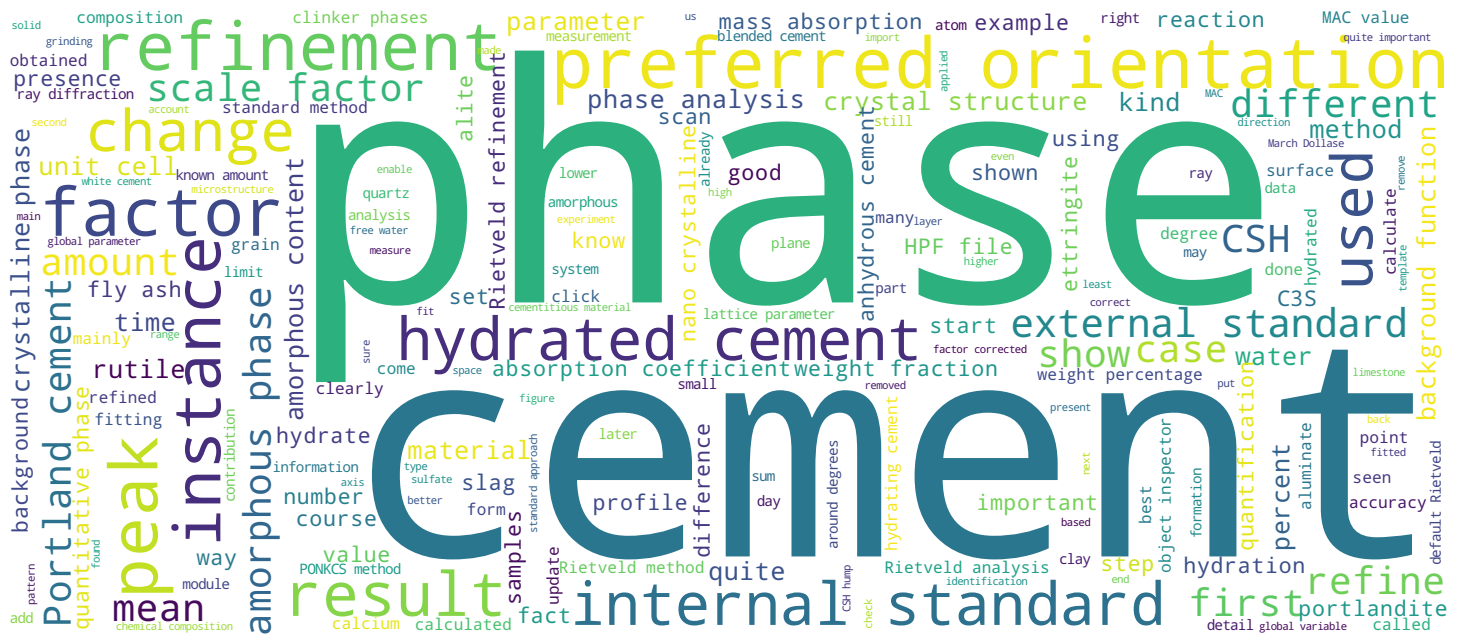


Rietveld quantitative phase analysis

Cement Chemistry and Sustainable Cementitious Materials

Dr. Ruben Snellings



Search MOOC



Video



Rietveld quantitative phase analysis

$$y_i(\text{calc}) = \sum_{j=1}^{N_{\text{phases}}} S_j \sum_{k=1}^{N_{\text{peaks}}} L p_k |F_{k,j}|^2 G_j (2\theta_i - 2\theta_{k,j}) A_j P_{k,j} + b k g_i$$

- Phase scale factors S_j yield mass fractions m_j

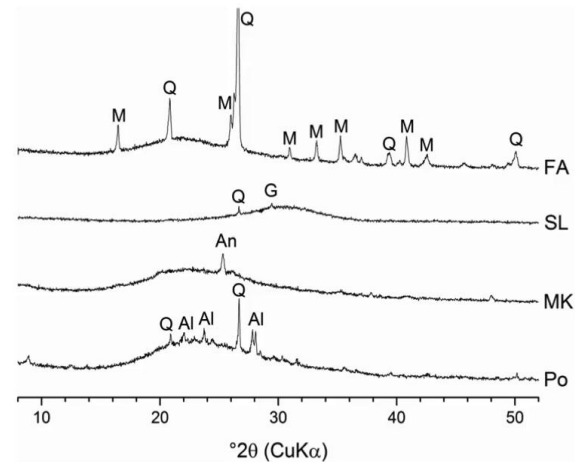
$$m_j = \frac{S_j (ZMV)_j}{\sum_i S_i (ZMV)_i}$$

M = mass per formula unit

Z = number of formula units per unit cell

V = unit cell volume

- If **amorphous** or unidentified phases are present, absolute QPA can be obtained using **internal** or **external standard addition**.



This lecture concludes the course by diving into quantitative phase analysis of cement. First, the standard quantification approach in the Rietveld method is extended to the samples that contain amorphous material. This we need because many cements contain a nano crystalline phase or an amorphous phase. Then we give a number of examples that involve anhydrous and hydrating cements along with some practical guidelines in the end. It is very helpful to also have a look at separate demonstration videos in which you can follow such analysis step by step. Let's go back to the intensity equation for a powdered diffraction experiment. The scale factor is obtained in the refinement, scale linearly, with the phase volume fraction. So if you assume that the sum of crystalline phases is 100 percent then the phase weight fraction can be calculated by normalizing the product of the scale factor with Z, the number of formula units per unit cell, the mass per formula unit and V, the unit cell volume, over the sum of these products over all crystalline phases. It should be noted that only relative proportions of weight fractions can be obtained if the sample contains amorphous phases or if any additional crystalline phases were not included into the Rietveld refinements.

Notes

Summary



0m 04s

Rietveld quantitative phase analysis

$$y_i(\text{calc}) = \sum_{j=1}^{N_{\text{phases}}} S_j \sum_{k=1}^{N_{\text{peaks}}} Lp_k |F_{k,j}|^2 G_j (2\theta_i - 2\theta_{k,j}) A_j P_{k,j} + bkg_i$$

- Phase scale factors S_j yield mass fractions m_j

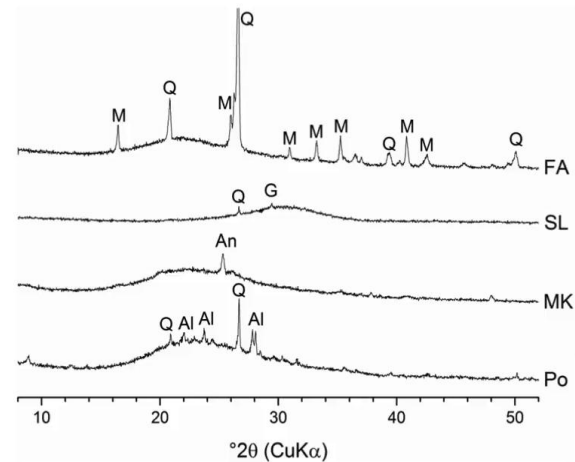
$$m_j = \frac{S_j (ZMV)_j}{\sum_i S_i (ZMV)_i}$$

M = mass per formula unit

Z = number of formula units per unit cell

V = unit cell volume

- If **amorphous** or unidentified phases are present, absolute QPA can be obtained using **internal or external standard addition**.



This approximation is often used in quantitative phase analysis of Portland cement or clinker, one would expect only small or negligible levels of amorphous phase. However, this assumption is not valid for cements containing SCMs which are mostly amorphous, for instance as you can see on the right hand side. Different methods were thus developed to take into account the presence of nano crystalline or amorphous phases. The presence of these amorphous phases can be quite easily seen in the figure on the right where you can see the broad hump which is indicative for amorphous phase.

Notes

Summary



1m 31s

- Approaches to determine the amorphous content:

- 1. Internal standard approach:**

Addition of a known amount of standard to the sample

- 2. External standard approach:**

The absolute phase contents are calculated by comparison to a separately measured standard monitor sample (the standard must be measured using identical measurement conditions as the sample)

- 3. PONKCS method**

Calibration needed of individual amorphous phases. Different amorphous phases can be quantified separately.

There are several ways to deal with amorphous content, here we will consider three different approaches. The first one is to add a known amount of internal standard into the sample, this is called the internal standard approach. The second one is the external standard approach in which the quantification results are rescaled based on a comparison to a separately measured monitor sample, the external standard. And then finally, the third method that will be introduced is the PONKCS method, which stands for Partially Or Not Known Crystal Structure method. This method requires separate calibration of the amorphous phase, but on the other hand it enables the quantification of different amorphous phases, more than one in the same sample.

Notes

Summary



2m 10s

- **Internal standard method: calculation**

The weight fraction of phase k is calculated as follows:

$$w_k = \frac{(ZMV)_k S_k}{(ZMV)_s S_s} w_s \frac{1 + f_s}{f_s}$$

where w_s = known crystallinity of the internal standard;
 f_s = weight fraction of the standard in the sample.

Or departing from the Rietveld calculation output:

$$W_k = W_{j,app} \frac{W_s}{W_{s,app}}$$

$$W_{Amorphous} = 1 - \sum_n W_n$$

The most common approach is the internal standard approach. In fact, in this method it is required to spike the sample with a known weight fraction, known amount of a crystalline standard. A given expression, shown here on the top, can be used to calculate the absolute phase weight fractions from the scale factors. The index S here identifies standards, W_s corresponds to the crystallinity or the purity of the internal standard itself, and f_s to the weight fraction of the standard that was added to the sample. Alternatively, the weight fractions can be calculated using the equation below, where the apparent weight fraction of the internal standard can then be for instance higher than the weighted amount, for instance let's say 25 percent when we added 20 percent of rutile, and this indicates the presence of amorphous or unidentified crystalline material. Or the second case is that it can be equal, so 20 percent for 20 percent to the weighted amount, and this indicates that there is no or very little amorphous or unidentified materials. And then finally the third case is that there is a lower amount of standard quantified than the amount that was weighted, and this is of course an indication that there are some problems in the experiment or in the data analysis procedure.

Notes

Summary



3m 00s

- **Internal standard method: calculation**

The weight fraction of phase k is calculated as follows:

$$w_k = \frac{(ZMV)_k S_k}{(ZMV)_s S_s} w_s \frac{1 + f_s}{f_s}$$

where w_s = known crystallinity of the internal standard;
 f_s = weight fraction of the standard in the sample.

Or departing from the Rietveld calculation output:

$$W_k = W_{j,app} \frac{W_s}{W_{s,app}}$$

$$W_{Amorphous} = 1 - \sum_n W_n$$

The total weight fraction of all amorphous and/or unidentified components can be calculated as a difference between the sum of all the crystalline components and one. So the sum of all the crystalline components and the difference with 100 percent is the amorphous phase fraction.

Notes

Summary



- Internal standard method: sample preparation and choice of standard
 - Avoid amorphisation during mixing/grinding (use McCrone micronising mill)
 - Avoid reactions between the sample and the lubricant or the internal standard during grinding
 - Choose the correct internal standard:
 - Should be completely crystalline (or of known crystallinity)
 - Should have the right Lin. Absorption Coefficient (LAC)
 - Should have the right hardness
 - Should preferably be highly symmetrical with peak positions not overlapping with sample phases
 - The standard should not be present in the sample
 - Choose the correct amount of internal standard
- To remember:
 1. No knowledge of sample chemistry required
 2. Additional sample preparation needed (mixing and grinding)

The internal standard method requires appropriate sample preparation. For instance, it is very important to homogeneously mix the standard into the sample. If the sample and standard are ground together, then one should take care that there is no over-grinding of the sample by co-grinding with a harder standard material. Over-grinding for instance would lead to peak broadening and partial amorphization, creation of amorphous content by destroying softer phases by the harder ones. Especially hydrated phases in the cement base are vulnerable to this kind of decomposition. Not only by grinding but also by dehydration and carbonation one would really change the hydrate assemblage and one would not measure the original content of the hydrated sample. Another property is that the internal standard should be of known crystallinity. This actually means that its amorphous content should be known and should not be present in the sample. Preferably, standard materials should have a high crystal structure symmetry and have peaks that do not overlap with the main reflection peaks and the phases present in the material.

Notes

Summary



4m 54s

- Internal standard method: sample preparation and choice of standard
 - Avoid amorphisation during mixing/grinding (use McCrone micronising mill)
 - Avoid reactions between the sample and the lubricant or the internal standard during grinding
 - Choose the correct internal standard:
 - Should be completely crystalline (or of known crystallinity)
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 - Choose the correct amount of internal standard
- To remember:
 1. No knowledge of sample chemistry required
 2. Additional sample preparation needed (mixing and grinding)

And in addition, it is also good if there is no micro absorption problems that would occur, for instance if there is a large X-ray absorption contrast between the phases in your sample and the standard. If this would be the case, the micro absorption problems may occur and one would have a falsified or a biased quantification. The obtainable accuracy of the quantification of the amorphous and unknown phases strongly depends on the amount of internal standard added. Small quantities of amorphous phase of a few percent are therefore very difficult to quantify precisely, while higher levels can be quantified with greater accuracy. For hydrating cements that may contain between about 30 and 60 percent of amorphous and nano crystalline phases, a good compromise between accuracy on both amorphous and crystalline phases would be to use additions of internal standard of around 20 weight percent. And it has been demonstrated that the presence of a significant amount of internal standard inside a hydrating base itself changes the kinetics of the hydration by a filler effect, it is therefore best not to include the standard in the sample, and instead to include a sample or add the sample after stopping the hydration.

