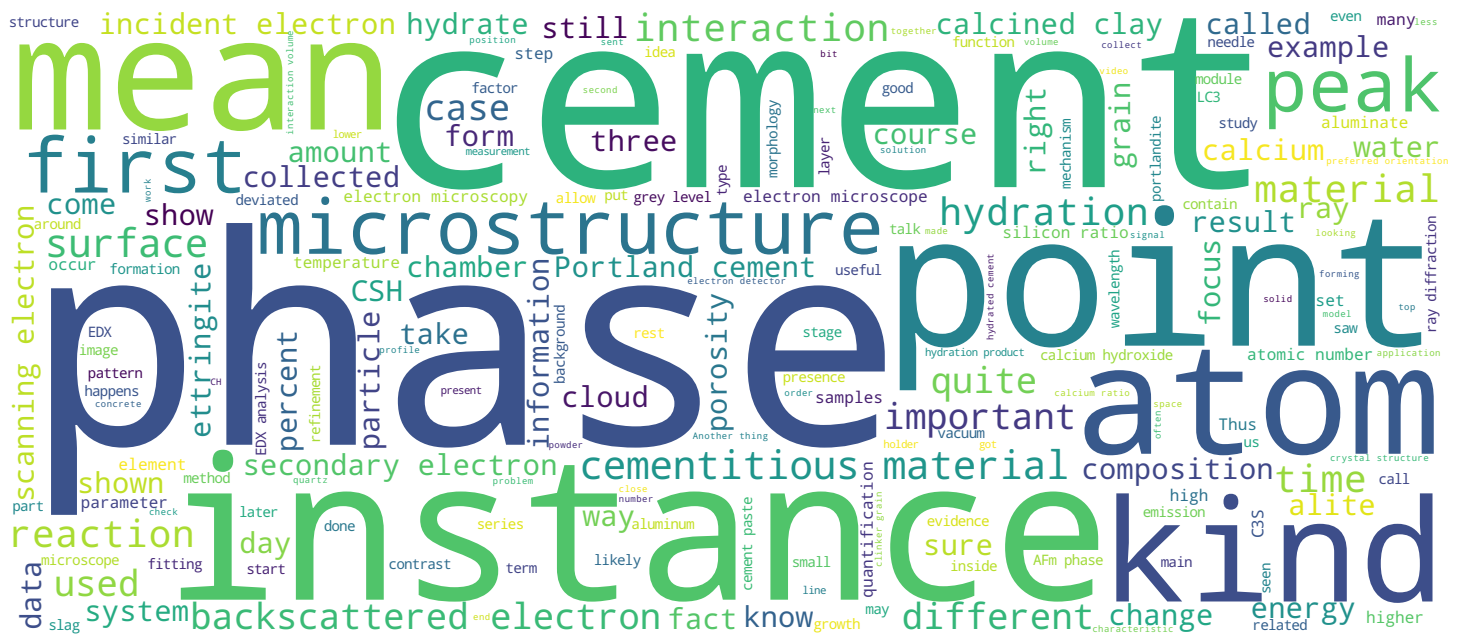


Cement Chemistry and Sustainable Cementitious Materials

François Avet





- Microstructure characterization by Scanning Electron Microscopy
- How does a microscope work?
↓
- Interactions electron / matter

Hello my name is Francois Avet and I will show you in this MOOC, the different information you can get using scanning electron microscopy, for the characterization of the microstructure of cementitious material. We first need to understand how a microscope works and what happens when electrons are sent to a sample and hit the surface of the material.

Notes

Summary



0m 04s

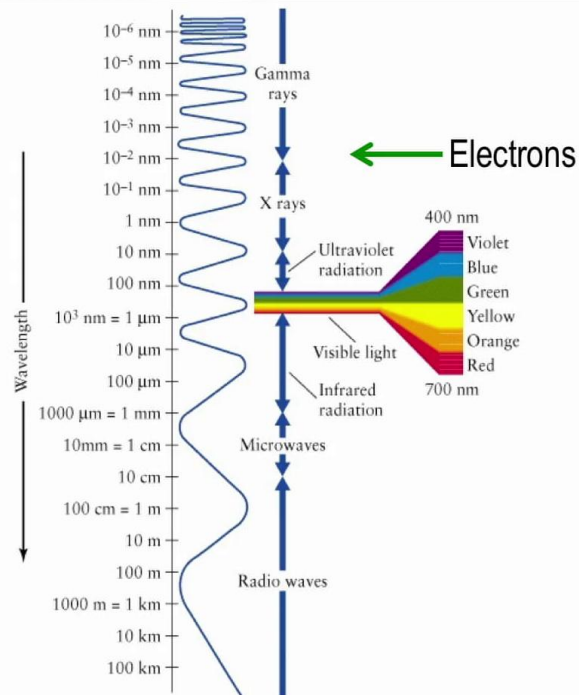
Electron microscopy

- Electrons instead of light



- Higher resolution limit

<http://science-edu.larc.nasa.gov>



So the first question we could ask is why do we use electrons rather than visible light? The first approach for observing the micro-structure is the use of optical microscope, using the light as the source of emissions. However the resolution of light microscopy is limited by the wavelength of the visible light, between 400 to 800 nanometers. The wavelength of electrons is actually much smaller, around 1 to 10 picometers. It allows to observe much smaller objects and to get a much better resolution. In the case of electron microscopy, the resolution is actually not limited by the wavelength of electrons but by the aberrations inside the microscope which are kinds of physical deviations caused by the microscope lenses.

Notes

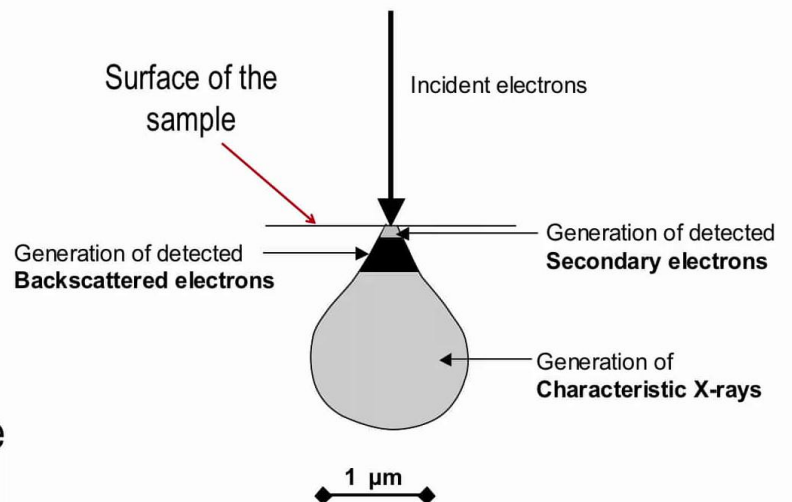
Summary



0m 25s

Interactions in Scanning Electron Microscopy

- Electrons emitted by the source
- Sent to the sample
- Series of interactions with the sample
- Volume of occurrence of these interactions = interaction volume



