CHARACTERISATION OF SOME CLAYS USED FOR WHITEWARE CERAMICS

I. MINERALOGICAL COMPOSITION

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ABSTRACT. In order to obtain a semiquantitative mineralogical composition of raw materials used for whiteware ceramics, four different clay types were analysed by X-ray diffraction. Studies were carried out by using a combination of analyses of the bulk sample, and of the fine fraction. Using a well-established pre-treatment methodology (use of chemicals, ultrasonic treatment, dispersion procedures), clay mineral concentration by centrifugation and sedimentation, oriented and random powder preparation, cation saturation, expansion/dehydration methods, 12 X-ray diffractometer traces were obtained from each sample. Based on these informations it was possible to establish the qualitative mineralogical composition, and also a semiquantitative one using peak intensities and peak area corrected by various factors. Scanning electron microscopy was also used in order to illustrate the identified mineral phases.

Key words: clays, clay minerals, X-ray diffraction analysis

INTRODUCTION

The quantitative mineralogical composition of clays is very important in a variety of geological, technological, and economic aspects. However, one of the main problem in any comparison of quantitative clay analyses derives from the different analytical methods used, e.g., application or not of a pre-treatment, methods of preparation, and qualitative evaluation procedures for the clay mineral components. Based especially on X-ray diffraction, and electron microscope images, the paper presents the mineralogical composition of four different clay types used for whiteware ceramics. The second part of this paper is focused on the correlation between mineralogical, and chemical composition vs. the technological characteristics.

ANALYTICAL TECHNIQUES

The bulk samples were initially dried for some weeks at room temperature. Subsequently, the aggregates were ground in a Fritsch Pulverisette and than analysed by X-ray diffraction (XRD) between 2°-70° 2θ using a Philips PW 1710 diffractometer equipped with Bragg-Brentano geometry, copper anticathode (45kV, 40 mA), and graphite monochromator.

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To establish the mineralogical composition of the < 2 µm fraction, the following methodology was applied:

- The bulk samples with natural humidity were treated several days with 35% hydrogen peroxide in order to remove the organic material, and to obtain a better dispersion. At the end of the reaction, after the removal of the excess hydrogen peroxide in a boiling water bath, the samples were treated 5 minutes in an ultrasonic device.
- Using distilled water, the < 63 µm fraction was sieved off, and than, by repeated centrifugation, the < 2 µm fraction was obtained.
- 40 ml from the previously obtained suspension were mixed with 10 ml KCl 4N, respectively with 10 ml MgCl₂ 4N solutions, the mixtures being homogenised for 12 hours. Finally, Cl⁻ ions were removed by repeated washing and centrifugation.
- Both K⁺ and Mg²⁺ saturated suspensions were used to obtain oriented samples by absorption on ceramic tiles (about 10 mg/cm²). These samples were dried several days in an NH₄NO₃ exicator and subsequently were analysed by XRD between 2°-40° 2θ.
- Further on, the oriented, and Mg²⁺, respectively K⁺ saturated samples were expanded with ethylenglycol (12 hours at 70°C) and analysed by XRD between 2°-40° 2θ.
- The K⁺ saturated samples were treated with dimethylsulfoxide (DMSO) (24 hours at 70°C) and than analysed by XRD between 2°-40° 2θ.
- The DMSO was removed by evaporation and subsequently, both the Mg²⁺ and K⁺ saturated samples were dehydrated by thermal treatment (2 hours at 300°C, and 550°C). After each heat treatment, the samples were analysed by XRD between 2°-14° 2θ.
- For a better redispersion and analysis of the fine clay fraction, the rest of the untreated samples (< 2 µm fraction) was dried by freezing in a Heutosic FD3 device, than ground and analysed by XRD between 2°-70° 2θ and 58°-64° 2θ (step-scan procedures using long count times and small scale factor) in order to identify the (060) reflections.

Thus, 12 X-ray diffractometer traces resulted for each sample, which were used to establish the qualitative mineralogical composition according to Brindley & Brown (1980), Moore & Reynolds (1987) and Thorez (1975). Semiquantitative evaluation was done by using peak intensities and peak areas corrected by factors according to Riedmüller (1978) and Tributh (1991).

To argument and illustrate the identified mineral phases, a Philips XL30 ESEM (environmental scanning electron microscope) was also used.

RESULTS AND DISCUSSION

The interpretation of the X-ray diffractometer traces of the bulk samples, and of the fine clay fraction (< 2 µm) led to the identification of the following mineral phases: quartz, kaolinite, vermiculite, illite, and „mixed layers” (smectite/illite) (Table 1).
Quartz is the most common and easy to identify mineral, thus our attention was focused on the other minerals.

The identified mineral phases in the analysed clays

<table>
<thead>
<tr>
<th>Mineral</th>
<th>UIII / 4806</th>
<th>UII / 4807</th>
<th>CARO / 4808</th>
<th>ESV3 / 4809</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>(+)</td>
<td>+</td>
<td>(+)</td>
<td>+</td>
</tr>
<tr>
<td>Illite</td>
<td>+</td>
<td>(+)</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>ML</td>
<td></td>
<td></td>
<td>(+)</td>
<td></td>
</tr>
</tbody>
</table>

ML = "mixed layers" (smectite/illite); (+) = small amounts

The best arguments for the presence of well crystallized kaolinite are the X-ray diffraction patterns obtained on the DMSO expanded samples (Fig.3). In this case, the main, characteristic reflection shifts to 11.2 Å (~ 8° 2θ). In addition, the transformation to metakaolinite after thermal treatment at 550°C (Fig.4) complete the diagnosis. The images obtained by SEM illustrate the well-shaped, large crystals of clear hexagonal outline (Fig.8) or much smaller, fine-grained crystals (Figs.7, 9 and 10).

