THE RIETVELD METHOD AS A TOOL FOR ASSESSING HEAVY-METAL IMMobilization IN S/S TREATMENT INVESTIGATIONS

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X-Ray Powder Diffraction

- Determines the average mineralogical composition of a solid sample
- Can only detect crystalline phases
- Each crystalline phase reflects X-rays in a unique way according to the morphology and composition of the crystal
- X-Ray Powder Diffraction employs random orientation of crystals in a sample, in order to obtain an intensity function that is the sum of the reflections produced by all crystal planes over a range of diffraction angles -> this is the XRPD pattern
Why use XRPD in S/S treated media?

The success of an S/S treatment is commonly evaluated using regulatory leaching tests (Toxicity Characteristic Leaching Procedure in the U.S., EN 12457 in the E.U.)

Regulatory tests alter the S/S matrix and are not designed to address the immobilization mechanisms of hazardous compounds (e.g. precipitation of heavy metals as insoluble compounds, sorption on CSH, etc.)

XRPD allows for the identification of crystalline phases prior and following the S/S treatment and possibly also the speciation of hazardous species

Knowing the speciation of hazardous compounds and most importantly heavy metals is critical in predicting solubility and applying geochemical reaction and fate-and-transport modeling

The properties of the cementitious matrix itself are elucidated by XRPD analysis
XRPD quantitative analysis by Whole Pattern Fitting (WPF)

The qualitative analysis of an XRPD pattern consists in matching all observed peaks with crystalline phases.

It is important to recognize that the observed peak intensity of each phase does not necessarily reflect its quantity in the sample.

Basic principle of WPF:
Fitting the experimentally observed diffraction pattern with a synthesized pattern using the phases identified in the qualitative analysis

-> the minimization of the difference between the two patterns is performed by a mathematical algorithm.

H.M. Rietveld was the first to introduce this method into XRD analysis in 1969.
Steps for WPF application

- Perform qualitative analysis in order to match all observable peaks
- Load identified phases into Whole Pattern Fitting dialog window of commercially available software
- Run software algorithm in order to produce a calculated pattern
- Refine model parameters to minimize the difference between experimental and calculated pattern
- Read quantitative results based on the optimized set of parameters
Refinable parameters

Global parameters (refer to entire pattern)
- *Background curve*
- *Angular corrections*
- *Amorphous humps*
- *Profile function*

Phase parameters (refer to each compound loaded)
- *Lattice constants*
- *Peak Intensity*
- *Peak width*
- *Preferred Orientation parameters*
- *Position and type of atoms in the crystal*
Mathematical model

- The refinement model is a least-square model that seeks to minimize the residual between the observed and the calculated intensity, summed over all data points.

\[ S = \sum_{i} \frac{(y_i - y_{ci})^2}{y_i} \]

The weight percentages are then calculated based on the integrated intensities (peak areas) and the Reference Intensity Ratios (RIR) of the loaded phases.
Criteria of fit

Numerical criteria
- R-factor
- Goodness of fit indicator

-> these depend largely on counting statistics and pattern complexity and are to be used as guiding numbers rather than as absolute criteria

Graphical criteria
- Plot of residual pattern

-> particularly useful as it indicates “problem areas” e.g. unidentified peaks, poor choice of minerals, preferred orientation phenomena
Example of residual pattern plot
Important considerations

- WPF is a mathematical model -> it minimizes the residual regardless of the physical meaning of parameter values

Peak broadening may be a result of poor degree of crystallization -> manual restriction of FWHM (peak width) to the instrument-specific broadening is necessary to avoid overestimation of phases

Significant shift in lattice constants may indicate a poor choice of mineral or have a physical meaning e.g. change in the state of hydration

The analyst must be in position to judge what adjustments to make, even though the goodness of fit may be worse, in order to avoid mathematical curve fitting
Mass balances

- *An indirect method to check WPF results is by performing a mass balance*

  1. Calculate distribution of elements in the mineral phases used to conduct WPF
  2. Multiply with the quantitative results to obtain element distribution of the phase in the analyzed sample
  3. Add the results for all mineral phases to obtain elemental composition of sample
  4. Compare with wet chemistry data
Example of WPF and mass balance in COPR

<table>
<thead>
<tr>
<th></th>
<th>Rietveld</th>
<th>Ca (40)</th>
<th>Fe (56)</th>
<th>Al (27)</th>
<th>Mg(24)</th>
<th>CrVI (52)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brownmillerite</td>
<td>10.4%</td>
<td>3.42%</td>
<td>2.40%</td>
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<td>Portlandite</td>
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<td>8.11%</td>
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<td>Calcite</td>
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<tr>
<td>Periclase</td>
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<td>Brucite</td>
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<td>Quartz</td>
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<td>Hydroandradite</td>
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<td>Katoite</td>
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<td>1.08%</td>
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<tr>
<td>Sjoegrenite</td>
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<td>2.77%</td>
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<tr>
<td>Ettringite</td>
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<td>0.65%</td>
<td></td>
<td>0.15%</td>
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<td>CAC-14</td>
<td>4.4%</td>
<td>1.04%</td>
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<td>0.34%</td>
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<tr>
<td><strong>SUM</strong></td>
<td><strong>99.9%</strong></td>
<td><strong>26.41%</strong></td>
<td><strong>6.22%</strong></td>
<td><strong>2.14%</strong></td>
<td><strong>6.65%</strong></td>
<td><strong>0.34%</strong></td>
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<td><strong>Total analyses</strong></td>
<td><strong>25.09%</strong></td>
<td><strong>6.49%</strong></td>
<td><strong>3.15%</strong></td>
<td><strong>4.92%</strong></td>
<td><strong>0.84%</strong></td>
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<td><strong>Difference</strong></td>
<td><strong>1.32%</strong></td>
<td><strong>-0.27%</strong></td>
<td><strong>-1.01%</strong></td>
<td><strong>1.73%</strong></td>
<td><strong>-0.50%</strong></td>
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</tbody>
</table>

Mass balance evaluation

- Elements with higher percentage present the maximum discrepancies (uncertainty increases in major phases)

- Isomorphic substitutions (Mg$^{2+}$ -> Ca$^{2+}$, Fe$^{3+}$, Cr$^{3+}$ -> Al$^{3+}$) can account for minor discrepancies

- Systematic errors may appear as consistent over- or underestimation in one or more elements
Applications of Rietveld

- Is the only available method to provide info on the average mineralogy of all types of solids. Application in S/S design and evaluation is possible in order to investigate the immobilization mechanisms of hazardous compounds (heavy metals).

- Can provide insight into compositional questions (solid solutions, hydration states, variation in minerals) but this requires good knowledge of crystallography.

- Can provide information on solid state chemistry and physics, when single-crystal X-ray diffraction is applied.
Limitations of Rietveld

- XRPD detection limit (can be as low as 0.01% for very well crystallized phases but is generally assessed between 1 and 5%)
- Identification of amorphous phases very limited -> problem for S/S applications with CAH/CSH gels
- Uncertainty in results (1-5% depending on quantity), precision in the evaluation of immobilization is limited
- Substitutions by hazardous metals in known phases are not always detectable; despite of large number of PDFs, natural and engineered systems always present large variations in composition
Thank you

Questions?