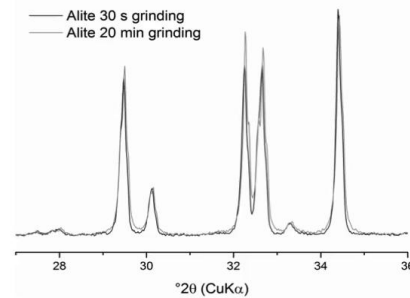
Summary



0m 04s

## 1. Powder fineness

- For representative measurements:
  - High number of particles need to diffract (particle statistics)
  - Particle sizes < 10-20  $\mu\text{m}$  required
  - Ideally 1-5  $\mu\text{m}$
  - Too large particles give spiky patterns and misfits, resulting in higher “unknown/amorphous” contents
- Extensive dry grinding may lead to amorphization
- Wet grinding preferable
- Sample spinning improves statistics



[Snellings et al. 2014]

So now looking at powder fineness in more detail it is obvious that not only you have to take a representative subsample but we also need to make a powder which has a high number of particles that can diffract. If we have a powder that has a large number of fine particles then we get a representative XRD measurement in which the peaks can be repeatably measured. Basically this means that in practice particle sizes of about 10 to 20 micrometers or less are required, ideally even smaller, smaller than 1 to 5 micrometers. In the graphs on the right side you can see for instance the effect of material fineness on the XRD patterns. On the upper right, you can see 2 XRD scans of the same material, an alite, synthetic alite ground for two types. One was thirty seconds which resulted in a rather coarse alite with a medium grain size of about 36 micrometers. The other one was a long grinding time of about 20 minutes which resulted in alite particles of about three micrometers. You can see that for the sample that has been ground for a longer time, the peaks are a little bit broader and they are actually, when looking at it in a mathematical way, they are more regular.

Notes

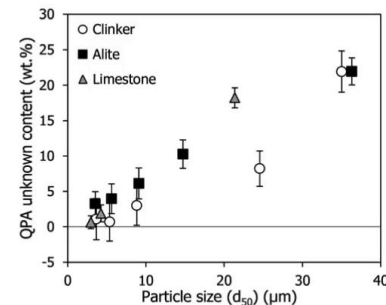
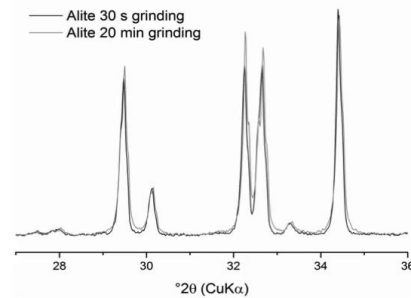
Summary



1m 32s

## 1. Powder fineness

- For representative measurements:
  - High number of particles need to diffract (particle statistics)
  - Particle sizes < 10-20  $\mu\text{m}$  required
  - Ideally 1-5  $\mu\text{m}$
  - Too large particles give spiky patterns and misfits, resulting in higher “unknown/amorphous” contents
- Extensive dry grinding may lead to amorphization
- Wet grinding preferable
- Sample spinning improves statistics



[Snellings et al. 2014]

In fact having two large particles gives something like a spiky pattern and results in misfits which then again results in larger amounts of unknown or amorphous contents. This can for instance be seen in the figure on the lower right there as a function of particle size of the powder, one has on the y axis the unknown content or amorphous content analyzed by Rietveld analysis. Here clearly one can see that if one has two large particle sizes, one is actually measuring an apparent or artificial amorphous content. This is not true and this is actually related to sample misfits or XRD pattern misfits. So just grinding the sample to the appropriate fineness will enable to give you a much more accurate assessment of the amorphous phase level. However one should be careful in grinding because extensive dry grinding in a dry medium may lead to amorphization of sensitive soft phases. So therefore for any phases that cannot be affected, what grinding is preferable? This can be done on any kind of clinker, alites, limestone, anhydrous phases for instance by using grinding media like isopropanol, acetone or ethanol. However this is not possible for hydrated cements where even this kind of treatment may change the vulnerable hydrate assemblage.