Notes

Summary



- Internal standard method: sample preparation and choice of standard
 - Avoid amorphisation during mixing/grinding (use McCrone micronising mill)
 - Avoid reactions between the sample and the lubricant or the internal standard during grinding
 - Choose the correct internal standard:
 - Should be completely crystalline (or of known crystallinity)
 - Should have the right Lin. Absorption Coefficient (LAC)
 - Should have the right hardness
 - Should preferably be highly symmetrical with peak positions not overlapping with sample phases
 - The standard should not be present in the sample
 - Choose the correct amount of internal standard
- To remember:
 1. No knowledge of sample chemistry required
 2. Additional sample preparation needed (mixing and grinding)

In mixing the sample into the hydrated material, you should be very careful not to alter the hydration products and therefore the mixing operations should be thorough but gentle, and sample exposure to air should be limited as much as possible. Since this can be quite tedious to do in practice, perhaps the less labor intensive external standard method is preferable for routine analysis.

Notes

Summary



7m 44s

- **External standard method: calculation**

- The weight fraction of phase k is calculated using:

$$w_k = \frac{(ZMV)_k}{(ZMV)_s} \frac{S_k}{S_s} w_s \frac{\mu_m}{\mu_{ms}}$$

where w_s is the **crystallinity of the standard**

μ_m and μ_{ms} are the **mass attenuation coefficients** of the bulk sample and the standard, resp.

μ_{ms} is calculated from the chemical composition including bound water

- Again, the amorphous weight fraction is:

$$W_{Amorphous} = 1 - \sum_n W_n$$

In the external standard approach, phase quantification is carried out through the comparison of the phase scale factors of a sample through the scale factor of a well-characterized standard material measured under identical diffractometer measuring conditions. In this procedure also the different mass absorption coefficients of the sample, μ_m and the standard μ_s , need to be taken into account. As can be seen in the expression given here, the W_s , the weight fraction of the standard phase in the external cement material, is also to be known.

Notes

Summary



8m 14s

Rietveld quantitative phase analysis

MAC calculation

Chemical composition needs to be known:

Calculation:

$$MAC_{SAMPLE} = \sum_i W_i MAC_i$$

To note:

H₂O has a low MAC,
cement pastes will have much
lower MACs than anhydrous
cement.

Oxide	MAC [cm ² /g]
CaO	124.04
SiO ₂	36.03
Al ₂ O ₃	31.69
Fe ₂ O ₃	214.9
MgO	28.6
Na ₂ O	24.97
K ₂ O	122.3
SO ₃	44.46
TiO ₂	124.6
P ₂ O ₅	39.66
H ₂ O	10.07
SUM	
MAC	

White cement anhydrous	Slag anhydrous	White Cement w/c 0.4
mass fraction	mass fraction	mass fraction
0.7221	0.3388	0.5158
0.2136	0.3067	0.1526
0.0143	0.1881	0.0102
0.0035	0.0040	0.0025
0.0086	0.1148	0.0061
0	0.0044	0.0000
0.0011	0.0038	0.0008
0.019	0.0192	0.0136
0.009	0.0157	0.0064
0.004	0.0001	0.0029
		0.2857
0.9952	0.9956	0.9966
101.46	66.86	75.26

Although the obvious advantage of the method, of this external standard method, is that the sample does not need to be intermixed with an internal standard and it does avoid sample preparation and homogenization problems. This approach does demand the mass absorption coefficient of the sample to be known. In the most practical of ways it is obtained by calculating the mass absorption coefficient for the used X-ray wavelengths or the chemical composition. This can be seen for instance in the table here where for each oxide from the chemical composition one has the MAC, the mass absorption coefficient, given for copper k alpha radiation. The linear combination of the mass absorption coefficients with the mass fractions will enable you to measure the mass absorption coefficient of that sample. In the table one can see the calculation done for a white cement which was not hydrated, which comes from MAC of about 101.5 square centimeters per gram, one can also see how it is calculated for a slag, as the slag contains less calcium which is a X-ray absorbing compound because it is heavier than for instance the silicon. One can see that here the total mass absorption coefficient is lower in the slag than for the white cement.

Notes

Summary



Rietveld quantitative phase analysis

MAC calculation

Chemical composition needs to be known:

Calculation:

$$MAC_{SAMPLE} = \sum_i w_i MAC_i$$

To note:

H₂O has a low MAC,
cement pastes will have much
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K ₂ O	122.3
SO ₃	44.46
TiO ₂	124.6
P ₂ O ₅	39.66
H ₂ O	10.07
SUM	
MAC	

White cement anhydrous	Slag anhydrous	White Cement w/c 0.4
mass fraction	mass fraction	mass fraction
0.7221	0.3388	0.5158
0.2136	0.3067	0.1526
0.0143	0.1881	0.0102
0.0035	0.0040	0.0025
0.0086	0.1148	0.0061
0	0.0044	0.0000
0.0011	0.0038	0.0008
0.019	0.0192	0.0136
0.009	0.0157	0.0064
0.004	0.0001	0.0029
		0.2857
0.9952	0.9956	0.9966
101.46	66.86	75.26

For a hydrated white cement, for instance showing in the last column, one can see that it is next to the cement content, there is also water in there. So, calculating the mass absorption coefficient of the total mix will show that for a hydrated mix, the mass absorption coefficient is quite a lot lower.

Notes

Summary



Rietveld quantitative phase analysis

- Partial Or No Known Crystal Structure (PONKCS) method
- Calibration of a phase of unknown structure:
 - Mix of the amorphous phase α and a standard (weight fractions known)

$$W_{\alpha} = W_s \frac{S_{\alpha} \rho_{\alpha} V_{\alpha}^2}{S_s \rho_s V_s^2}$$

- In unknown mixes the refined amorphous phase scale factor can then be recalculated into a weight fraction

↓

Peak phase calibration factor ← $\rho_{\alpha} V_{\alpha}^2 = \frac{W_{\alpha} S_s \rho_s V_s^2}{W_s S_{\alpha}}$

A promising development is a so-called PONKCS method, which stands for 'Partial Or No Known Crystal Structure approach. This method takes into account the contribution of a phase that has no or no known crystal structure by calibration of a phase constant, which is shown below. This phase constant can then be used in combination with the refined scale factor to calculate the phase weight fraction on mixes.

Notes

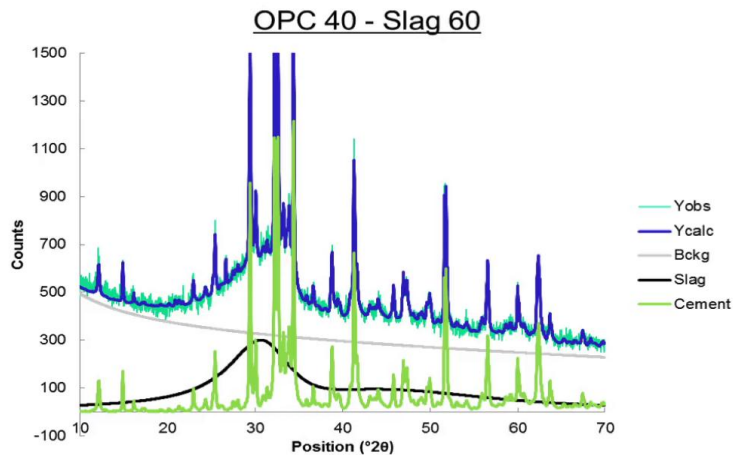
Summary



10m 44s

Rietveld quantitative phase analysis

- Partial Or No Known Crystal Structure (PONKCS) method (Scarlett & Madsen, 2006)
- Application to cements (Snellings et al., 2014)
- E.g. Anhydrous blended cement



% Measured	Slag	58.2
σ	Slag	0.3
% Weighed	Slag	59.0
Absolute deviation	Slag	0.3

This method was recently applied to the quantification of the grief reaction of the metakaolin alkali activated systems, but also to the quantification of CSH by XRD in the early hydration of alite. The precision and accuracy of the PONKCS method was tested by making model mixes of cement and SCMs, as for instance shown in this graph. Here, a mix of 40 percent Portland cement and 60 percent slag is shown. One can clearly see the crystalline phases in green from the cement and the slag contribution in black in the X-ray diffraction pattern. The weighed in amount here is 60 percent. By calibrating separately the slag and calibrating the phase constant for the slag and using it in a PONKCS method approach, one can actually measure directly the amount of this slag in the sample. As you can see on the right hand side the results were very good. We measured using the PONKCS method about 58.2% of slag, while we weighed in about 59%. So in general for mixes in which the SCMs were the only unknown amorphous component next to a number of crystalline phases, an excellent precision is obtained of around 1 weight percent and the accuracy over a large number of samples was about 2 - 3 weight percent.

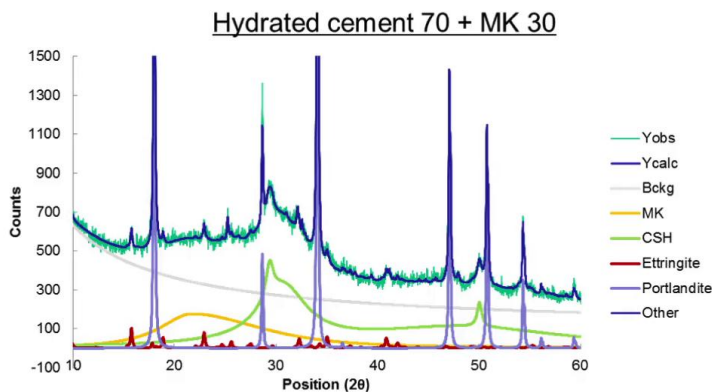
Notes

Summary



Rietveld quantitative phase analysis

- Partial Or No Known Crystal Structure (PONCKS) method (Scarlett & Madsen, 2006)
- Application to cements – model mixes (Snellings et al., 2014)
- E.g. hydrated blended cement – distinction MK/C-S-H



Binary mix	Average	σ	Weighed	Absolute deviation
Sample	Wt% MK	Wt% MK	Wt% MK	Wt% MK
White Cement 70 – MK 30	27.5	0.5	27.8	0.3

In more complex mixes the errors and detection limits are expected to be larger. A particular difficulty in decomposing hydrated systems is acquiring a suitable model for the CSH phase. In the figure shown here you can see a white Portland cement hydrated for seven years, that was mixed with a known amount of metakaolin. You can recognize some of the crystalline phases present in the hydrated Portland cement such as ettringite or portlandite, and you can see also in green the contribution by the CSH phase and in yellow the contribution by metakaolin. Again when we did the analysis by PONKCS, the accuracy and precision were very good. This was mainly because the CSH was the only amorphous phase in the hydrating cement and we could construct a CSH peak model that fitted nicely and could be used to decompose also model mixes, so meaning the hydrated cement with a known amount of slag or metakaolin and so on and so forth. However, the situation unfortunately becomes more complex when we have different kinds of CSH formed and blended cements of different composition, and therefore the peak profiles start to change or there is the presence of other amorphous phases that can actually limit or bias the quantification.

Notes

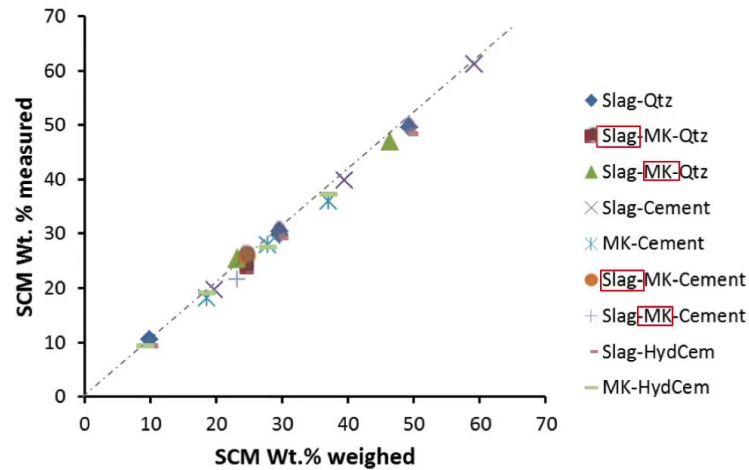
Summary



12m 50s

Rietveld quantitative phase analysis

- Partial Or No Known Crystal Structure (PONKCS) method (Scarlett & Madsen, 2006)
- Application to cements – model mixes (Snellings et al., 2014)



In blends however, synthetic blends, the method can be used very well as shown in the figure here. Better is an excellent correlation of the weighted amount of SCM on the x axis and the measured amount by PONKCS analysis on the y-axis. This may be very useful for instance in process control, in the production of ternary or quaternary blended cements where one needs to check whether the mixing has been done correctly.

Notes

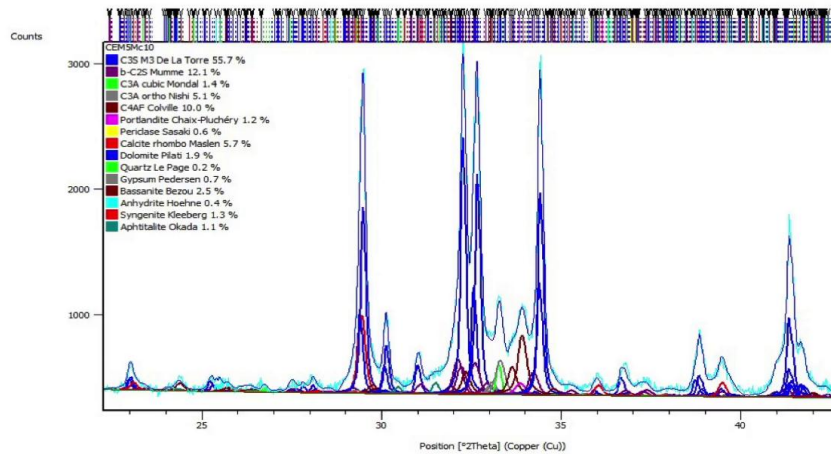
Summary



14m 23s

Rietveld quantitative phase analysis

Portland cement is a complex mix of phases, whole pattern fitting methods (e.g. Rietveld) can deal with peak overlap in the XRD scans



Differences in strength development and durability can be correlated with the phase composition

Traditional XRD quantitative phase analysis methods were based on single peak heights or on single peak integrated heights and one compared these heights to the height of an internal standard. This has not been very successful for cements. Why? This has been introduced before, this is because there is a high degree of overlap between the main peaks of the major phases, and this gives significant problems and significant error when applying such simple methods. There are a number of additional problems such as variability in composition and crystal structure such as the presence of polymorphs that could actually cause significant variations in peak positions and also intensities. For instance in the case of Portland cements one knows that there is a lot of solid solutions, substitutions of minor elements such as alkalis or magnesium or sulfate in the major phases and this is common and it leads often to the stabilization of different polymorphs which is then difficult to relate to a certain quantity. Therefore, the development of the whole pattern fitting methods such as the Rietveld method has enabled to largely overcome most of these peak overlap problems and it has found such widespread application.

