Characterization of Construction Materials

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Lecture - 41

Scanning Electron Microscopes- Working Principles – Part 2

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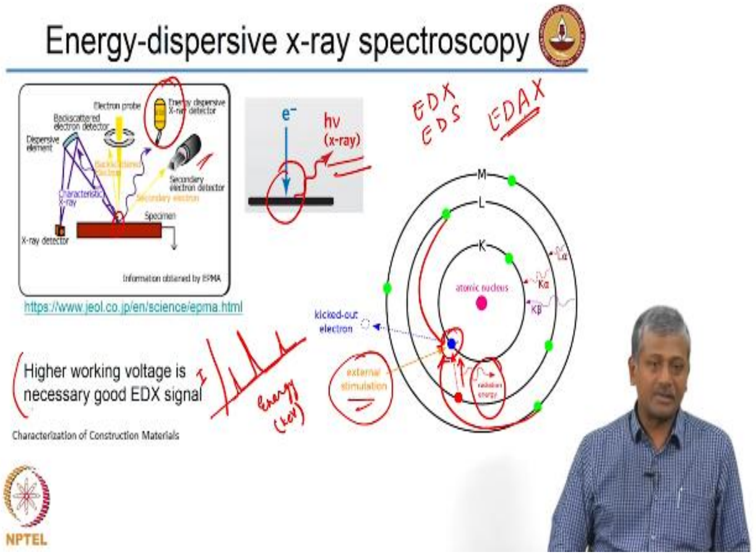

Energy-dispersive x-ray spectroscopy

https://www.jeol.co.jp/en/science/epma.html

Higher working voltage is necessary good EDX signal

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The other concept that is of extreme importance as far as SEM is concerned is the presence, not all the time, of X-ray detector. Now in most SEMs, you will only have the secondary detector. So, basic SEMs will have only secondary detectors. If you are willing to pay a certain extra price over it, you will be able to get the backscatter detector. But you also have to sometimes invest in the EDS or EDX detector. So, sometimes it is called EDX, sometimes it is called EDS; Energy-dispersive X-ray analysis or Energy-dispersive Spectroscopy. Now, sometimes people wrongly call it EDAX. EDAX is the name of a commercial product for EDS. So technically, when you write your papers and describe this process in your papers, you cannot be calling it as EDAX; EDAX is actually a commercial name. So the actual scientific name is EDX or EDS.

So what is happening here? We know that the electron beam is now striking your sample and we said that, secondary electrons are basically the outer shell electrons getting dislodged, low energy electrons which are collected by the secondary detector. We have the backscattered electrons which are going straight up and collected by the annular detector or annular ring which is placed around the objective lens. Now, again what is the difference between secondary and backscattered electrons? Secondary electrons are electrons from the atoms in the sample, backscatter electrons are the same electrons as the incident electrons which are going back.

Now what is happening here is these incident electrons are obviously of high energy and when you have a high energy, you can also knock off the inertial electrons of the sample. If you have a sample atom, let’s say silicon or calcium present, these electrons have high enough energy that they go and knock off the inertial electrons. So what happens here is quite similar to what happens in the process of generation of X-rays in the X-ray tube. So instead of X-rays being the external simulation, in this case the external simulation is done by the high energy electrons. So they are now dislodging the inertial electrons.

So what will happen now is, an electron from the outer shell will try to jump in. So just like what is shown here, an electron from the next higher shell will now try to jump in. When it jumps in there is an energy difference, which is released as heat and as X-rays. So radiation is basically composed of heat as well as X-rays**.** So these X-rays are Characteristic because they define a very clear energy transition, for example here, from the L-shell to the K-shell. You can also have M to K, but the possibility of that happening is much lower than L to K. So that is why whenever you look at X-ray intensities that are generated from the target metal in an X-ray tube, you see you generate a larger intensity of the K_α and K_β as opposed to L_α and L_β.

So here we are talking about characteristic X-rays which are generated from the atoms in the sample. Much like what we talked earlier about X-ray fluorescence. X-ray fluorescence is practically the same thing, instead of the electron beam that we have here, the external stimulation is by X-rays. So actually truly speaking what happens inside your X-ray tube? In the X-ray generation device is nothing but X-ray fluorescence. But there again the external simulation is your high energy electrons which are accelerated through the potential difference. They hit the target metal and generate the target metal's X-rays. If it is copper, we generate copper X-rays, if it is cobalt we generate cobalt X-rays, and so on and so forth. So here energy-dispersive X-ray spectroscopy is related to the detection of the X-rays that get fluoresced from the atoms in the sample as a result of interaction with the electron beam.

