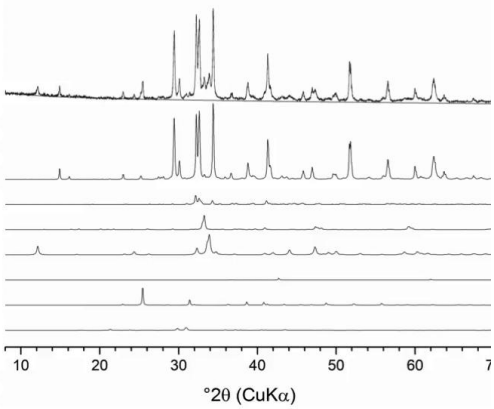
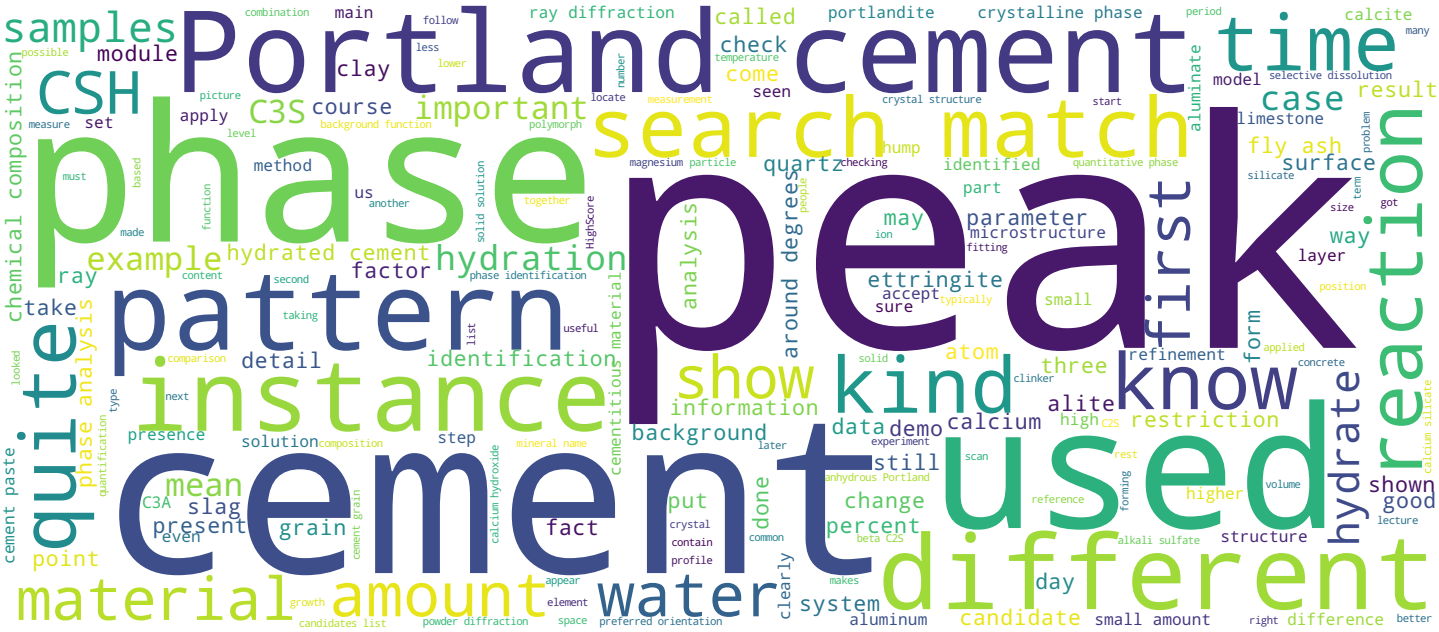


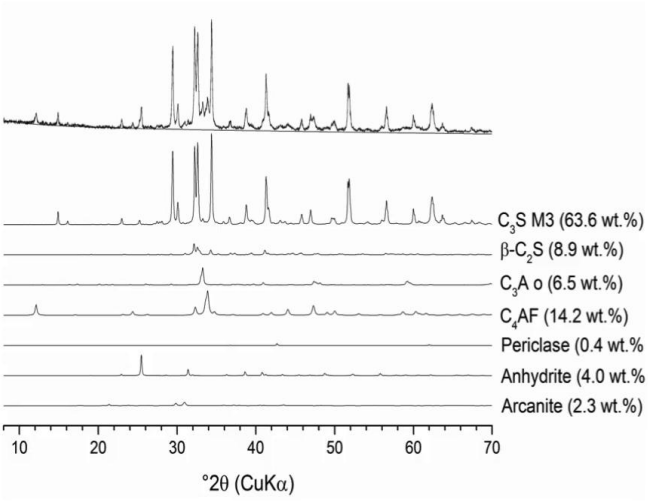
Qualitative X-ray diffraction analysis

Cement Chemistry and Sustainable Cementitious Materials

Dr. Ruben Snellings



Qualitative X-ray diffraction analysis



- Identification of crystalline phase based on characteristic peak «fingerprint» patterns

Database of «trustworthy» PDF patterns includes

- Major clinker phases and polymorphs (Ca silicates, aluminates, ferrites)
- Minor clinker phases (alkali sulfates, oxides)
- Sulfate addition phases
- Common SCM phases (except natural pozzolans)
- Hydrate/carbonate phases

Search/match table for rapid manual identification

- Often many phases are suggested by the software, difficult to find plausible matches for minor phases

