Materials for geopolymers

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1. Basic materials for geopolymer synthesis: raw or waste materials
   - Non-thermal treated raw materials
   - Thermal treated raw materials

2. Additives
   - Inert
   - Active

3. Waste materials: Advantages and disadvantages, economical aspects
Basic materials for geopolymer synthesis

1. Clay material with proportion of Si/Al molar quantities - Chemical and mineralogical analyses (XRF and XRD)
   - Minimum value – 48% of clay material

2. The quantity of transformed of Al$^{3+}$ ions from natural six-fold coordination to oxygen to the five and four-fold coordination.
   - Minimum value – 45% of Al$^{3+}$ ions five and/or four-fold coordination.
Basic materials

- Industrially prepared materials
  - Non-thermal treated materials (waste)
  - Naturally thermal treated materials

- Non-thermal treated materials
  - So-called „white waters“ from ceramic production
  - Extracted but not used clays
  - Clays washed from sandstones (glass sand)
  - Volcanic materials
  - Coal burning ashes
  - Wastes from metal production (slags)
  - Schistous clay

- Thermal treated materials
Industrially prepared materials: Non-thermal treated materials

- Kaolin – up to 94 wt.% of kaolinite content, the rest: mica, SiO$_2$, feldspar
- Guaranteed chemical composition
- Necessity of thermal activation (750°C, dwell 4 - 6 hours)

The chemical composition of kaolin Sedlec 1a (in wt. %)

<table>
<thead>
<tr>
<th>Oxides</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>CaO</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>L.O.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin</td>
<td>47.30</td>
<td>36.70</td>
<td>0.85</td>
<td>0.18</td>
<td>0.27</td>
<td>0.23</td>
<td>0.95</td>
<td>0.03</td>
<td>12.90</td>
</tr>
</tbody>
</table>
Industrially prepared materials: Thermal treated materials

- **Mefisto L – metakaolinite**
  - Sub product of shistous clay firing
  - Thermal activated during shistous clay firing – 80 % of $\text{Al}^{3+}$ in tetra coordination
  - Particle size: 1-10 $\mu$m

<table>
<thead>
<tr>
<th>Oxides</th>
<th>$\text{SiO}_2$</th>
<th>$\text{Al}_2\text{O}_3$</th>
<th>$\text{Fe}_2\text{O}_3$</th>
<th>$\text{TiO}_2$</th>
<th>$\text{CaO}$</th>
<th>$\text{MgO}$</th>
<th>$\text{K}_2\text{O}$</th>
<th>L.O.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mefisto L (wt. %)</td>
<td>52.90</td>
<td>41.90</td>
<td>1.08</td>
<td>1.08</td>
<td>0.13</td>
<td>0.18</td>
<td>0.77</td>
<td>1.40</td>
</tr>
</tbody>
</table>
Non-thermal treated waste raw materials

- Necessary steps before use:
  - Extraction, transportation
  - Material treatment (washing, drying, milling)
  - Chemical and particle size analyses
  - Thermal treatment (activation)

- All mentioned preparative steps are costly and use of the material should be on the beginning judged from economic point of view.
Raw materials: „white waters“ from ceramic production (porcelain and sanitary ware)

- All ceramic producers applied similar sort of water clearing, using generally sedimentation tanks and filter-pressing the sediments of the unfired ceramic mass.

- Containing about **48 – 52 wt.%** of kaolin, feldspar and quartz and indefinite remnants of glazes.
  - The geopolymer matrix will be formed only from clayed proportion, means **48 - 52 wt %** of total weight.

- Ceramic mass is finely milled than one economic obstacle could be omitted
Raw materials: „white waters“ from ceramic production (porcelain and sanitary ware)

- White waters from Bechyně, Horní Slavkov, Teplice ceramic factories.
- 1 producer: 600t/month
- The water content: 18 - 20 wt. %
- Material must be dried, disintegrated and thermally activated.