So if you have an Energy dispersive X-ray detector, it will now collect all the X-rays that are coming from different elements in the sample. If you have cement, obviously you will get everything from calcium, silicon, iron, magnesium, sodium, potassium, everything you will be able to collect and display that in a plot between the Intensity and the Energy. Energy typically will be in kilo electron volts (keV). So what you will get is, plots like this (as shown in Figure 1). So, each one of these peaks will correspond to a specific element.

Figure 1 Plot between Intensity and Energy

Accelerating voltage for a very dense material, you may not be able to generate sufficient energy to have these inertial transitions taking place, but in all cases when you select the right level of accelerating voltage with a high energy electron beam, you will be able to generate X-rays from the sample.

In scattering we are talking about the scattering of the incoming radiation. Whenever we talk about scattering, it is the incoming radiation that is getting scattered in different directions.

So here this is fluorescence, this is the electrons in the sample atom which are undergoing transitions producing X-rays. So this is X-ray fluorescence from the sample.

So very important to understand is you need a high working voltage to get a good EDX signal. Again the same effects will happen in this case also, you need a shorter working distance. Why do you need a shorter working distance? Because again, you can focus with a very strong current and you will be able to generate the X-rays. But there is a practical difficulty.

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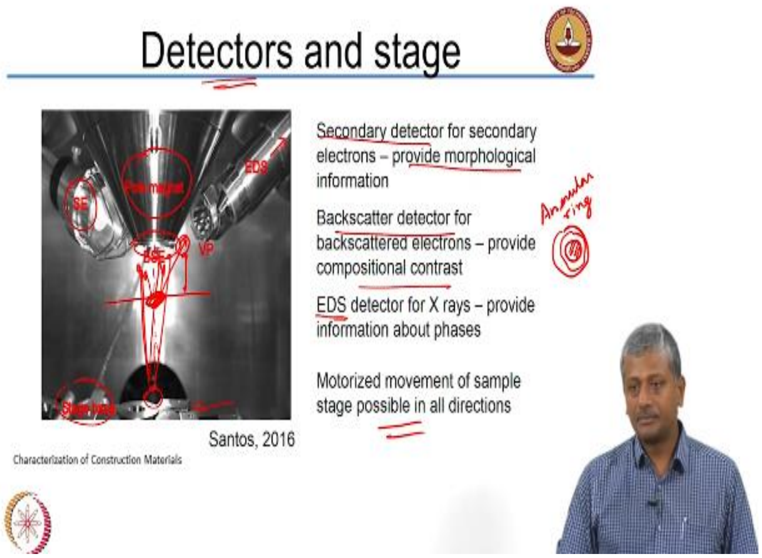

Detectors and stage

Secondary detector for secondary electrons – provide morphological information

Backscatter detector for backscattered electrons – provide compositional contrast

EDS detector for X rays – provide information about phases

Motorized movement of sample stage possible in all directions

Santos, 2016

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Angular ring

So, there is a practical difficulty. What happens often is, when your working distance is small, if your sample is, let us say here, and it is generating these backscattered electrons, it is generating the X-rays which have to go towards the EDS detector. So very often if the short working distance is there, which is required for a good quality collection of X-rays, what will happen is many of these X-rays that are going, will get blocked by your backscattered electron detector. It may actually happen to be in the path, it may just not let your X-rays go towards a detector. So very often what you may have to do is take a backscattered image for the area that you are interested in, but then remove the detector so that it does not come in the path of your X-rays that are going towards the X-ray detector.

Very often when you actually do the SEM analysis that is what your technician will tell you to do, to collect better X-rays you may have to move the backscatter detector out of the path. Otherwise very often, the backscatter detector tends to block the path of the X-rays because you are working at a low working distance. If your working distance is high, definitely these X-rays will be able to go quite easily to the X-ray detector; you will not have a problem with blockage. But then to get a large number of X-rays you need to reduce the working distance.

