Advanced Topics in the Science and Technology of Concrete
Electron Microscopy
Professor Karen Scrivener
LMC, EPFL, Lausanne, Switzerland
Part 2: Microstructural characterisation of cementitious materials

In this second part we are going to look at electron microscopy, which is really one of the most powerful techniques for micro structural characterization, although more able to quantify that is really, I think the compact X-ray diffraction and thermo gravimetric analysis we have not talked about are very good for quantification, whereas, electron microscopy is much more visual. It gives you an overall idea of things, but the quantification is more tricky.

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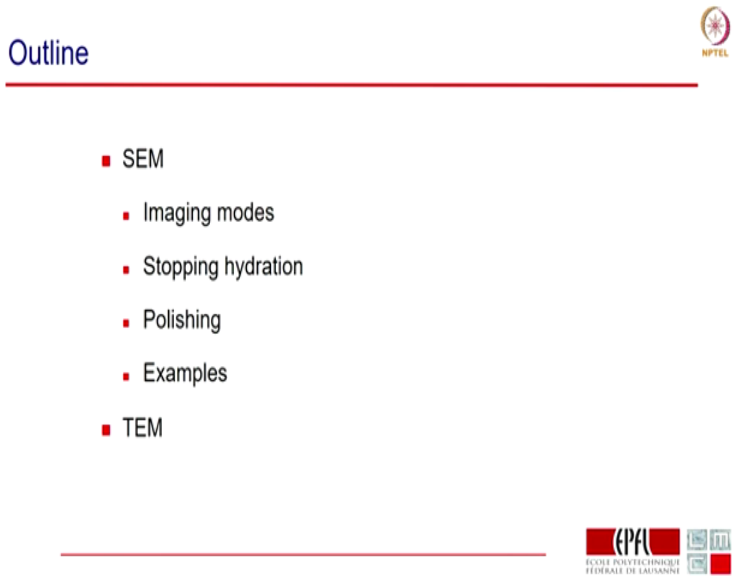

Outline

- SEM
  - Imaging modes
  - Stopping hydration
  - Polishing
  - Examples
- TEM

So, we are going to talk mainly about S E M, imaging modes, stopping hydration and particularly polishing, which is the most important thing and we will look at some examples and at the end, I am just going to show a couple of examples of transmission electron microscopy which is a very powerful technique but not for the faint hearted because it really will take you about six months to a year to be able to transmission electron microscopy which is not practical for most studies.

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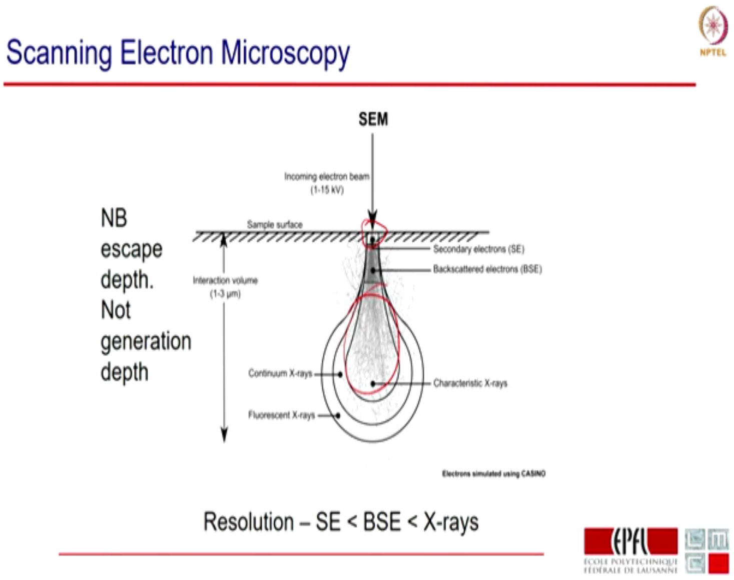

Scanning Electron Microscopy

NB escape depth. Not generation depth

Resolution – SE < BSE < X-rays

So, what is happening in electron microscopy, it depends on the interaction between the incoming electrons and the sample. So, this is shown in this diagram above, we have this beam of incoming electrons and then they interact with the matter in the sample through what is called Interaction volume, which is over size of a few microns and here we can see from a Monte Carlo simulation with trajectories of the different electrons and the different signals we are using have different characteristics.

So, the main three signals we're using in the S E M are, first of all secondary electrons, which come from just the very small area close to the surface because they have very low energy. So the all secondary electrons generated everywhere, it is just that at greater depths, they do not escape from the sample. Then we have the backscattered electrons which have a slightly bigger depth but still they are focused in a quite narrow area and finally, we have the characteristic x-rays which really come in from this whole volume here and that is where we have the most problem of the fact that we saw playing this volume of several microns.

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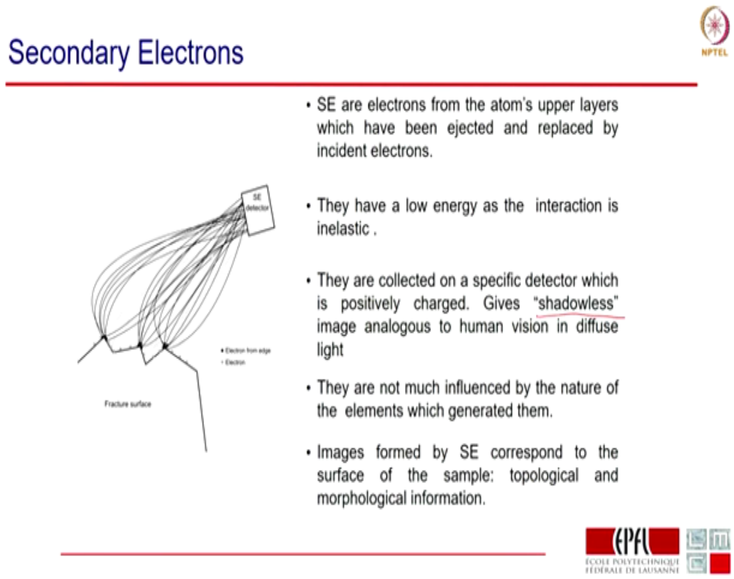

Secondary Electrons

- SE are electrons from the atom's upper layers which have been ejected and replaced by incident electrons.
- They have a low energy as the interaction is inelastic .
- They are collected on a specific detector which is positively charged. Gives "shadowless" image analogous to human vision in diffuse light
- They are not much influenced by the nature of the elements which generated them.
- Images formed by SE correspond to the surface of the sample: topological and morphological information.

So, let us look at each of these in turn and what we can do with them. Now, first of all, the secondary electrons are electrons from the outer layer of the atoms, that have been ejected from the sample. Now, they have a low energy and because they have a low energy, you can collect them with a detector which has a slight positive bias and this give us what is called a shadowless image.

Now, shadowless image is actually kind of what we used to seeing, because even though we know we have shadows, light can be quite diffused, collecting light from all around your face and not just the part facing to me and this means that the secondary electron images, we tend to like a lot, because they kind of ensure that we can relate most of them in tell and probably you all have seen these nice micrographs. The problem is that these are not really such good for looking at thing is in a quantitative way, they are really a very qualitative technique.

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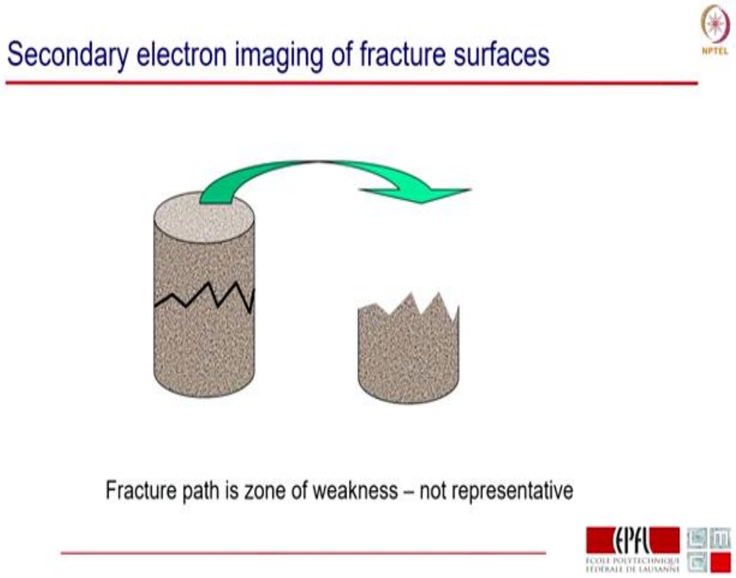

Secondary electron imaging of fracture surfaces

Fracture path is zone of weakness – not representative

So how do we use secondary electrons?, Well generally we look at fractured surfaces, these are very easy to prepare you just take a piece of your sample, smash it with a hammer, pick up a little piece, closer toward other and put it in the electron microscope.

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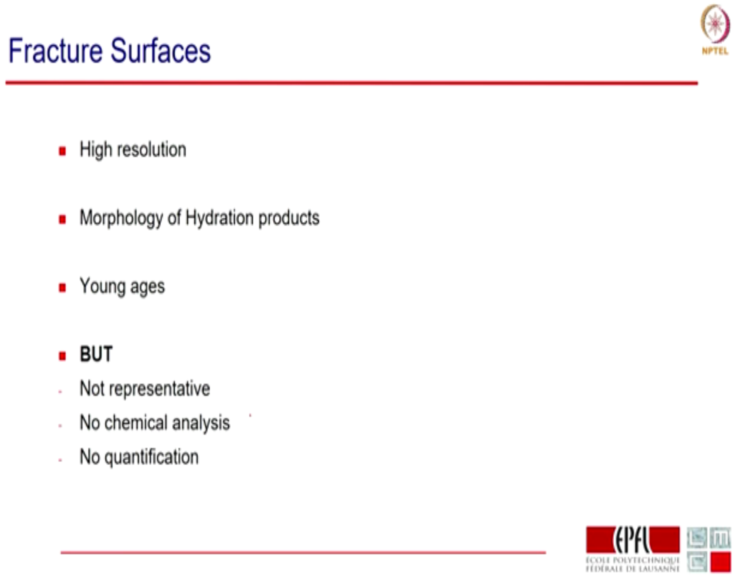

Fracture Surfaces

- High resolution
- Morphology of Hydration products
- Young ages
- **BUT**
  - Not representative
  - No chemical analysis
  - No quantification

And this has the advantage, we have very high resolution and we can see the morphology of hydration products and that can be very powerful techniques. But it is not representative because we have made this fracture, we are only seeing the weak areas. We cannot get any chemical analysis, so do not believe any kind of chemical analysis done on fracture surfaces, it is not reliable and we cannot quantify anything.