Scrivener (2004)

The most common type of microscopy to observe a microstructure of cementitious materials is scanning electron microscopy which is actually more accessible and easier to use than transmission electron microscopy. In a scanning electron microscope, electrons are emitted from the electron source, they pass through a series of lenses which focus them, and then the electrons reach the surface of a sample here. And they undergo a series of elastic and inelastic collisions with the atoms of the sample. Different signals can be collected from these collisions. When we talk about the scanning electron microscope it means that actually the surface of a sample would be analyzed point by point and the final image is actually the assemblage of the information from all these points. An incident electron as you can see here, faces a series of interactions before its energy is fully dissipated. Thus all these interactions from this incident electron and the electrons of the sample does not occur exactly at the entering point of the electrons but they occur in a more global volume which is called the interaction volume. These interactions can be either elastic with no energy loss or inelastic.

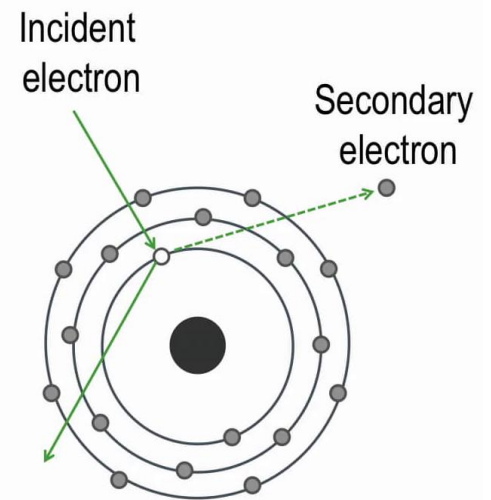
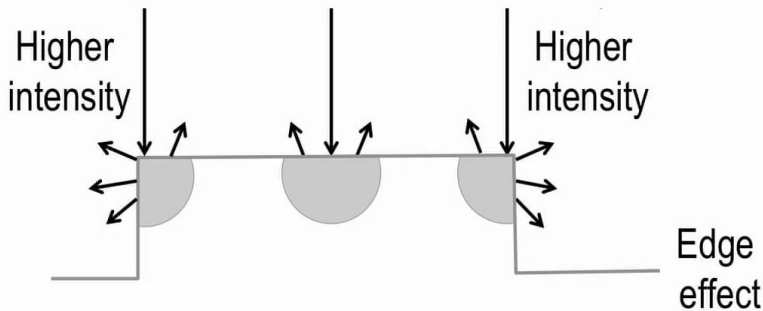
Notes

Summary



Inelastic interactions: Secondary electrons

- Collision \Rightarrow Ejection of a secondary electron
- Very low energy
 - \Rightarrow can only escape from the near surface
 - \Rightarrow topography contrast



The first kind of interaction which can occur between the incident electron and the atoms of a sample is if an incident electron, as shown here, collides with an electron of the atom of the sample. From this collision the incident electron is deviated like this, and the bound electron is ejected. This ejected electron is called a secondary electron or also called SE. The energy of the secondary electrons is typically lower than 50 electrovolt which is actually very small. Thus, if these electrons want to be collected by a detector, they have to be formed very close to the sample surface. If they are formed deeper in a sample then these electrons would face some interactions before reaching the sample surface, they would be absorbed in the sample due to very low energy and they would not be collected by a secondary electron detector. So thus, the contrast we can obtain with the secondary electrons is a topography contrast as you can see here. Here is shown three points where incident electrons are sent and you can see that actually this volume here is a volume where secondary electrons can escape and can be then detected. And you can see that at the edges more electrons can escape the surface.

Notes

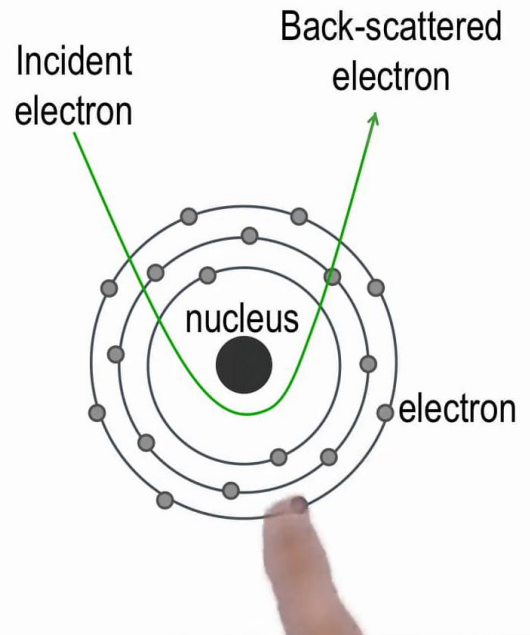
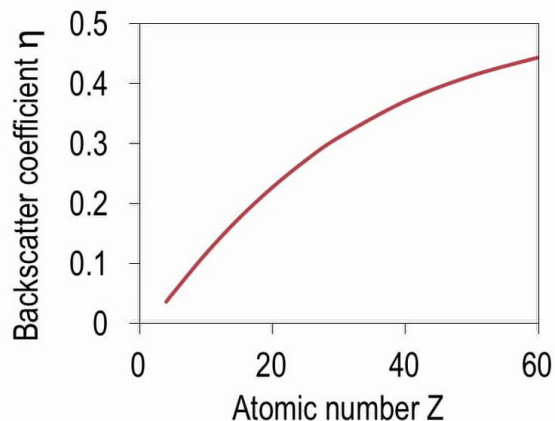
Summary



2m 45s

Elastic interactions: Back-Scattered electrons

- Coulomb interaction with nucleus
- Intensity proportional to the atomic number of the atoms \Rightarrow Z-contrast



And thus can be collected. This means that on the image on these specific points we get more signal and we have a brighter contrast. This is called the edge effect. Another kind of interaction which can occur is when an incident electron feels the Coulomb interactions with a nucleus of an atom of a sample. This incident electron is deviated because of this Coulomb interaction. If this deviation leads to high angle diffusion, then the electron can leave the surface and it can be collected by the backscattered electron detector. So this electron which is scattered back is called backscattered electrons or BSE. This interaction is almost elastic. There is almost no energy transfer which means that the energy of the backscattered electrons is very similar to the energy of the incident beam. So which information can we obtain with backscattered electrons? Well, the coulomb force with a nucleus increases with the atomic number Z . Indeed with the increase of the atomic number, the number of positive charges of the atom increases. Thus the incident electron has a higher likelihood to be deviated. If more electrons are deviated more will also be collected.