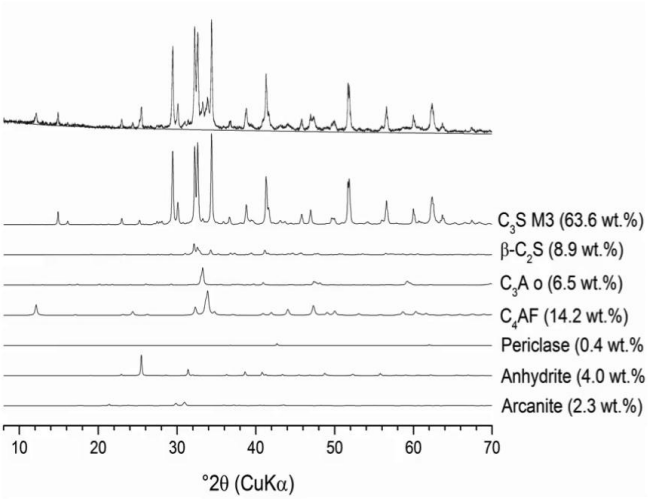
Now that you know how to prepare and measure your sample, it is time to have a look at the analysis of the resulting data. The first step in this analysis is to find out which phases are present in your sample. This lecture will give you a brief overview on how we identify phases in a so-called qualitative phase analysis on your X-ray powder diffraction data. The qualitative phase analysis is based on a comparison of the peaks in a measured XRD pattern to a large database containing peak patterns of many known phases. Usually a database such as the powder diffraction file database, the PDF database published by the ICDD is used and this database allows searching and matching in combination with chemical or categorical filters to restrict the number of candidates that can match your pattern. Also open source databases exist such as the COD database and the american mineralogist database. As general in the helping phase identification we have supplied you with a list of common phases found in cement. And this is also given as a supplementary material to this course. This list can be used to build a custom database for cement phases for your system and it can be used in combination with your specific available search/match software.

Notes

Summary

0m 04s

Qualitative X-ray diffraction analysis



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Alternatively, there is also the classical way of doing search/matching by rapid manual identification, by comparison for instance between a list of XRD peaks of certain phases and peaks in your pattern. We have also supplied such search/match table as a supplementary material to this course and you can use it to find difficult phases such as minor phases which have very low peaks for instance. In the graph on the left side you can see that there is the main problem of identification which is peak overlap. If you look for instance at the overlap between the C3S and the beta C2S patterns, then you can see that the major peaks are actually completely overlapping which makes it very difficult for any automatic phase identification software to find for instance beta C2S in the system.

Notes

Summary

1m 41s

Qualitative X-ray diffraction analysis

- Identification of all phases in a cement is not trivial: additional information is very useful:
  - **Microscopic** observations
  - Bulk sample **chemistry**
  - Knowledge of the **origin** of the materials
  - **Phase enrichment** using selective dissolution is particularly useful to identify minor phases

This way we also need to rely on other information such as microscopic observations or knowledge of the bulk sample chemistry or just knowing what kind of phases can be present in your material. Specifically for Portland cement and anhydrous Portland cements, it is very useful to do some selective dissolution to identify minor phases.

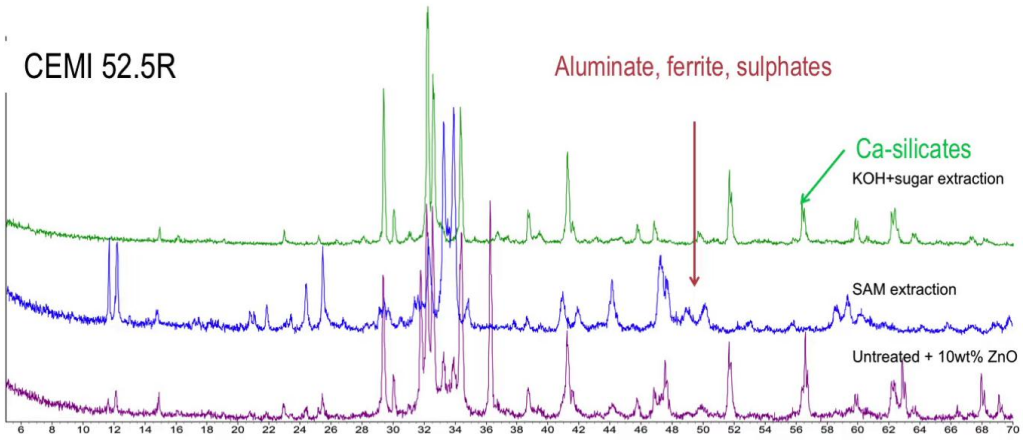
Notes

Summary

2m 48s

Qualitative X-ray diffraction analysis

- Selective dissolution: OPC
  - OPC is a complex mixture of phases, several phases show strongly overlapping reflection patterns
  - Selective dissolutions concentrate minor phases: important aid in identification



Having looked at the example in this figure you can see that for anhydrous Portland cement we have done two extractions, two selective dissolutions that either concentrate the calcium silicate through its phases, this happens with a potassium hydroxide plus sugar extraction in the green curve or we did an extraction, selected a solution with salicylic acid and methanol in which we have a residue, a solids residue that is concentrated in the aluminates, ferrites and alkali sulfates phases. For instance when comparing the bulk sample in purple below with the SAM extracted sample, you can see that there is a very large increase in the peaks of ferrites and alkali sulfate phases, for instance ferrite around 12 degrees and alkali sulfate phases in the range of 20 to 25 degrees 2 theta. This selective dissolution method can also be used to identify whether there is any polymorphs in your sample. For instance, one may really look at whether there is any polymorphs of C2S or there is orthorhombic or cubic C3A in the Portland cement.

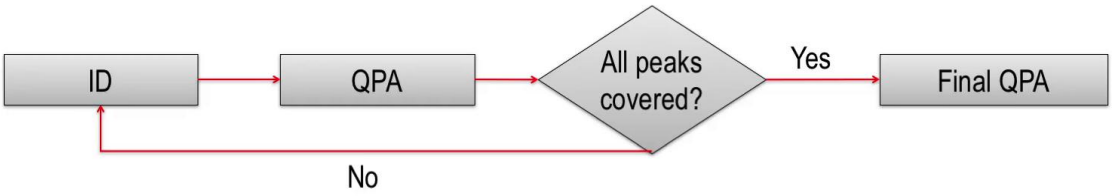
Notes

Summary

3m 12s

Qualitative X-ray diffraction analysis

- **Iterative procedure** between pattern fitting and identification helps to spot minor phases