Notes

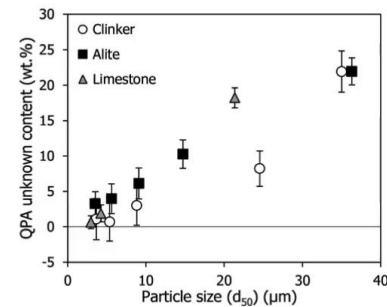
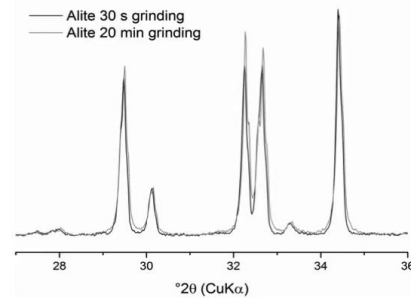
Summary



3m 02s

## 1. Powder fineness

- For representative measurements:
  - High number of particles need to diffract (particle statistics)
  - Particle sizes < 10-20  $\mu\text{m}$  required
  - Ideally 1-5  $\mu\text{m}$
  - Too large particles give spiky patterns and misfits, resulting in higher “unknown/amorphous” contents
- Extensive dry grinding may lead to amorphization
- Wet grinding preferable
- Sample spinning improves statistics



[Snellings et al. 2014]

And therefore in those cases it may be preferable just to gently dry the material and measure it as such or to actually cut a slice from a hydrated cement based and measure that fresh. It should be mentioned as well that spinning the sample in the horizontal plane improves the statistics enormously by a factor of about 5. So this is definitely to be encouraged or to be advised in your data collection strategies.

Notes

Summary



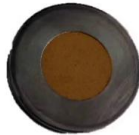
4m 46s

## 2. Sample mounting

Front-loaded



Back-loaded

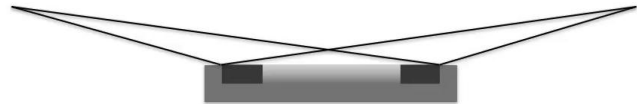


Slice  
(cement paste)



Beam overflow to be avoided  
Too low intensities of low angle peaks

(larger sample diameter, smaller divergence slits)



Sample surface should be flat, not rough, not tilted  
Causes peak shifts, broadening due to sample height differences



In mounting, the obtained powders and slices onto the sample holders for quantitative XRD, following aspects should really be considered. In flat plate reflection geometry care should be taken that the sample surface area and thickness are large enough to avoid any beam overflow at low angles. Also too small surface areas will lead to an underestimation of the peak intensities at low angles and thus cause also some diffraction peaks or increased backgrounds from the sample holder. In case smaller sample holders are used or are only available then one can still change the diffractometer optics by for instance choosing smaller divergence slits. Especially for phases that show high peaks in low angle regions such as ettringite or AFm phases, this beam overflow problem will lead to an underestimation of their content and quantitative phase analysis. Other requirements are that the mount surface should be flat without roughness and not tilted, in order to avoid peak displacement or broadening associated to sample height differences or misalignments. For hydrated cements where we use cut slices we should polish those slices to remove any inhomogeneities at the surface and also the slice surface should be carefully positioned at the aligned sample height for the measurements. Otherwise we will have shifts in peak positions.

Notes

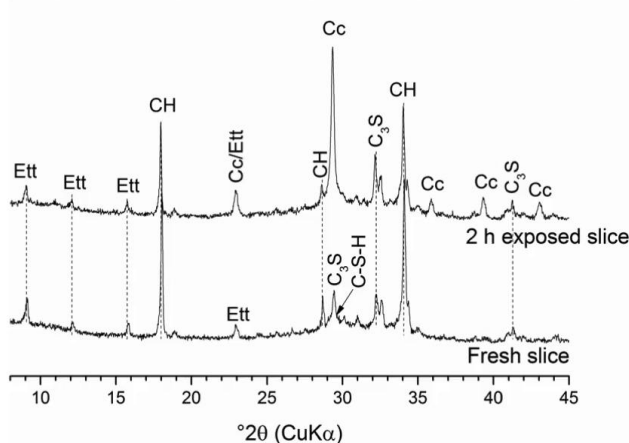
Summary



5m 17s

## 3. Sample preservation

- Hydrated cement samples are prone to carbonation
  - E.g. 2 h exposure of fresh slice to air
  - Both fresh and dried samples are sensitive to carbonation