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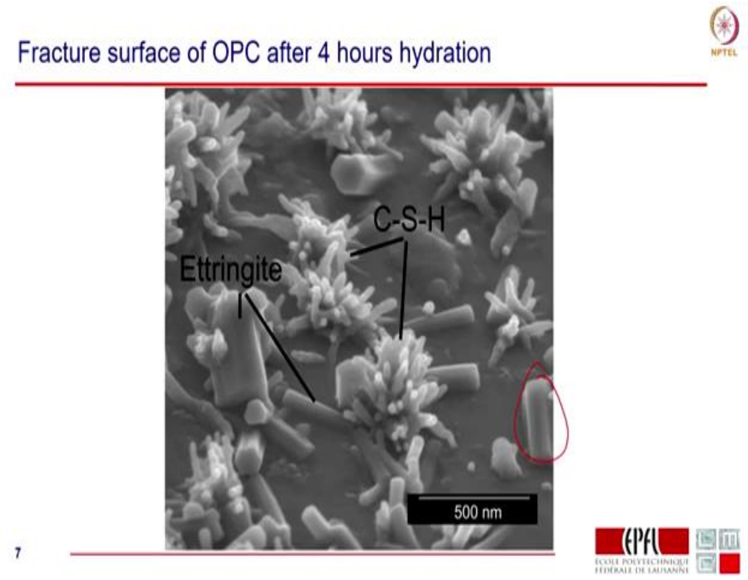

Fracture surface of OPC after 4 hours hydration

So, this is the kind of image we can get, here we see a very nice image of a cement paste during early hydration and we can see the different hydrates, we can see this crystal of ettringite, we can see the crystals of calcium silicate hydrate which are growing on the surface and incidentally I just want to point out here, you see there is no coverage of the surface and these ettringite needles are not what directly slows down the aluminate hydration, its sulphates ion. And level of detail we can get from it, we can clearly see that these ettringite crystals are not providing any kind of barrier to hydration.

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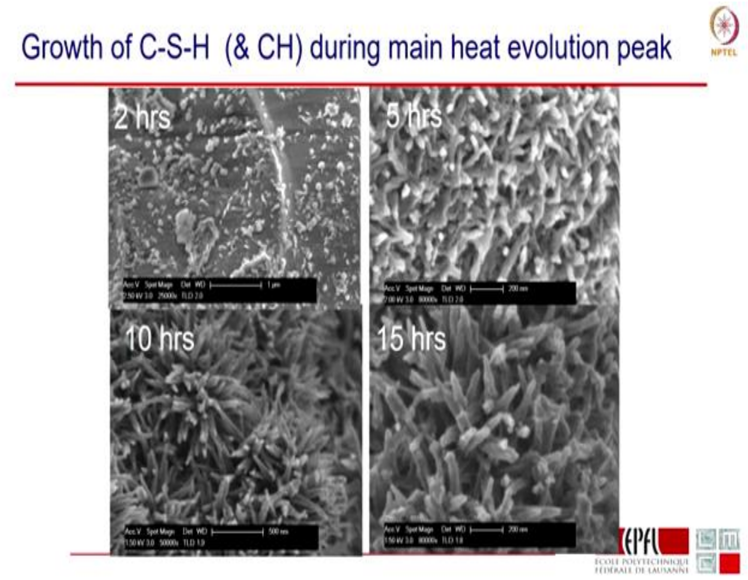

Growth of C-S-H (& CH) during main heat evolution peak

So, we can overturn that idea which was quite popular in the literature. And here we see some images, where we see the growth of C S H during the main hydration peak, we can see very nicely, how these C S H needles grow over time and that is all very good, the problem is that you know, any cement will look just the same so, if you have done it, you don't need to do it again.

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After few days everything looks the same

And the most for the problem is that, as soon as you get a sample which is few days old, everything really looks to same, well everything looks the same and not the same, because the problem is if you look at an individual image like this the microstructure in porous areas is completely different from unporous area, so you are going to have as much difference between within one sample as within any other sample. So here are supposedly four different samples but really you cannot say anything about whether they are really different or just variation or the same you see they have got big particles of aggregate in.

So, I mean it is really useless this I mean I am sorry but this is every day as editor of a journal, I see so many papers like this where people have spent time on the electron microscope taking pictures like this, it is just the waste of time, it is a waste of everybody's time, it is a waste of instrument time, waste of your time and a waste of my time having to reject your paper. So, you know please try not to do this.

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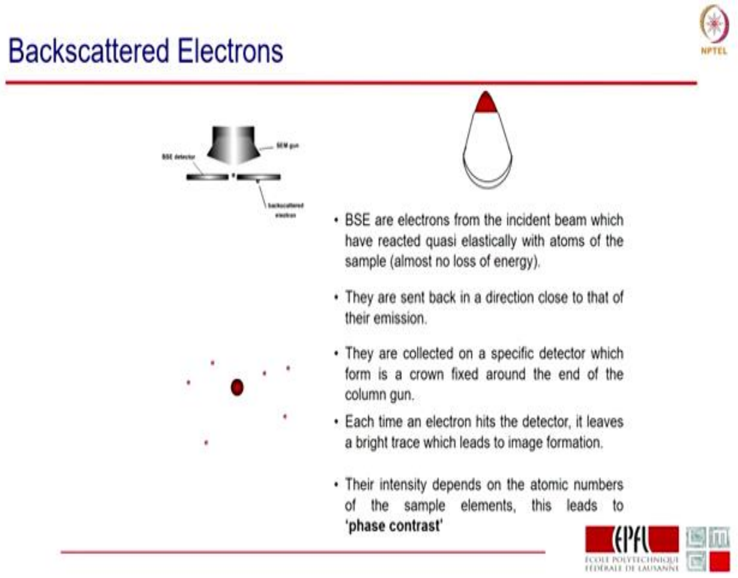

Backscattered Electrons

- BSE are electrons from the incident beam which have reacted quasi elastically with atoms of the sample (almost no loss of energy).
- They are sent back in a direction close to that of their emission.
- They are collected on a specific detector which form is a crown fixed around the end of the column gun.
- Each time an electron hits the detector, it leaves a bright trace which leads to image formation.
- Their intensity depends on the atomic numbers of the sample elements, this leads to **'phase contrast'**

Now, much more useful when we get to backscattered electrons and here what happens is the incoming electrons are deflected by the electrons surrounding the atom and they kind of bounce back, you can imagine it like a ball bouncing back from a wall and the probability, that the electrons bounce back goes up as the number of electrons and the atoms goes out that is to say as the atomic number goes up, okay.

So, you have this extremely useful contrast which depends on the atomic number which leads to what is called phase contrast.

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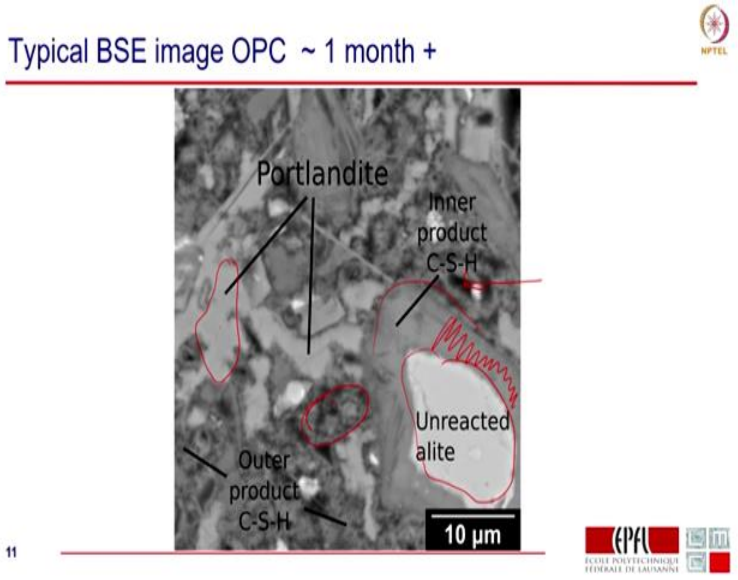

Typical BSE image OPC ~ 1 month +

And the kind of typical image you can see like the one above and this is where it is you know really so very powerful. Now we have a polished section the contrast is produced by the different atomic numbers, so we have the anhydrous phases which contain no water, which are the brightest then we have the calcium hydroxide and then we have the other hydrate phases and we cannot generally distinguished between the C S H and the other phases like a ettringite, they are all tend to be mixed up together but what we can see is the homogeneous regions of what we call inner product of C S H that is formed in the place of the original grain and then regions of outer product, which are formed between the grains.

So, this is very useful, we can really see very well the disposition of the different phases and of course the pores but as we will talk about in the next part the pores we see are only really the very large pores, so it is not so useful for porosity.

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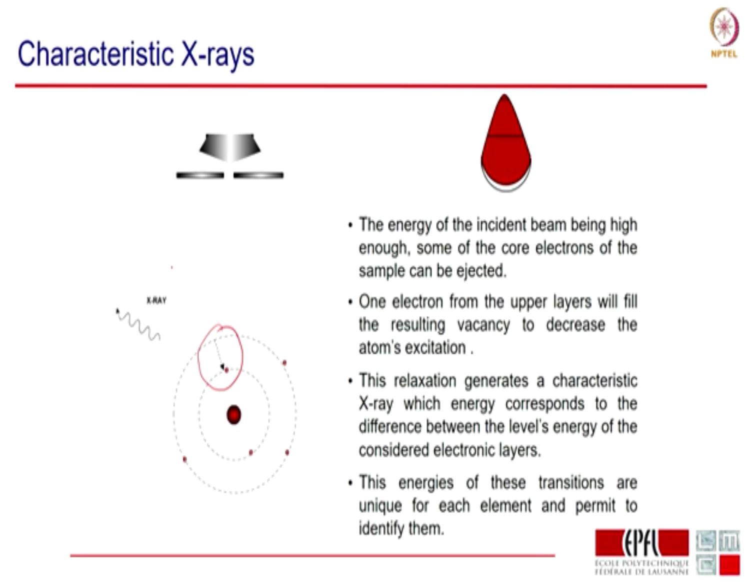

Characteristic X-rays

- The energy of the incident beam being high enough, some of the core electrons of the sample can be ejected.
- One electron from the upper layers will fill the resulting vacancy to decrease the atom's excitation .
- This relaxation generates a characteristic X-ray which energy corresponds to the difference between the level's energy of the considered electronic layers.
- This energies of these transitions are unique for each element and permit to identify them.

And the third technique we use is called characteristic x-rays. What happens here is that we have an incoming electron that knocks out an electron from the shell of the atom and then we have the relaxation of another electron into its place with the emission of an x-ray and of course because the energy between these different shells is quantized and depends on the atomic number, the energy of this x-ray that is given off is characteristic of the atom.

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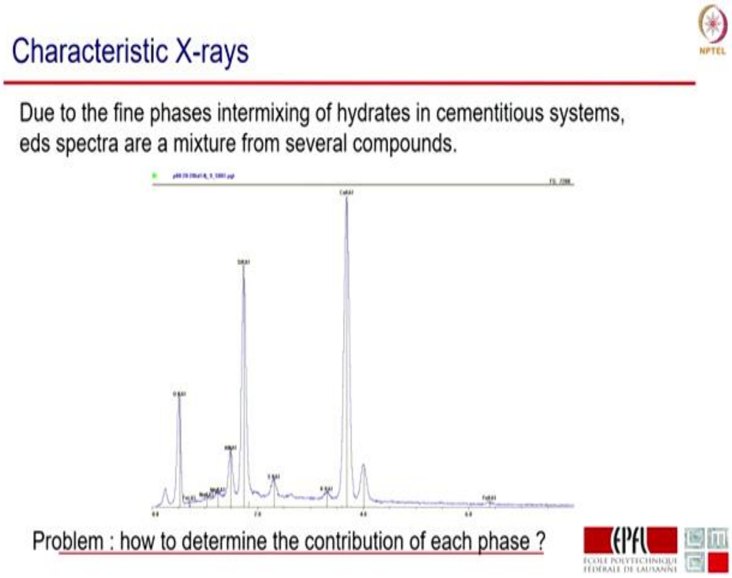

Characteristic X-rays

Due to the fine phases intermixing of hydrates in cementitious systems, eds spectra are a mixture from several compounds.

Problem : how to determine the contribution of each phase ?

And so, if we look at a typical spectra, well we can see different peaks according to the different element, comes is then how to determine the contribution of each phase and particularly where we have this intermixing.