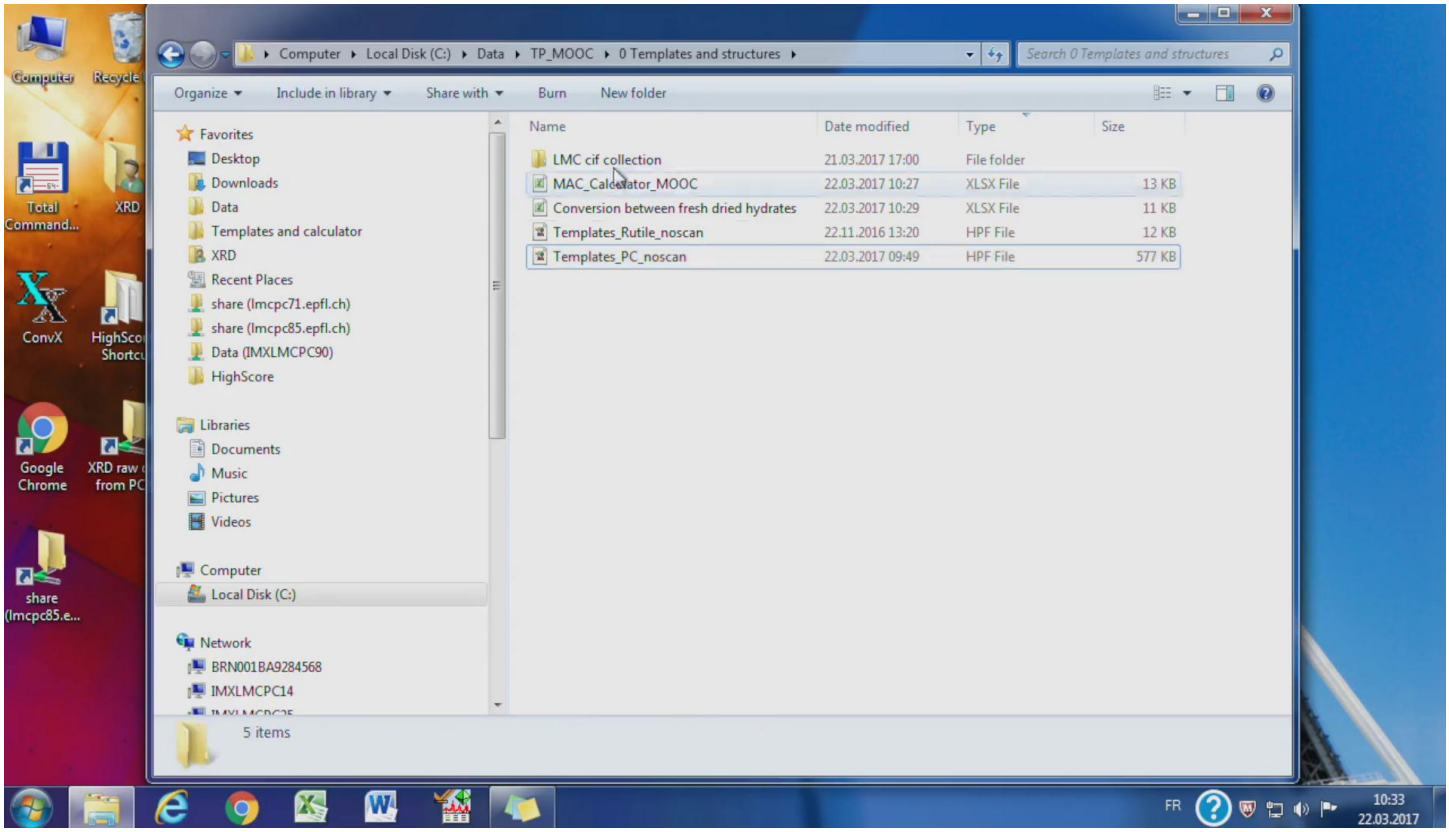


Finally the XRD pattern fitting procedures in quantitative phase analysis often indicate a presence in the difference or residual curves of minor or trace phases that were previously hidden by extensive peak overlap with major phases. Therefore, an iterative procedure that goes back and forth between phase identification and phase quantification is very common and very useful in obtaining a complete analysis.