It should be clear that the hydrate assemblage of cement and particularly in hydrated cements is sensitive to surface exposure. As an example, this figure shows the changes in mineralogy of a fresh slice that was measured before and after a two hour exposure to air inside the diffractometer. Not only fresh samples but also samples of which the hydration was stopped are sensitive to air exposure. Hydration stoppage does reduce the sensitivity so much that it cannot overcome these effects.

Notes

Summary

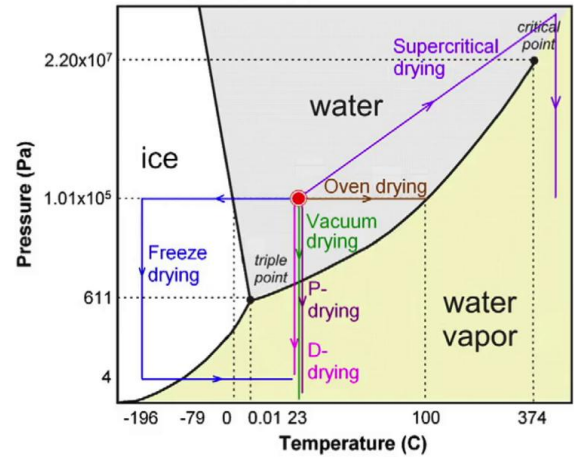


7m 00s



## 3. Sample preservation

- Hydration stoppage for:
  - Storing samples
  - Measuring a certain material property (e.g. porosity, TGA, etc.)
  - Analysing samples at the same age with different techniques
- Different techniques possible:
  - Oven drying
  - Freeze drying
  - Vacuum drying
  - Solvent exchange (by isopropanol)



[Zhang and Scherer, 2011]

Most characterization techniques of hydrated cements need the hydration of the cement to be stopped or the sample to be dried. Even if the hydration stoppage is not strictly necessary for XRD based studies this is common practice mostly for practical reasons. Arresting the hydration enables sample storage and the characterization of the same sample at the same degree of hydration by different techniques. The primary aim of the various available methods for hydration stoppage is that the properties of interest of the hydrating cement, the phase composition in the case of XRD, are preserved as much as possible. To stop the hydration of cement the unbound water present in the capillary pores needs to be removed. Water present in smaller gel pores or chemically bound into the hydration products should preferably be retained as its removal may really cause the alteration of the hydrates or even the decomposition and micro structural changes. There are two main ways to remove the water, either by direct drying techniques such as oven drying, vacuum drying or freeze drying, or second group of measurements by solvent exchange in which water is replaced by an organic solvent, mostly isopropanol which evaporates afterwards.

Notes

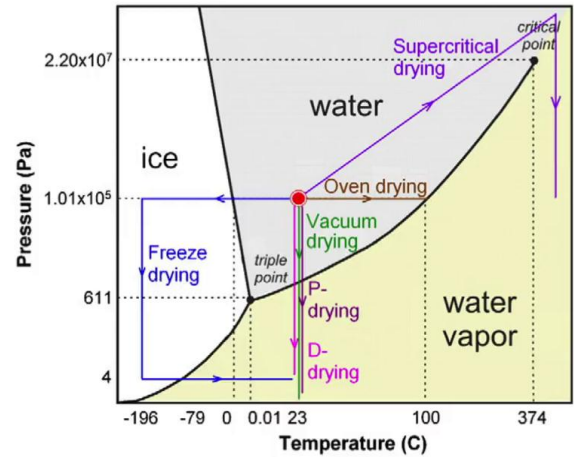
Summary





## 3. Sample preservation

- Hydration stoppage for:
  - Storing samples
  - Measuring a certain material property (e.g. porosity, TGA, etc.)
  - Analysing samples at the same age with different techniques
- Different techniques possible:
  - Oven drying
  - Freeze drying
  - Vacuum drying
  - Solvent exchange (by isopropanol)



