Proved materials for geopolymers

Ivana Perná
Tomáš Hanzlíček

Institute of Rock Structure and Mechanics of Academy of Sciences of the Czech Republic
V Holešovičkách 41, 18209 Praha 8
Czech Republic

Program

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 (^{27}Al MAS-NMR in solid state).
   - Minimum value – 45% of Al^{3+} ions in five and/or four-fold coordination.

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

Industrially prepared materials: Non-thermal treated materials

- Kaolin – up to 94 wt.% of kaolinit 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. %)

Oxides	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	L.O.I.
Kaolin	47.30	36.70	0.85	0.18	0.27	0.23	0.95	0.03	12.90

Industrially prepared materials: Thermal treated materials

- Mefisto L – metakaolin (producer ČLUZ, Czech Republic)
  - Sub product of shistous clay firing
  - Thermal activated during shistous clay firing – 80 % of Al^{3+} in tetra coordination
  - Particle size: 1-10 μm

Oxides	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	L.O.I.
Mefisto L (wt. %)	52.90	41.90	1.08	1.08	0.13	0.18	0.77	1.40

Non-thermally treated waste raw materials

- Necessary steps before the 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 cleaning, using generally sedimentation tanks and filter-pressing the sediments of the unfired ceramic masse.

- 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.

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 μm only 25 wt. %.) ⇒ <u>reaction velocity is than lower</u>
- Economic obstacles: Treatment of the material before activating (washing, drying) and eventual milling.
- The clays have generally very high content of alumina.

Raw materials: Extracted, but non-used clays

- Kamenná Panna (Central Bohemia Region):
  - Refractory (kaolinitic) clay contains up to 42 wt.% Al_2O_3
  - 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 (SiO_2).
- 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 thermally activated clay.

Thermally treated raw materials

- **<u>Naturally thermally activated</u>**

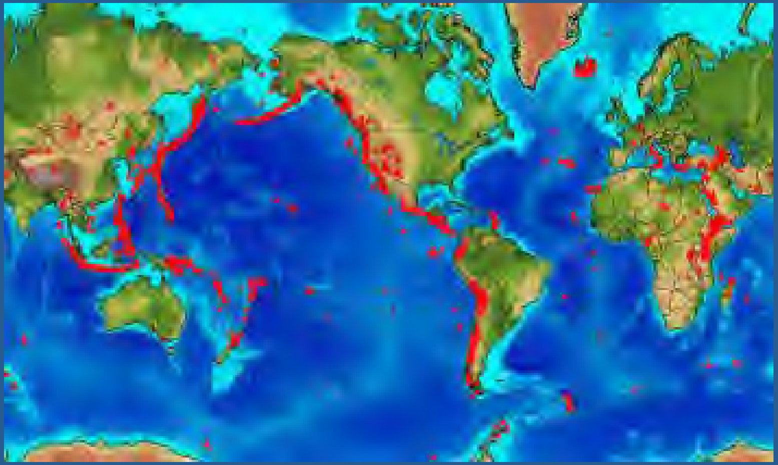
- Necessary steps before use:

  - Extraction, transportation
  - Material preparation (drying, separating, milling)
  - Chemical and granulometric analyses
  - Unguaranteed and changeable content of [4] $Al^{3+} \rightarrow$ ^{27}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 thermally activated material



Samples from Nicaragua:

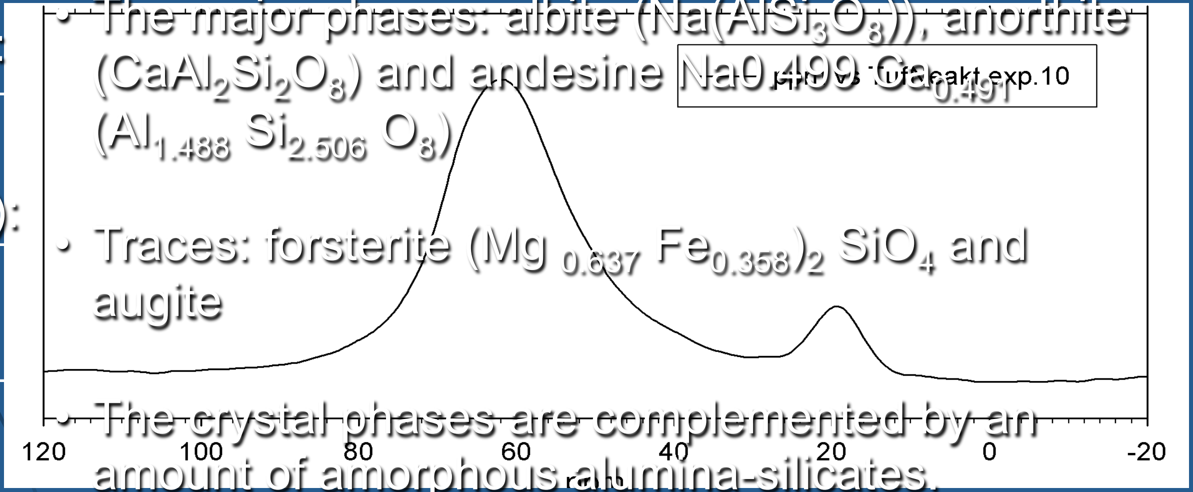
- Chemical analyses (XRF):

Oxides	SiO_2	Al_2O_3
Tuff	58.10	15.21

Roentgen analyses (XRD):

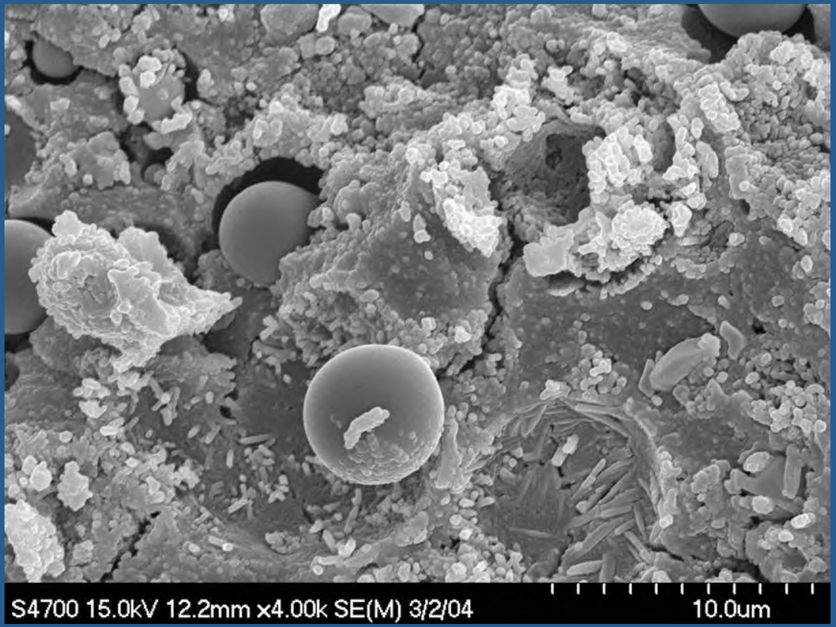
- The major phases: albite ($Na(AlSi_3O_8)$), anorthite ($CaAl_2Si_2O_8$) and andesine Na0.499 $Ca_{0.491}$ ($Al_{1.488}$ $Si_{2.506}$ O_8)
- Traces: forsterite ($Mg_{0.637}$ $Fe_{0.358})_2$ SiO_4 and augite
- The crystal phases are complemented by an amount of amorphous alumina-silicates.

^{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



T. Jílek, dissertation, ICT Prague, 2004

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

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:**

Oxides	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	SO_3	L.O.I
Slag	22.38	8.09	2.31	0.51	37.44	3.51	1.27	<0.11	7.46	14.7

- **Mineralogical composition** of calcareous blast furnace slag: gehlenite $Ca_2Al(AlSi)O_7$, merwinite $Ca_3 Mg(SiO_4)_2$, syn. syngenite $K_2Ca(SO4)_2 \times H_2O$ and wollastonite $CaSiO_3$

- The industrial utilization of slag as basic material is limited by high concentration of alkalis.
- Very perspective material in admixture with activated clay.