Notes

Summary

4m 31s

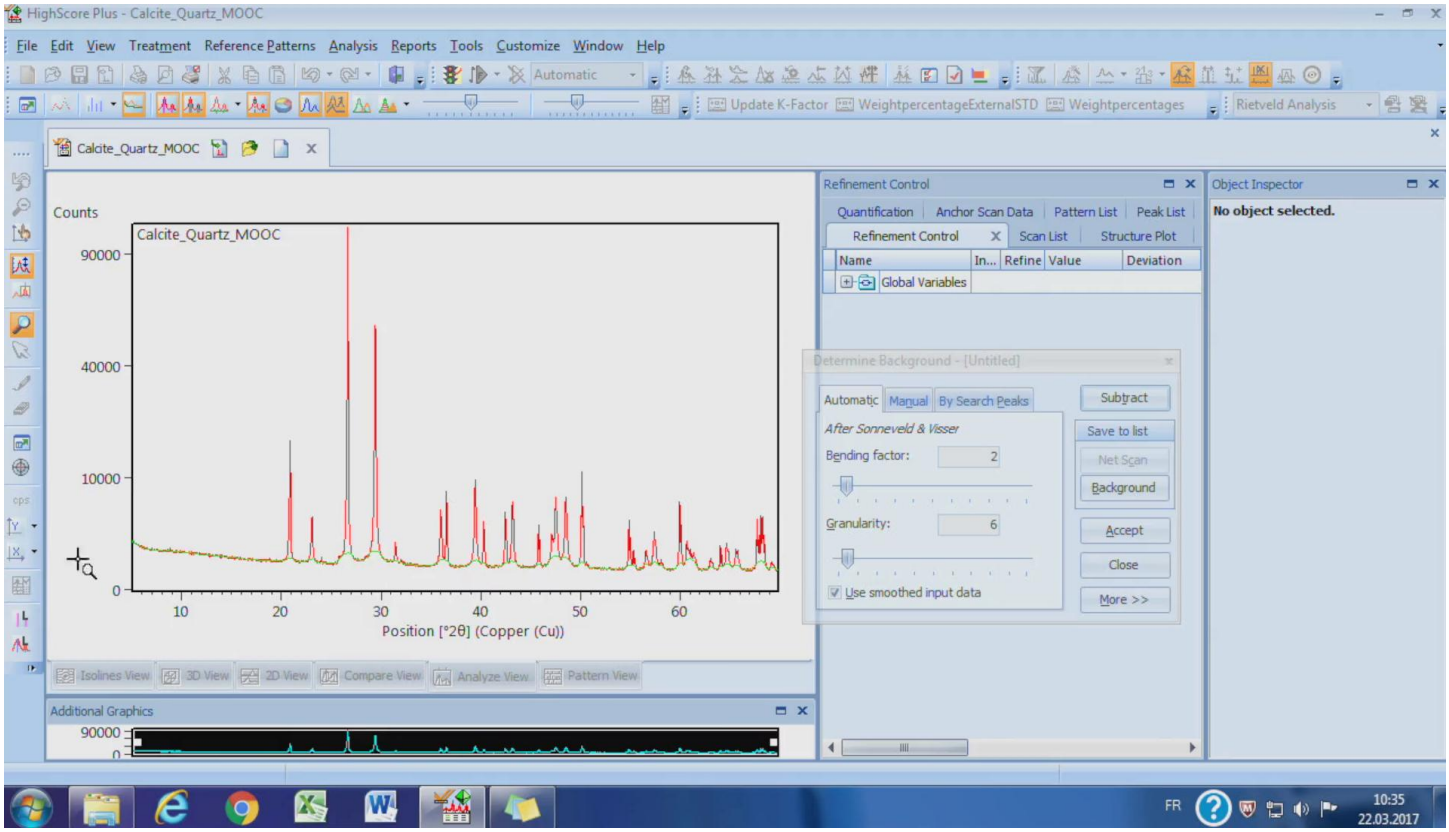


From this session on we will show you how do analysis using XRD data. Here are the files we are going to use for the demo. You can find the templates as well as the conversion file and the MAC calculator in excel files. All of the cement related structures are available in zip files in this folder.

Notes

Summary

5m 05s

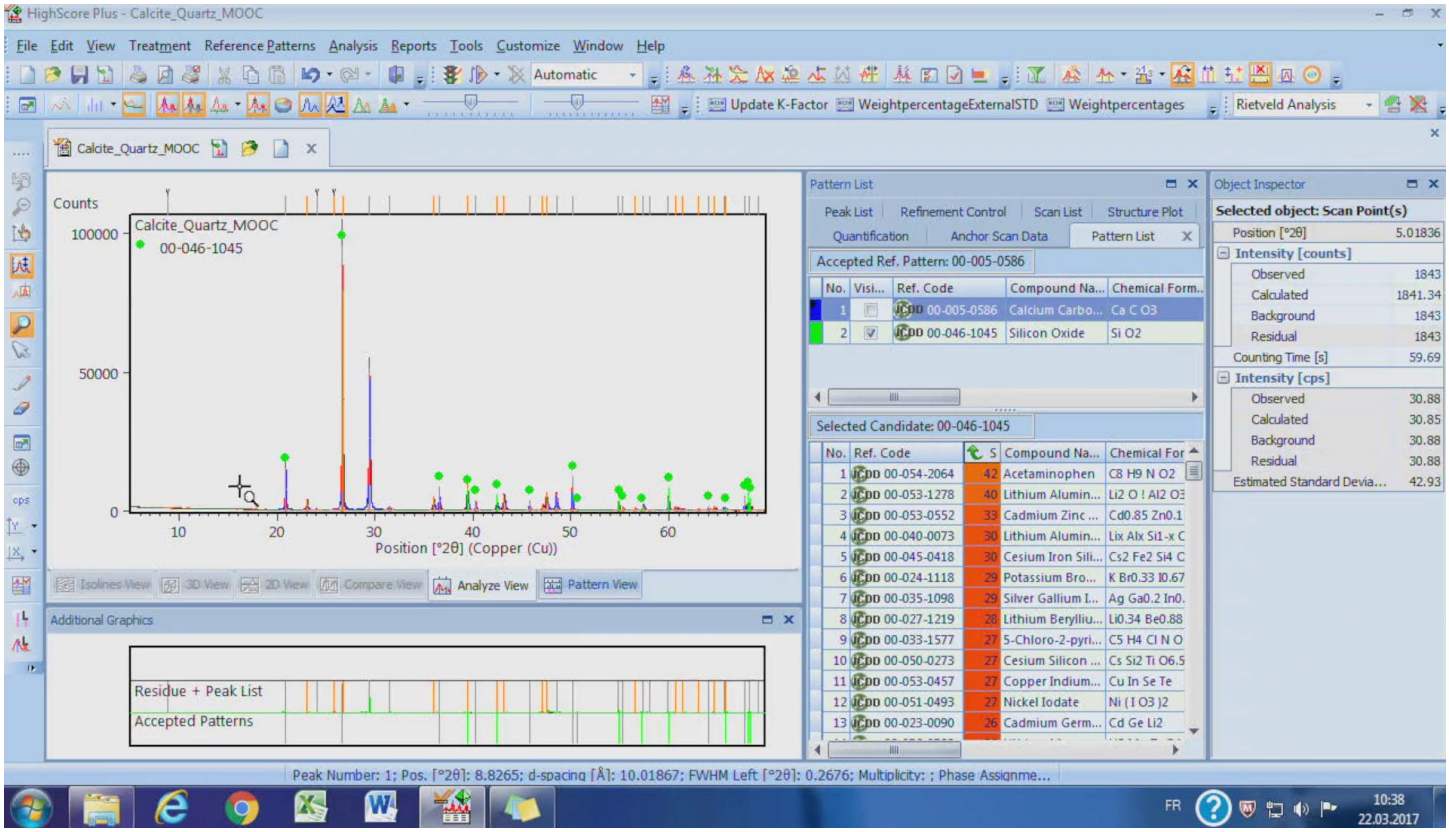


The demo will be shown step by step. Part one is the identification, part two shows simple Rietveld analysis and part three will be the advanced quantitative phase analysis. The samples used for demo videos are simple binary mixture made of calcite and quartz, anhydrous Portland cement, typical SCMs including fly ash and slag and finally hydrated cement. The demo videos are mainly based on the software called Highscore plus from Panalytical. A quick demo on how to use the open source software QualX2 for identification and GSAS II for quantification will also be covered for you to be able to practice in case there is no access to HighScore plus. Let's get started with the qualitative analysis. Simple demo using calcite and quartz mixture. Open the HighScore plus software, then create a new file. Now insert the file. Now insert the data. You can change the scales of the y-axis to linear, square root or log scale to check the details of the peaks. More details such as the configuration of the diffractometer in the scan can be found in the object inspector. To do the identification, there are three steps. First, determine the background of the pattern. Second, search the peaks in the pattern.