Notes

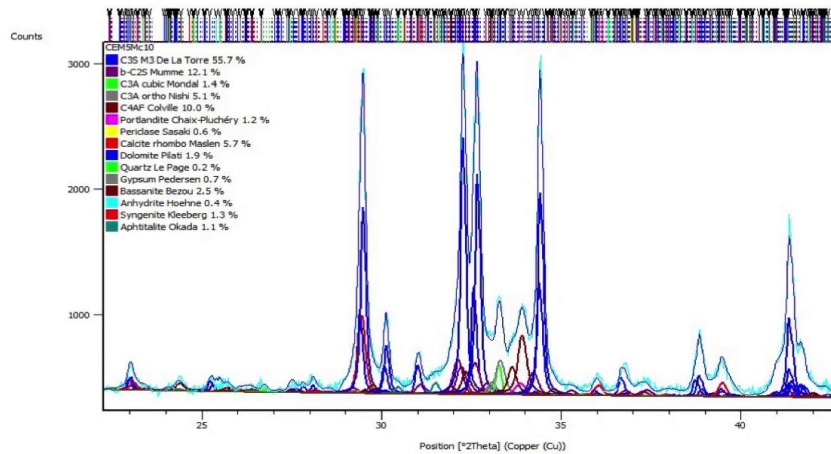
Summary



14m 55s

Rietveld quantitative phase analysis

Portland cement is a complex mix of phases, whole pattern fitting methods (e.g. Rietveld) can deal with peak overlap in the XRD scans



Differences in strength development and durability can be correlated with the phase composition

Since the phase composition such as the alite content can be related to properties such as strength development or durability, these kind of XRD analysis by the Rietveld method have found really a lot of use in both cement research and production quality control.

Notes

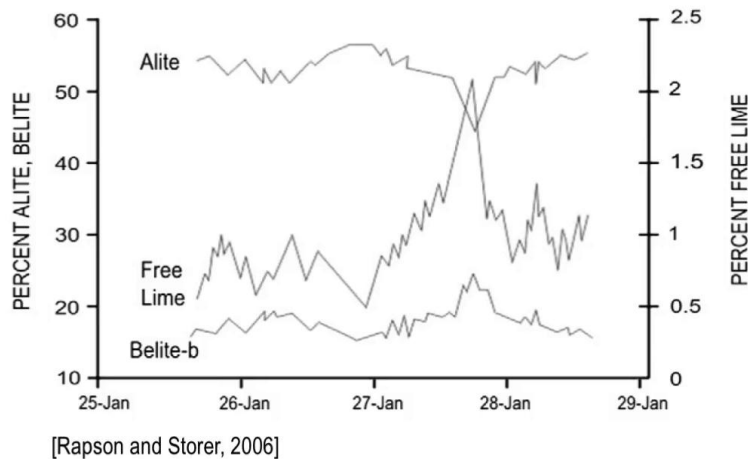
Summary



16m 20s

Rietveld quantitative phase analysis

- Rietveld QPA in production process and quality control in cement plants

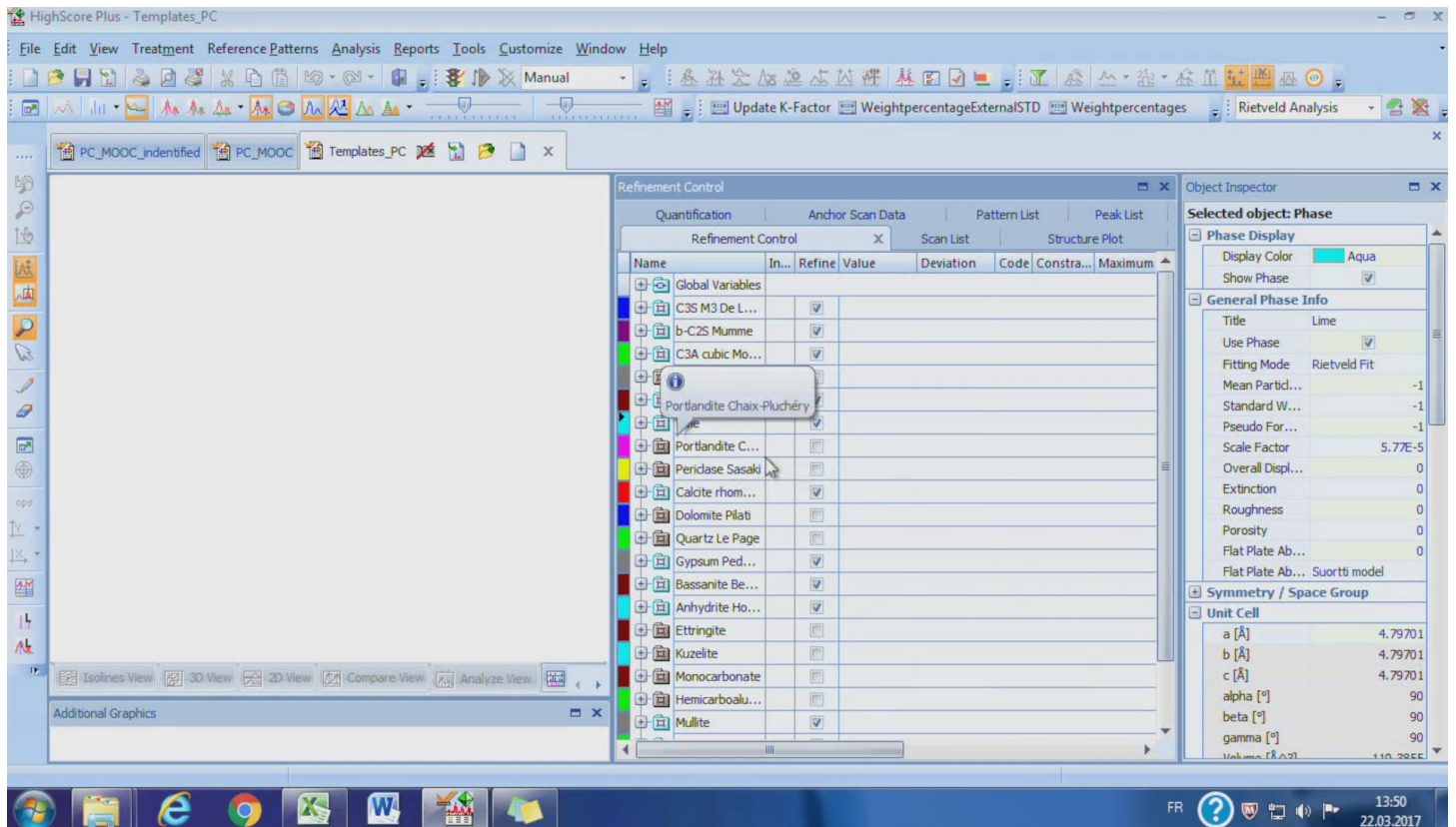


For instance, this figure shown here shows a monitoring of the alite, belite and free lime contents by XRD during a period of Portland cement production of an industrial site. And here you can clearly see that at some point there was some for instance temperature lowering in the kiln and we can see a drop in alite levels, free lime coming up and belite increasing as well.

Notes

Summary





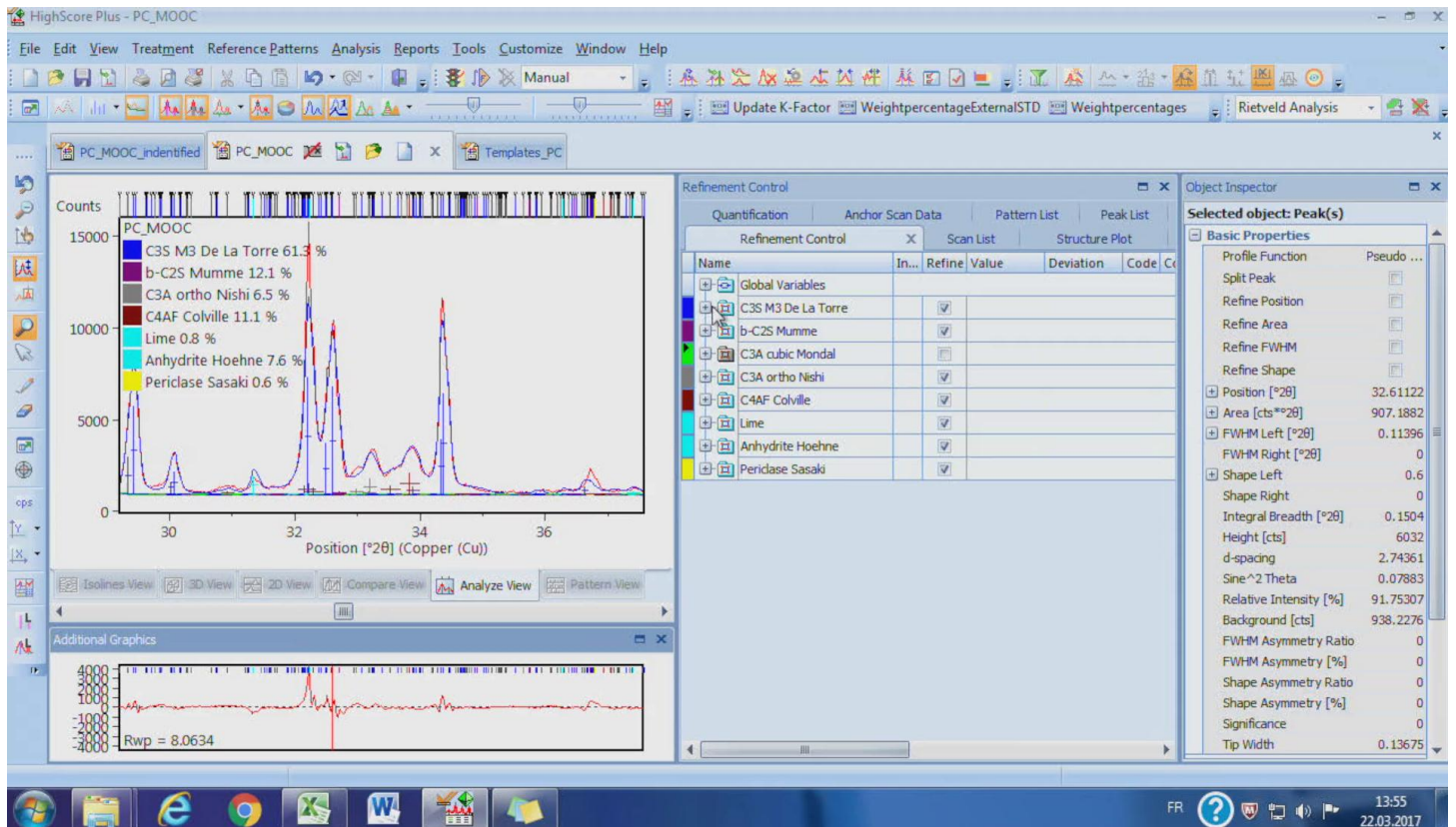
A step by step demonstration of phase quantification of anhydrous cement will be shown in one of the demonstration videos. As we already did the identification of the cement, now we need to import the structure for each phases. First, import and set the phases for the refinement. Import the structure for C3S. Let's change the name. For each phase, the scale factor, unit cell and profile should be refined. Constraints of 1% of variation on the unit cell were applied to secure the refinement. Limit of 0.0001 to 0.2 to the profile W was applied. The application of constraints to the refined parameters will improve the stability of the overall refinements when especially we are analyzing complex samples such as the hydrated cement. Do the same steps for the rest of the phases, for example the C2S, C3A and C4AF as well as some other minor phases. Herein we keep the two most common polymorphs for C3A, namely the cubic and orthorhombic ones. Alternatively, if you already have an HPF file with all the phases you can also copy the phase from one HPF file to another. Right click on the phase, copy to the new HPF file you need. We set all the limits and the parameters to be refined in the template, in the template HPF file, previously using the same steps.