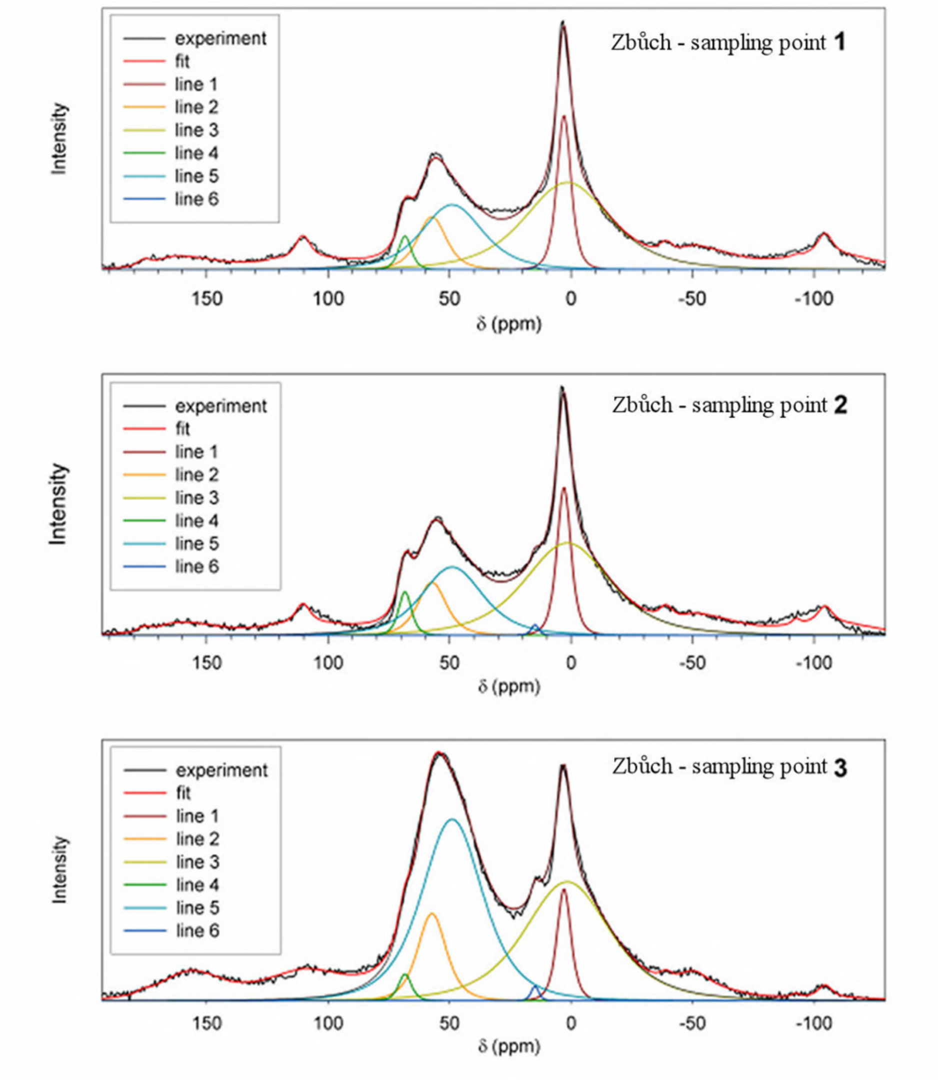
Thermally treated materials: Schistous clay

- 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:

Sampling point	[4] Al^{3+}	[6] Al^{3+}
1	38.0%	62.0%
2	38.3%	61.7%
3	45.9%	54.1%



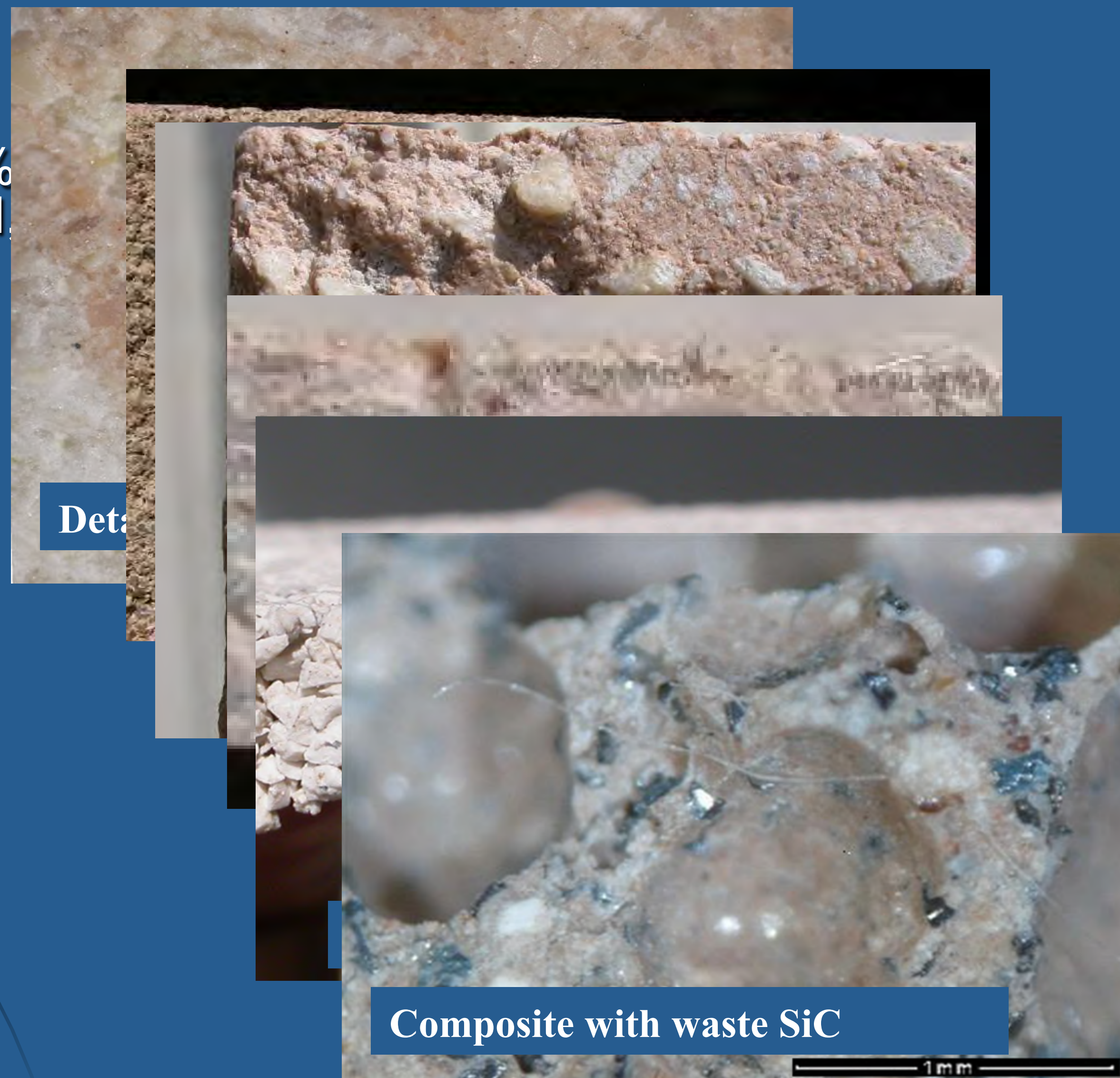
Additives

- <u>Suitable choice of additives:</u> 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