Notes

Summary

5m 26s

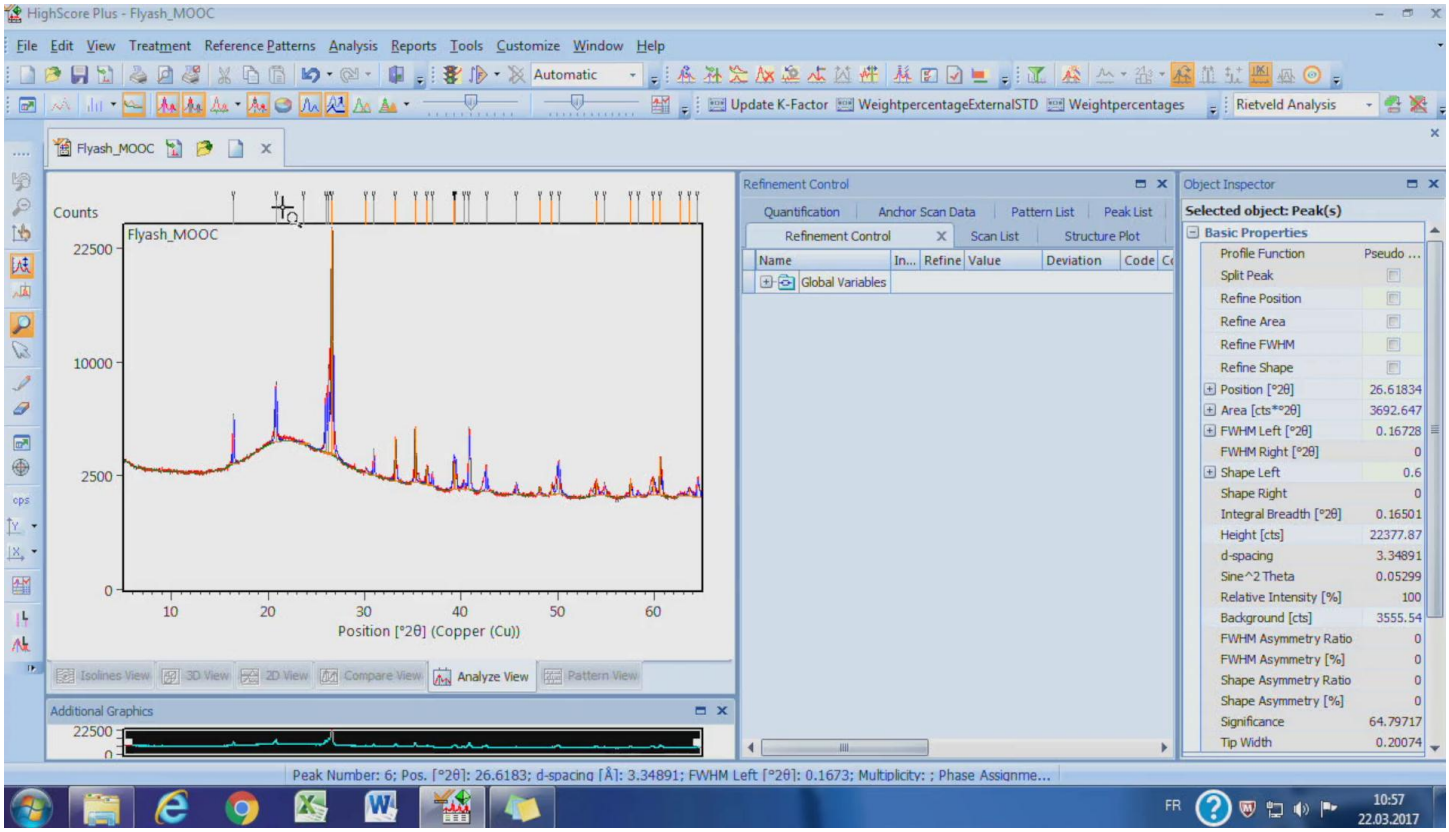


You can see the peaks on top of the pattern, the black v marks mean that the peaks are not identified. Then the search match. There are a lot of cards in the database. It is better to know some background information of the sample, such as the category of the sample, for example inorganic or organic, chemical compositions, crystallography information and the potential phases in the mixture. The restrictions can be very helpful to improve the search match. We will show you all these functions in the coming demo. Here we just search high quality cards using star indexed. After the search/match the candidates are shown in the candidates list. The score indicates how good the candidates match the experimental pattern. You can check the details of this card by double clicking the selected cards. We accept the first proposed candidate, the calcite. The V marks are removed for all the matched peaks with calcite. After taking the next candidate, quartz, most of the peaks are identified. For each phase we picked, it is recommended to check the relative strength match by eye focusing on the three strongest peaks. The remaining tiny peaks are from the K beta residue. The demo on QualX2 for identification.