[Zhang and Scherer, 2011]

The figure on the right shows a working principle of the different direct drying techniques. In oven drying, the temperature is increased at constant pressure until the phase boundary, the boiling point, is reached and water starts evaporating. On the contrary, in freeze drying, the sample is rapidly cooled by immersion in liquid nitrogen and then the frozen water is being removed by first decreasing the pressure and then heating the sample until reaching the phase boundary at which the water is removed by sublimation. Then, in vacuum drying, water is being removed by just reducing the pressure by a vacuum pump and evaporation at low vacuum conditions.

Notes

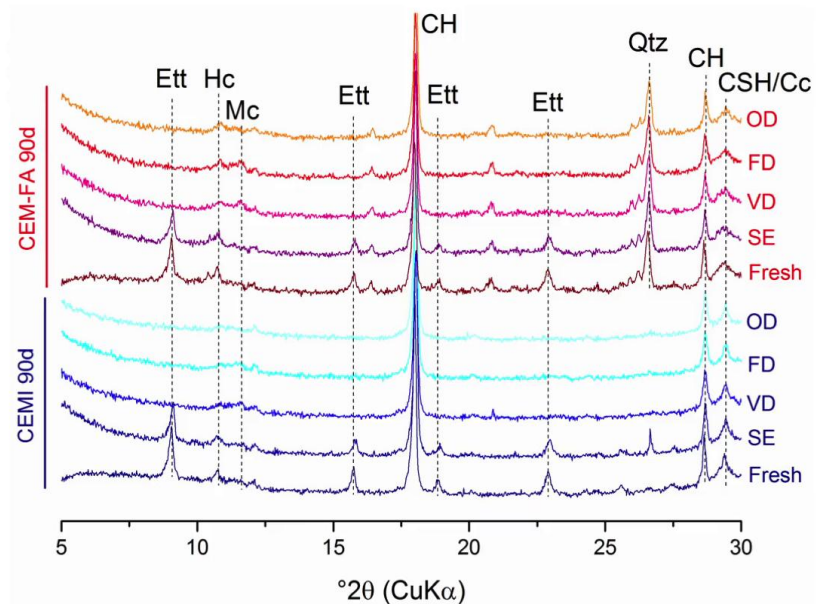
Summary



9m 09s

## 3. Sample preservation

- Different hydration stoppage techniques
  - Oven drying
  - Freeze drying
  - Vacuum drying
  - Solvent exchange (by isopropanol)
- All drying affects ettringite



The results of a round robin test on hydration stoppage clearly show that none of the hydration stoppage methods leave the hydrate assemblages entirely intact. In particular ettringite and AFm phases are affected by drying. Oven drying, freeze drying and vacuum drying result in the removal of structural water and thus the decomposition of the ettringite in the AFm phases. Oven drying was observed to be more destructive than vacuum drying. And it appears that all direct drying methods result in the dehydration of cement hydrates. In case of crystalline products, this may lead to decomposition and an underestimation of the phase content on the hydration stop samples. Solvent exchange techniques represent a more gentle way of removing the water and that preserves better to microstructure and the hydrate assemblage. In the figure, you can see that the ettringite peak can still be recognized quite clearly in the methods that have used solvent exchange.