Notes

Summary

17m 05s





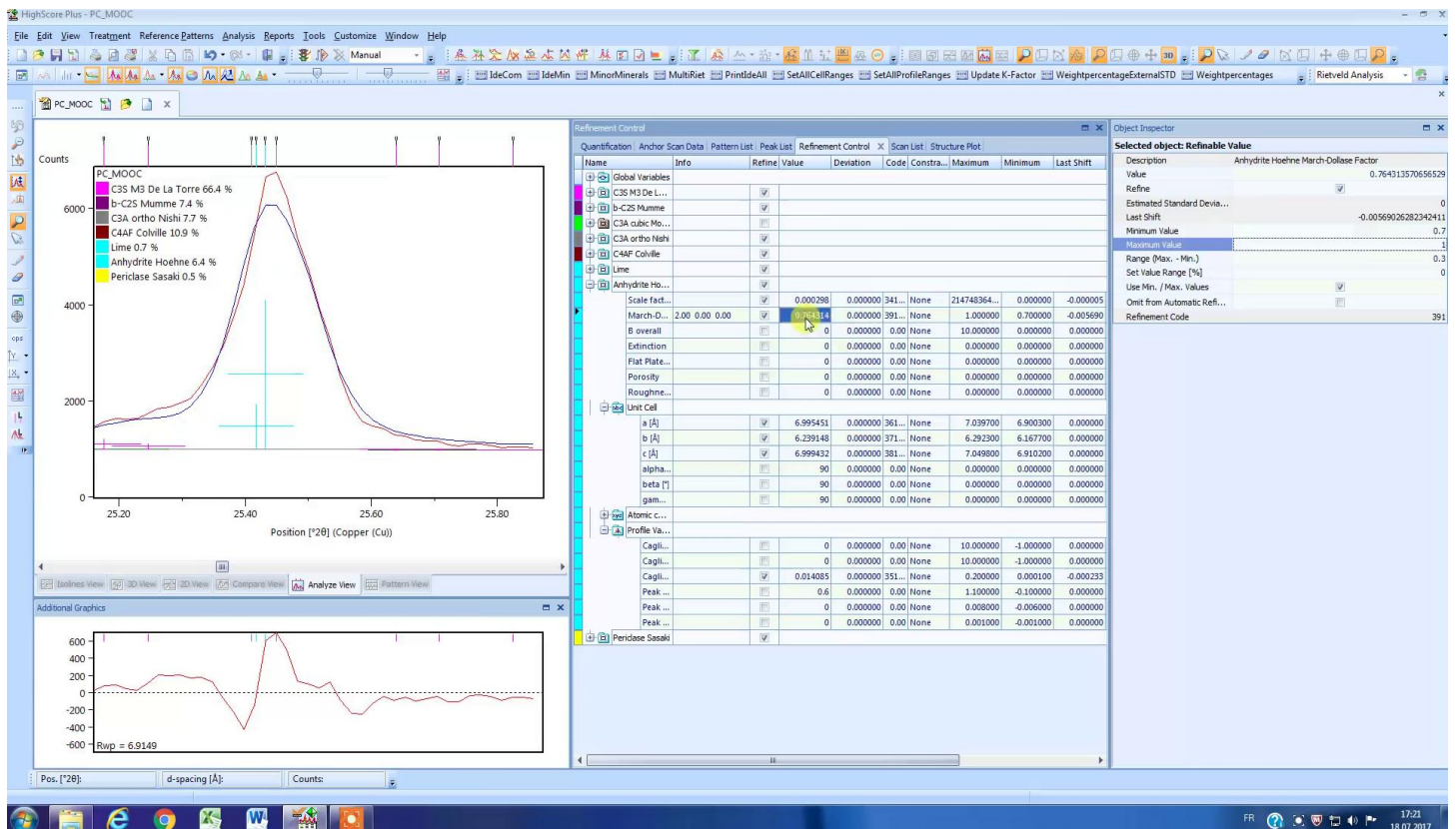
Check all the parameters for the phases. Secondly, set the global parameters: the specimen displacement, background function are usually refined. For the background functions, the polynomial function with five coefficient were used. We use manual mode for refinement as all the refinement parameters were set manually. After all the parameters were set, the refinement can be executed by pressing the refine button here. After the first run, we can see that there is not much cubic C3A in the cement. Now we can kick it out for further refinement. As we have so many phases in the cement, it takes several runs to reach the global minimum for the refinement. Open the additional graphics for the difference plot to visually check the fitting. The most common mismatching is from the cloud of the peak around 32 degrees. In this range we have the main peak for C3S and of course some other peaks which were overlapped. The mismatch is mainly because of the preferred orientation of C3S here. You can find out the direction by pointing the mouse onto the peak which is not well fitted. Here it is the 6 0 -6 plane for M3 alite.

Notes

Summary

18m 51s





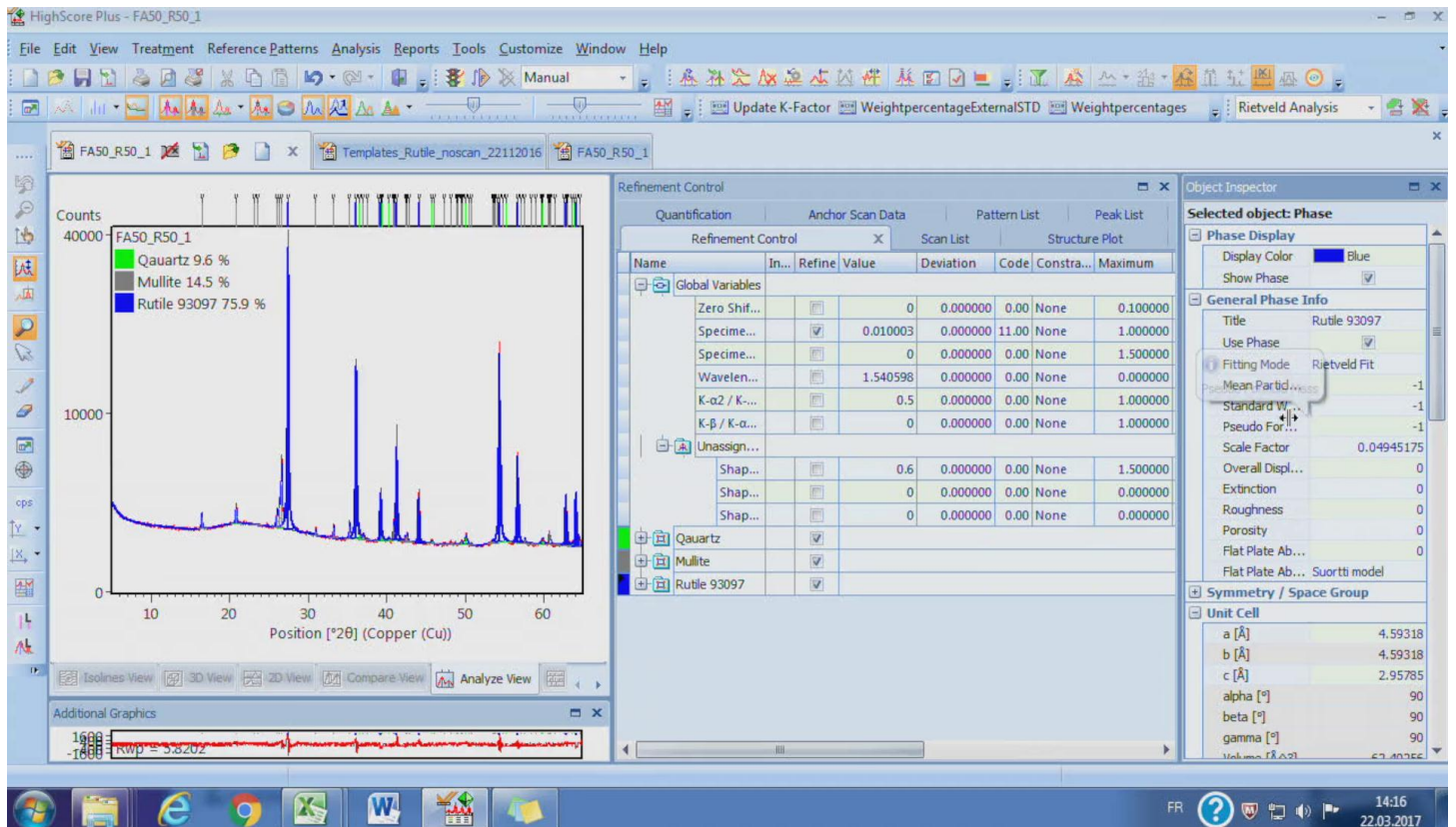
To set the preferred direction you can click on the C3S in the refinement control then in the object inspector for C3S you will find the item called preferred orientation. The March/Dollase model is recommended. Specify the direction, h, k, l of the plane for the preferred orientation. After setting the direction, check the refinement for the March/Dollase factor. Like the other parameters, we put the limit for the refinement of 0.7 to 1. The value 1 means there is no preferred orientation at all, the smaller the more preferred orientation. In most cases 0.7 should be low enough. If the value is too small, it means the sampling is not well done. A repetition of the XRD pattern collection with more attention on reducing the preferred orientation, in this case, is recommended. By refining, the fitting of this peak is much improved. Another phase that can be easily preferred orientated is the anhydrite. Do the same for the preferred orientation of anhydrite for the for the 2 0 0 direction. Refine. There are some improvements for the goodness-of-fit and the weighted R profile. The Rwp value is now 6.947% showing in the additional graphics.

Notes

Summary

20m 15s





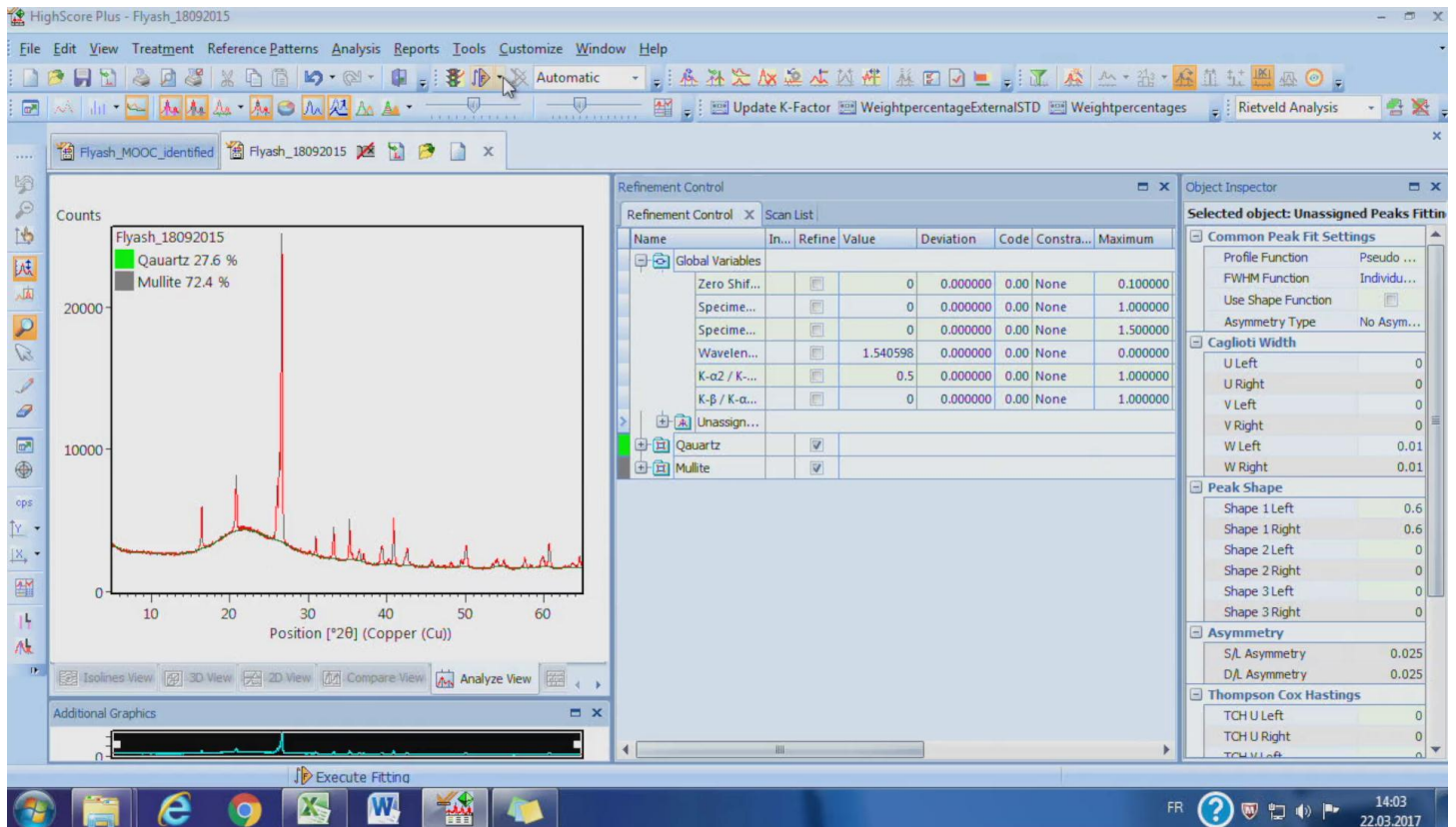
Now execute the refinement. The overall fitting is quite good. When checking in details, we can see that there are some peaks which are not well fitted, for example the peak at 27.4 degrees, the main peak for rutile. When placing the mouse onto the peak, it shows the HKL of the corresponding peaks for the phase. Here is the 1 1 0 plane for rutile. Actually this is the preferred orientation of the rutile. When the preferred orientation is set, set the March/Dollase factor to refine. Now the refinement is done with an Rwp value of about 5.8%, which is very good. To show the results in internal standard, go to customize, fitting Rietveld panel, change the “show weight percentage” to “as received”. Here we have three options: normal refers to the default Rietveld output, as received means the renormalized internal standard results, finally, the external k-factor corrected means the results based on external standard. The last step is to specify how much internal standard we added. Choose the rutile in the refinement control, locate general phase information, there we have the item called standard weight percentage. Type the actual weighed amount, here 48.1, as the crystallinity of the rutile we use is 96.2%.

