Materials for geopolymers

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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.
   - Minimum value – 45% of Al^{3+} ions five and/or four-fold coordination.

- Basic materials
  - Industrially prepared materials
    - Non-thermal treated materials
    - Thermal treated materials
  - Non-thermal treated materials (waste)
    - So-called „white waters “ from ceramic production
    - Extracted but not used clays
    - Clays washed from sandstones (glass sand)
  - Naturally thermal 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 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. %)

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 – metakaolinite
  - 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-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 masse.

- Containing about **48 – 52 wt.%** of kaolin, feldspar and quartz and indefinite remnants of glazes.

Industrial filter-press

- 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

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

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 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 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.% 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 thermal activated clay.

Thermaly treated raw materials

- **<u>Naturally thermal 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 thermal activated material

<u>Samples from Nicaragua:</u>

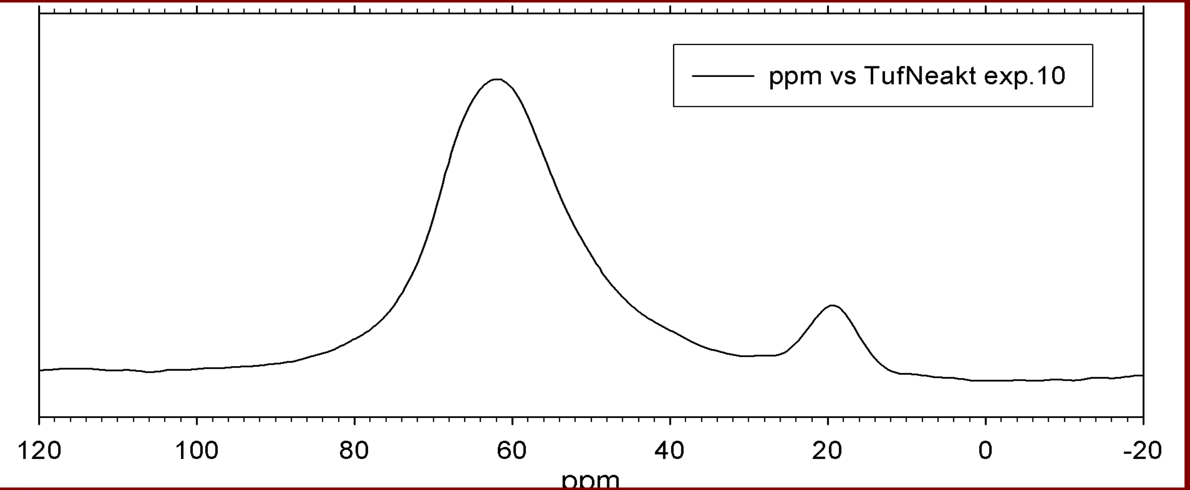
Chemical analyses (XRF):

Oxides	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	SO_3	L.O.I
Tuff	58.10	15.21	9.51	0.96	6.39	2.78	1.21	2.64	-	3.76

Roentgen analyses (XRD):

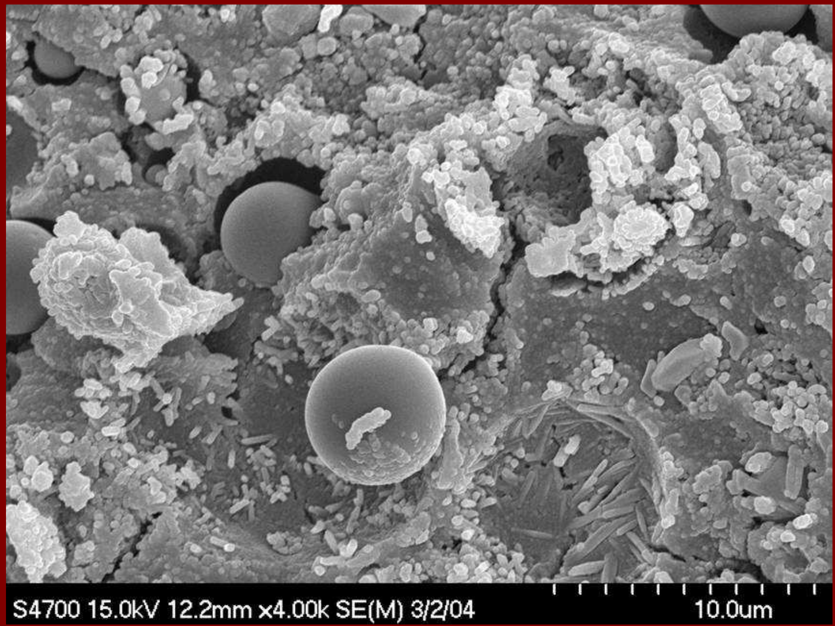
- The major phases: albite ($Na(AlSi_3O_8)$), anorthite ($CaAl_2Si_2O_8$) and andesine Na0.499 $Ca_{0.491}$ ($Al_{1.488}$ $Si_{2.506}$ O_8)
- Traces: forsterite ($Mg_{0.637}$ $Fe_{0.358})_2$ SiO_4 and augite
- The crystal phases are complemented by an amount of amorphous alumina-silicates.