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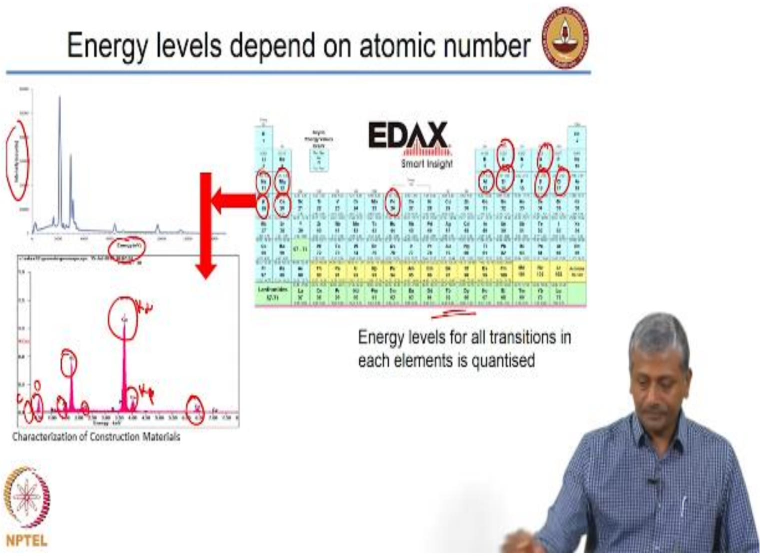

Energy levels depend on atomic number

Energy levels for all transitions in each elements is quantised

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As I said earlier, energy levels depend on the atomic number. So what you will get is a plot between the intensity and energy; or the number of X-rays that are collected for a specific level of energy, so energy is plotted here in eV.

So one example is given here, we have a calcium silicate system like C-S-H for instance, if you look at the energy dispersive spectroscopy pattern for C-S-H, you will see calcium. There are two peaks for calcium, why do you think that happens? Because you are getting both K_{α} and K_{β}. What is K_{α}? It is when the transition happens from L-shell to K-shell. K_{β} is when the transition happens from M-shell to K-shell. So the probability of α transitions are much more than β transition, so you get a higher intensity of α radiation and lower intensity of β radiation. You have silicon here, you do not really see the secondary peaks of silicon, you only see the primary K_{α} peak. You have aluminium, you have some sulphur.

So what you can do is, once you actually collect the X-ray signal, you can turn off and on, the kind of elements that you want. So that means that you need to have a prior idea of what you think should be there in the system. That is not too difficult. Now if you are working with cementitious systems, you know that you need to have calcium, you need to have probably sometimes magnesium, sodium, potassium, you need to have silicon. There may be carbon, however carbon produces your lowest energy level X-rays, and so very often people do not rely on EDS to detect carbon. However, you can detect carbon because carbon peaks will appear for example, if you are looking at a phase like calcium carbonate, you will be able to see calcium, oxygen and carbon. So the second peak is oxygen, the first peak is carbon, so you will be able to see that so generally we also select carbon, oxygen. What else will you select? Iron, aluminium, probably sulphur. If you are looking at a chloride contaminated sample, you may have chloride phases; you will be able to detect chloride also. It is very rare that you will have anything else apart from these. We have covered all the major elemental species that are likely to be in your cement.

But the issue is, without knowing what is actually there in your sample, you cannot really make a good judgment about it. Then you will have to rely on the auto-detect capabilities of your software and the software may actually end up detecting unnecessary elements which may or may not be there. Sometimes what happens in this process is that you may also be able to detect the coating, in some cases. If your coating thickness is too large, like gold-palladium coating if you are putting on top, if your coating thickness is large, you will also get the X-rays from the coating. So in some cases, you may also produce peaks for gold. So that may confuse your spectrum quite a bit. But anyway, you need to be aware of what you need to select to do an analysis, because the same elemental composition that you get from the energy dispersive spectroscopy can be quantified. I am not going into the process of quantification, but there are methodologies to actually quantify this to actually get a good elemental-level composition of your sample.