Notes

Summary



23m 23s



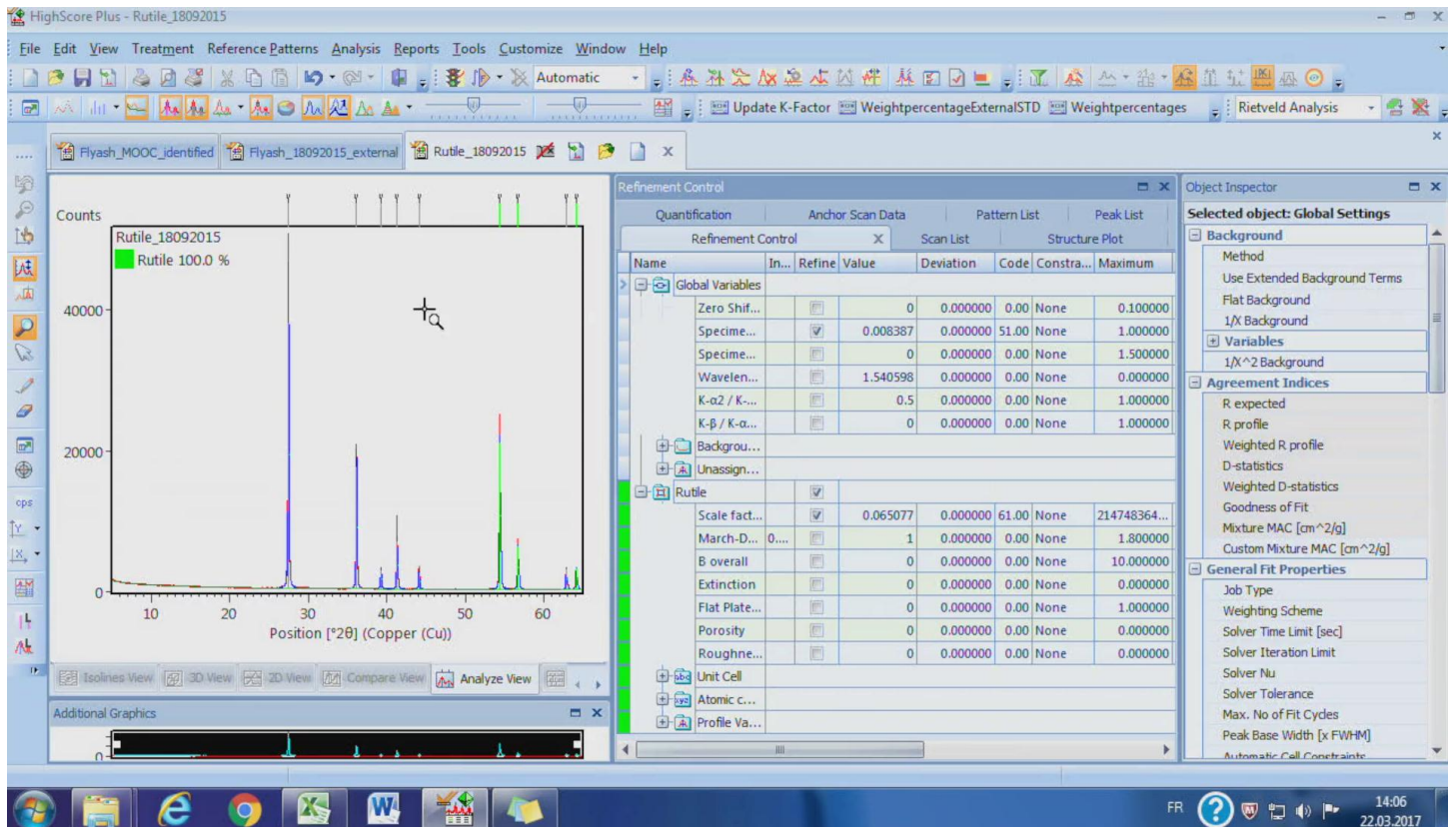
Now the final results are shown in the analyze view window. Export the data using the weight percentage button or simply load it down. The basic for external standard is that the k-factor can be determined using the external standard measured under the same condition. Then the absolute content of the crystalline phases can be calculated using the k-factor method. For the case of the external standard method, you will need two XRD patterns: one for the sample and another for the standard. And we also need to know the chemical composition for the sample to compute the mass absorption coefficient, the MAC value. The calculation was provided in the template files. Step 1: refine the fly ash pattern. Open the scan for fly ash, insert the phases, namely the quartz and mullite. Change the name of the phases. Manually determine the background. Make sure the background is following the lowest point of the pattern but it should not go into the peaks. Change the background function from polynomial to use available. For simple Rietveld refinement system with few phases, we can start with the automatic Rietveld refinement by clicking on the default Rietveld.

Notes

Summary

25m 02s





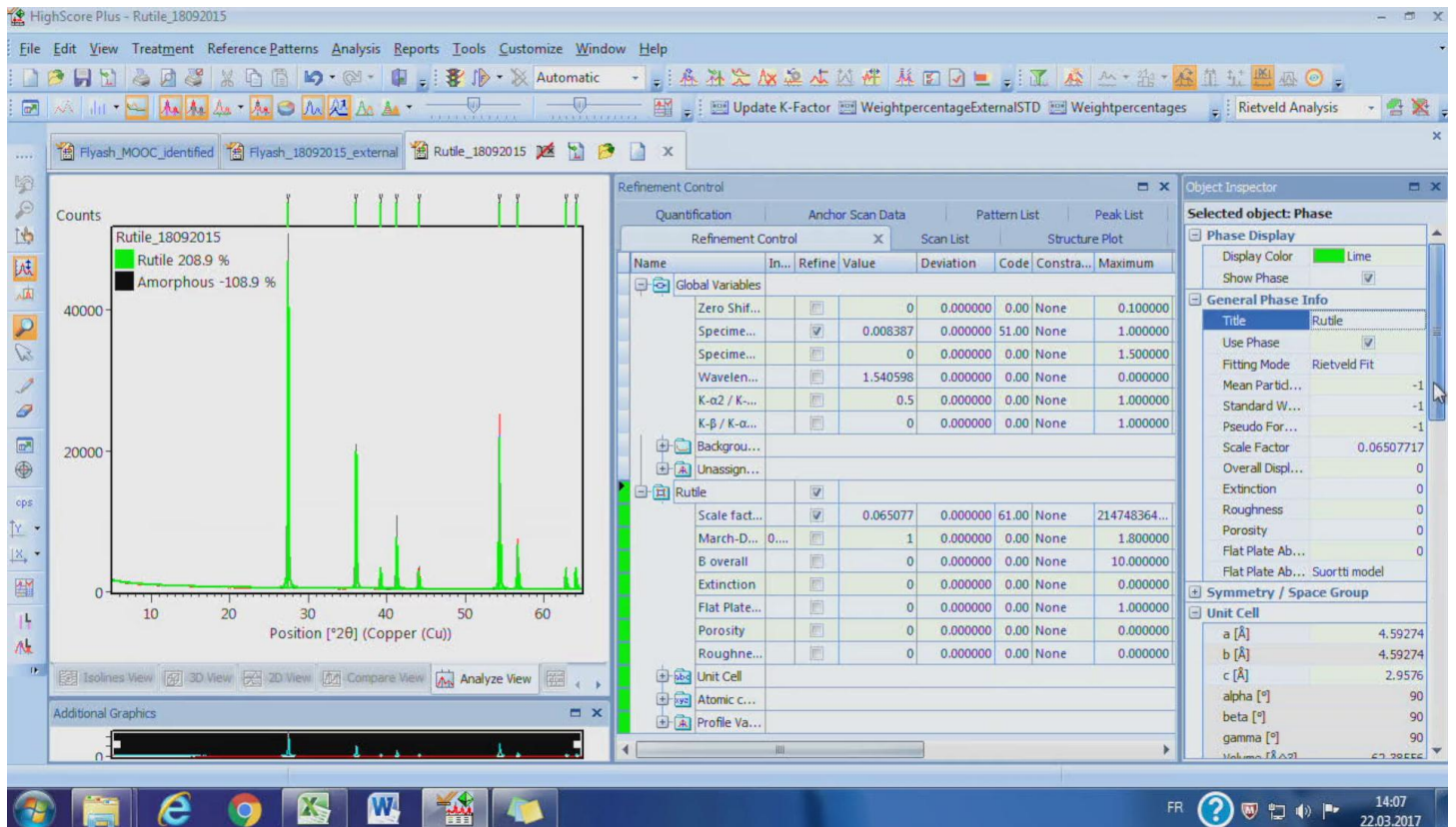
The automatic Rietveld will refine the scale, unit cell and the profile step by step. After several runs of automatic refinement then change the refinement to manual mode to further refine the pattern. Take a look at the peak at 26.5 degrees, the unfitted peak is because of the preferred orientation of quartz at 1 0 -1 plane. Set the direction of the preferred orientation and set for refinement. Also, add limits for the preferred orientation, then execute the refine. Save the HPF file. Step 2: calculate the k-factor using the standard scan. Create a new file, then insert the rutile scan. There is only one phase in the rutile, insert the phase. The standard scan is quite a simple scan to refine, so the automatic Rietveld refinement is enough. Several runs of the default Rietveld refinement is recommended to get the global minimum. After the refinement, save the HPF file under the same folder as the sample we analyzed. You may notice that I didn't refine the preferred orientation for the rutile. The standard was pressed on purpose to have some preferred orientation to compensate the amorphous content in the standard. The rutile we used contains 3.8% of amorphous content.

Notes

Summary

26m 30s





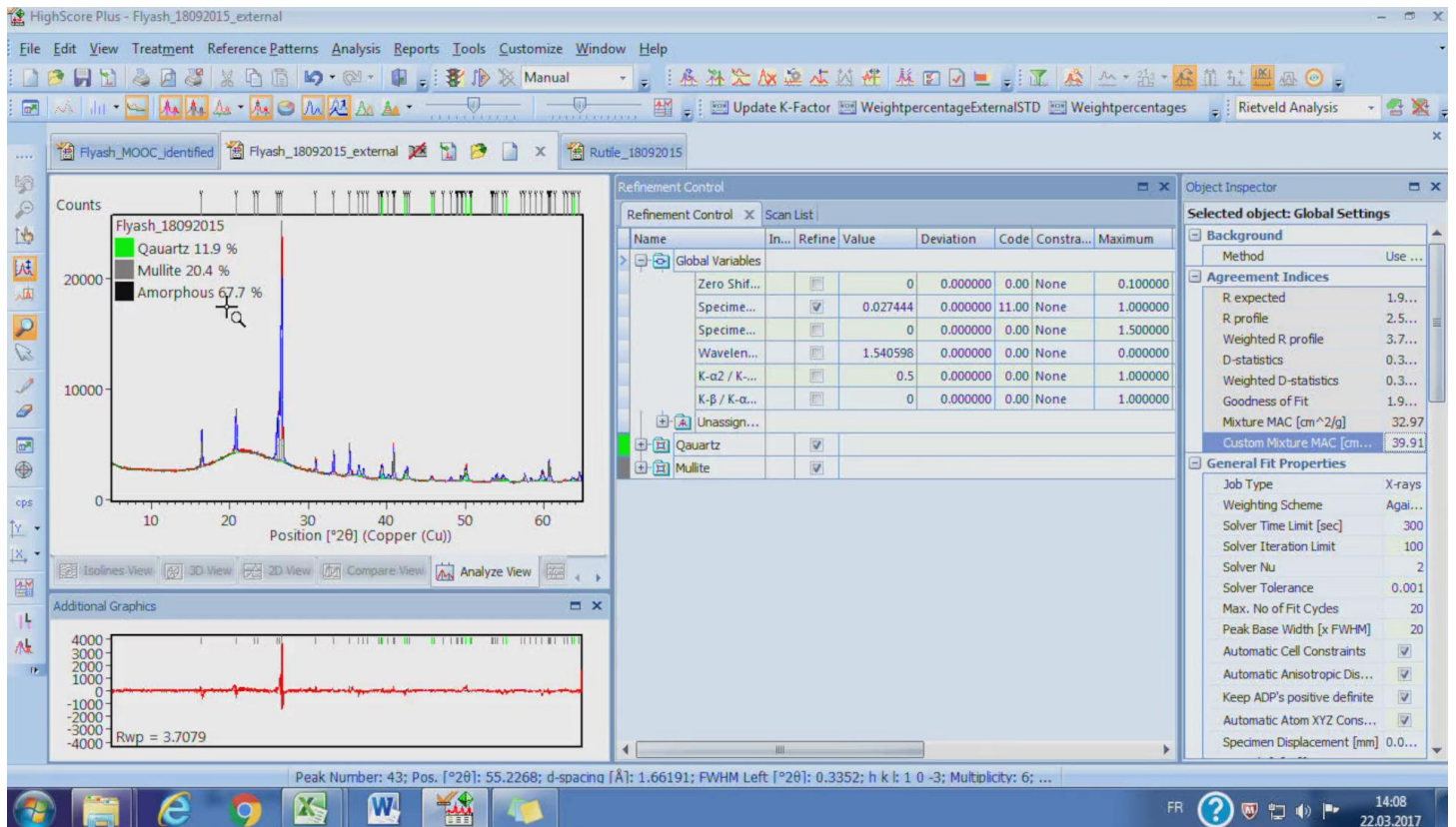
The deliberately introduced preferred orientation results in a k-factor which is 100% of crystalline rutile. To present the external standard results, go to customize, program settings, fitting Rietveld panel, then you will have three choices to show the weight percentage: normal, as received or external k-factor corrected. Take the external k-factor corrected for the external standard method. Here the three choices are: normal refers to the default Rietveld output by normalizing all the crystalline phases to 100%. As received means the renormalized internal standard results, by taking out the standard. Finally, the external k-factor corrected means the results based on external standard. Now we have amorphous content shown in the analyze view window. The value is strange now, as the k-factor is not updated yet. We can check the k-factor in customize, default, external standards. The k-factor is a global parameter for HighScore Plus, which means we have to update it whenever the value is changed. Another place to find out the value of the k-factor is here. Click on the phase rutile, in object inspector you can find the derived data where the copper k-factor is located.

Notes

Summary



27m 55s



For this standard, the k-factor is 791.28. Right click on the k-factor and then choose “take current k-factor as standard”. Now you should see the 0% of the amorphous for the standard, which means that the k-factor is the right one. Step three, update the MAC for the fly ash. After updating the k-factor, go back to the fly ash scan. There is a value for the amorphous content. The value is not valid because the MAC value here is not updated yet. Click on the global variables in the object inspector find the custom mixture MAC under agreement indices. Change the value to the calculated one using XRF results. Here is the Excel used to calculate the MAC for cement related materials. You can also calculate the MAC using the HighScore Plus MAC calculator in the tools menu. In the MAC calculator you can find all the MAC values you need. The fundamental behind is the same. Update the MAC to 39.91 for the fly ash, now the amorphous content is correct.