Notes

Summary

7m 04s

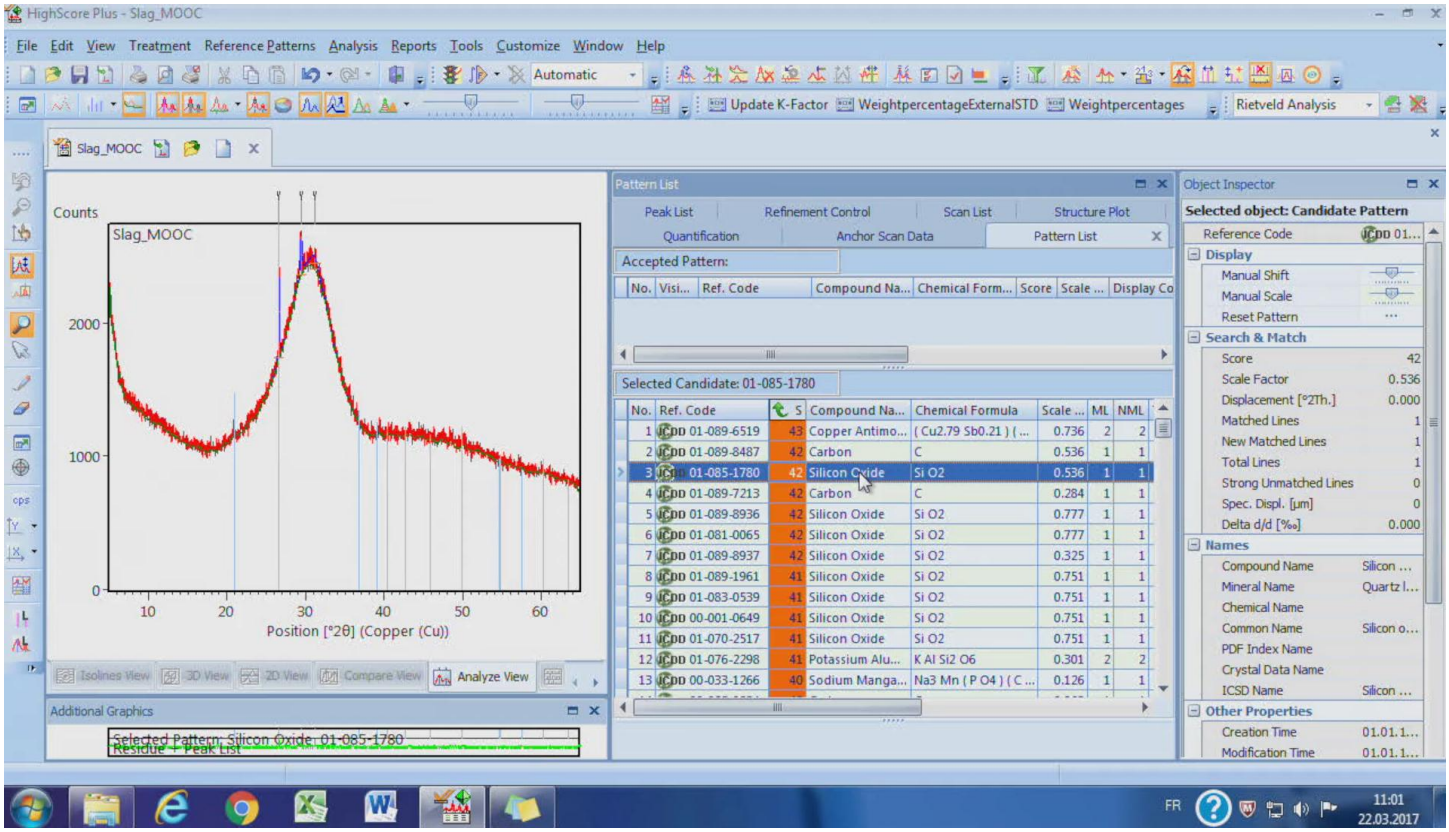


Import a diffraction data then go to search to search/match. Pick the candidates from the candidates list and accept the matched phases. Similar rules to HighScore plus will be applied to check the matches of the peaks. Make sure all or most of the peaks are matched. Demo on fly ash and slag. For these 2 demos, we will show you the typical patterns for the amorphous humps. As the samples are mainly amorphous with small amounts of crystalline phases, it is more challenging to make the decision of the final candidates in the samples if there is no information about the samples. For such kind of samples, the identification must be done with special care by taking as much information as possible such as the chemical composition. For fly ash, there are a lot of amorphous content which give us a hump here. For this case the background function should be modified to follow the hump and just keep the peaks by changing the parameters. The background function should just follow the trend of the lowest points of the pattern but should not go into the peaks. Let's search peaks, then search match. We can always pick the star and indexed cards for the identification With a search match, the best match was the mullite followed by the quartz.