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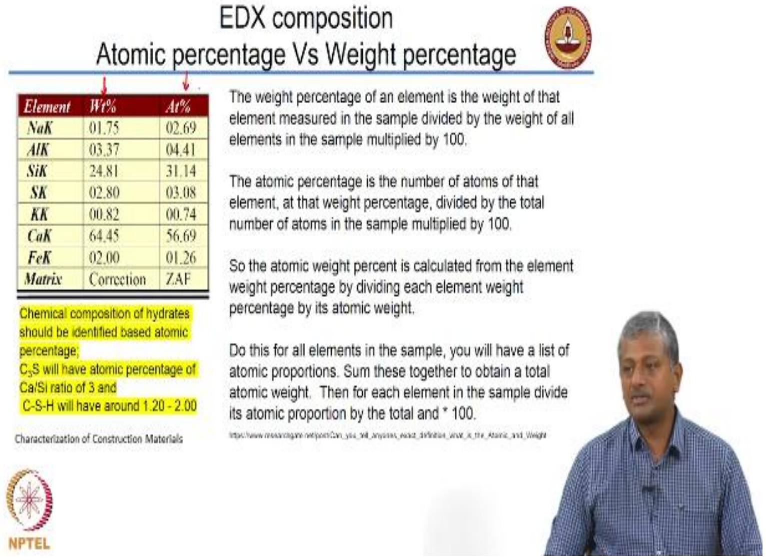

EDX composition
Atomic percentage Vs Weight percentage

Element	Wt%	At%
NaK	01.75	02.69
AlK	03.37	04.41
SiK	24.81	31.14
SK	02.80	03.08
KK	00.82	00.74
CaK	64.45	56.69
FeK	02.00	01.26
Matrix	Correction	ZAF

Chemical composition of hydrates should be identified based atomic percentage;
C_3S will have atomic percentage of Ca/Si ratio of 3 and
C-S-H will have around 1.20 - 2.00

The weight percentage of an element is the weight of that element measured in the sample divided by the weight of all elements in the sample multiplied by 100.

The atomic percentage is the number of atoms of that element, at that weight percentage, divided by the total number of atoms in the sample multiplied by 100.

So the atomic weight percent is calculated from the element weight percentage by dividing each element weight percentage by its atomic weight.

Do this for all elements in the sample, you will have a list of atomic proportions. Sum these together to obtain a total atomic weight. Then for each element in the sample divide its atomic proportion by the total and * 100.

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And this composition is typically presented in terms of weight percentage. It can also be presented in terms of atomic percentage. Now what do you mean by weight percentage and atomic percentage? Suppose you take calcium carbonate, so the total molecular weight of calcium carbonate is 100 (Ca – Atomic number = 20, Atomic weight = 40; O - Atomic weight = 16; C - Atomic weight = 12). So what is the weight percentage of calcium in calcium carbonate? 40% (40 divided by 100). So if you take a pure calcium carbonate and do an energy dispersive spectroscopy on it, you will get a weight percentage of 40% for calcium.

However, if you want to do the atomic percentage, it is basically the proportion of the calcium atoms in the structure of $CaCO_3$. So how many atoms totally are there in $CaCO_3$? Ca, carbon and 3 oxygen atoms, so there are 5 atoms. So what is the atomic percentage of calcium? 1 divided by 5, which is 20%. So while the weight fraction is 40% the atomic fraction is 20%. So that is what is presented in this case, weight fraction and atomic fraction.

Now, let us say you are looking at C_3S, which is $3CaO.SiO_2$. So if you do EDX of this, what will be your atomic fraction of calcium? (3/9). Oxygen is 5/9, silicon is 1/9. So if you do an EDS on C_3S phase, what should be your approximate height difference or rather percentage height between calcium and silicon? Ca by Si should be how much? ($\frac{3}{1}$ =3), that is what you will see typically in most x-ray patterns. However, of course, it is not the exact thing. What you will see here in the intensity is more likely to be corresponding to the weight fractions and not to the atomic fractions. But when you do an elemental analysis from the surface and you resolve the weight and atomic fractions, from this you can actually start calculating, what the likely composition of the phase that you are observing is.

For example here, your calcium is 56.69, silicon is 31.14. Let us say you have a little bit of aluminium, sodium is there, and you have some sulphur. All these could be just incorporated in the structure of the calcium-silicate itself, and you have a little bit of iron. And typical methodology of doing this quantification is called the ZAF methodology; we do not have time to go into that in detail. But in reality, what we are seeing is when you have C_3S, the atomic percentage of calcium to silicon (Ca/Si) will be about 3. If you look at C-S-H, the elemental fraction of Ca/Si will be in the range of 1.2 to 2. We know that typical C-S-H produced by ordinary Portland cement hydration has a Ca/Si ratio of about 1.5 to 2. When you replace cement with fly ash or slag or silica fume, you tend to reduce the Ca/Si towards 1.5 or less than that.