Notes

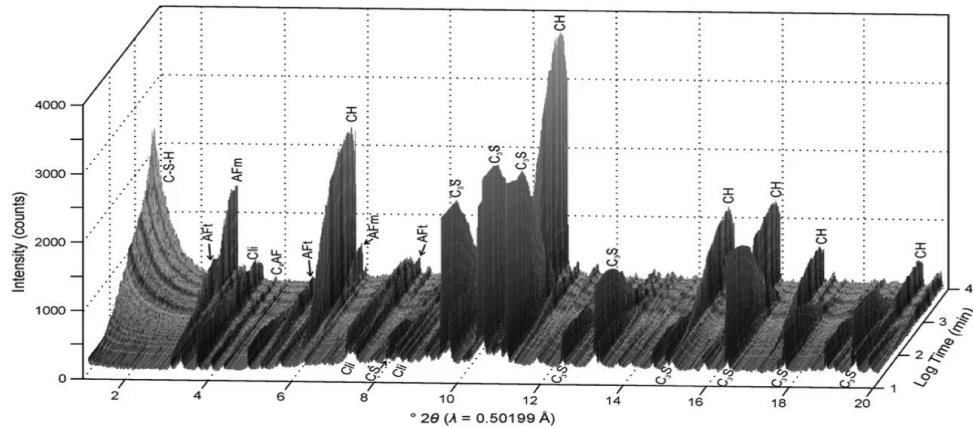
Summary



29m 25s

Rietveld quantitative phase analysis

- In-situ XRD of a hydrating zeolite blended cement



[Snellings et al., 2010]

Next to analyzing an anhydrous cement of course also time series of hydrating cements can be analyzed. Here the figure shows the 3D stack of XRD measurements of a hydrating zeolite blended cements. You can clearly see the formation of cement hydrates such as ettringite and portlandite, while clinker phases and clinoptilolite zeolite are being consumed.

Notes

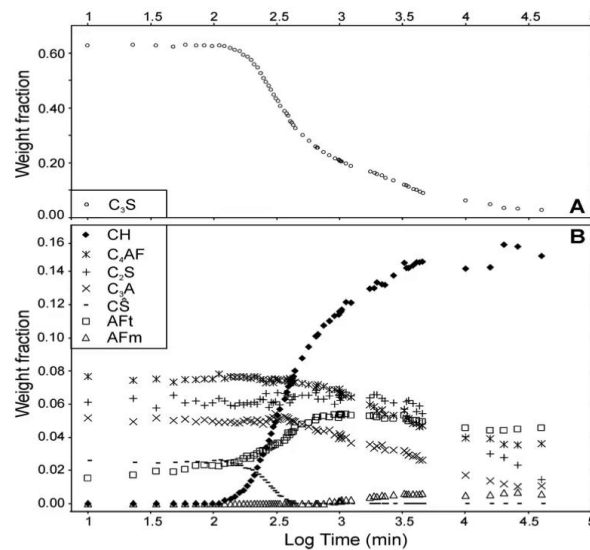
Summary

30m 42s



Rietveld quantitative phase analysis

- In-situ synchrotron XRD of a hydrating cement paste



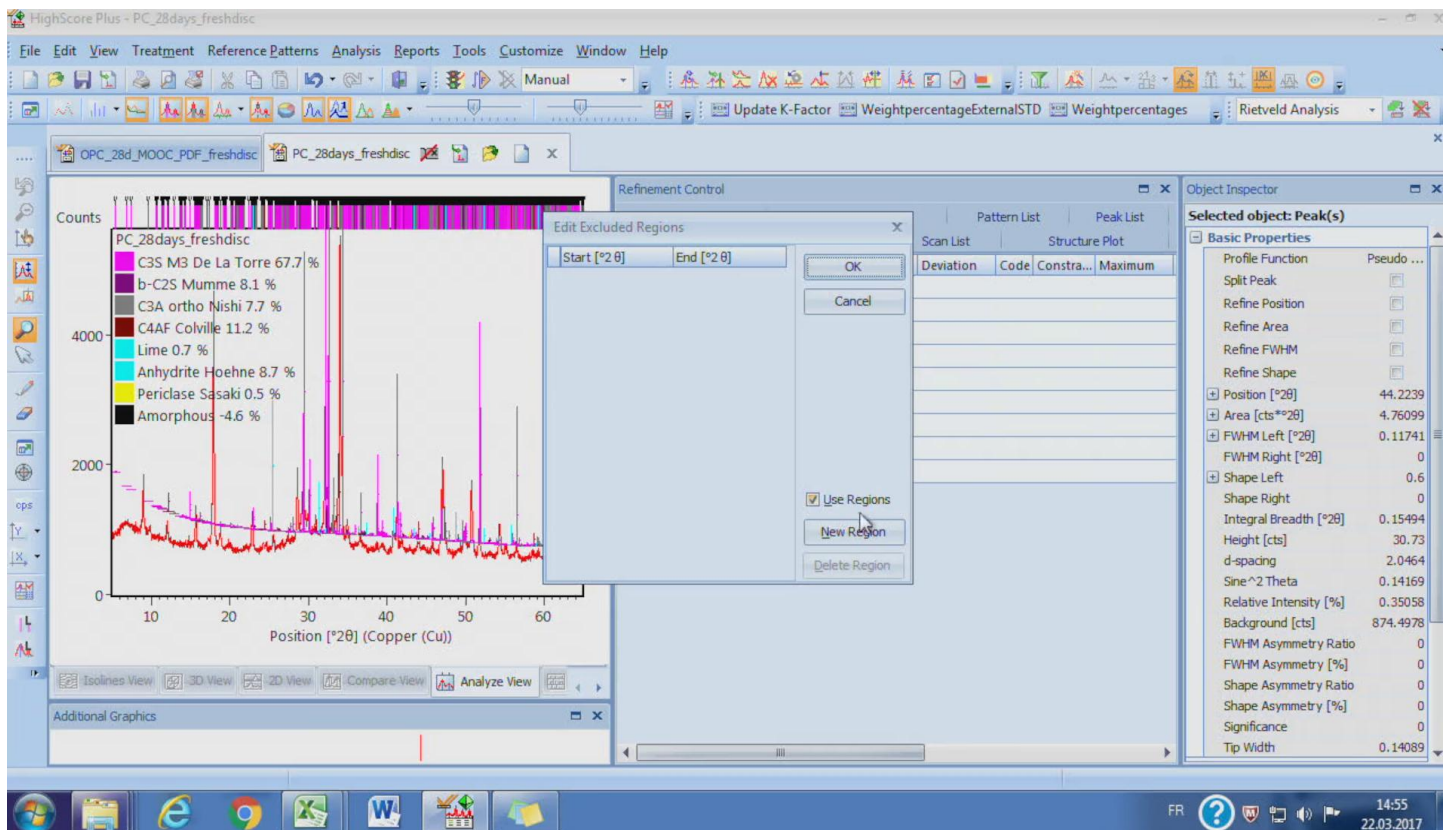
[Snellings et al., 2010]

Processing these data and by Rietveld analysis, gives you quantitative results on the consumption and formation of the solid phases. And these data can then be used on its turn as input for hydration models or to establish reaction mechanisms.

Notes

Summary





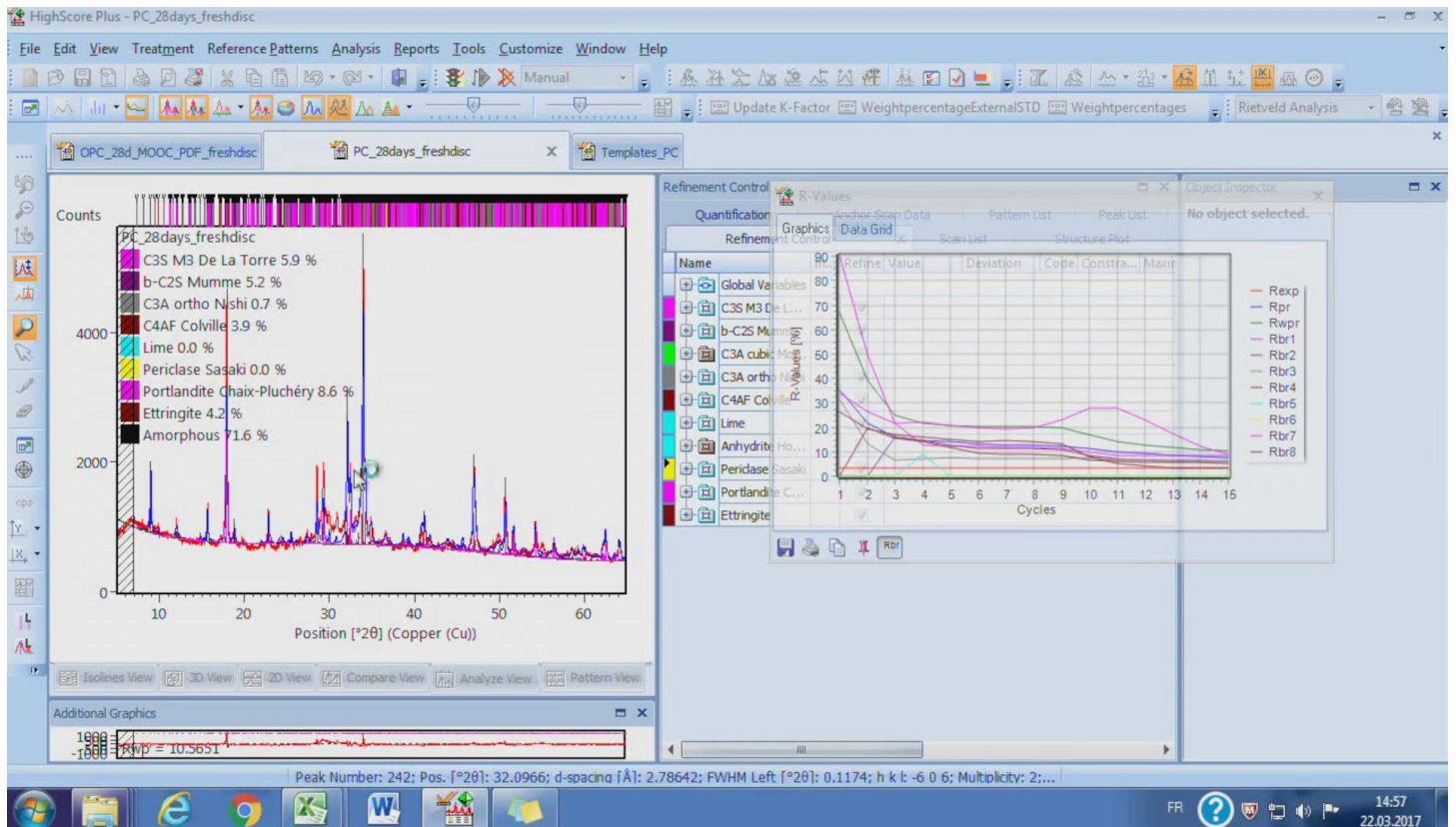
The video demonstration will show you a step-by-step phase quantification of a hydrated cement. It is advised that you have a look at this as it will show you the major difficulties and the major steps to be taken in the hydrated cement. The hydrated cement is much more complex compared to the anhydrous cement. The existence of the nano crystalline C-S-H, the main hydrate of cement is the first challenge for the quantitative analysis. In most of the hydrated cement or blended cement, there are many minor phases which bring more difficulties for the Rietveld analysis. As the existence of the amorphous phases, here the nano crystalline CSH, in the samples, the quantitative analysis of hydrated cements needs to be done with the internal standard or external standard method. The Rietveld analysis for hydrates is based on the analysis of the anhydrous cement. Open the analyzed HPF file for the anhydrous cement, remove the scan for the anhydrous cement, then insert the scan for the hydrated cement. The refinements will be constrained within the range of 7 degrees to the end. Go to analyze menu, fittings, edit excluded regions. Create a new excluded region from 0 to 7 degrees.