Notes

Summary

8m 32s

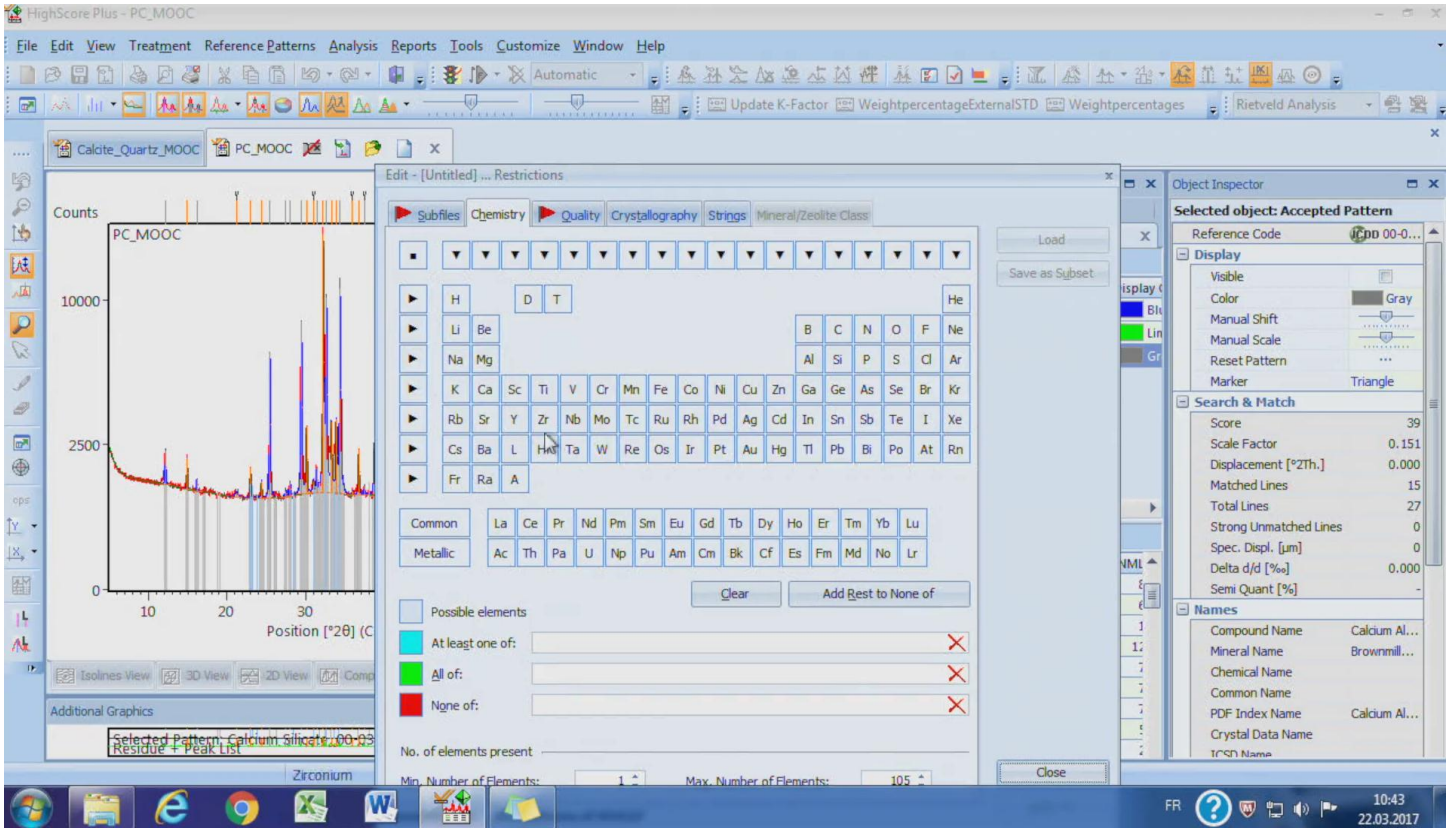


We accept these two candidates for the match by dragging the candidate into the accepted area. However there are still some tiny peaks which are not matched, for example the peak around 30 degrees. By checking the rest of the candidates another polymorph of silicon oxide named stichovite matches the peaks. Now all the peaks are identified. For slag, we also see the amorphous hump. The strategy for the background is similar to the one for fly ash: follow the lowest points of the pattern but never go into the peaks. If we search peak quickly, there are only three peaks in the pattern. We apply the search match without any restrictions, most of the candidates are quite strange as the elements are those for sure that didn't exist in the sample. This is mainly because of the relatively low concentration of the crystalline phases in this sample. Let's put some restrictions to the search match, for example the subfile mineral related cards. Refine the search match and then we get the quartz on the top list. When checking the chemical composition of the sample, We know that there are small amounts of silicon oxide in the sample. So the presence of quartz is reasonable.

Notes

Summary

10m 00s

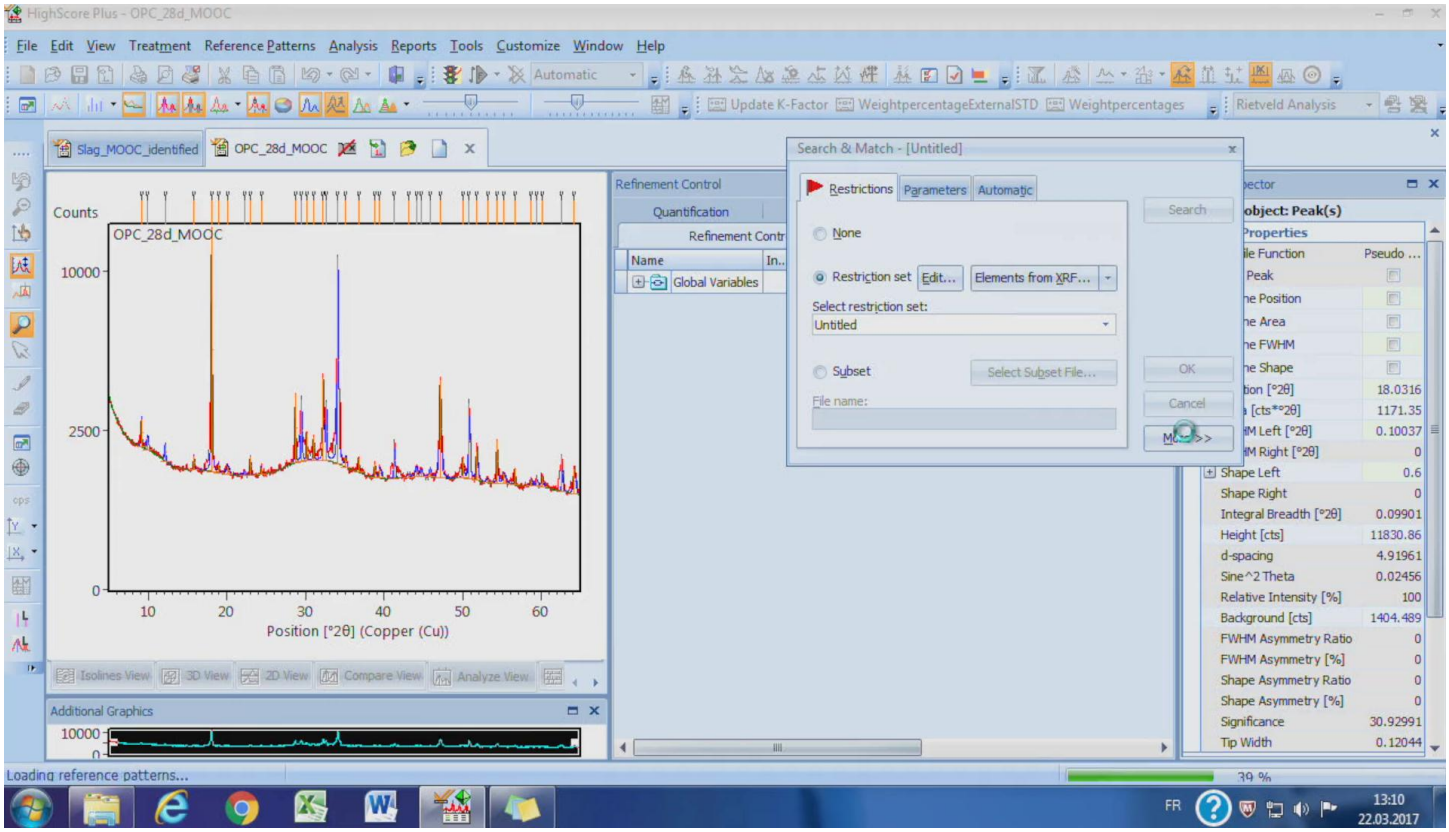


Then there are some other strange candidates such as the ice and some rare earth elements compound. The possible candidates would be the calcium carbonates, namely the calcite, according to the chemical composition from XRF. A demo on Portland cement. For Portland cement, the challenge for the identification is from the complexity and similarity of the pattern for C3S and C2S. A lot of peaks are overlapped which makes the situation more difficult. We do the same steps for the data of Portland cement, insert the scan, determine the background and then search the peaks. As we know, it is the cement so the restriction of cement and hydration product in the subfiles is applied. The first candidate is the solid solution for C3S with magnesium and aluminum. The second one is C3S. Both give similar match score while the C3S matches better when checking the peaks at around 15 degrees. Right click to accept the candidate. Next is the anhydrite. Then, it is the C4AF, namely the Brownmillerite if you have a quick look into the details of the card. For the rest of the phases you can get help from the different types of restrictions to locate. For instance, there might be some free lime left in the cement if the sintering is not well done.