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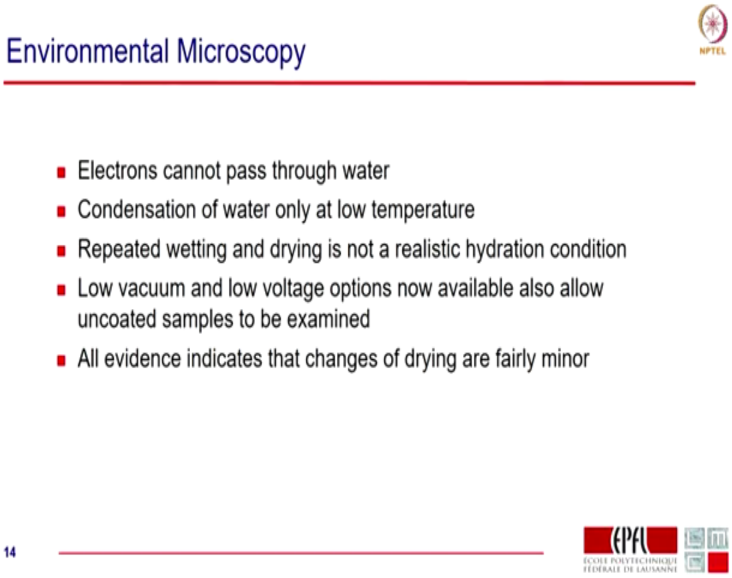

Environmental Microscopy

- Electrons cannot pass through water
- Condensation of water only at low temperature
- Repeated wetting and drying is not a realistic hydration condition
- Low vacuum and low voltage options now available also allow uncoated samples to be examined
- All evidence indicates that changes of drying are fairly minor

So, we go on to look at some examples. I want to say a word about environmental microscopy because many people say “oh! this is a solution we can look at hydration in-situ”. No you cannot. First and foremost, electrons do not pass through water, I mean they go maybe into one micron level.

So if you have got any water on your sample, they are just going to bounce off the water and you are just get to see the surface of water which is not very interesting, then what people say is very good in these electron microscopes is that you could condense water and then you can remove it. Well you can do that, but the point is the whilst condensation of water in the environmental electron microscope only occurs at a very low temperature so the water is only there when the temperature is very low and the hydration is not really going to be going at temperature. Secondly, you are putting water there then you are removing it, that is not at all a realistic hydration condition.

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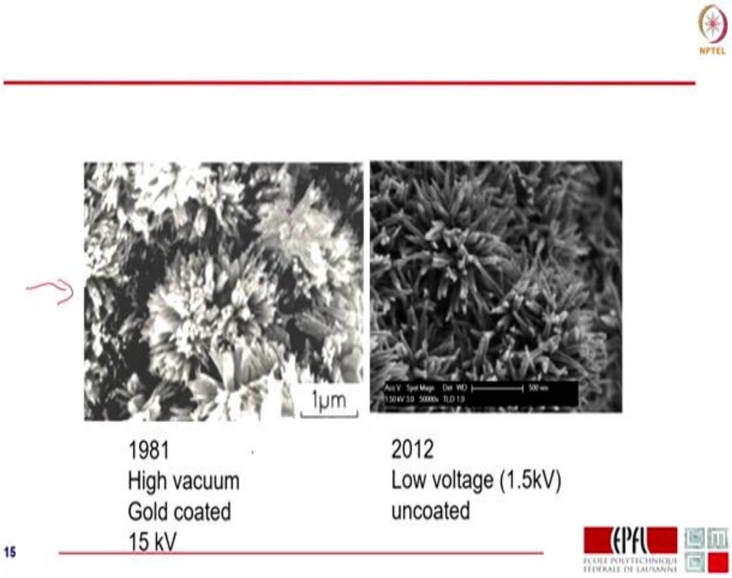

1981
High vacuum
Gold coated
15 kV

2012
Low voltage (1.5kV)
uncoated

So, you know really the use of environmental microscopes for cementations materials I think is a very limited, maybe it is useful where you have something like a polymer addition or something like that but otherwise, I do not really recommend it. Nowadays even on conventional S E M S you have many options for low vacuum, you can also look at uncoated samples and particularly, if we look at the picture above, which I took in my PhD thesis in 1981, it was taken in a completely conventional S E M high vacuum gold-coated, this is a picture taken by my student Emily Barzani which was done at low voltage no coating.

Now, basically you are seeing the same thing, you know this, it is C S H and even this condition of high vacuum and gold coating has not really completely changed that structure. So do not be afraid when people say “oh! you have got water there”, yes you have to be careful about the coating on that but you can do it.

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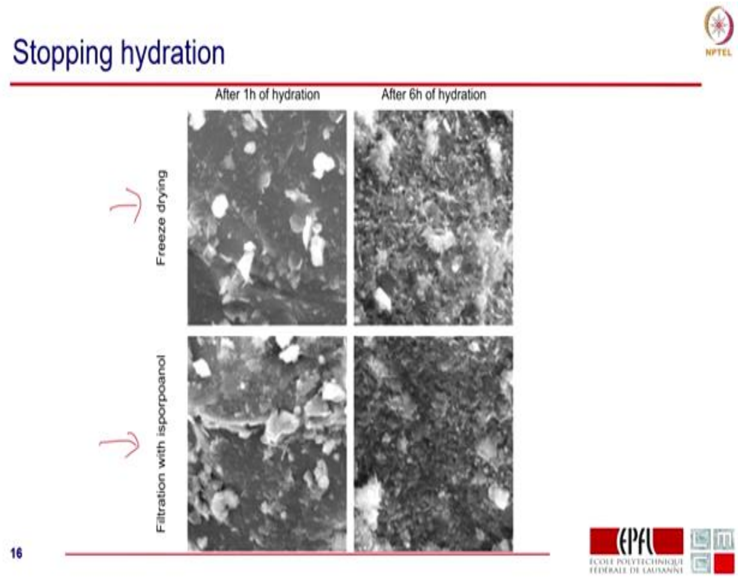

Stopping hydration

And above we see some examples for the different methods of stopping hydration, so at the top we have example with freeze drying and then we have an example where we have looked with isopropanol, this is been done with a powder, so it is been done with a quick flight filtration and basically you do not see any difference. They are pretty much the same in the two samples.

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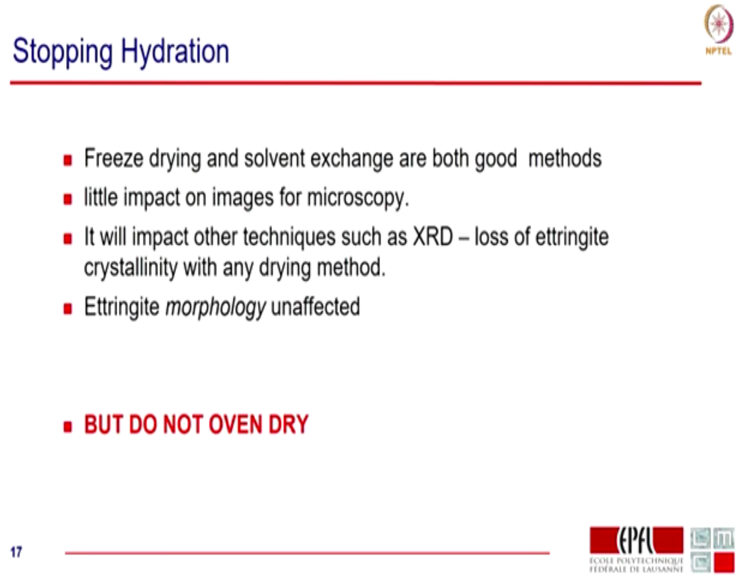
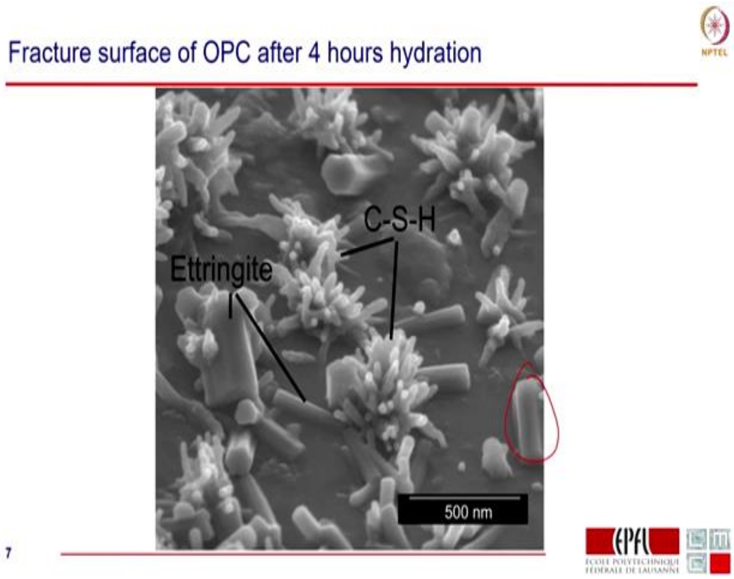


Stopping Hydration

- Freeze drying and solvent exchange are both good methods
- little impact on images for microscopy.
- It will impact other techniques such as XRD – loss of ettringite crystallinity with any drying method.
- Ettringite *morphology* unaffected

- **BUT DO NOT OVEN DRY**



Fracture surface of OPC after 4 hours hydration

So, both of these are very good methods for electron microscopy. They have little impact on the images, of course they impact x-ray diffraction we just talked about but that is not what we are worried here and in above picture as we can see the ettringite needles, these will not be crystalline anymore, this will not show up in the x-ray diffraction but in the morphology it is unaffected.

Do not oven dry as I have said, because oven dry, it looks a complete mess I am sorry I do not have a picture of an oven drive sample. I should I did one a long time ago but I have not got it anymore and I obviously needs to take one again.

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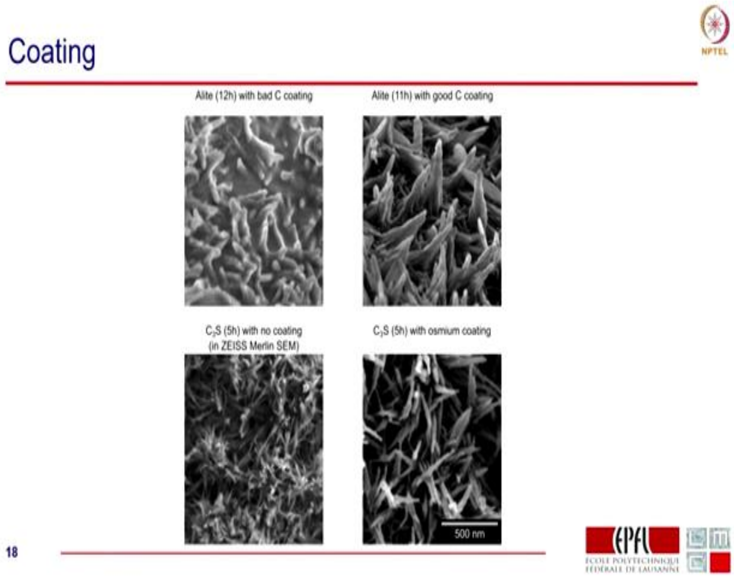

Coating

Alite (12h) with bad C coating

Alite (11h) with good C coating

C_3S (5h) with no coating (in ZEISS Merlin SEM)

C_3S (5h) with osmium coating

So, the other thing is coating. Now if you are not careful you can get a lot of damage of your sample by not doing the coating well so this is what is called poor coating but if you do good coating with carbon, you can see in the picture above that we have preserved the needle structure very well and there are some examples with no coating and osmium coating. It is pretty much all the same, so you know if you do things well, then you can preserve the morphology of the hydrate.