Notes

Summary

31m 24s





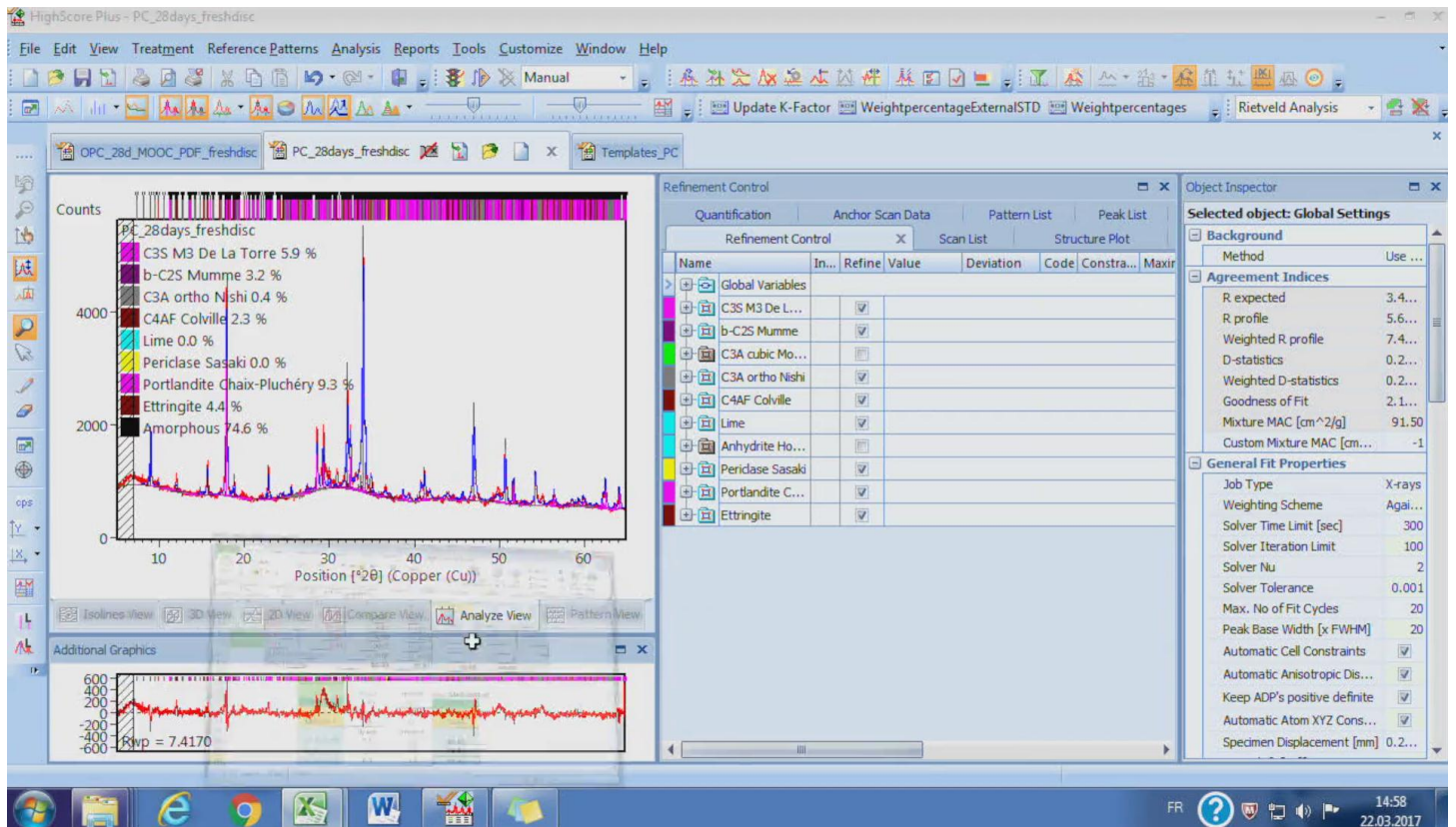
In this file, we already have all the clinker phases so we need the phases for the hydrates, namely the portlandite, ettringite etc. We can import the phase directly from the CIF files, or we can copy the phases we need from the templates where we already have the phases. The reason we use refined phase from the same cement is that all the clinker phases will be constrained using the same cell parameters and profile, only the scale factor will be refined in the hydrated cement. By applying such constraints, the refinement of the hydrated cement is more stable than the large numbers of phases presented. Specifically all the preferred orientation of the clinker phases should be removed and set to default 1. Remove the refine flag for the other clinker phases, namely the unit cell profile. The anhydrate will be dissolved quickly with the first day, so we also removed it. Right click any space in the refinement control, collapse root nodes. For the hydrates, namely the portlandite, we refine the unit cell profile as well as the scale factor first. We will do the final check of the refinement of the portlandite by refining the preferred orientation. Similar rules will be applied to the ettringite.

Notes

Summary

32m 54s





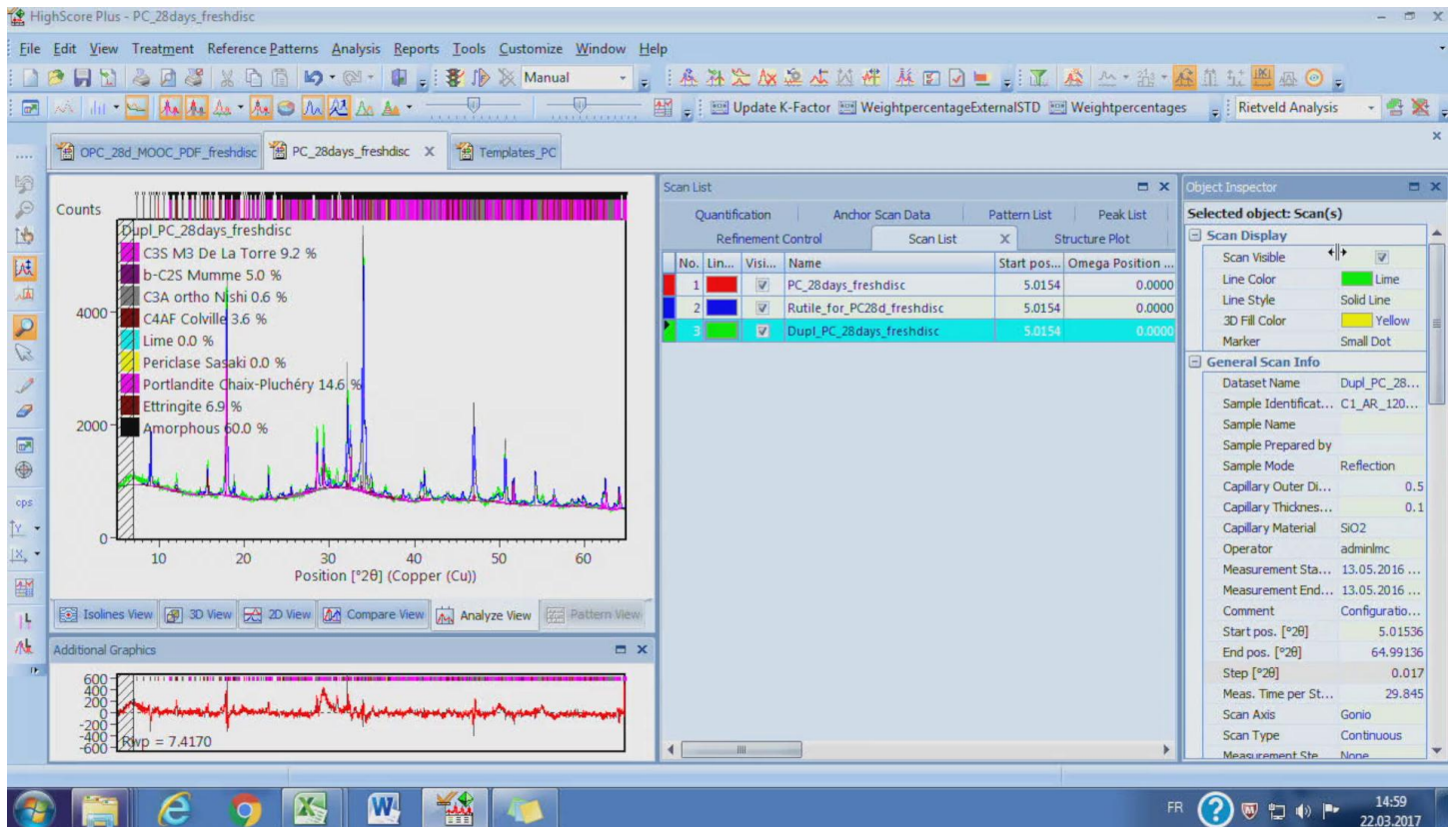
As you can see, the polynomial function is not powerful enough to fit the wide hump from the CSH contribution in the hydrated cement. So we change the background function to the manually determined one. Click on the global variable, then background, change the type of background function in the object inspector from polynomial to use available background. In this way we can define the background function by ourselves using the determined background. By changing the granularity and blending factors, we should have a background curve following the lowest background of the patterns. Refine again, you should get a much better fitting of the pattern. Let's refine the preferred orientation of the portlandite. Now the fitting is much better except the cluster of peaks at around 29 degrees. We will deal with this later, as it is mainly from the CSH nano crystalline hump. Overall, the manually determined background works for the hydrated cement. After the refinement of the pattern, we can output the results. There are two steps: update the MAC value for the sample, update the k-factor. Find out the calculated MAC for the hydrated cement, here it is 72.03. in HighScore Plus click on the global variables.

Notes

Summary

34m 25s





It will show you the object inspector. In the agreement indices you can find the item called custom mixture MAC, update the value to the calculated one, here 72.03. The k-factor was obtained using the scan of rutile under the same condition as the sample scan within the same day. Insert the rutile scan, copy the phase rutile to the rutile scan, then execute the profile fit default Rietveld twice. Now you should be able to see the amorphous content. Update k-factor will update the k-factor in the system showing you a 0% of amorphous for the standard which means that we have the correct k-factor for this measurement. To export the results, we should activate the sample scan by double clicking the scan in the scan list, and then click on the weight percentage external standard button. This is the customized exporting button. You can find the way to configure the button in the help files. Otherwise simply note down the values showing in the fitted window. Let's make a duplicate of the refined scan and label it as CSH PC 28 days. This is a technique to optimize the fitting for CSH hump. Instead of using the manual background we can introduce a profile for CSH.

Notes

Summary

35m 49s



Output_for demo - Microsoft Excel

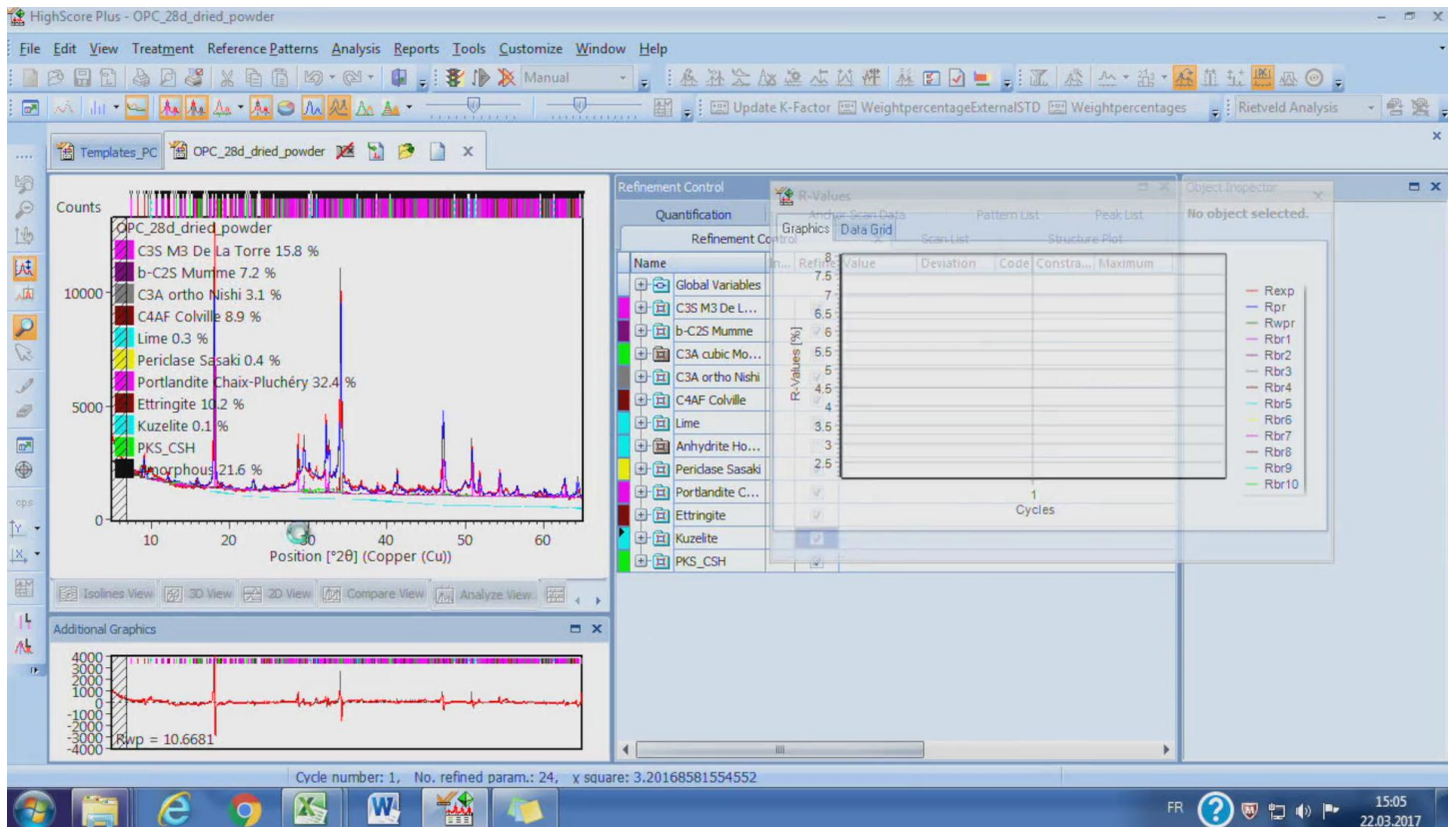
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
13	Fly ash internal	C:\Data\Ti 9/30/2015 F2_R_2_handm			12.58	19.09	68.33	50	4.041	2.189	#####							
14	Fly ash internal	C:\Data\Ti 9/30/2015 F2_R_1_handm			12.61	19.06	68.33	50	4.277	2.259	#####							
15	Fly ash internal	C:\Data\Ti 9/30/2015 F2_R_2_handm			12.17	18.91	68.93	50	4.54	2.512	#####							
16	Fly ash internal	C:\Data\Ti 9/29/2015 F2_R_1_handm			13.17	20.59	66.24	50	3.919	2.131	#####							
17	Fly ash internal	C:\Data\Ti 9/29/2015 F2_R_2_handm			12.76	19.68	67.56	50	4.082	2.227	#####							
18	Fly ash internal						67.878											
19	Fly ash internal						0.927306											
20																		
21		Path:\Scar Scan Date, Sample ID			Calcite rh	Quartz Le	Amorph %	RProfile	G.O.F.	Date/Time								
22	Slag	C:\Data\Ti 9/18/2015 Slag1_Xuerun			0.47	0.58	98.95	2.334	1.062	#####								
23		Path:\Scar Scan Date, Sample ID			C3S M3 De	b-C2S Mui	C3A cubic	C3A ortho	C4AF Colv	Lime %	Anhydrite	Periclase	Quartz %	Mullite %	PKS_SFA %	Amorph %	RProfile	G.O.F.
24																		
25	Blended cement	C:\Data\Ti ##### F2_50_Blendec			29.96	2.15		3.61	4.59	0	3.53	0	6.78	12.32		37.06	3.428	1.992
26		C:\Data\Ti ##### F2_30_Blendec			42.57	3.26		5.34	6.52	0.09	6.46	0.01	4.58	7.51		23.65	4.255	2.443
27		C:\Data\Ti ##### F2_10_Blendec			55.48	5.71		6.96	8.46	0.03	7.19	0.01	1.45	2.43		12.27	4.693	2.508
28																		
29	Hydrates 28d fre	Path:\Scar Scan Date, Sample ID			C3S M3 De	b-C2S Mui	C3A cubic	C3A ortho	C4AF Colv	Lime %	Anhydrite	Periclase	Portlandit	Ettringite %		Amorph %	RProfile	G.O.F.
30	Fixed background	C:\Data\Ti 5/13/2016 C1_AR_120520:			9.22	4.97		0.61	3.64	0		0	14.59	6.95		60.02	5.603	2.131
31	CSH background w	C:\Data\Ti 5/13/2016 C1_AR_120520:			8.84	5.7		1.43	4.75	0.19		0.23	14.32	7.53		57	5.516	1.996
32																		
33																		
34																		
35																		

The profile was obtained by fitting white cement hydrated for 7 years using the 14 angstrom tobermorite structure. The extracted profile only contributes to the background fitting without quantitative information. We will only refine the scale factor of the extracted profile for CSH but keep all the other parameters constant, as in general most of the CSH hump are similar. The background function can be simplified to the polynomial one when the CSH profile was employed. Let's change it here. Three parameters for the background, the flat background function 1 over X background and coefficient 1 will be sufficient enough to give us a good fit. If not, you can add more coefficients into the background function. Let's refine again. Now the Rwp file has decreased and the fitting is much better, especially the fitting around 29 degrees where the CSH hump was located. Check the k-factor and the MAC, makes sure they are correct, then we export the results. Here is a summary of the results for the hydrated sample, using different background methods. The results using CSH background is better as the improved fitting. There are not much differences in the portlandite content, the main differences are those phases present peaks close to the CSH hump.