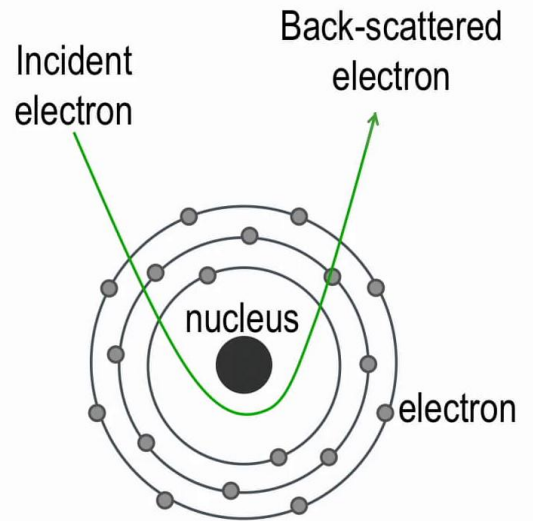
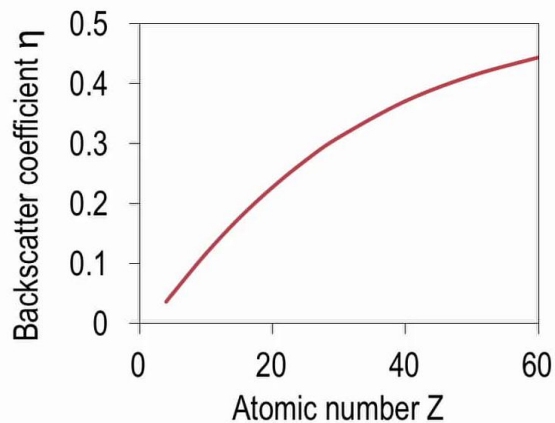
Notes

Summary



Elastic interactions: Back-Scattered electrons

- Coulomb interaction with nucleus
- Intensity proportional to the atomic number of the atoms \Rightarrow Z-contrast



Thus the contrast will be brighter on the image for a higher Z of the atom. This graph here shows you that the brightness increases with the atomic number. This is here the backscatter coefficient which is related to the intensity of the signal as a function of the atomic number and you can see that if you have a material with a higher average Z inside, you can see that actually you will see something brighter on your image because you will collect more backscattered electrons.

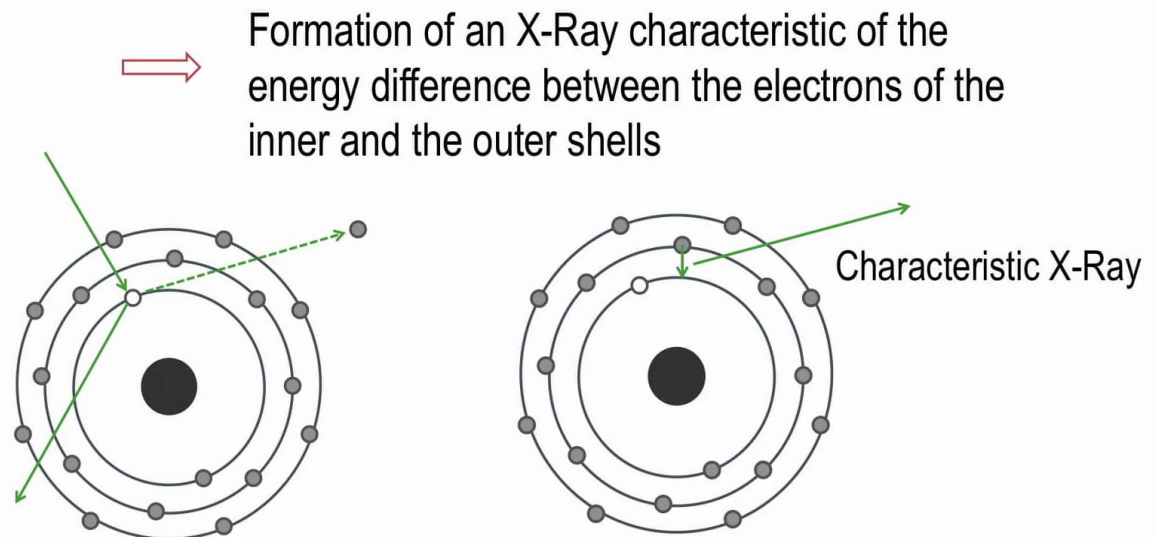
Notes

Summary



Characteristic X-Rays

- Electron fall from an upper shell



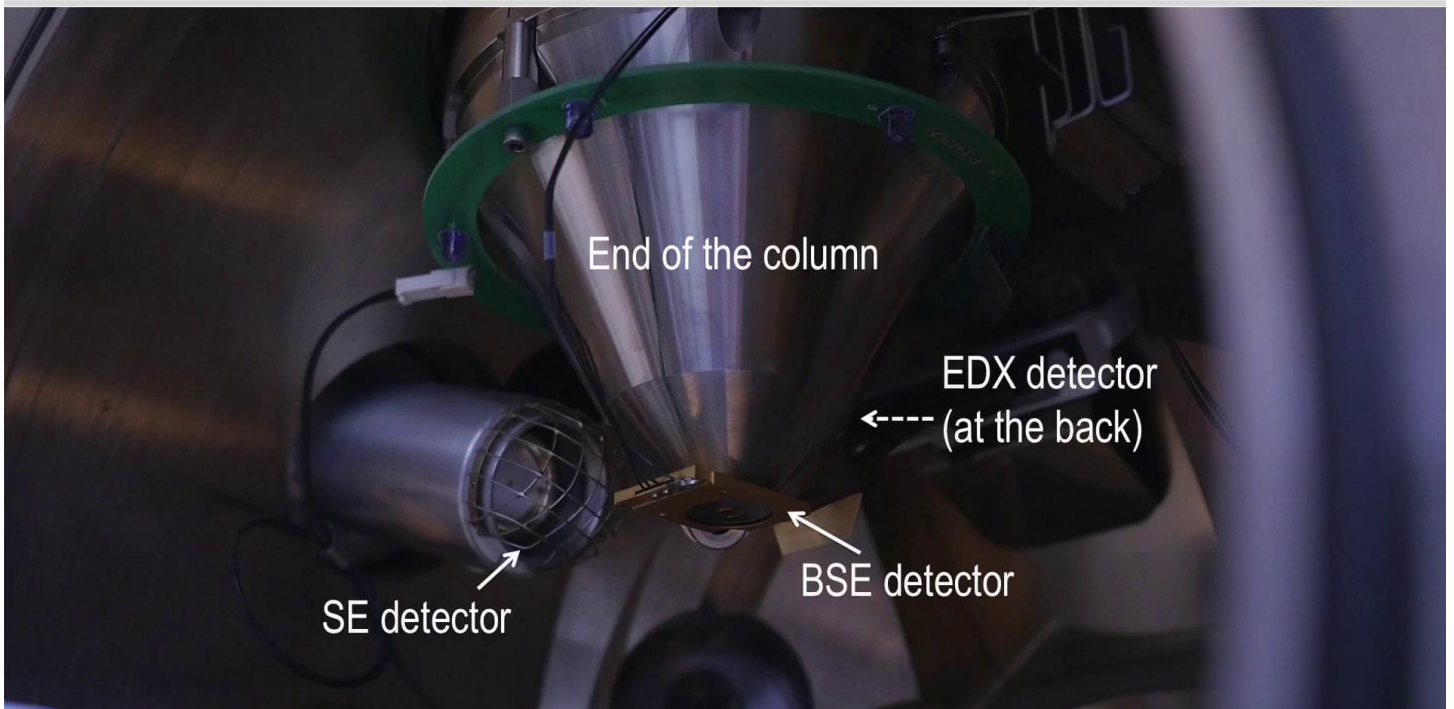
The third kind of interaction which is very useful for the characterization of a microstructure of cementitious materials is the formation of characteristic X-rays. After the emission of a secondary electron shown here, an electron is missing in the layer of the atom. This atom is ionized. If this missing electron originates from an inner electron shell of the atom this atom is energetically unstable. In order to reach a more favorable energetic level, an electron falls from an outer shell with a higher energy to fill the vacancy. This release of energy during this relaxation phenomenon leads to the formation of an X-ray. And what is important is that the energy of this X-ray is related to the energy difference of the two-shell levels here. Thus the energy of these X-rays is characteristic of the atom they come from. The element these X-rays come from can thus be identified and the atom content can be quantified for a selected spot of a microstructure.