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Polishing

Do NOT use water!!!!

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So now we are going to look at polishing, because as I hope I have convinced you, backscatter electron imaging is by far the most useful technique, but to get these backscatter electron, it is a really important prerequisite that we have a perfectly polished sample and most polishing machines can work quite well but do not use water. It seems kind of obvious you have got cement which is reacting with water. Obviously, if you are going to use water during the polishing, you're going to wreck everything, but every day I am talking to people and they say “why cannot I get good polishing?” then we find out that, they are polishing with water, because they have taken it maybe to the geology laboratory or the metals laboratory and if you what looking at rocks or metals, you are not worried about water, so the standard procedure is water.

Now generally what we are usually using is a deodorize petrol because we found this is a good lubricant that does not pick up water. The problem with many other lubricants like ethanol, is if you have it lying around in the lab it will pick up water and then that is the same thing, it kind of destroy your sample the same way and you have a polishing disk, you either have separate disk or you very carefully wash between the different stages and then you use the different diamond sprays.

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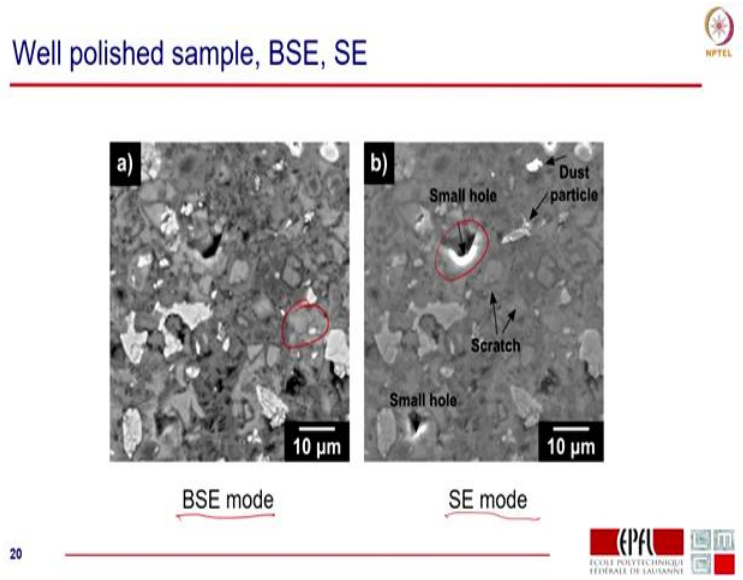

Well polished sample, BSE, SE

BSE mode

SE mode

In above image,what we are aiming at is that, in the backscattered electron mode, we can see the nice contrast between the different phases, we can see the areas of calcium hydroxide and to check it, we can go into secondary electron mode and In the secondary electron mode you can see there is some small holes which you will always have. There is a very fine scratch but that is okay and sometimes you can even see particles of dust, that is what you have to be careful about, because if you leave your sample lying around on the bench it will get particles of dust that fall on it but this is really not bad.

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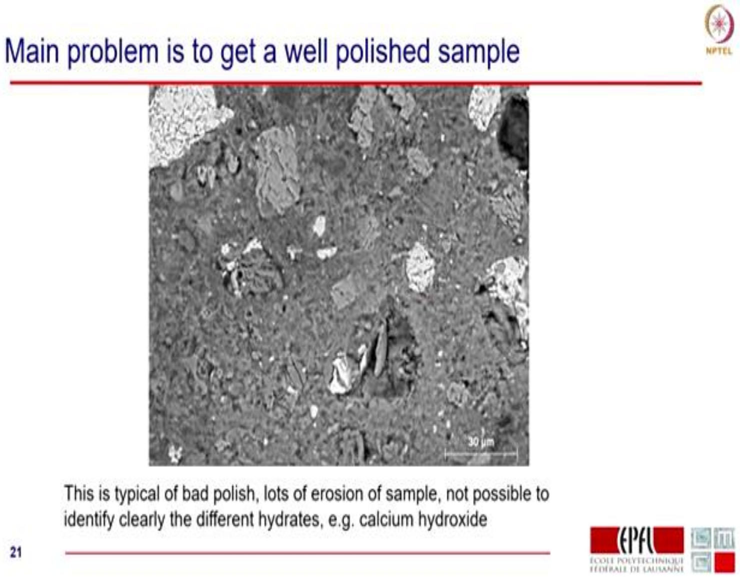

Main problem is to get a well polished sample

This is typical of bad polish, lots of erosion of sample, not possible to identify clearly the different hydrates, e.g. calcium hydroxide

In contrast, many people hang out with the difficulty in acquiring well-polished sample, above is a very typical polished sample and the problem here is that, the sample was not well impregnated with resin, so the phases are ripping out and you have ended up with a very rough surface. You cannot identify the calcium hydroxide, you can sort of see the cement grains but they are very rough and this is really no good for anything.

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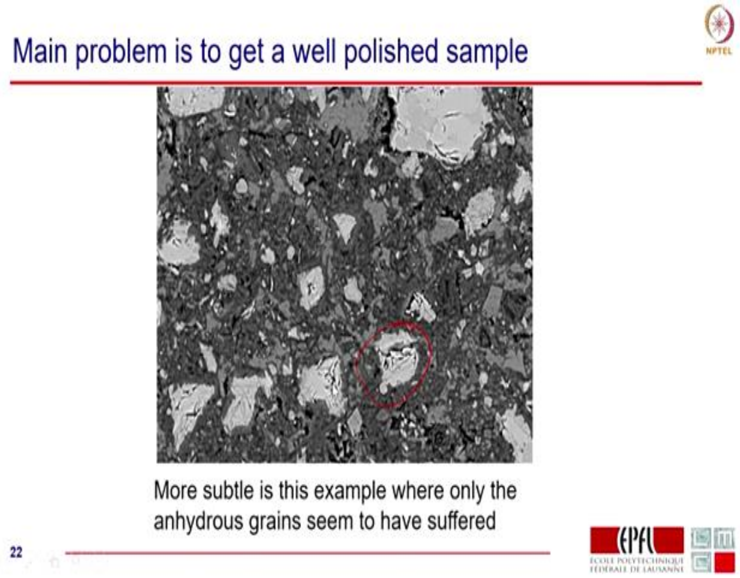

Main problem is to get a well polished sample

More subtle is this example where only the anhydrous grains seem to have suffered

Here is a example where you see the most of the hydrate part is well polished but these cement grains have been attacked, maybe it was polished with ethanol which had picked up water, you see then these anhydrous cement grains have really heavily attacked and that is not really useful.

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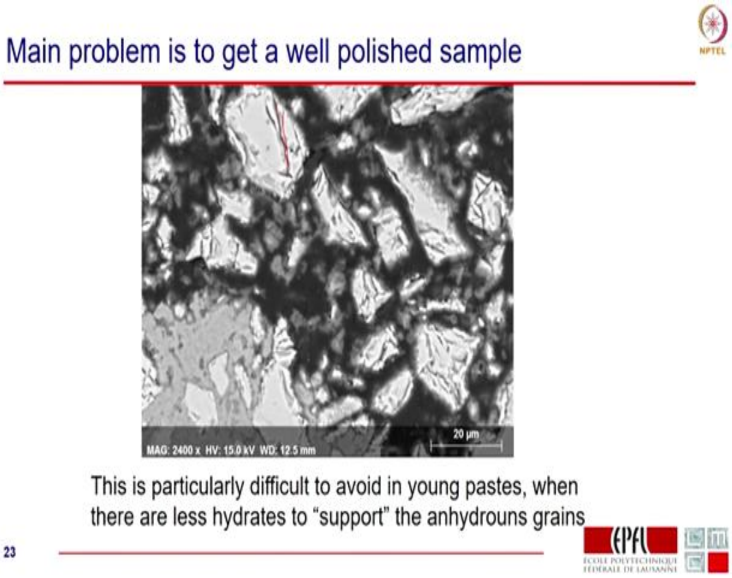

Main problem is to get a well polished sample

This is particularly difficult to avoid in young pastes, when there are less hydrates to “support” the anhydrouns grains

If you have very young samples it can be very challenging, your cement grains will be much harder than the hydrate phases and so you tend to get this damage and cracks. So, it is particularly advised that, do not try to polish sample for about one day.

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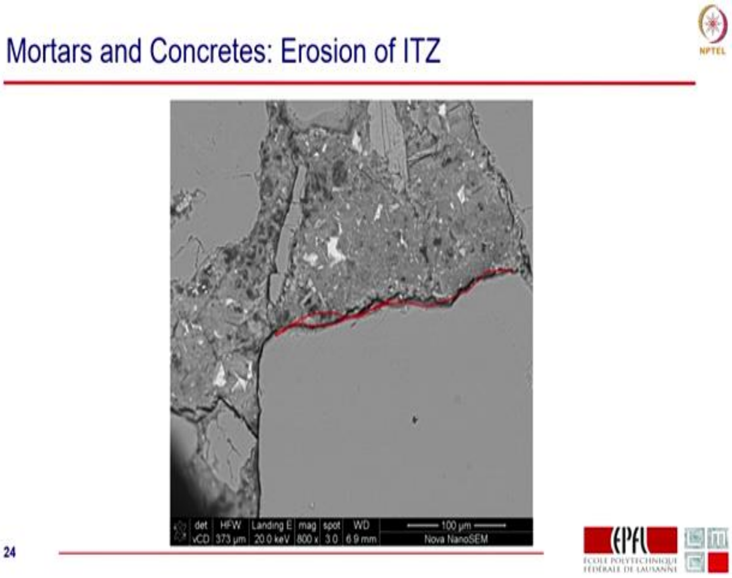

Mortars and Concretes: Erosion of ITZ

It is really very different and then when you want to go to Mortars and concretes, It becomes even more difficult because now, we have a very hard aggregate here and the softer paste and what often happens is you really rip out all the material. So, these kind of gaps has really been caused by the polishing because of the different hardness.

So, the problem we have in mortars and concrete is that we have a very different hardness between the aggregates and the softer cement paste and this means, it is quite easy to get to the erosion of material here at the interface between the two. So, you have to be careful of that.

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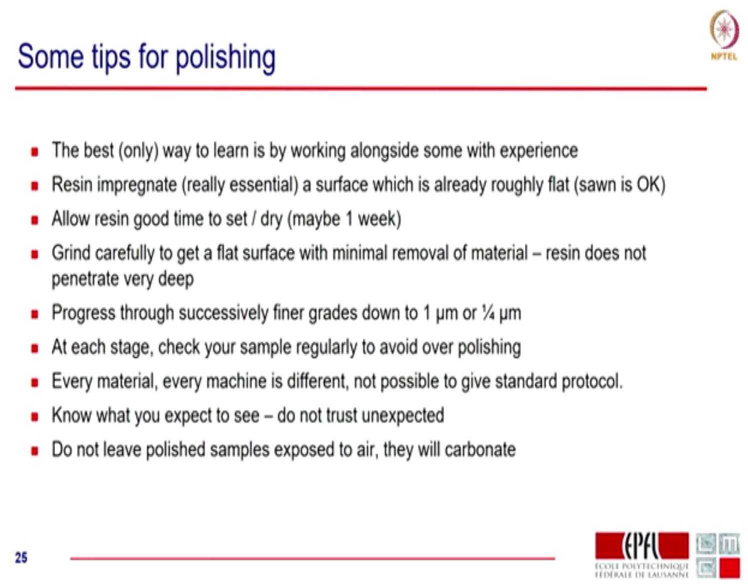

Some tips for polishing

- The best (only) way to learn is by working alongside some with experience
- Resin impregnate (really essential) a surface which is already roughly flat (sawn is OK)
- Allow resin good time to set / dry (maybe 1 week)
- Grind carefully to get a flat surface with minimal removal of material – resin does not penetrate very deep
- Progress through successively finer grades down to 1 µm or ¼ µm
- At each stage, check your sample regularly to avoid over polishing
- Every material, every machine is different, not possible to give standard protocol.
- Know what you expect to see – do not trust unexpected
- Do not leave polished samples exposed to air, they will carbonate

So some tips and the first tip is may be not all of that helpful because the first tip says that really if you want to learn to polish a sample well, you have to work with somebody who know is what they are doing, I cannot stand up and tell you what to do, even if you go and read the book, it gives you some advice but it is you know, there's nothing like really working with somebody because the point about polishing is you have to be checking what is going on all the time.