Notes

Summary

11m 21s

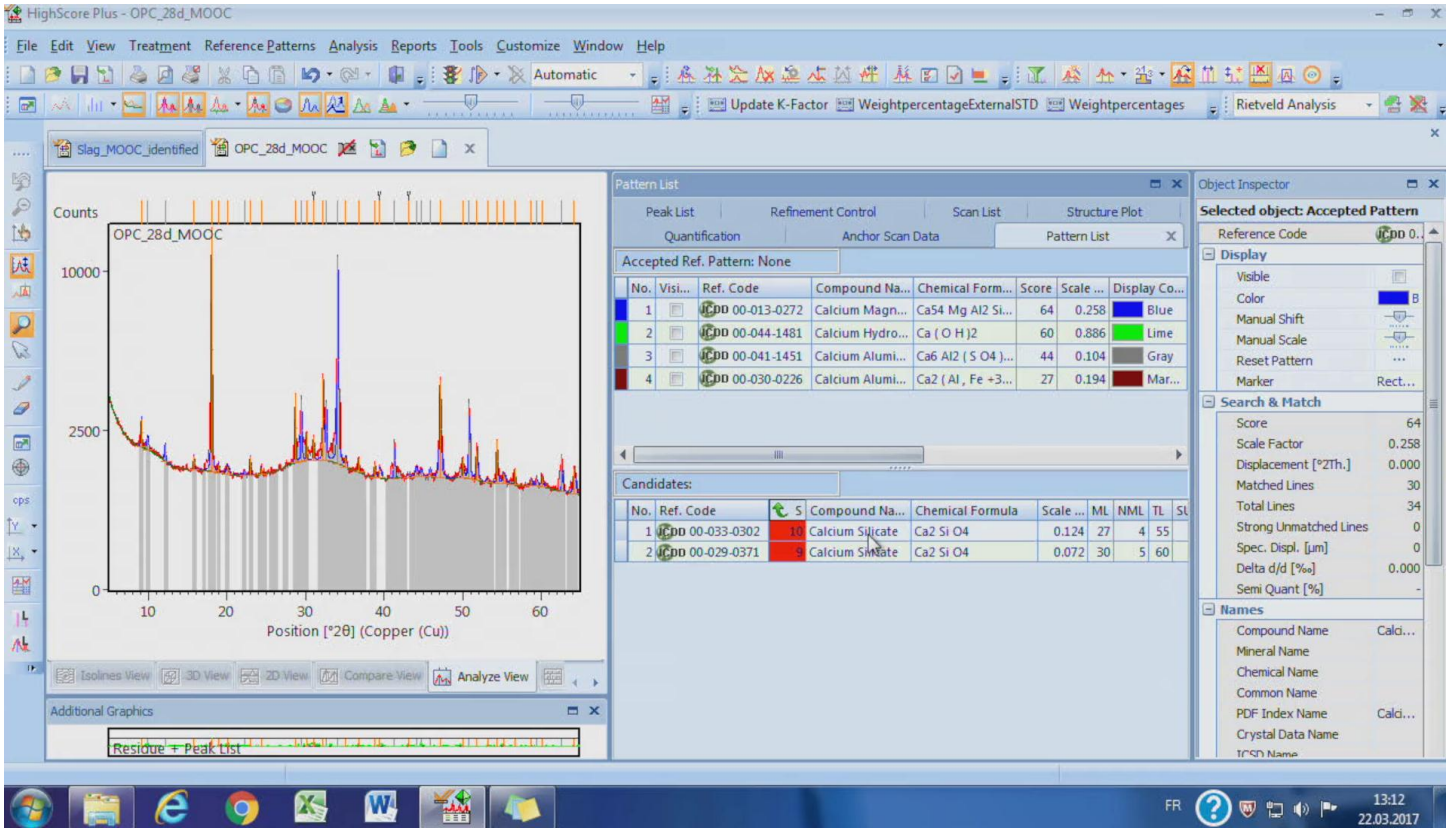


The restrictions based on elements can be used: we pick the calcium and oxygen. In this sample, there is only very small amount of free lime. For Portland cement, there must be some C2S. As we know, the mineral name of the beta C2S is called Larnite. Let's try the restriction using strings. Before we use another restriction, the previous one must be cleared. Indeed, if we apply the restriction based on the mineral name, it will be easier to locate the exact phase. If we just use the element restrictions for the same chemical composition, there are some polymorphs which need to be distinguished. Until now, most of the peaks are identified. But there is no C3A found in the candidates list. We put some element restrictions to find the C3A. There is the C3A we need. All the peaks match the pattern now. Demo on hydrated cement. Now we take a look at the hydrated cement. You can see clearly the hump for CSH around 30 degrees with copper radiation. So the background should be treated similarly to the fly ash and slag, following the trend of the patterns. As we know, it is cement hydrates, so we apply the subfile restriction with cement and hydrates. The suggested matches are alite.

Notes

Summary

12m 53s



Here it appears as a solid solution of the C3S with some magnesium and aluminum. Then it is the Portlandite which is the main hydrate for cement. Then you can find the ettringite which appears as calcium aluminate sulfate hydroxide hydrate. Also check the peaks in the patterns. The hydrated cement being complex, sometimes the software cannot find out the potential candidate easily. Then the restrictions can be used to simplify the search match process. Generally, the C4AF reacts slowly during the hydration process. Let's locate this phase with the mineral name of Brownmillerite. The same routine can be used for the C2S, namely Larnite. Up to now, all the crystalline phases in the hydrated cement space was identified. Unsurprisingly, we cannot find the candidates for CSH in the database as it is nano-crystalline which presented a hump instead of a set of peaks. The closest crystalline structures to CSH are the 11 angstrom and 48 angstrom tobermorite structure which is the most used starting structure to model the CSH structure.

Notes

Summary

14m 20s