Notes

Summary



Electron tube and detectors



This image shows you how the chamber of a microscope looks like. So you have here the end of a column, so this is the incident beam coming here, leaving through this hole to the chamber. So the sample holder is right below here. So you send electrons to the sample. You will have all these interactions which then will be collected by different detectors. We have here the secondary electron detector with this grid on top. The golden plate here is this BSE detector and the EDX detector is right at the back, a bit hidden. So we can collect all of these information in one microscope.

Notes

Summary



7m 44s



- Applications
- Secondary electron imaging
- Backscattered electron imaging on polished cross-section
- Energy Dispersive X-Ray Spectroscopy

These three types of interactions are very useful to characterize the microstructure of cementitious materials, In the next section, you will see how to set a nice image and some applications of these three types of interactions for cementitious materials.

Notes

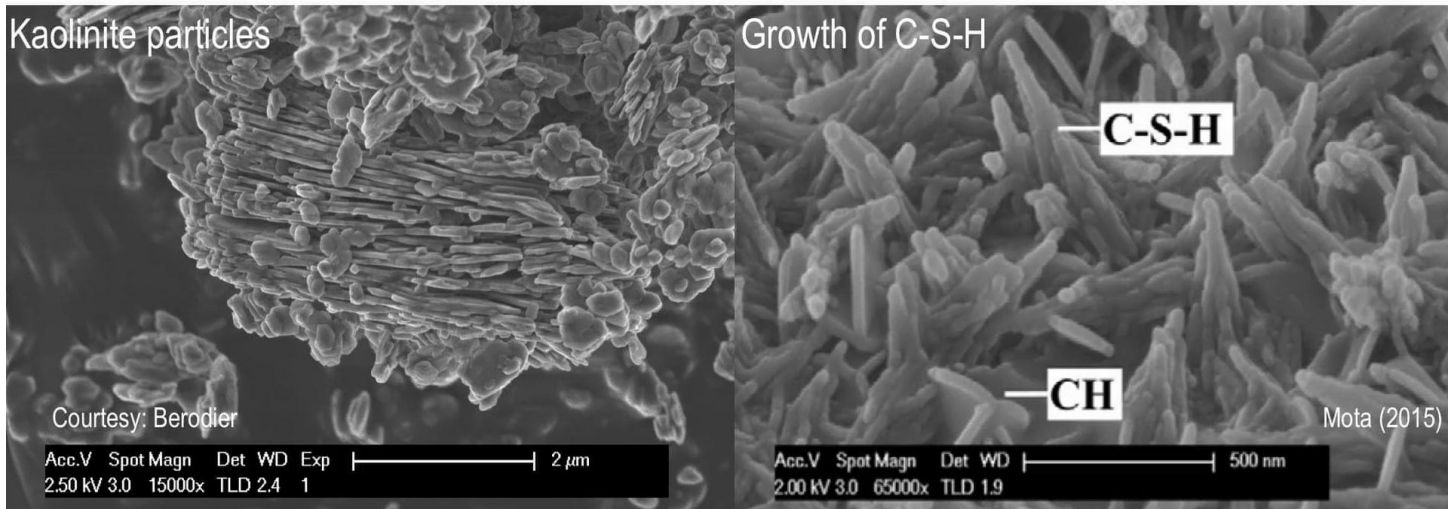
Summary



8m 23s

Morphology study

- Raw materials or hydration products at very early age
- Qualitative analysis



The first application for secondary electrons is the study of the morphology of particles. You can see here you have two very nice images showing you the morphology for instance here of kaolinite particles, so an anhydrous material. And here for the growth of C-S-H, which is hydration product at a very early age of hydration. These secondary electrons are used because of this topographic contrast which permits to really see nicely the morphology of the particles. This analysis is only qualitative. We can't get any quantitative analysis from this study. But still, it permits to really have a look the different morphologies we can find in cementitious materials.

Notes

Summary



8m 39s

Study of a polished cross-section sample

- Sample put in a sample holder and positioned on the microscope stage



So after talking about secondary electrons, we can now focus on backscattered electrons. To do so, it is always better to prepare your sample as a polished cross-section. As you saw before in the sample preparation course. So the sample is put in a sample holder like this, we just clip it. And then we will install it inside a microscope. So the chamber of a microscope is always under vacuum to avoid any contamination. And first vacuum was broken using nitrogen gas. And then the sample is gently put on the sample stage. We use a small giraffe, just to check the height of a sample to make sure that we are not too far from the good focus and then we close the chamber and we apply a vacuum again.