- Generally, this waste is excellent main material for the geopolymer syntheses.
- Compressive strength from 13 to 21MPa according to filling agent and content of additive.
# Results summary of different type and changing content of additives

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Additives</th>
<th>Content (wt. %)</th>
<th>Compressive strengths (MPa)</th>
<th>Flexural strengths (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Glass from TV screens</td>
<td>48</td>
<td>16.8</td>
<td>5.8</td>
</tr>
<tr>
<td>2.</td>
<td>Graveled limestone</td>
<td>43</td>
<td>21.0</td>
<td>3.1</td>
</tr>
<tr>
<td>3.</td>
<td>Fly ash</td>
<td>66</td>
<td>18.0</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>Sand</td>
<td>22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Crushed porcelain</td>
<td>50</td>
<td>14.7</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Filling content depends on particle size of additives.
Raw materials: Extracted, but non-used clays

- Clayed materials omitted by ceramic industry or superficial clayed layers.

- These, not used clays are generally contaminated by organic matters or/and by ferric/ferrous and titan impurities.

- Distribution of clay particles is rather bigger than found in typical kaolin ($< 20 \mu m$ only 25 wt. %.) $\Rightarrow$ reaction velocity is than lower

- Economic obstacles: Treatment of the material before activating (washing, drying) and eventual milling.

- The clays have generally very high content of alumina and especially: The use must be very carefully judged - cost of treatment and eventual price and quantities of final products.
Raw materials: Extracted, but non-used clays

- Kamenná Panna (Central Bohemia Region):
  - Refractory (kaolinitic) clay contains up to 42 wt.% Al₂O₃
  - Geopolymer, example of sandstone bonded by white clay
Raw materials: Clays washed from sandstones

(main production of snow-white glass sand)

- Kaolinitic clay washed from sandstones contains 54 - 55 wt.% of clayed material.
- Rest is very fine part of remnant quartz sand (SiO₂).
- Clayed substances are double layered clay and after thermal activation apt for easy hydration and reaction with alkalis.
- This clay is fully suitable for geopolymer syntheses.
Raw materials: Clays washed from sandstones (glass sand)

- Střeleč, sandstone deposit (East-North Bohemia).
- High content of Lepidocrocite (γ-FeO(OH)) in clay – causing red color of the thermal activated clay.
Thermally treated raw materials

- Naturally thermal activated

- Necessary steps before use:
  - Extraction, transportation
  - Material preparation (drying, separating, milling)
  - Chemical and granulometric analyses
  - Unguaranteed and changeable content of [4] $\text{Al}^{3+} \rightarrow ^{27}\text{Al}$ MAS NMR analyses in solid state

- All mentioned preparative steps are costly and use of the material should be on the beginning judged from economic point of view.
Thermally treated materials: Volcanic materials

- Regions with volcanic activity
- Tuffs, volcanic ashes, laterites, pumice
- Naturally thermal activated material

Samples from Nicaragua:

Chemical analyses (XRF):

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<tr>
<th>Oxides</th>
<th>SiO₂</th>
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<th>TiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>SO₃</th>
<th>L.O.I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tuff</td>
<td>58.10</td>
<td>15.21</td>
<td>9.51</td>
<td>0.96</td>
<td>6.39</td>
<td>2.78</td>
<td>1.21</td>
<td>2.64</td>
<td>-</td>
<td>3.76</td>
</tr>
</tbody>
</table>
Roentgen analyses (XRD):

- The major phases: albite (Na(AlSi$_3$O$_8$)), anorthite (CaAl$_2$Si$_2$O$_8$) and andesine Na$_{0.499}$Ca$_{0.491}$ (Al$_{1.488}$Si$_{2.506}$O$_8$)
- Traces: forsterite (Mg$_{0.637}$Fe$_{0.358}$)$_2$SiO$_4$ and augite
- The crystal phases are complemented by an amount of amorphous alumina-silicates.

$^{27}$Al MAS NMR in solid state
Thermally treated materials: Ashes

- Fly ashes from classic combustion: prof. Palomo, Spain or prof. Škvára, Czech Republic
- High resistance against sulfate and chlorine corrosion
- Very good mechanical properties

- High concentration of alkali activator limits the industrial acceptation of fly ashes as basic material.