Notes

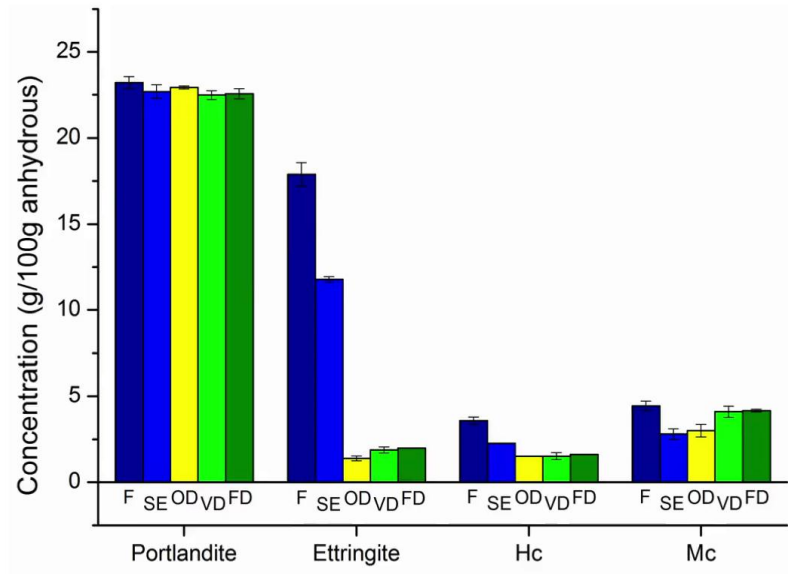
Summary



9m 57s

## 3. Sample preservation

- Different hydration stoppage techniques
  - Oven drying
  - Freeze drying
  - Vacuum drying
  - Solvent exchange (by isopropanol)
- All drying affects ettringite



However when we look at the quantification results it is clear that also the ettringite is lower in the solvent exchange samples compared to a fresh sample. However portlandite is much more resistant towards hydration stoppage and remains, within error, preserved.

Notes

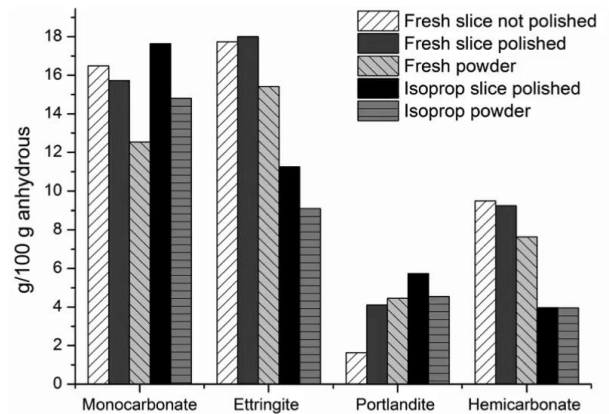
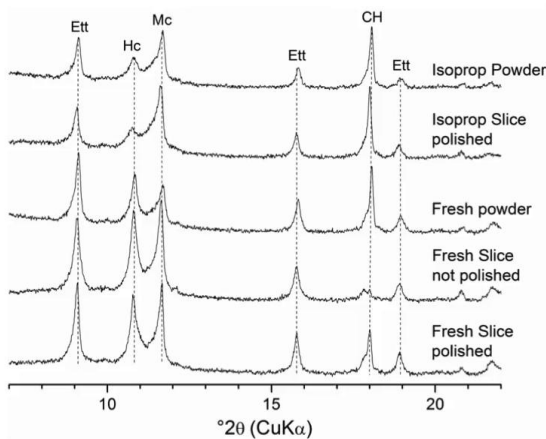
Summary



11m 08s

## 3. Sample preservation

- New XRD detectors enable fast measurements (15 min) – measurement on undried samples is possible
- Example: fresh vs. hydration stopped; cut slice vs. powder



The effective hydration stoppage by solvent exchange on the hydrate assemblage is illustrated by XRD patterns and quantification results for 28 days hydrated blended cement containing fly ash and limestone as shown in the figures below. A comparison is made here between cut slices and crushed powders that are either measured fresh immediately after cutting or crushing the sample or after hydration stoppage by isopropanol exchange during one week. The cut slices were measured with and without surface polishing to see the effect of this polishing action. You can see that isopropanol exchange during one week resulted in a reduction of the ettringite and hemicarboaluminate quantification results of about 50 percent. The monocarboaluminate and portlandite phases appear much more resistance to solvent exchange. Sample crushing led to a decrease in monocarboaluminate peak intensities and quantities. And unpolished fresh slices were deficient in portlandite and contained about one half of percent of calcite more indicating that there was some surface carbonation or decomposition of portlandite during the cutting. It should be mentioned as well that procedures that involve a shorter solvent exchange period on finer powders may result in less ettringite decomposition.