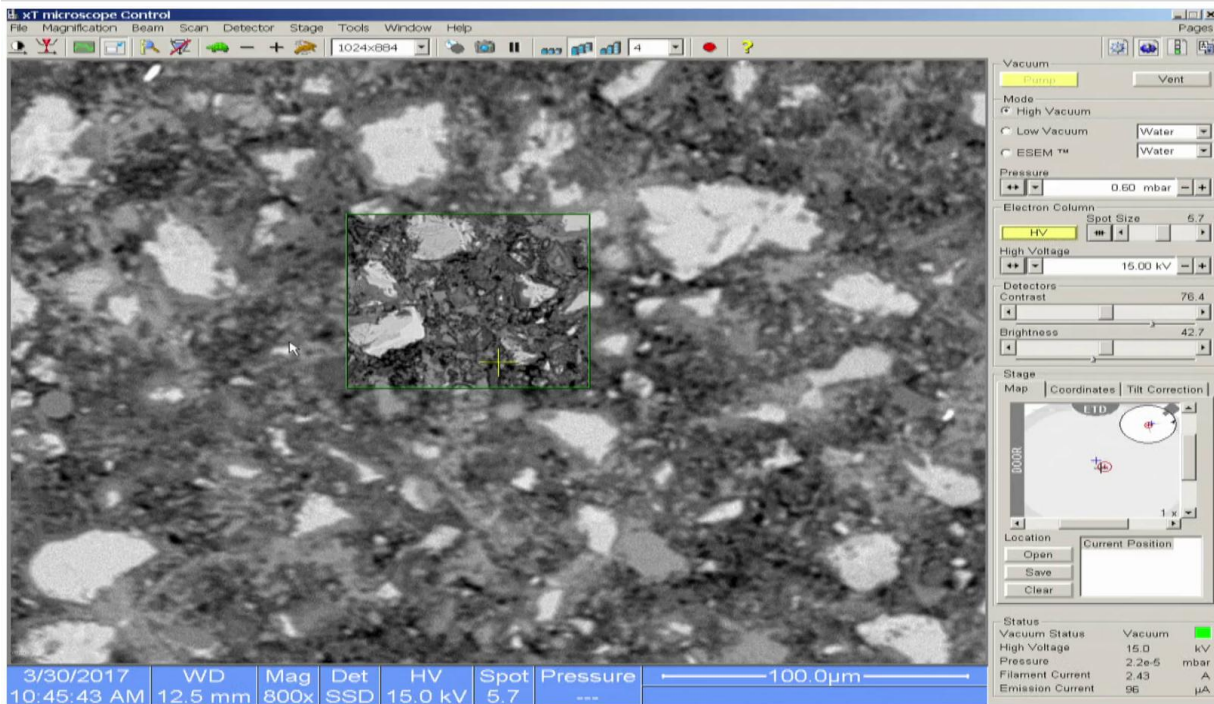
Notes

Summary



9m 27s

Setting of a good image



So now the sample is inside the microscope and we just waited for a good vacuum to be done to make sure that we won't have any contamination. Moreover it is very important to have a good vacuum otherwise the electrons, which are sent to a sample, could interact with air molecules inside the chamber. So it is very important to remove as much as possible air molecules present inside the chamber. When the vacuum is good enough, we can start applying a voltage, which will lead to an emission of a current, an emission of electrons sent to the sample. You just click HV here, And progressively we will see an image appearing on the screen. We start collecting backscattered electrons and this is the contrast you can see there. We have some really nice grey contrasts showing the backscattered electrons collected and so the different phases we have seen as cementitious material. As you can see the image is a bit blurry because we are not exactly in focus. So first we need to set the focus to make sure that we have the best resolution possible. So to change our focus, we simply adjust the Z position of the stage to make sure that the sample is at a good height and a good working distance.

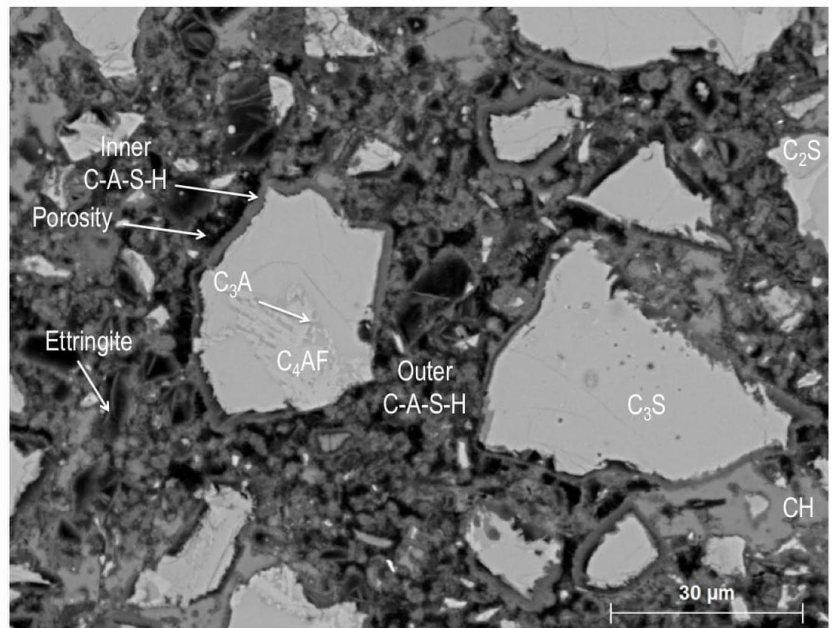
Notes

Summary



Microstructure of hydrated sample

- OPC sample at 28 days
- Formation of hydration products filling the space between cement grains



So we can see here the typical microstructure of a plain Portland cement sample for which the hydration was stopped at 28 days. So different areas can be clearly distinguished. We can first observe bright grey areas. These bright areas correspond to anhydrous clinker grains. Between these anhydrous grains a matrix of hydration products fills the space, fills the porosity with time. So in these bright grains we can clearly identify C₃S with this angular shape of grains. We can also see that for some grains we have not only one grey contrast but several at the same time which means that actually clinker grains are polyphased and not all monophased. So I put on this screen some phases which are likely to be there. With BSE you cannot directly know what is what. But we can demonstrate it, we can prove it later, doing an EDX on these phases. Concerning the hydration products we can first easily identify portlandite or calcium hydroxide or CH. It is this kind of uniform microstructure you can see here. Uniform grey level which is actually brighter than the other hydrates. Otherwise the main phase filling the rest of the porosity is this C-S-H phase as you can see a bit everywhere.