T. Jílek, dissertation, ICT Prague, 2004
Thermally treated materials:
e.g. slag from metal production

- First studies from the fifties of the past century (prof. Gluchovsky, Ukraine, 1959; prof. Krivenko)

- **Blast furnace slag** (dumps of iron and steel production at Kladno town, cca 10,000,000 tun)

- **Chemical composition:**

<table>
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<th>Na₂O</th>
<th>SO₃</th>
<th>L.O.I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag</td>
<td>22.38</td>
<td>8.09</td>
<td>2.31</td>
<td>0.51</td>
<td>37.44</td>
<td>3.51</td>
<td>1.27</td>
<td>&lt;0.11</td>
<td>7.46</td>
<td>14.7</td>
</tr>
</tbody>
</table>

- **Mineralogical composition** of calcareous blast furnace slag:
gehlenite Ca₂Al(AlSi)O₇, merwinite Ca₃Mg(SiO₄)₂, syn. syngenite K₂Ca(SO₄)₂ x H₂O and wollastonite CaSiO₃

- The industrial acceptation of slag as basic material limits a necessity to use high concentration of alkalís.

- Very perspective material in admixture with activated clay.
Thermally treated materials: Schistous clay

- Zbůch (West Bohemia region), only 45 wt.% of clayed mineral
- Dumps of over layered material-coal mining
- Containing a proportion of coal
- Delayed after flame burning (50 years)
Thermally treated materials: Schistous clay

- Naturally long-term burning processes – thermal transformation
- Chemical analyses
- $^{27}$Al MAS NMR in solid state:

<table>
<thead>
<tr>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>38.0%</td>
<td>62.0%</td>
</tr>
<tr>
<td>2</td>
<td>38.3%</td>
<td>61.7%</td>
</tr>
<tr>
<td>3</td>
<td>45.9%</td>
<td>54.1%</td>
</tr>
</tbody>
</table>
Additives

- Suitable choice of additives: mechanical properties, color, porosity, structure, freeze-thaw resistance, etc.

- Inert:
  - Sand
  - Ceramics
  - Glass fibers
  - Limestone
  - SiC
  - Mica
  - Etc.

- Active:
  - Blast furnace slag
  - Fly ash
  - Biomass ash
  - Shistous clay
  - Etc.
Inert additives

- Sand
- Desert sand (75%)
- Limestone
- Glass fibers
- Grinded porcelain
- Waste from SiC production
- Micas
- Wood chips
- Paper
- Stone powders
- Etc.

Detailed view on sand grains
Sandstone from salted desert sand
Limestone grains
Composite with glass fibres
Composite with grinded porcelain
Composite with waste SiC
Active additives

- Shistous clay
- Blast furnace slag
- Fly ashes
- Biomass ashes
- Stone powders
- Etc.

Multi-layer composite from biomass ash
Waste material:

- **Advantages:**
  - Low costs material
  - The ecological aspects (cleanup of old industrial brown fields and dumps)
  - Utilization of different local materials (slag, ash, etc.)

- **Disadvantages:**
  - Non-constant chemical composition – necessity of testing
  - Non-constant particle size – necessity of milling, separating and granulometric analysis
  - The efflorescence
  - Lower mechanical properties
  - Lower filling by additives
Industrially prepared primary material:

**Advantages:**
- Guaranteed chemical composition
- Guaranteed particle size
- High finesse of particles
- No mechanical or thermal treatments
- Use of lower amount to make a resulting material (content of clay mineral – 100 %)
- Lower risk of efflorescence
- Staff, time and energy saving

**Disadvantages:**
- Higher material costs
- Transport charges
Possibilities

1. Use of industrially prepared primary material for matrix
   - Filling by different additives – up to 90 wt.%
   - Sandstone – desert sand, sand with higher content of undesirable oxides (Fe, Ti, etc.)

2. Use of waste material for matrix
   - Lower filling by different additives
   - Utilization for specific application
   - Shistous clay matrix: compressive strength – 48 MPa

3. Use a combination of primary and waste raw material (from 1:1 to 1:2) to make a matrix
   - Waste raw material: slag, ash, schistous clay
   - Filling by different additives
   - Mefisto / slag matrix: compressive strength – 75 MPa
Conclusion

- Mentioned material sources could be used as main, 3D net forming, substance or as additives.
- There is a possibility to find a specific application for these materials.
- Any type of treatment means increasing costs and is one of the limitation factors.
- The economic factors play very important role in the case of industrial production.
Thank you for your attention