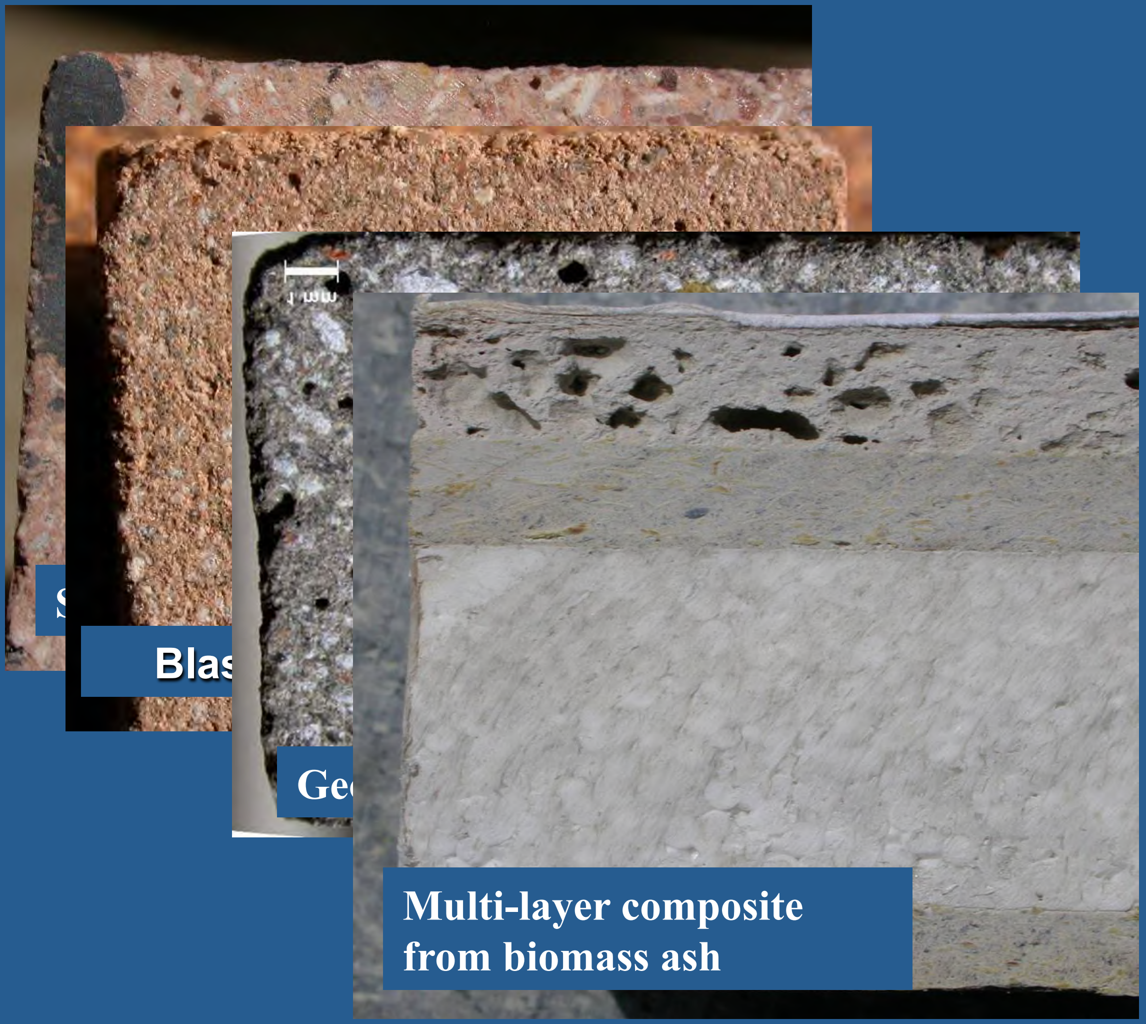
- Sand
- Desert sand – up to 75% (85 wt. % of quartz sand, 10 wt. % of calcite and other minority phases)
- Limestone
- Glass fibers
- Grinded porcelain
- Waste from SiC production
- Micas
- Wood chips
- Paper
- Stone powders
- Etc.



Composite with waste SiC

Active additives

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



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.
- The economic factors play very important role in the case of industrial production.

Thank you for your attention