Notes

Summary



## 3. Sample preservation

### Fresh

- Limited disturbance of hydrates
- Limited sample preparation
- Freshly cut sample are prone to carbonation/desiccation
- Requires fast data collection (15 min) and immediate measurement

### Dried

- Aft/AFm reflections reduced by direct drying
- Also isopropanol treatment has an effect on Aft/AFm phases
- Possible carbonation after 2 weeks of storage
- Bound H<sub>2</sub>O has to be measured by TGA for quantification

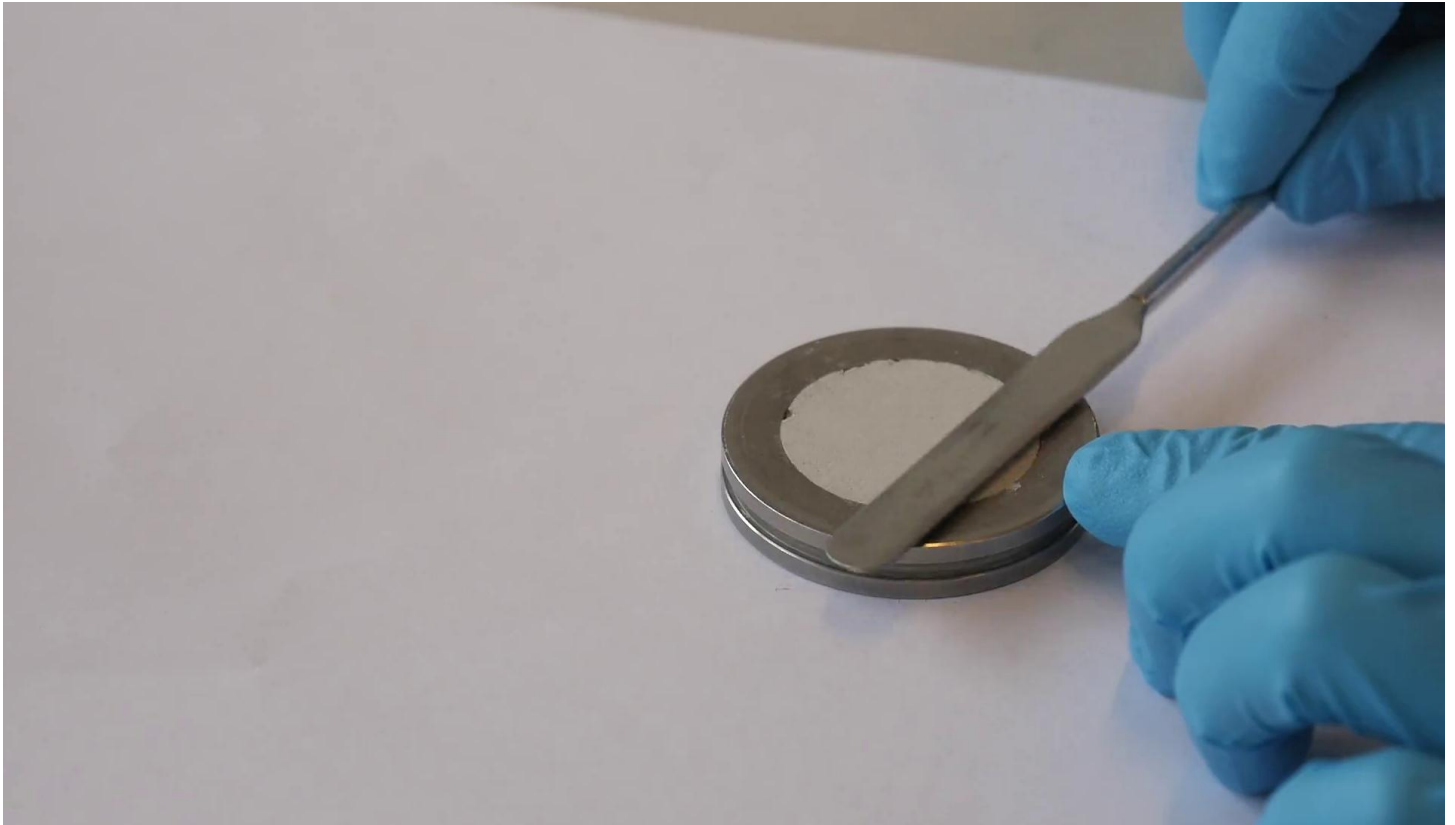
This slide really summarizes the advantages and disadvantages of working with fresh or dried hydrated cement samples. The major advantage of measuring on fresh slices is that the hydrate assemblage is practically undisturbed if one can measure immediately and rapidly. This is not possible if XRD measurements take time or if the machine is not immediately available. On the other hand dried samples resist much more or much better to carbonation and offer more flexibility in terms of timing of the measurement and storage of the samples. However also there it is advisable to limit the time between stoppage and measurements as much as possible. Samples stored for more than two weeks in a protected atmosphere start showing signs of carbonation or decomposition already. The major downside is thus that the ettringite and AFM reflections are being reduced by any drying operation.