So, you can use an optical microscope to check for scratches, to check you have not got too much erosion for your sample etc. Really for pace we have to impregnate with resin, it is very important but to get , you need to have a sample that is roughly flat first because the resin does not generally penetrate all that much, so you can lightly level your sample or some sandpaper or something or even a good sawn cut is okay and then impregnate with resin.

Allow the resin to harden properly, this is a very common error. People are trying to rush things, if you are going to have a properly hard and resin it, generally needs to leave it for one week. If you are really in a rush you can maybe put in an oven at 40 degrees but no more. Grind carefully to get a flat surface, so that you do not remove too much material because otherwise you are going to get rid of all that resin, you spent time to put in and then progress successively through finer grades down to generally one micron or quarter micron but in each stage you need to check your sample regularly because it say is even easy to over polish as to under polish. If you have under polished, you will still see scratches from the previous stage but if you over polish, you get to that situation where I showed you of the bad polish where everything is gouged out.

So, both are very easy to do and that is the problem. And once you have over , you need to start again there is nothing you can do, you got to level that sample re-impregnate, take well best thing is take a new sample. Every material every machine is different so you cannot have a standard protocol so I can give you one protocol it works very well allow machines at EPFL but it is going to have to be adjusted to your machine there and then you know if you have a paste that is one thing, if you have a mortar that is another thing, if you have a young sample that is one thing, an old sample that is another thing each thing you need to think about thing is like what is the load on the sample what is the speed of polishing all of these things can be very important.

So, it is difficult and it is a question of really learning by experience, but last of all, know what you want to expect so we have seen some nice micrographs here and you know hopefully then if your sample is not looking like that then it is probably your polishing. It is probably not, that you have discovered this new miracle cement that reacts differently from everything else, it is probably you did not do the polishing right and once you have polished your samples do not leave them lying around in the lab, because they will carbonate because they will pick up dust and then you spent all this time polishing and then you wreck it by leaving it around. So, use a bit of common sense.

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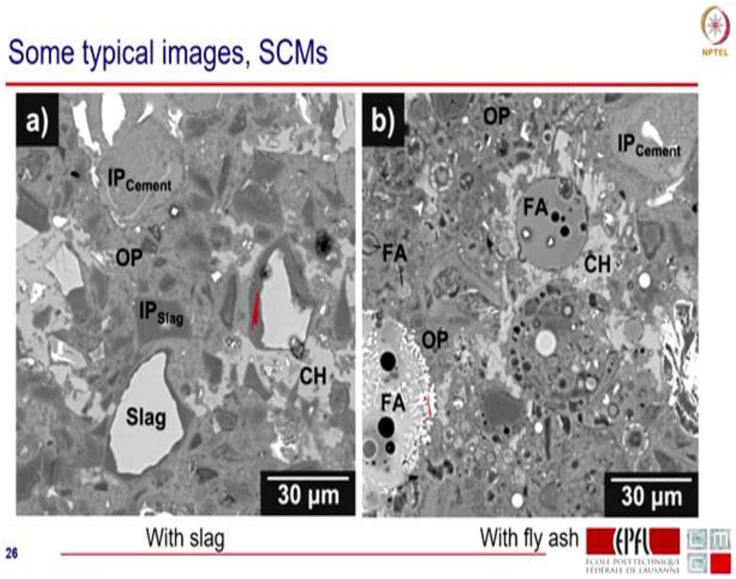

Some typical images, SCMs

With slag

With fly ash

So, we have got our nice polished samples in above image and then we can see really a lot of things, so two very nice examples I like very much which show the two most common type of supplementary cementitious materials. So, in this one we can see the slag, we can see how, for example this inner product, this dark area around the slag. It is darker because all the magnesium that was in the slag is in the same part.

In this fly ash, we can see all the different fly ash particles here we can see we have had some cuts and crystalline hydrates in the fly ash here we have got different compositions etc. So, we have got to lot a visual information but again quantifying it is really challenging.

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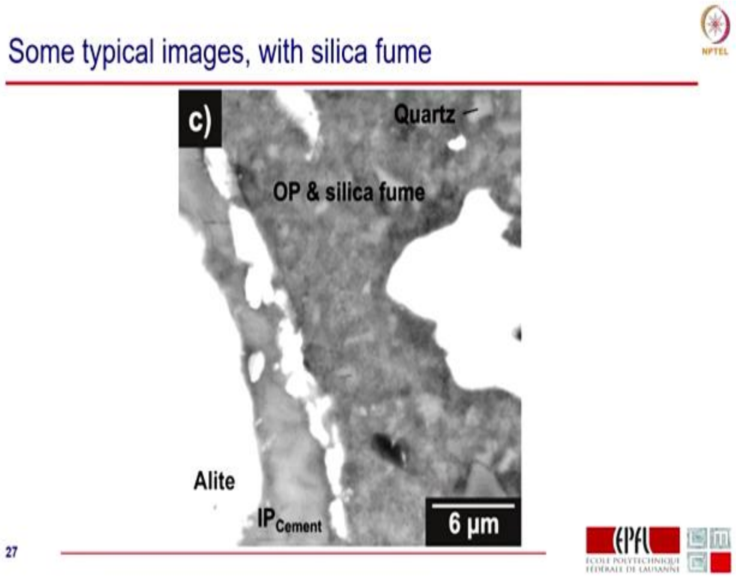

Some typical images, with silica fume

Here is silica fume, of course silica fume will generally be at a scale which we cannot resolve very well but we cannot sort of just about make up the individual very fine silica fume particles here. Certainly, it would be very useful to check that your silica fume is well dispersed because that is a huge problem with silica fume you tend to great big clumps and those you can see very easily.

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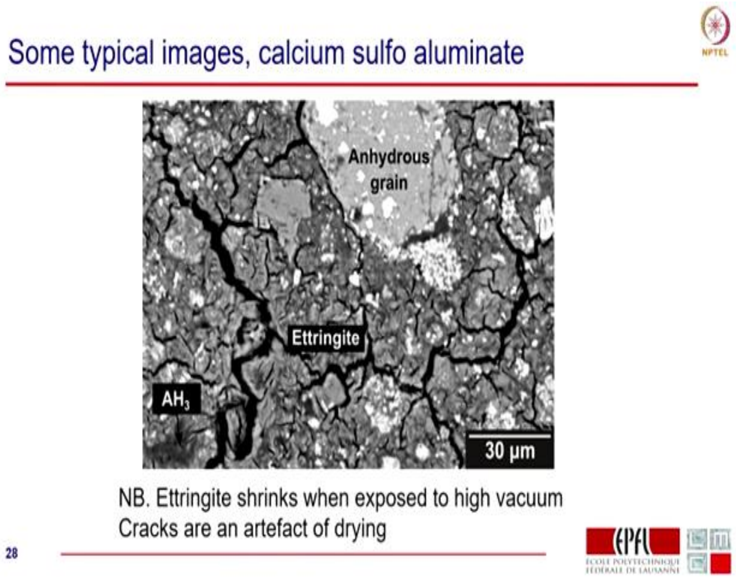

Some typical images, calcium sulfo aluminate

NB. Ettringite shrinks when exposed to high vacuum
Cracks are an artefact of drying

If you look at other cements, so for example calcium or aluminates you can get some problems, like when you have got samples with lots of ettringite because it loses a lot of water on drying forms these big cracks and that is an artefact the samples not really as cracked as that.

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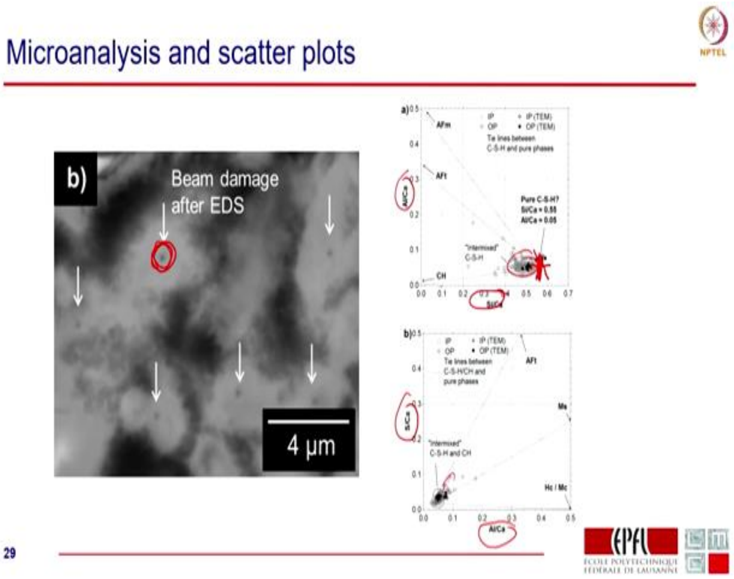
Microanalysis and scatter plots

29

Microanalysis of course is very important and we are going to talk about that later in terms of quantification. There is a lot of detail again behind that and as most of that is written in the book but also, we wrote a paper and materials characterization on this. Now because you have got this large interaction volume of a few microns, so you can see in above image, you have got this beam damage, this spot looks very small but in fact underneath the sample, if you remember that diagram at the beginning we are actually analysing an area that is sort of this kind of size, which will usually contain C S H intermixed mix with other phases and we can look at that intermixing, if we make the plots.

Above are the two most useful kind of plots we use, we can have the one where we have an ammonium calcium against silicon calcium and there, we see this cluster of points for the C S H and when we have point is going on the line, which will be the mixtures with calcium hydroxide. When we have points which is going up, that way this will be mixtures with a AFm phase or ettringite and to distinguish between the modest mono phases and the ettringite, then it can also be very useful to have the other plot, where we have now sulphur/calcium against aluminium/calcium and here we see that, very fine C S H is intermixed with small amounts of ettringite and of monosulphate.

So, this can really be useful and as we are going to talk about you can use the extremity of this cluster. This is the least intermixed point. This is quite good value of the composition, the real composition of the C S H.