Notes

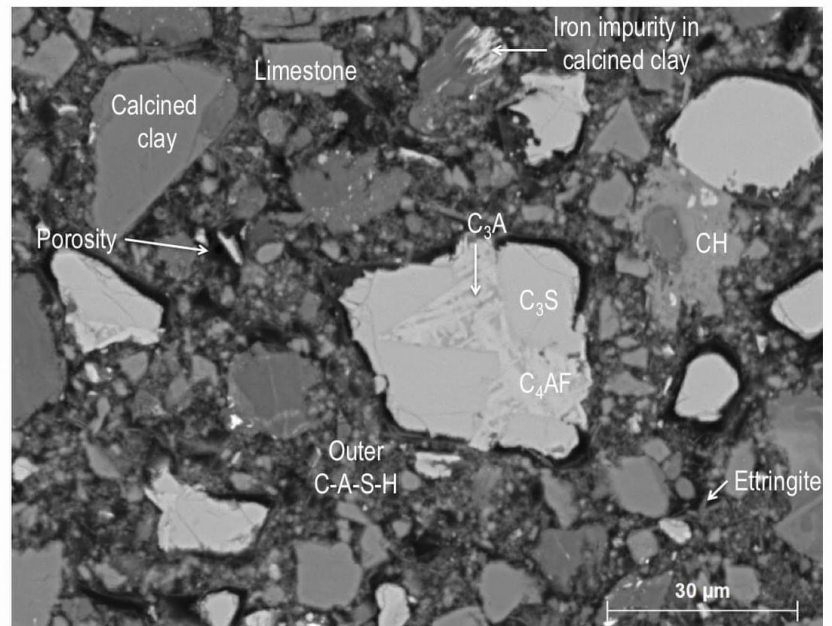
Summary



11m 46s

Microstructure of hydrated sample

- Limestone Calcined Clay Cement (LC³) at 1 day
- Clay with fairly low kaolinite content (50%)



We can see either outer C-S-H, here or also inner C-S-H which grew inside the initial boundary of clinker grains. Ettringite can also be observed, these kind of needles here. And the rest which is black is the porosity...which is dark is the porosity. Why is the porosity dark? Simply because we are sending electrons to these points and we do not collect anything back which is why the contrast is dark like this. Another question we could ask is why is the contrast of anhydrous phases brighter? Because hydrated phases contain water. Which significantly decreases the average Z coefficient of the phase. Moreover they are also less dense which makes them look darker on the image. So we can have a look at plain PC systems but also the main interest of using SEM is to look at other types of blends. Here is an example of limestone calcined clay cement, or LC3, at one day of hydration. In this system the clay used is not a pure calcined clay of pure metakaolin but it is a clay with only 50 percent of kaolinite calcined inside. So the microstructure shows some differences compared to the plain cement observed before. First we can observe limestone particles here, here, here, also there, with a regular shape with a small rim of C-S-H growing at the surface.

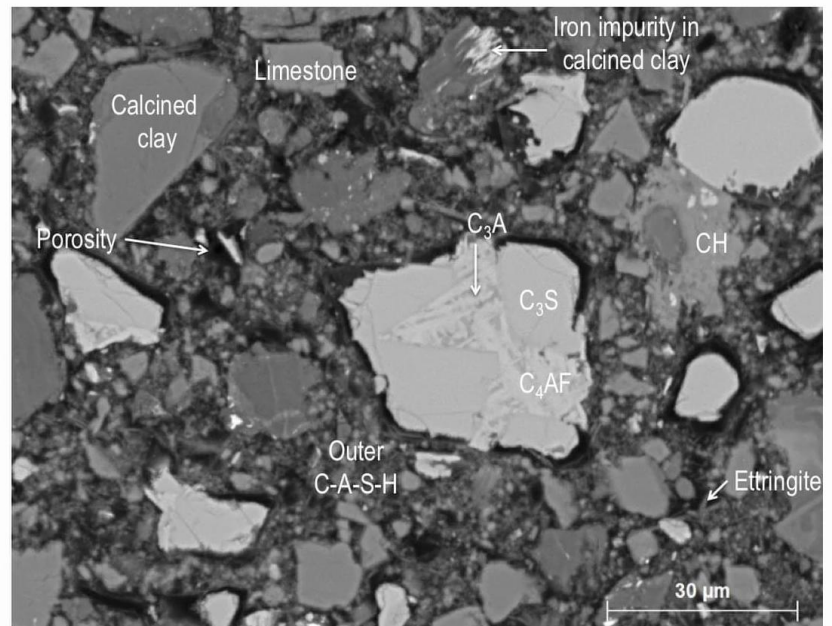
Notes

Summary



Microstructure of hydrated sample

- Limestone Calcined Clay Cement (LC³) at 1 day
- Clay with fairly low kaolinite content (50%)



In LC3, in limestone calcined clay cement, we can also of course observe calcined clay particles. And what you can see with these calcined clay particles like here, here, here, also there, there also is that the grey level is not uniform everywhere. Why so? It means that we have actually impurities in calcined clay. As I said before this clay here contains only 50 percent of kaolinite which means that the rest is impurities. For instance this particle here on the top of this image shows a much brighter area on the right side. And this indicates that there is likely to have elements with a higher atomic number or higher Z in this area which is likely to be actually an iron impurity in the calcined clay.

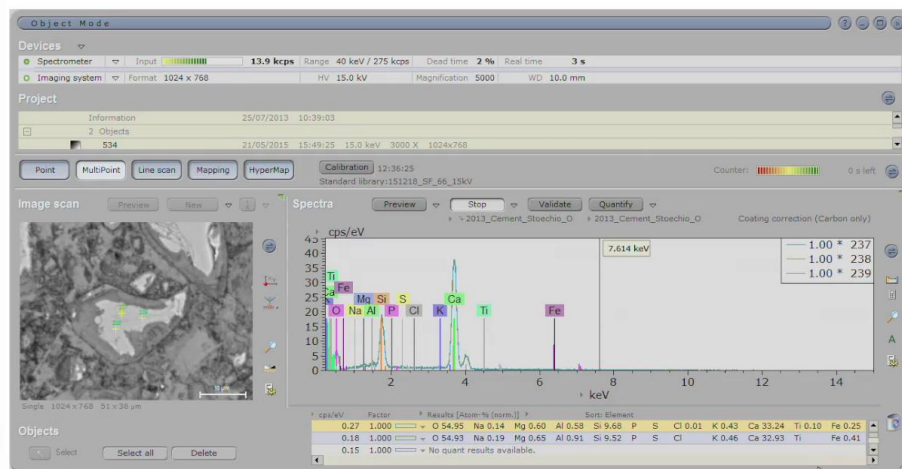
Notes

Summary



EDX: characteristic X-Ray

- Can be only applied on polished cross-sections
- Impossible to quantify hydrogen
- Quantification of oxygen not reliable
- Better to use atomic ratios from chemical analyses



So with backscattered electron imaging we can have a very nice information on the repartition of the phases in the microstructure. But for the identification of phases we do not have any evidence, any chemical evidence of the phases. Let's just try now to carry out an EDX analysis on this microstructure to identify several phases that we assumed to be present before. On this video is shown the quantification of alite phase. We spot several points of alite in the microstructure in these grains here and we are going to start with the EDX analysis to get the chemical composition of the phase. As you can see the quantification is very fast. And now we can have a look at the results. For EDX there are some tricks to be aware of. First it is impossible to quantify hydrogen. As we saw before, to form an X-ray we need to have an electron fall from an upper player of the atom. For hydrogen is impossible because there is only one electron. So we cannot quantify hydrogen with EDX. Another thing is that the quantification of oxygen and other light elements is not extremely reliable. Because of the extremely low energy you need to ionize oxygen and the other light elements. So that is why it is not very accurate.