Notes

Summary





For powdered hydration stopped samples, it is a little bit different, so here I will show a lot of examples with the powdered sample. There are not much differences in the refinement procedures for the patterns obtained on the hydration stopped powder. There are three aspects that need to be addressed when analyzing hydration stopped powders: first, the potential carbonation of the samples, second, the preferred orientation, third, the normalization of the results. We save the previous analysis base on the fresh disk as a template, then remove the scans in the HPF file. Thus there are only the phases and the refined parameters left. Actually, this is the way we made templates for the analysis which will reduce a lot of work to import and set the parameters for the refinement. Insert the scan, then refine. We can see some unmatched peaks around 10 degrees. According to the identification we made before, this is the peak of a monosulfoaluminate. Copy the phase, here it is a kuzelite from the template. Further refine the pattern with kuzelite. The fitting is much improved. The preferred orientation of the portlandite in the powdered sample is much severe compared to the fresh disk.

Notes

Summary

39m 02s



Output_for demo - Microsoft Excel

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
19	Fly ash internal						0.927306									
20																
21		Path:\Scar Scan Date, Sample ID		Calcite rh	Quartz Le	Amorph %	RProfile	G.O.F.	Date/Time							
22	Slag	C:\Data\T\9/18/2015 Slag1_Xuerun		0.47	0.58	98.95	2.334	1.062	#####							
23																
24		Path:\Scar Scan Date, Sample ID		C3S M3 De	b-C2S Mur	C3A cubic	C3A ortho	C4AF Colv	Lime %		Anhydrite	Periclase	Quartz %	Mullite %	PKS_SFA %	Amorph % RProc
25	Blended cement	C:\Data\T\##### F2_50_Blendec		29.96	2.15		3.61	4.59	0	3.53	0	6.78	12.32			
26		C:\Data\T\##### F2_30_Blendec		42.57	3.26		5.34	6.52	0.09	6.46	0.01	4.58	7.51			
27		C:\Data\T\##### F2_10_Blendec		55.48	5.71		6.96	8.46	0.03	7.19	0.01	1.45	2.43			
28																
29	Hydrates 28d fresh	Path:\Scar Scan Date, Sample ID		C3S M3 De	b-C2S Mur	C3A cubic	C3A ortho	C4AF Colv	Lime %		Anhydrite	Periclase	Portlandit	Ettringite %		Amc
30	Fixed background	C:\Data\T\5/13/2016 C1_AR_120520		9.22	4.97		0.61	3.64	0		0	14.59	6.95			
31	CSH background with polynomial	C:\Data\T\5/13/2016 C1_AR_120520		8.84	5.7		1.43	4.75	0.19		0.23	14.32	7.53			
32																
33		Path:\Scar Scan Date, Sample ID		C3S M3 De	b-C2S Mur	C3A cubic	C3A ortho	C4AF Colv	Lime %		Anhydrite	Periclase	Portlandit	Ettringite	Kuzelite %	PKS_CSH %
34	Hydrates 28d dried	C:\Data\T\11/16/201 OPC_28d_1611		9.21	4.14		1.73	5.32	0.2	8.72	0.3	17.81	5.5	2.04		
35	Hydrates 28d paste base			7.98	3.59	0	1.5	4.61	0.17		0.26	15.44	4.77	1.77	0	
36																
37																
38																
39																
40																
41																

This is mainly because of the sampling procedure when we are doing powder samples. There are also some preferred orientations for the ettringite phase. Find out the plane: 1 0 0, set the March/Dollase direction to 1 0 0 for this phase and then refine. Calculate the k-factor of the measurement and update it. Update the MAC value for the dried paste. The MAC value of the dried paste should also be updated by taking the removal of the free water in the sample. Generally, you need the result from TGA to calculate the updated background. Delete the previous output TXT file then output the results. The dried basis should be converted into the fresh paste or anhydrous basis for comparison. The bound water from TGA results will be needed to finalize the conversion. Alternatively, we can directly measure the free water content to finalize the calculation. Calculation templates using the TGA bound water were provided in the template. The end.

Notes

Summary



- **General guidelines**
 - start with good literature structure models (see supplemental material)
 - minimize the number of refined variables
 - final refinement should include all varied parameters
- **In QPA**
 - Refine only scale factors and lattice parameters
 - Constrain parameter variation within a sensible interval
 - Check fit and contribution of individual phases visually
 - Check for parameters hitting limits of preimposed interval

Overall one could conclude that quantitative phase analysis of hydrated cement is not so straightforward and it is quite important to say that XRD data of complex systems should actually not be analyzed by black box approaches. Experience has shown that quantitative phase analysis and the accuracy of the results, even for simple systems, depend really a lot on the strategy of analysis and also the skill and experience of the analyzer, the analyst. You should try to have at least a basic understanding of the underlying crystallography and of course also of the cement chemistry to be able to guide the Rietveld refinement and to judge that the quality of the results is fine. You can actually gain some of this practical experience by practicing on simple model mixtures that you make yourself and you can also follow some trainings from more experienced researchers in your group or of other groups. So a Rietveld quantitative phase analysis can be subdivided at least into two parts. So as we discussed, there is the quality phase analysis part in which we identify which phases are present and we select the crystal structures that are most suited for the quantitative phase analysis that comes next.

Notes

Summary



41m 41s

- **General guidelines**
 - start with good literature structure models (see supplemental material)
 - minimize the number of refined variables
 - final refinement should include all varied parameters
- **In QPA**
 - Refine only scale factors and lattice parameters
 - Constrain parameter variation within a sensible interval
 - Check fit and contribution of individual phases visually
 - Check for parameters hitting limits of preimposed interval

So the second step is the quantitative phase analysis where we do the data fitting of the whole powder pattern to a calculated pattern. So as general guidelines we could say that it is very good to start with good literature structure models and we have supplied in the database a number of supplementary materials, a folder which contains crystallographic information files from which you can extract the information you need to run a Rietveld analysis. So it is very useful to have a look at these, because you can find a lot of different entries in the literature databases and they may be more or less applicable to cement systems. So we already made some sort of pre-selection for you from which you can start and do your analysis. What is quite important as well is that at least initially, but also it is best to do this over the whole analysis, Rietveld analysis, is that you minimize the number of refined variables. Why? Well that is often already 10, 20, 30, 40, 50 different variables that are being fitted in the Rietveld refinements and that is not that much information that it can be completely left and constraint.

Notes

Summary



43m 10s

- **General guidelines**
 - start with good literature structure models (see supplemental material)
 - minimize the number of refined variables
 - final refinement should include all varied parameters
- **In QPA**
 - Refine only scale factors and lattice parameters
 - Constrain parameter variation within a sensible interval
 - Check fit and contribution of individual phases visually
 - Check for parameters hitting limits of preimposed interval

Of course, once you have selected a number of parameters that should be varied, you should, in the final step of your refinement, refine them altogether so you come to your final optimized results. So basically it means that you have optimized all the variables and you have at least obtained a sort of stable global solution. So it is quite important that for quantitative phase analysis that at least in the first steps you refine only scale factors and lattice parameters. And then later on you can include other corrections perhaps like a preferred orientation correction. Also it is quite important that for lattice parameters you constrain parameter variation within a sensible interval. As discussed before, one can vary lattice parameters to a large extent or the program could do that. And then you might end up with the crystal structures which are just chemically and reasonable. Bond lengths may be stretched too much while you are changing or allowing to change lattice parameters to vary. Also it is important to check the fit and the contributions of the different individual phases visually. Why?

Notes

Summary



44m 42s

- **General guidelines**
 - start with good literature structure models (see supplemental material)
 - minimize the number of refined variables
 - final refinement should include all varied parameters
- **In QPA**
 - Refine only scale factors and lattice parameters
 - Constrain parameter variation within a sensible interval
 - Check fit and contribution of individual phases visually
 - Check for parameters hitting limits of preimposed interval

Because then would see what a certain parameter or change in a certain parameter is really doing in the fitting whether for instance then a small contribution of a minor phase is really significant, whether it is really there or whether it is just a misfit of another phase. And also a good hint is when you have imposed this, let's say intervals for instance for lattice parameter, you could say: well it may vary about 1-2% from the literature data, but when you did the refinement, when you run the refinement and you check for parameters that hit these limits, that you have just pre-imposed, that actually there you might have indication for some problems maybe there is another phase, maybe there is a problem with your crystal structure model that you selected, or there can be other stuff.

Notes

Summary



46m 04s

- Parameters to be refined for QPA

Reflection peak properties	Crystal structure parameters	Refined in Rietveld QPA
Position	Lattice symmetry	Not applicable, fixed
	Unit cell parameters	Yes
Intensity	Atom type	No
	Atomic fractional coordinates	No
	Site occupancies	No
	Atomic displacement parameters	No
Profile shape, width	Crystallite size	Yes, usually part of analytical peak shape function
	Lattice strain	No

So this table gives you some sort of overview of what you can vary during the refinement. So basically we start with phase scale factors, unit cell parameters, peak shape parameters, and micro structural parameters, and even needed preferred orientation parameters. Of course next to the phase dependent parameters, also so-called global parameters need to be defined such as a specimen displacement correction and coefficient of the background fraction. In complex systems such as cement, the refinement of crystal structure parameters such as atomic positions and displacement factors should best be avoided. The crystal structure refinement by the Rietveld method should best be reserved just to pure systems. The other in which the parameters are very generally dependent on the distance to their final values is the so-called parameter shifts. But overall, it is suggested that you first start with global parameters to be refined and then phase dependent parameters.

Notes

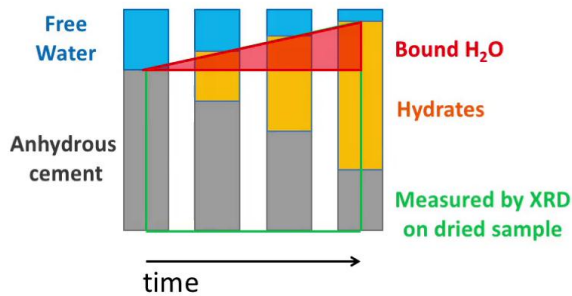
Summary



46m 58s

Rietveld quantitative phase analysis

- Rietveld QPA results need to be rescaled to take into account the incorporation of bound water
- Calculation of the **Degree of Hydration** (DOH):
- Correction must be made for the **dilution effect**



$$W_{k,dilution\ corrected} = W_{k,XRD} * (1 + H_2O_{bound,TG})$$

In case of hydrating cements, the amount of solids varies during the bonding of water into the hydration products. Therefore a final step into the quantification should be to rescale the results to a common basis such as the initial clinker content or the cement content to enable an easy comparison and a straightforward comparison between different times of reaction. This is also called the dilution effect. On the figure here you can see how for instance over time the amount of solids increases. Now when you remove the free water by hydration stoppage you should of course account for this effect and let's say that for instance 10% in the anhydrous cement would not be the same as 10% on the final solids in the hydrated cement. This is especially and particularly important for the calculation of the degree of hydration, but you would always need to of course refer to the same kind of basis because 10% of alite in the initial system could be different than 10% of alite in the final system. The formula given on the right side here gives you a way of how to correct this Portland cement.

Notes

Summary

48m 05s



Rietveld quantitative phase analysis

- fresh specimen (disc):
 - per 100g paste $m=m_{\text{XRD}}$
 - per 100g anhydrous $m=m_{\text{XRD}} \cdot (1+w/c)$
- dried specimen (powder):
 - per 100g paste $m=m_{\text{XRD}} \cdot (1+H_2O_{\text{bound}})/(1+w/c)$
 - per 100g anhydrous $m=m_{\text{XRD}} \cdot (1+H_2O_{\text{bound}})$

H_2O_{bound} on ignited basis

Some of the recalculation formula show that they actually depend on whether free water is removed to stop the hydration reactions. If the sample is assumed to be hand dried in cut or fresh slice, then the correction factor should contain the water to cement ratio of the phase. So what you initially put is water into the cement. If the sample is dried the separate measurement of the bound water content on ignited basis measured for instance by thermogravimetry is needed to rescale the results. The given expressions here are developed for the case of a hand dried fresh hydrated sample and for a dry hydrated sample. And you can use this for your recalculation.

Notes

Summary



49m 23s