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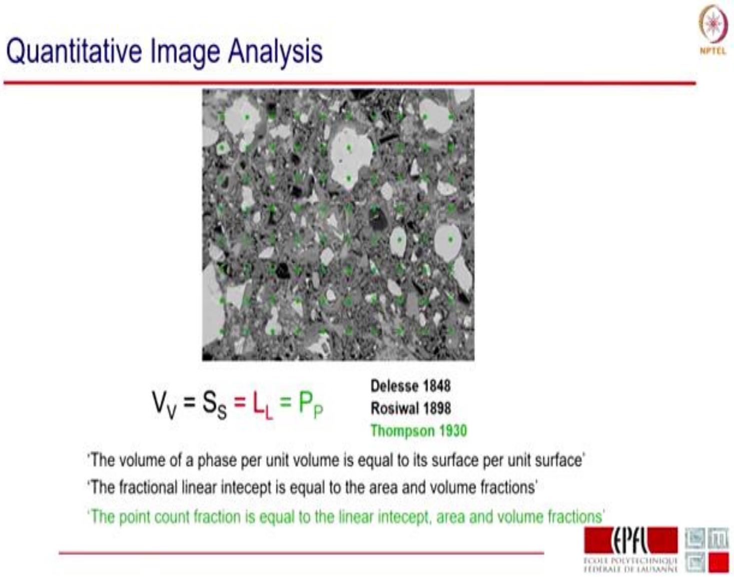

Quantitative Image Analysis

$V_V = S_S = L_L = P_P$

Delesse 1848
Rosiwal 1898
Thompson 1930

'The volume of a phase per unit volume is equal to its surface per unit surface'
'The fractional linear intecept is equal to the area and volume fractions'
'The point count fraction is equal to the linear intecept, area and volume fractions'

Now we can also use image analysis based on gray levels for quantification and all the time people say to me "well, how do you know that the area you measure on a poly section is the same as the volume fraction?", well I know that very well because it was proved already in 1848, so more than 150 years ago this was proved mathematically. If you measure the area fraction on a surface it is the same as the volume fraction providing the sample is statistically isotropic, you do not have very preferred orientation and providing your sampling is big enough.

So, you have to do a good sampling and in fact you can also do line intercepts or you can do point counting they're all equivalent. You do not need to worry about that, it is been proved mathematically no problem. If you want to look at other things like particle size distribution then it is a lot more difficult, basically, I do not strongly recommend it because it is rather complicated but we have not got time to go into it here.

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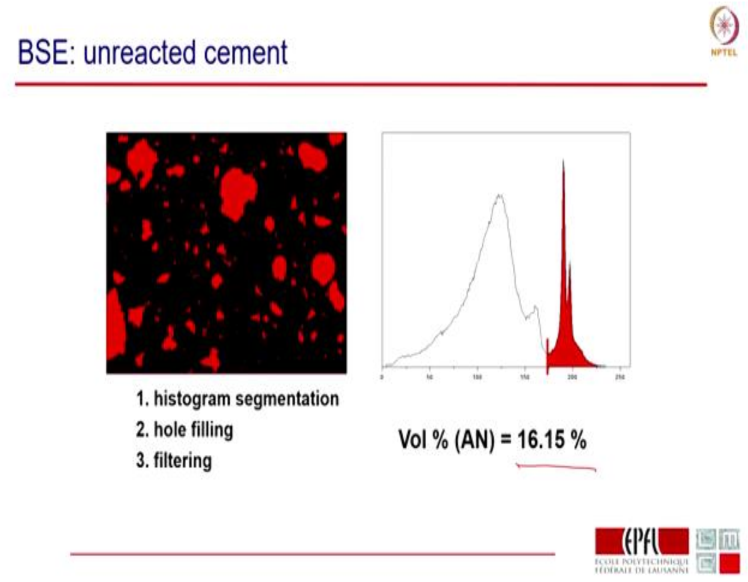


BSE: unreacted cement

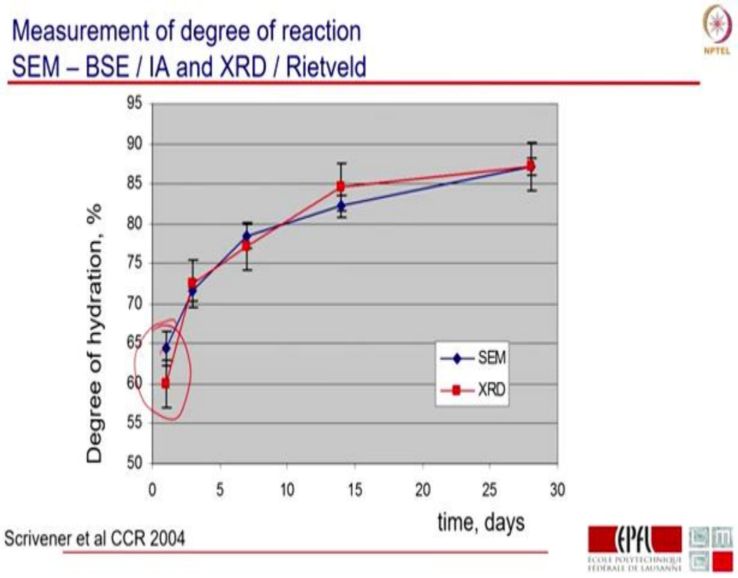
1. histogram segmentation
2. hole filling
3. filtering

Vol % (AN) = 16.15 %

So, this is very useful, particularly for looking at degree of hydration because of the phase this is most easy to distinguish here are the unreacted cement grains. We can see in the gray level histogram, we can see this peak of the unreacted cement grains, we can make a threshold in here. we can identify those areas we can do a bit of filtering to clean up the noise and then we see that we have the anhydrous volume fraction, in this one image is sixteen point one five per cent.

So, if we had a water cement ratio of say point four at point four the original volume of anhydrous is roughly forty per cent so here, we know we have got a degree of hydration of seventy-five per cent or so. Of course, if you just do it on that one image that is not very reliable, we really generally average over a hundred images you cannot get away with less but if your machine can do automatic images then you can easily collect a hundred images in an hour or so. It doesn't take very long.

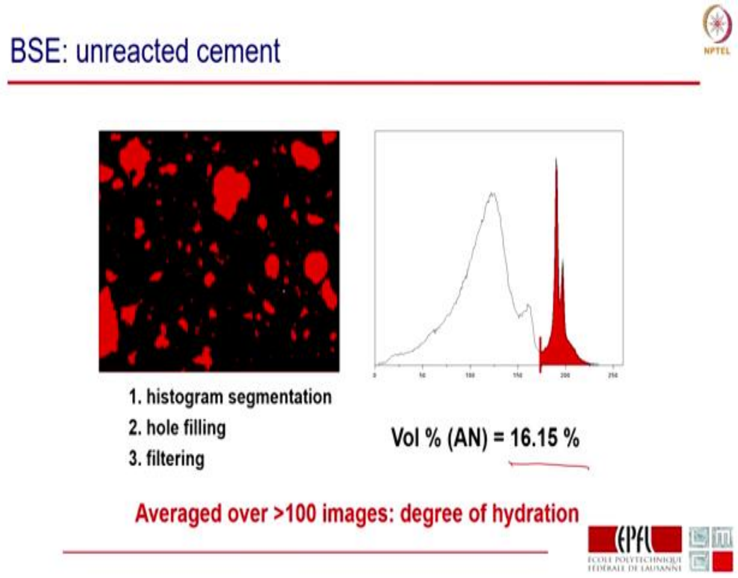
(Refer Slide Time: 26:10)


Measurement of degree of reaction
SEM – BSE / IA and XRD / Rietveld

Scrivener et al CCR 2004

And here we see that if we use image analysis to measure the degree of hydration or if you use x-ray diffraction Rietveld, we talked about earlier we can get very good agreement between the two techniques. It is kind of a you know, one is kind of validates the other we see that the problem comes at early ages at very early ages we tend to overestimate the degree of hydration by S E M because of the difficulty of detecting very small grains.

(Refer Slide Time: 26:38)


BSE: unreacted cement

1. histogram segmentation
2. hole filling
3. filtering

Vol % (AN) = 16.15 %

Averaged over >100 images: degree of hydration

So, you see with rather difficulty to take very small grains but at all for a day or so there are not any small grains left, so the problem becomes less of a problem.

(Refer Slide Time: 26:56)

Pore boundary?

If you want to look a porosity it is really challenging, because here if we look, here the question is, “where is the boundary?”, You cannot see a hard boundary between C S H and the porous structure, partly due to the resolution of the technique but partly due to the nature of the C S H this very fine, a very fine structure. You cannot really quantify porosity we are going to come back to that in the next lecture you can make a comparative measurement.

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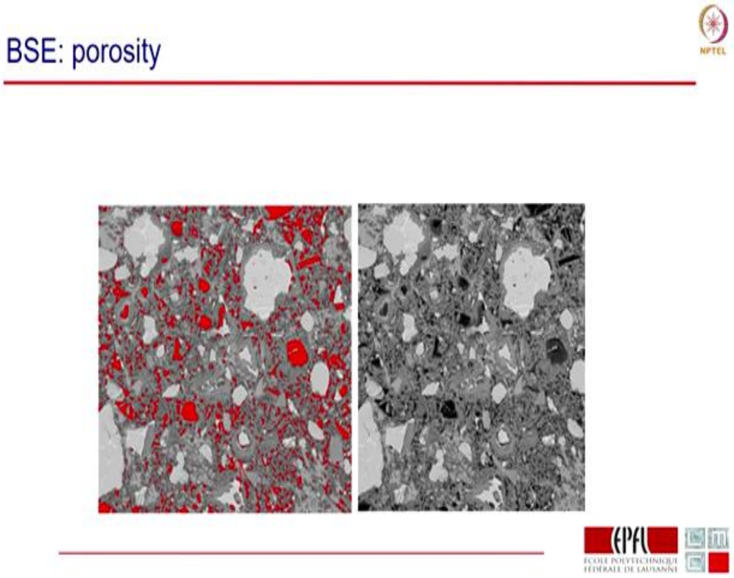

BSE: porosity

If you want to make a comparative measurement between one sample and another, as long as you use the same kind of thresholding technique, it does not matter too much what you use.

So typically, we can take the intercept and then we can threshold it and we can see visually the distribution of the larger pores. we are missing most of the ports.

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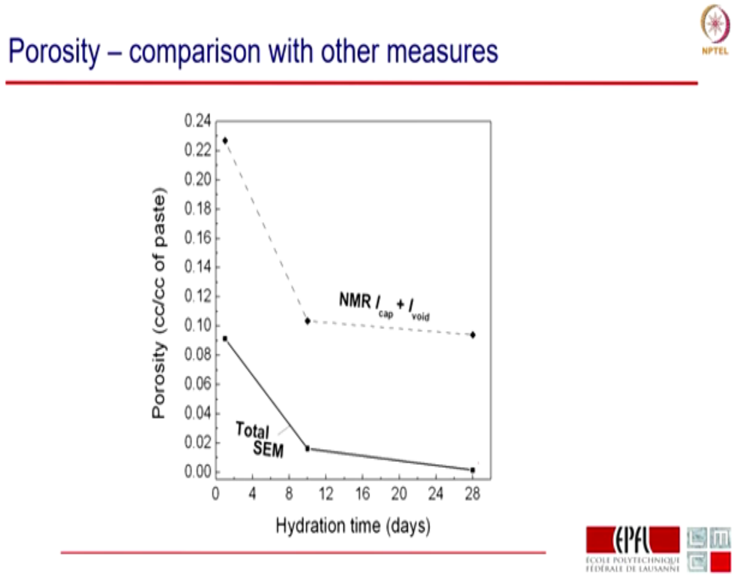
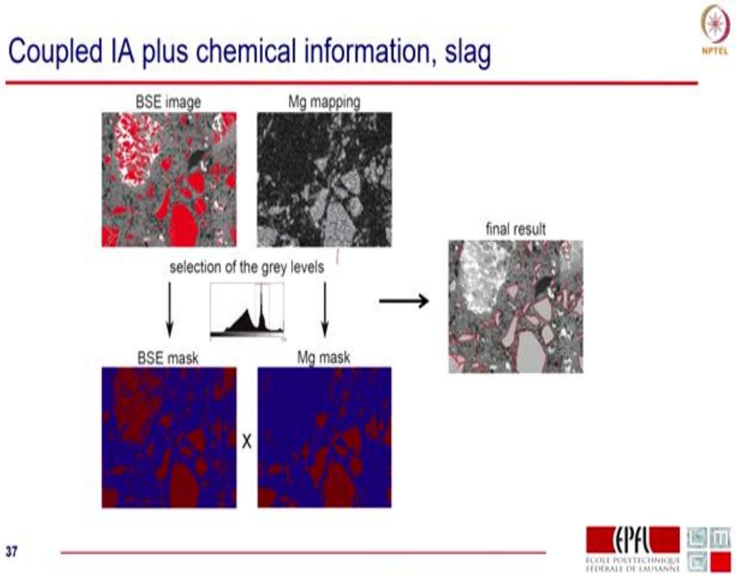


Porosity – comparison with other measures

So, above is a comparison between the porosity we measured by S E M and those we measure by N M R which we are going to see in the next lecture and we see that by the time we got 28 days we can see hardly anything by S E M but we still got a lot of porosity left by N M R. So particularly at older ages it is not that much useful porosity other than just give you a visualization.