Notes

Summary

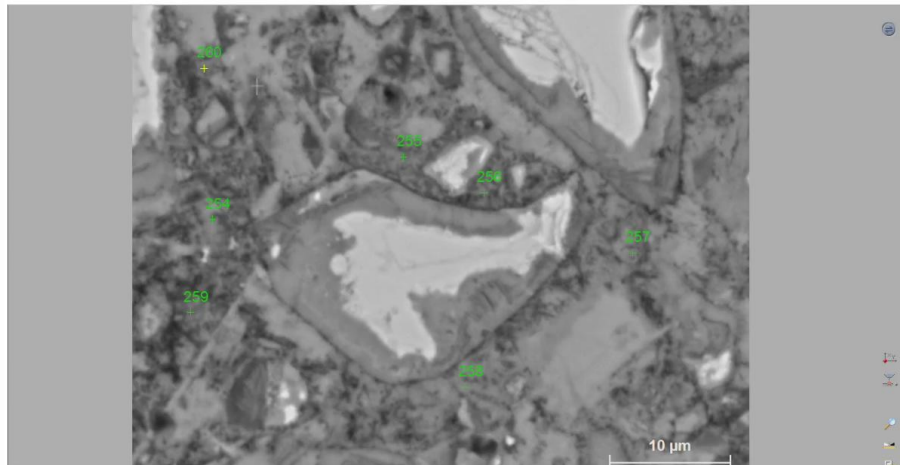


C(-A)-S-H composition

- Intermixing of phases is a big issue for C(-A)-S-H composition



- Use of 2D scatter plots to deal with intermixing problem



Thus it is better actually to use atomic ratios from the chemical analysis than direct values collected on the software. For instance for C3S here, instead of looking at the absolute value obtained we can have a look at the calcium to silicon ratio. We know that in alite we should have calcium to silicon ratio close to three, an atomic calcium to silicon ratio close to three which is the case here. So this evidence is the presence of C3S in this grain. We can do so for all the other phases, anhydrous or hydrates, to evidence their presence in the microstructure. The main issue for EDX analysis is the interaction volume we talked about at the beginning of this talk. When a specific spot is pointed actually the information which we collect does not come from this point only but comes from the interaction volume related to this point which is a few microns. Right? So if we are pointing just at the border between two phases it is very likely to have information from both phases. This is an issue especially for the determination of a C(-A)-S-H composition. So C-S-H and C(-A)-S-H are roughly the same thing. It is just that when there is a significant incorporation of aluminum in this C-S-H we call it a C(-A)-S-H.

- Notes

Summary

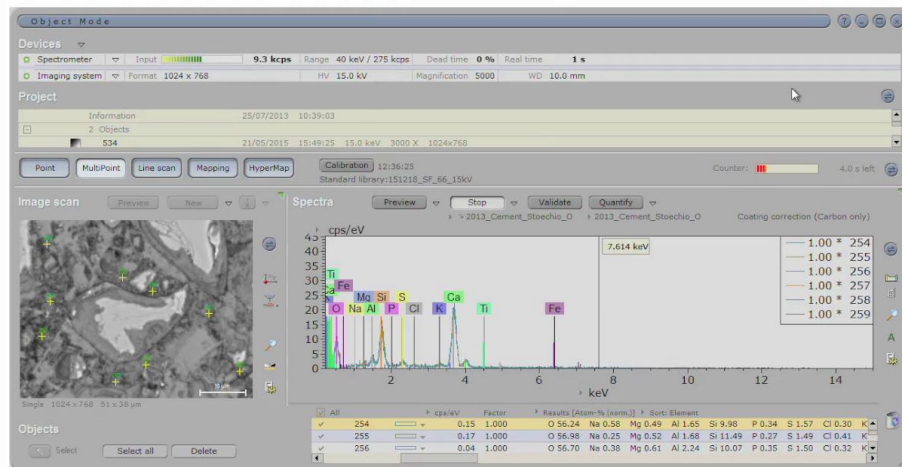


C(-A)-S-H composition

- Intermixing of phases is a big issue for C(-A)-S-H composition



- Use of 2D scatter plots to deal with intermixing problem



In the case of LC3 for instance we call it C(-A)-S-H. So when we point the C-S-H here, it is extremely likely to have information on other phases at the same time. Thus the idea to get an accurate composition of a C-S-H is to use 2D scatter plots to deal with intermixing problems. How does it work?

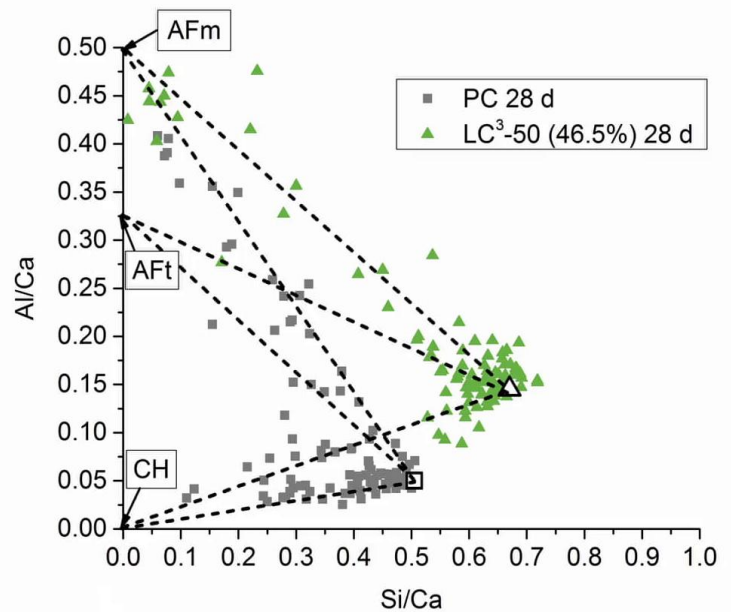
Notes

Summary



C(-A)-S-H composition

- Comparison of OPC and LC³-50
- Tie lines from pure phase composition to C(-A)-S-H
- C(-A)-S-H with the least intermixing at the right edge of the cloud of points



The best way of doing it is to plot the aluminum to calcium ratio here, the atomic composition aluminum to calcium ratio as a function of a silicon to calcium ratio. Why do we do that? Because the intermixing which can occur with portlandite or calcium hydroxide, with ettringite or with AFm phases can be directly observed. These phases I just mentioned are present on the left axis here because they do not contain any silicon. This way we can isolate the points which are really C-S-H from points which are coming with a bit of information of these pure phases here, portlandite, ettringite and AFm phases. If you do that, so this is shown for an OPC system at 28 days of hydration and LC3 system at 28 days of hydration, we can collect approximately 200 points per system and we get this kind of clouds of data. So if we have a look closer to the PC system for instance we have a cloud of data around this composition here. And we have some points deviating and going for instance here towards portlandite. If we take for instance this point here which is roughly in the middle between CH and this cloud of C-S-H it means that for this point we have information approximately about half from CH, from portlandite and half from this C-S-H.