Notes

Summary



12m 58s



In this video we are going to show you how to prepare a sample for XRD analysis. The typical sample used are powders. The fineness of the powders should be at least less than 20 microns, ideally 1 to 5 microns to ensure the particle statistics. If the samples are not powdered yet, a mortar and pestle can be used to comminute the samples. Wet grinding is preferred if you want to grind the particles very fine. Another way to improve the statistics of the powder is to spin the sample. For dried hydrated cement, the surface as well as the edges of the sample should be removed because they can be carbonated during the storage and sample preparation. Front loading should be the most widely used sample preparation method even though it is not the best because of the simplicity of the sample holder and the sample preparation. Take the sample and distribute it into the cavity. Further spread the sample in the cavity with the edge of the sample knife. At the end, plane the surface of the powders. Make sure the surface is smooth and the powder is well packed. Back loading is recommended for powder sample to avoid the potential preferred orientations.

Notes

Summary

14m 07s







The preferred orientation will be an issue for Rietveld analysis even if we can correct it mathematically. It is better to avoid it during the sample preparation. Clean the stage. Fix the top part of the sample holder on the stage, fill half the cavity with the powder. Spread the powder and press everything to pack them, then fill the rest of the space with more powder. Further spread the sample in the cavity with the edge of the sample knife. At the end, plane the surface of the powders and remove the excess powder. Unlock the top piece and put back the lower part of the sample holder. Turn over the sample holder together with the stage. Rotate the sample holder by about 10 degrees and then remove it from the stage. Clean the edges of the sample holder. When there are not enough samples to fill the cavity of the sample holder, the so-called zero-background sample holder can be used to support the limited amount of sample. First, fix the zero-background slice to the sample holder. Spread the tiny amount of sample on the disc, trying to make a smooth surface if possible. Specifically for hydrated cement paste, the cut slice can be directly used for XRD analysis.