(Refer Slide Time: 28:18)



Coupled IA plus chemical information, slag

We can couple the grey level information with chemical information and this is very good for detecting the amounts of supplementary cementitious materials. So, if we take the example of slag, slag has a very precise grey level but that may overlap with some of the anhydrous phases but the thing that is unique about slag, it is generally the only material that contains magnesium.

So, if you make a magnesium map, you can see quite well the slag grains, you can apply various filters, then you can very clearly identify the slag grains and this is probably the best technique for measuring the degree of reaction of slag.

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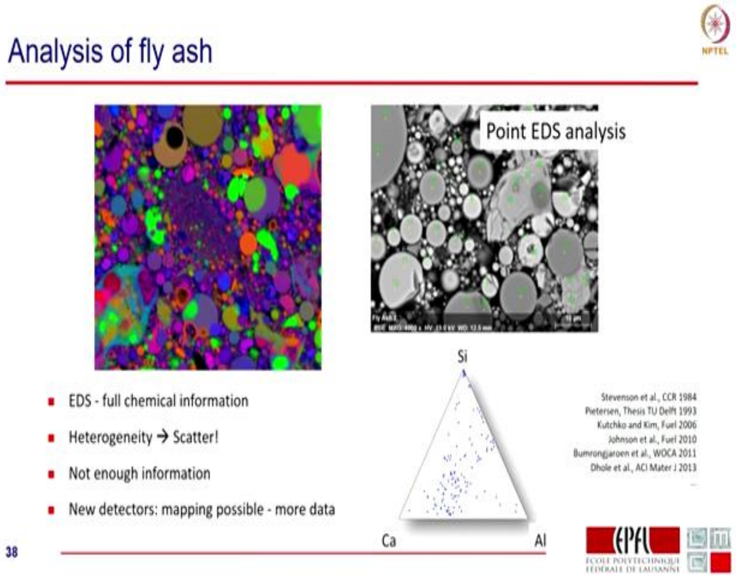

Analysis of fly ash

Point EDS analysis

- EDS - full chemical information
- Heterogeneity → Scatter!
- Not enough information
- New detectors: mapping possible - more data

Stevenson et al., CCR 1984
Pietersen, Thesis TU Delft 1993
Kutchko and Kim, Fuel 2006
Johnson et al., Fuel 2010
Bumrongjaroen et al., WOCA 2011
Dhole et al., ACI Mater J 2013

Fly ash is much more complicated because here is now the grey level is extremely variable. So, we got an extremely variable grey level we have also got an extremely variable chemistry, In points analysis of different point flash particles they are all over the place but we have developed a new technique recently where we take the full chemical map.

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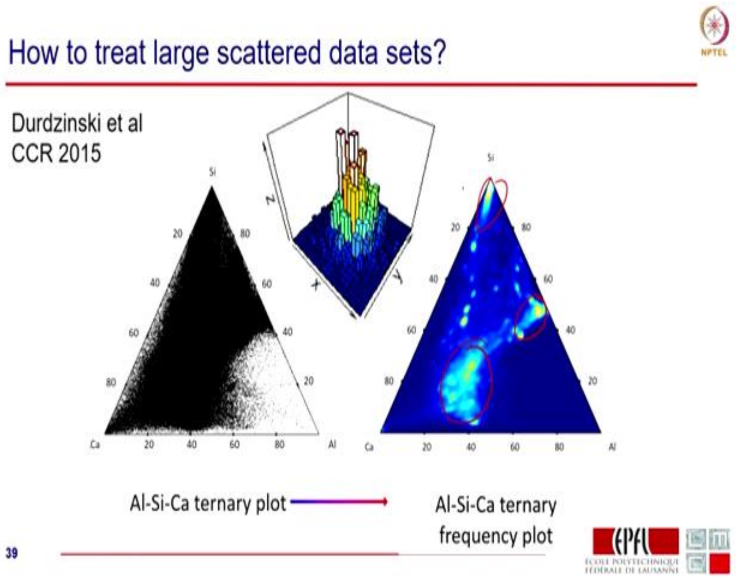

How to treat large scattered data sets?

Durdzinski et al
CCR 2015

Al-Si-Ca ternary plot → Al-Si-Ca ternary frequency plot

So this is all the analysis of points in the fly ash it is not much good like that because you see you have just got points everywhere, but if you now process that data to look at the density of points in the individual area, you can do not transform it to a map like above and now we can quite clearly see we have got different zones where we got different fly ash compositions and we can use that to actually classify that.

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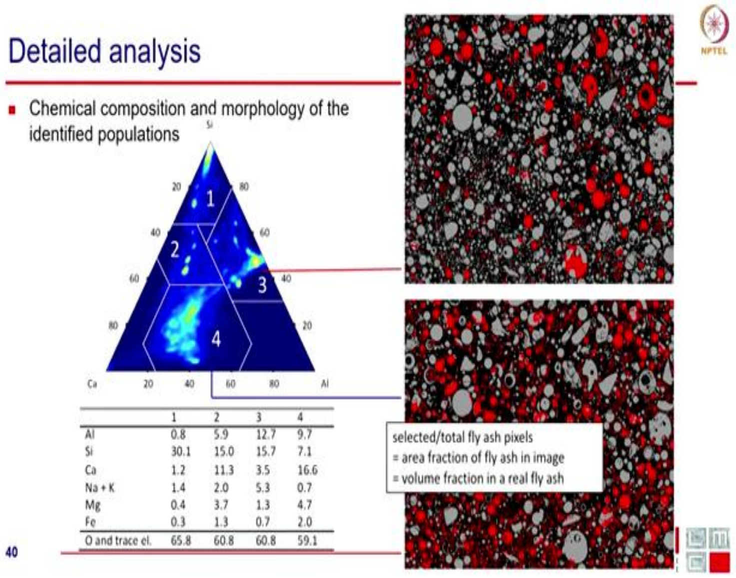

Detailed analysis

- Chemical composition and morphology of the identified populations

	1	2	3	4
Al	0.8	5.9	12.7	9.7
Si	30.1	15.0	15.7	7.1
Ca	1.2	11.3	3.5	16.6
Na + K	1.4	2.0	5.3	0.7
Mg	0.4	3.7	1.3	4.7
Fe	0.3	1.3	0.7	2.0
O and trace el.	65.8	60.8	60.8	59.1

selected/total fly ash pixels
= area fraction of fly ash in image
= volume fraction in a real fly ash

So above we have classified the different zones and then you can go back to the original image and you can see, what is the fly ash with the composition in this zone three and what is in zone four and then we can actually look at the individual chemical compositions of all these fly ashes. So, this is a method which we published and can be used now to quantify the different kinds is of fly ashes and also to measure their degree of hydration in fact.

It is a little bit time-consuming you generally you know, you really have to spend about two hours to collect these full chemical maps and you need 20 or 30 maps to make any kind of sense statistically, maybe twenty or even ten you can get away with and so if you collect overnight you can usually get enough data to get a valid measurement but it is slow.

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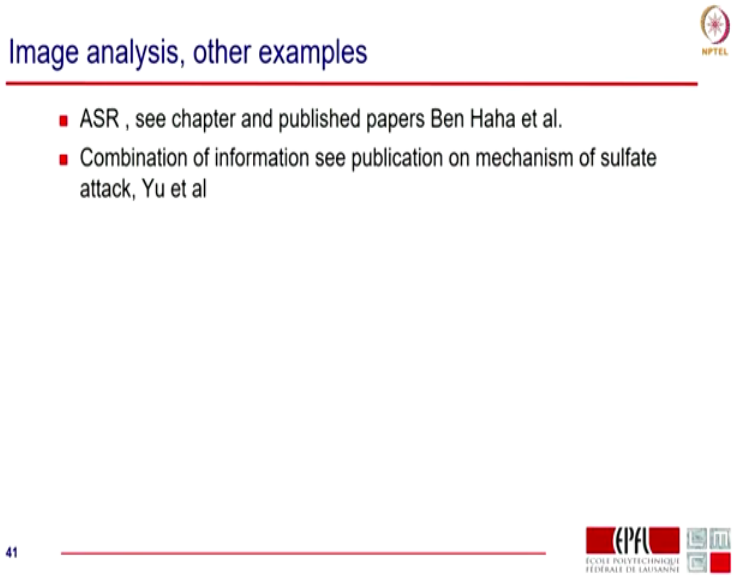

Image analysis, other examples

- ASR , see chapter and published papers Ben Haha et al.
- Combination of information see publication on mechanism of sulfate attack, Yu et al

So, we have got lots of other examples, we can look at alkali silica reaction, we can look at static sulphate attack these are examples and references that are written and also in the chapter you can look into those in more detail.

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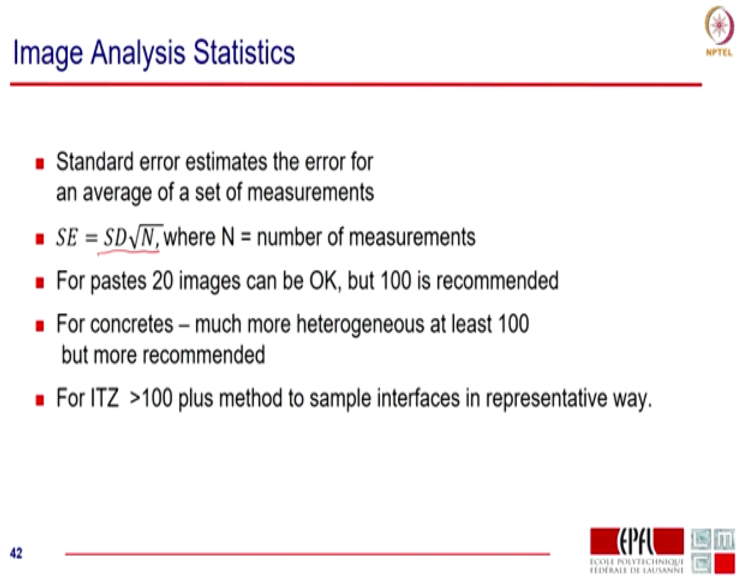

Image Analysis Statistics

- Standard error estimates the error for an average of a set of measurements
- $SE = SD\sqrt{N}$, where N = number of measurements
- For pastes 20 images can be OK, but 100 is recommended
- For concretes – much more heterogeneous at least 100 but more recommended
- For ITZ >100 plus method to sample interfaces in representative way.