So, you have weight proportions and atomic proportions. So you need to be careful about selecting the right one to depict your actual composition of the sample. Again, you will see some examples later on.

Quantification is done in XRD in that way, but here it is a little bit different. It is not the same as taking the area under the curve, we take the relative intensities and use that as a measure of what we will actually get based on the atomic weight of the sample. So there are some corrections to be applied in this case.

The weight and atomic fraction is calculated by the software based on the ZAF corrections, but you have to interpret what this material is. In the case of X-ray, it is not like that, in X-rays what you do is you compare your peaks or location of the peaks with the standard database. Here, there is nothing like that, you do not have a standard database as far as EDS is concerned. All you have a database of is, where exactly will you get the intensity lines of different elements, you do not have a database of different materials that will produce certain intensities in your sample. You need to collect that for yourself and look at the data yourself. We will see later how this data is actually plotted to make certain characteristic decisions about the type of phases that you are observing. So you will see how you need to represent this data. So these weight fractions and atomic fractions need to be represented carefully when you actually, want to do the analysis about the kind of phase that you are observing.

Now based on this atomic composition that has been presented here, what do you think would be the approximate composition of this material? What is this material that we are looking at? What is this phase for which the atomic composition is presented you think? Probably C-S-H, calcium silicate hydrate, because in C-S-H you have alumina also incorporated with the silicon, you have alkalis that are adsorbed into the C-S-H, you may also have sulphur based upon the kind of temperatures that are there during the hydration process. So this phase composition is for C-S-H. Now what is the Ca/Si ratio here, in this CSH? ($\frac{56}{31}$). Atomic fraction of calcium divided by atomic fraction of silicon, so that is $\frac{56}{31}$ that is approximately about 1.7 or 1.8. But in terms of weight fraction, it is $\frac{64}{25}$, so it is around 2.5-2.6, but atomic fraction is 1.7 or 1.8. So you need to convert the right numbers to assess the type of phase that you are actually looking at. So if you make a decision based on weight fraction this may appear to be something like an unhydrated phase, because Ca/Si is so high, but the true calculation should be done with the atomic fraction. So if you are looking at plain C_3S, your atomic fraction should be 3:1, so you should get 3 as your ratio of Ca/Si in the case of C_3S, but this is C-S-H.

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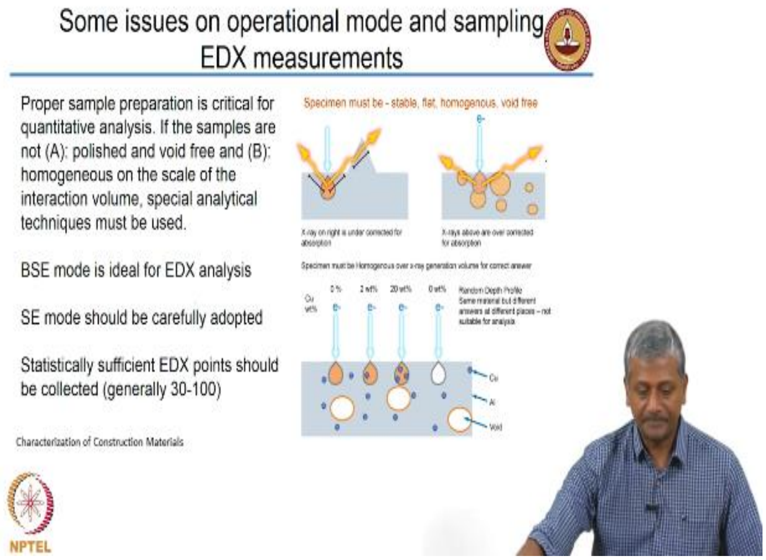

Some issues on operational mode and sampling EDX measurements

Proper sample preparation is critical for quantitative analysis. If the samples are not (A): polished and void free and (B): homogeneous on the scale of the interaction volume, special analytical techniques must be used.

BSE mode is ideal for EDX analysis

SE mode should be carefully adopted

Statistically sufficient EDX points should be collected (generally 30-100)

Specimen must be - stable, flat, homogenous, void free

X-ray on right is under corrected for absorption

X-rays above are over corrected for absorption

Specimen must be Homogenous over x-ray generation volume for correct answer

Random Depth Profile
Same material but different answers at different places – not suitable for analysis

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NPTEL

We will talk about some practical difficulties on how EDS is collected and what we are actually looking at as far as the EDS pattern is concerned.