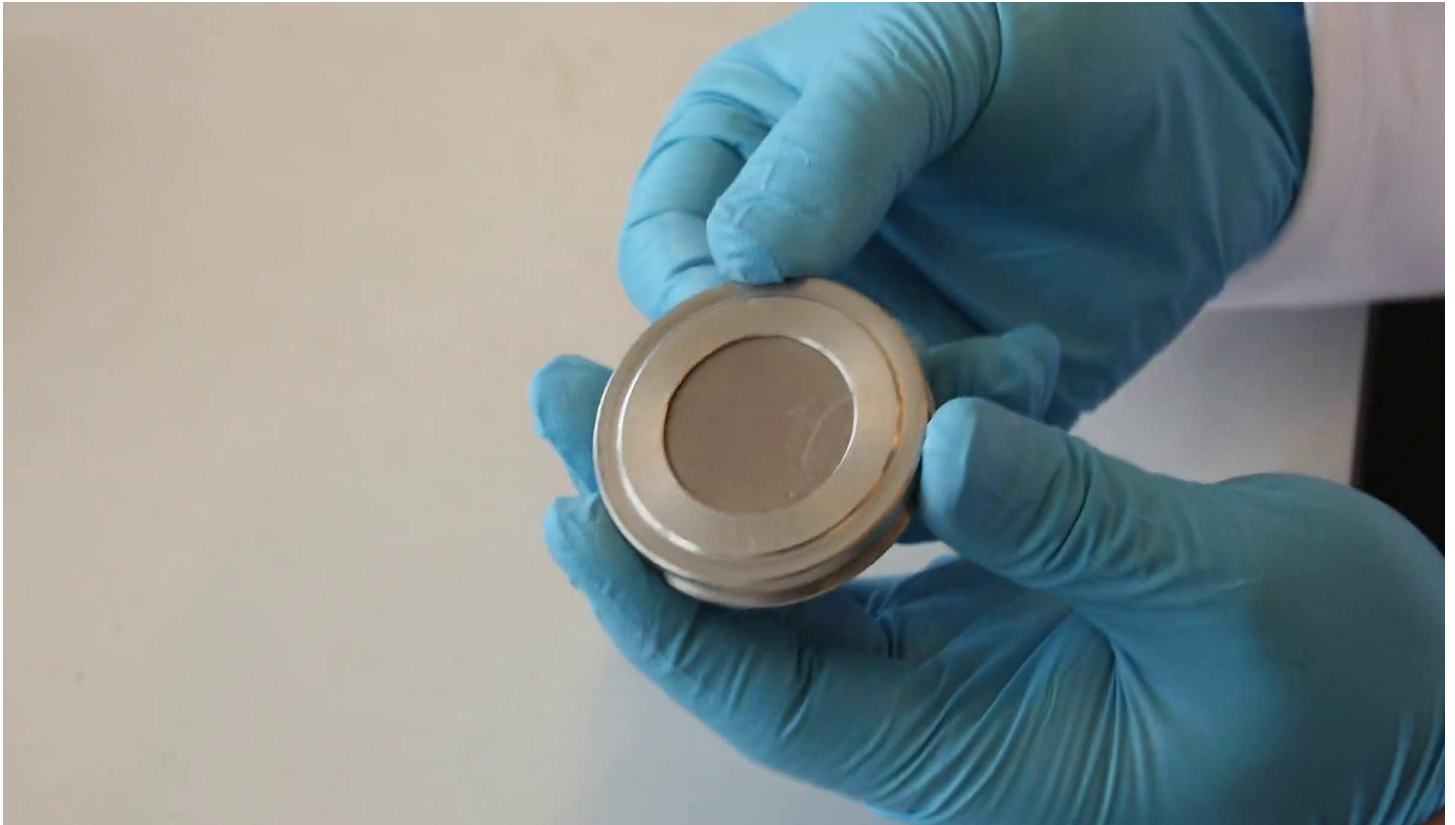
Notes

Summary



15m 31s





The fresh slice was proved to be the best sample status for hydrated cement as there is no damage for the hydrates such as ettringite. The freshly cut slice at specific ages is polished using a number 1200 sand paper to make sure the surface is flat and washed slightly with distilled water. A piece of tissue is immediately covered on the wet slice to prevent the water evaporation. Load the piece of sample in the sample holder and fix it. In the case of fresh discs, the data collection should be done as soon as possible, typically within 15 minutes. This is to avoid the drying and the carbonation of the samples. However, working with cut slice is more demanding to the availability of the X-ray diffractometer.

Notes

Summary

17m 00s