When you are making image analysis you have to be aware, that you do not want to look at the error between the standard deviation between different images because that will naturally be high, what we need to look at a standard error, whereas this is the standard deviation divided by the square root of the number of images.

$$SE = SD\sqrt{N}$$

Where,

N =Number of measurements.

SE=Standard error.

SD=Standard deviation.

So, if you have a paste and you want to measure degree of hydration, twenty is good enough but hundred is recommended. Concretes, which are more heterogeneous, we need at least a hundred and if you want to look at the specific area like the I T Z then you got to look at many more.

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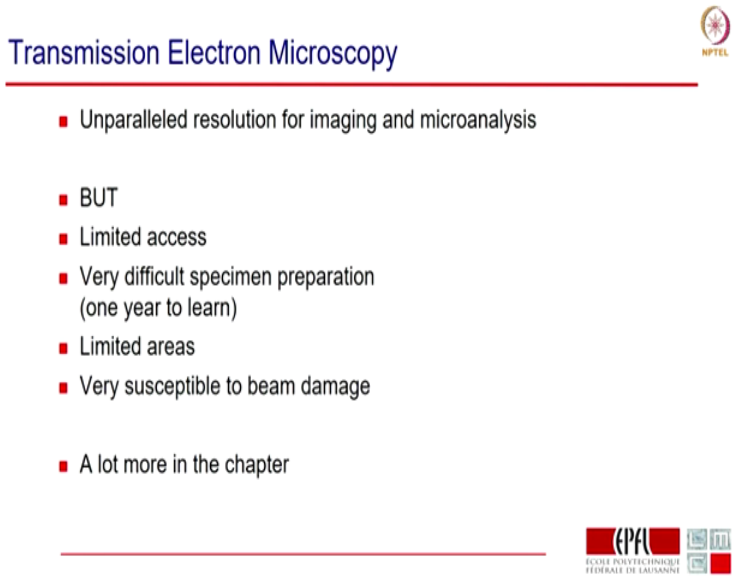

Transmission Electron Microscopy

- Unparalleled resolution for imaging and microanalysis

- BUT
- Limited access
- Very difficult specimen preparation (one year to learn)
- Limited areas
- Very susceptible to beam damage

- A lot more in the chapter

So just to finish this lecture, a quick look at transmission electron microscope, it is really got much higher resolution but the problems you have is that, you have got limited access to T E M s, they are generally not as much available as S E M s. it is very difficult to learn the specimen preparation, it might take a year and even then, you get very small areas you can see at one time. They are also very susceptible to beam damage.

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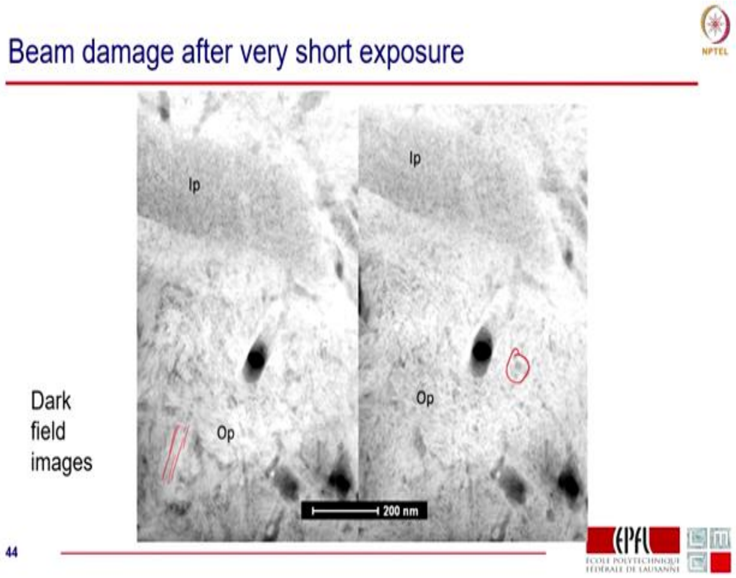

Beam damage after very short exposure

Dark field images

So just a quick example, above we see a quite an old paste and you can see in this image here you can see the very fine structure of the C S H. These kinds of plates you nearly structure here, even after a few minutes you can see that starting to bubble up and you have lost that fine structure and many micrographs in the literature, you can see, they just focus on these bubbles like this, this is just purely an artefact of the water in those hydrates, evaporating off.

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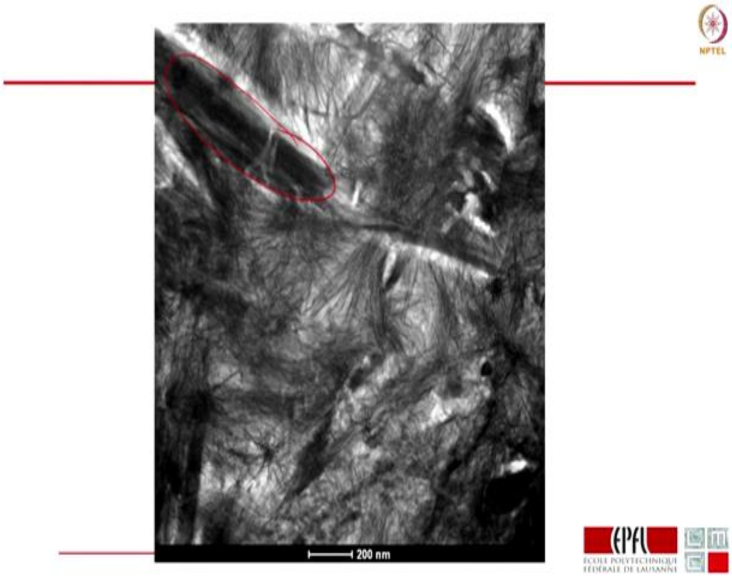

So, you got to be very careful but when you do it right you can get lovely images like above, it is my favourite image at the minute this is from limestone calcite clay cement. So, we can see there are the particles of the calcite clay and then we have got this very fine C S H and you can see how dense this microstructure is. So, in terms of durability, any aggressive agent has really got to penetrate between these fine structures of about 10 microns between the C S H and we are going to talk about this a bit more in the next lecture on porosity.

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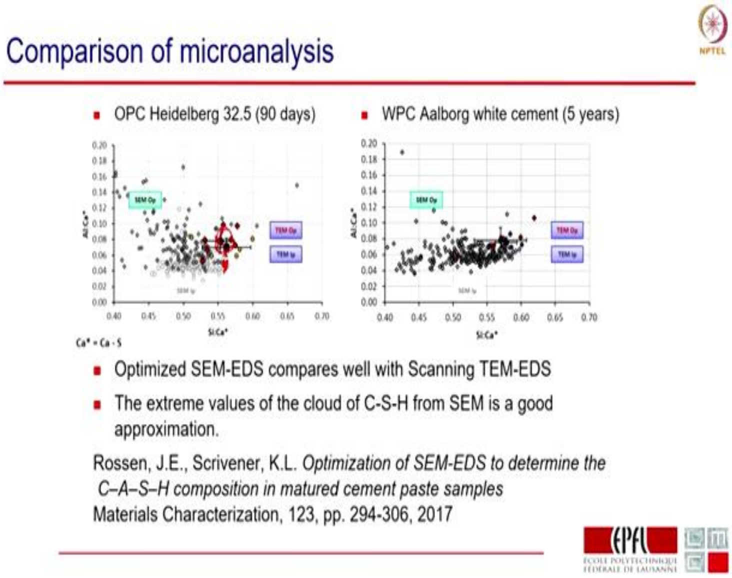

Comparison of microanalysis

- OPC Heidelberg 32.5 (90 days)
- WPC Aalborg white cement (5 years)

- Optimized SEM-EDS compares well with Scanning TEM-EDS
- The extreme values of the cloud of C-S-H from SEM is a good approximation.

Rossen, J.E., Scrivener, K.L. *Optimization of SEM-EDS to determine the C–A–S–H composition in matured cement paste samples*
Materials Characterization, 123, pp. 294-306, 2017

What T E M is particularly useful for is getting much more precise chemical analysis. So it shows you the kind of clusters, we saw in the S E M and now the points in the T E M and you can see that the points really verify that, if we take this outer edge of this distribution here in the S E M this is close to the unmixed composition of the C S H and that is all written about in the paper, where we really went into a lot of detail about how to determine the composition of the calcium aluminate silicate hydrate in cement paste.

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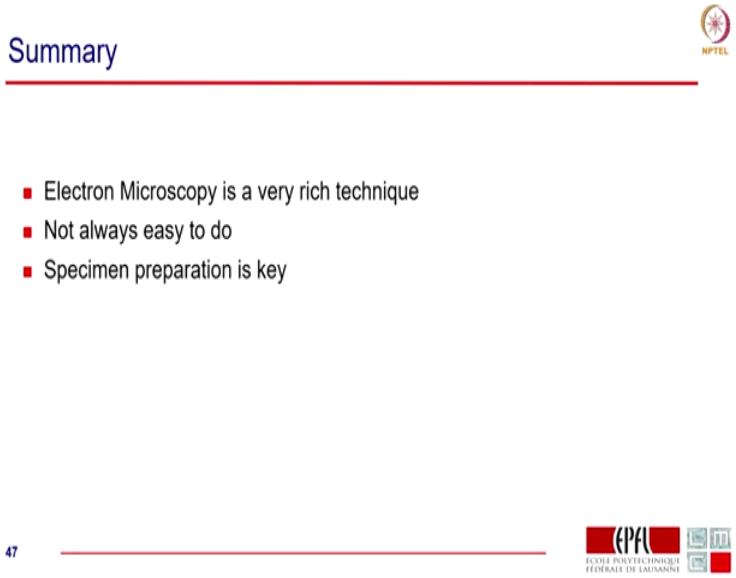

Summary

- Electron Microscopy is a very rich technique
- Not always easy to do
- Specimen preparation is key

So just to summarize it is really a very rich technique, it is not easy to do and specimen preparation is really the key.

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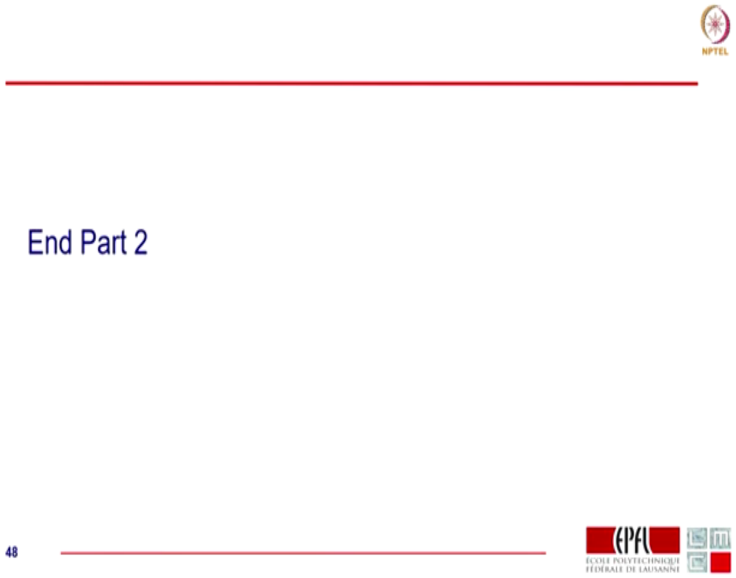

End Part 2

So that is the end of that part, thank you.