Vermiculite is more abundant in the UII (4807) and ESV3 (4809) clay types and less in UIII (4806) and CARO (4808) types. The 14 Å (6.3° 2θ) and 18 Å (4.9° 2θ) reflections identified in bulk samples, in the < 2 µm fraction, and especially in the Mg$^{2+}$ saturated samples (Figs.1, 2 and 5) highlighted the presence of two different vermiculite types (14 Å and 18 Å).

In the case of K$^+$ saturated samples (Fig.6), the vermiculite diffraction patterns are less visible, being covered by the illite reflection at 10 Å (~8.9° 2θ).

Illite 1M was identified using its characteristic reflections at 10 Å (~8.9° 2θ), 5 Å (17.7° 2θ) and 3.32 Å (26.8° 2θ) especially in the UIII (4806) and CARO (4808) clay types (Figs.1 and 2). The position of these reflections is not modified after swelling using organic solvents (ethyleneglycol) (Figs.5 and 6), nor by heat treatment at 550°C (Fig.4).

The SEM images are showing the filamentous aspect of illite crystals (Fig.10).

After this qualitative identification of mineral phases in the studied clay types, the next step was to obtain a semiquantitative result regarding the percentage of participation. In this respect, the peak intensities (mostly of a lower order), corrected by factors according to Riedmüller (1978), and Tributh (1991) were used. The results are presented in Table 2.
Table 2
Semiquantitative mineralogical composition of the analysed clays (wt.%)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Clay type / sample number</th>
<th>UIII / 4806</th>
<th>UII / 4807</th>
<th>CARO / 4808</th>
<th>ESV3 / 4809</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td></td>
<td>11.40</td>
<td>25.70</td>
<td>25.50</td>
<td>15.50</td>
</tr>
<tr>
<td>Kaolinite</td>
<td></td>
<td>77.50</td>
<td>57.35</td>
<td>51.40</td>
<td>63.55</td>
</tr>
<tr>
<td>Vermiculite</td>
<td></td>
<td>2.50</td>
<td>12.20</td>
<td>2.00</td>
<td>20.95</td>
</tr>
<tr>
<td>Illite</td>
<td></td>
<td>8.60</td>
<td>4.75</td>
<td>20.10</td>
<td>-</td>
</tr>
<tr>
<td>„mixed layers“</td>
<td></td>
<td>-</td>
<td>-</td>
<td>1.00</td>
<td>-</td>
</tr>
</tbody>
</table>

The chemical composition of the studied clays (determined by X-ray fluorescence at S.C. SANEX S.A. laboratory) is presented in Table 3. The behavior of the different clay types regarding their mineralogical and chemical composition vs. their technological properties will be discuss in the second part of the paper.

Table 3
Chemical composition of the studied clays (wt. %)

<table>
<thead>
<tr>
<th>Clay type</th>
<th>Oxides</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>TiO₂</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>L.O.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-III</td>
<td></td>
<td>48.13</td>
<td>33.82</td>
<td>2.00</td>
<td>1.06</td>
<td>0.65</td>
<td>0.50</td>
<td>0.00</td>
<td>0.35</td>
<td>13.48</td>
</tr>
<tr>
<td>U-II</td>
<td></td>
<td>59.43</td>
<td>26.39</td>
<td>1.77</td>
<td>0.98</td>
<td>0.45</td>
<td>0.35</td>
<td>0.00</td>
<td>0.40</td>
<td>10.22</td>
</tr>
<tr>
<td>CARO</td>
<td></td>
<td>53.35</td>
<td>30.33</td>
<td>1.23</td>
<td>0.99</td>
<td>0.09</td>
<td>0.47</td>
<td>0.13</td>
<td>2.06</td>
<td>11.35</td>
</tr>
<tr>
<td>ESV 3</td>
<td></td>
<td>53.12</td>
<td>31.01</td>
<td>2.30</td>
<td>0.95</td>
<td>0.60</td>
<td>0.36</td>
<td>0.02</td>
<td>0.40</td>
<td>11.26</td>
</tr>
</tbody>
</table>

CONCLUSIONS
The usage of standardized pre-treatment, preparation and evaluation methods and an exact qualitative identification in clay analysis could significantly decrease the variation of results. In particular, this applies to the quantification method with regard to the choice of peaks and the application of correction factors. A well-defined method of analysis could lead to an appropriate semiquantitative identification of mineral phases in any clayey raw materials.

ACKNOWLEDGEMENTS
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REFERENCES


Fig. 1. X-ray diffractometer traces of bulk samples

Fig. 2. X-ray diffractometer traces of the < 2 µm fraction
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Fig. 3. X-ray diffractometer traces of the expanded with DMSO samples

Fig. 4. X-ray diffractometer traces of the dehydrated (T=550°C) samples
Fig. 5. X-ray diffractometer traces of the saturated with Mg (M) and expanded with ethylenglycol (ME) samples.

Fig. 6. X-ray diffractometer traces of the saturated with K (K) and expanded with ethylenglycol (KE) samples.
Fig. 7. Sample 4806 (UIII clay type) – kaolinite plates

Fig. 8. Sample 4807 (UII clay type) – kaolinite crystals
Fig. 9. Sample 4808 (CARO clay type) – kaolinite crystals

Fig. 10. Sample 4806 (UIII clay type) – kaolinite plates and filamentous illite