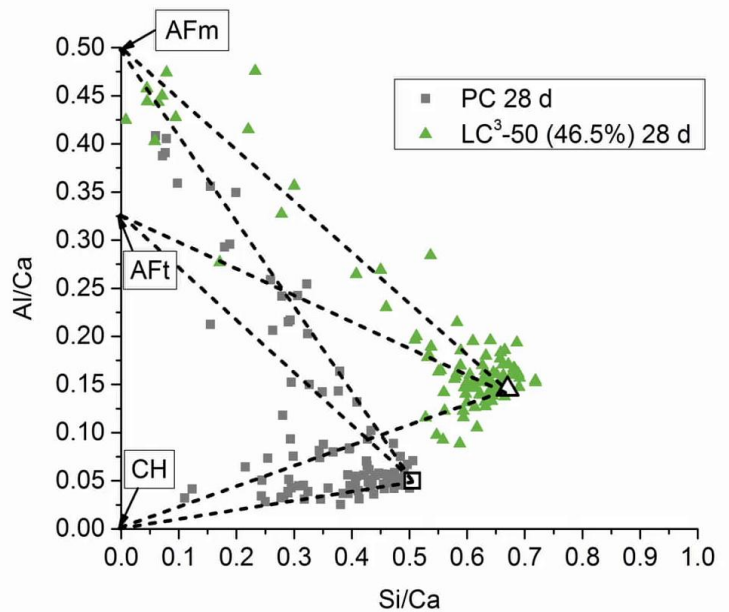
Notes

Summary



C(-A)-S-H composition

- Comparison of OPC and LC³-50
- Tie lines from pure phase composition to C(-A)-S-H
- C(-A)-S-H with the least intermixing at the right edge of the cloud of points



Now how to find the exact C-S-H composition? You have this cloud of data here. The more you are on the left side of this cloud the more you are intermixed with other phases. Which means that the right correct C-S-H composition is at the right edge of the cloud. So you can use these lines from these phases with fixed stoichiometrical composition to help you to find the real composition. The intersection of these lines from portlandite, ettringite and AFm phases should give you the good C-S-H composition. And what you can see then you can apply it to different systems which is the case here. So we have OPC and this LC3 system and what we can see is that we have really strong differences in terms of C-S-H composition between these systems. We have a strong silicon and aluminum incorporation in the C-S-H. This is a kind of valuable information you can get from EDX analysis.

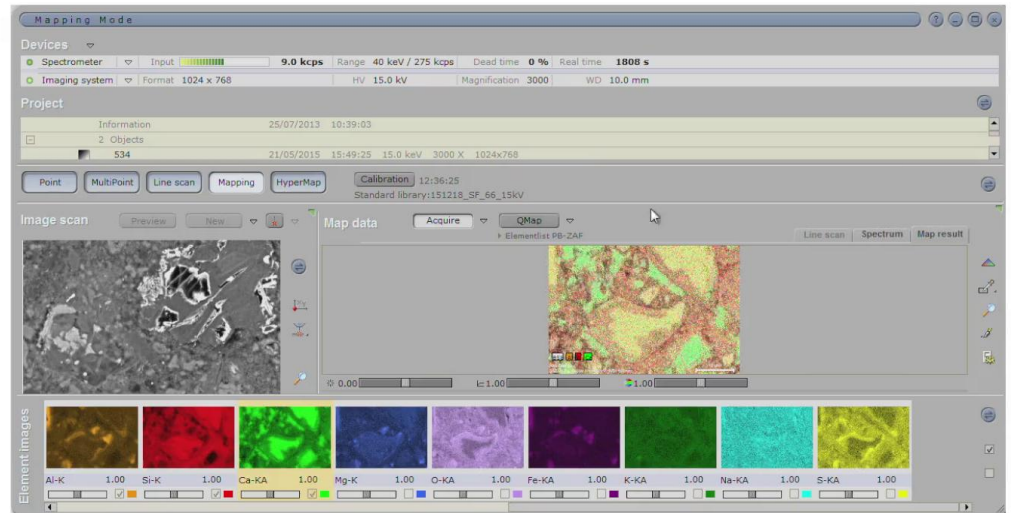
Notes

Summary



EDX mapping

- Phase distribution
- Porosity
- Qualitative size distribution
- Change in C(-A)-S-H density
- Characterization of damage (ASR for instance)



Another thing you can do with EDX which is more global I would say is to get a phase distribution not only on some points but on the whole map in your system. An example is shown here for an OPC system. So you simply select the elements you want aluminum, silicon, calcium, magnesium, iron, oxygen, potassium, sodium, sulfur and you can actually acquire and EDX but not on a couple of points but on each point of your map, so of course this takes more time.

Notes

Summary



22m 50s

EDX mapping

- Phase distribution
- Porosity
- Qualitative size distribution
- Change in C(-A)-S-H density
- Characterization of damage (ASR for instance)



But this also gives you some valuable indication on the phase distribution inside your microstructure. So that is another very nice example of how we can use microscopy for cementitious materials. There are many other applications which can be studied with a scanning electron microscope. For instance we saw the porosity, this kind of dark area in the microstructure. This porosity, which is of course a kind of coarse porosity, like coarser than approximately one micron, can be quantified using image analysis and we can get a rough estimation on the porosity of a system. The size distribution of particles can also be determined. Its qualitative it can give us an idea about the distribution of of the particle size. Another thing we can do with SEM is to look at the grey level, for instance of the inner C-S-H which you can see here on this microstructure. For instance with temperature we know that the density of the C-S-H changes, and depending on the grey level intensity we can calibrate it and know how much it changes with temperature. Finally mapping can also be very useful to characterize the damage. For instance for alkali silica reaction, it is extremely useful to follow the reaction of ASR and to know where the damage is and what really happens. It allows to better understand the mechanisms of these reactions.

Notes

Summary



23m 30s

Conclusion



- One of the most powerful techniques for cementitious materials
- Imaging
- Chemical analysis
- Various applications

To sum up what we saw, scanning electron microscopy is one of the most powerful technique for the study of cementitious materials. We can do really many different things with a scanning electron microscope from topography imaging to backscattered electron imaging, from chemical analysis. And there are really many applications for which scanning electron microscope really allows to better understand what is going on in a cementitious material. Thank you for watching.

Notes

Summary



25m 12s