^{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 $Ca_3Mg(SiO_4)_2$, syn. syngenite $K_2Ca(SO4)_2$ x H_2O and wollastonite $CaSiO_3$

- The industrial acceptation of slag as basic material limits a necessity to use high concentration of alkalis.
- Very perspective material in admixture with activated clay.

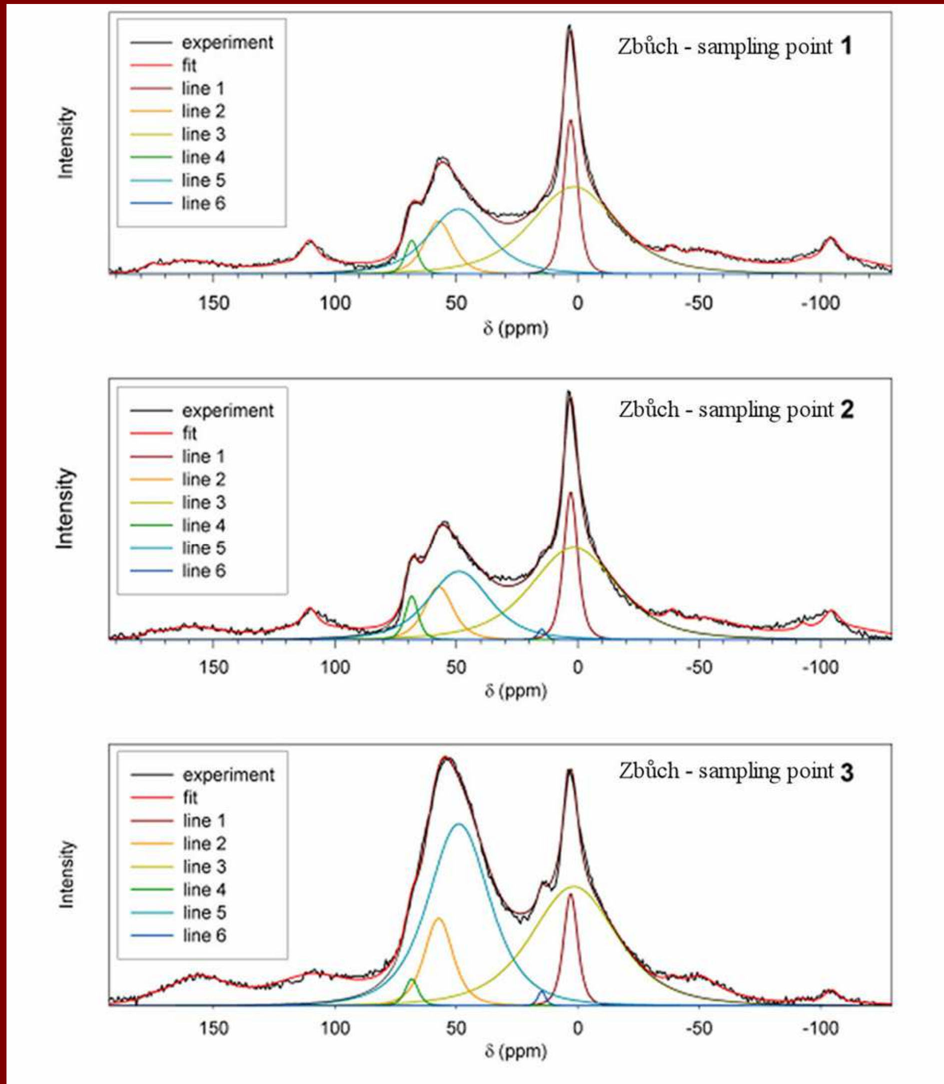
Thermally treated materials: Schistous clay

- 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

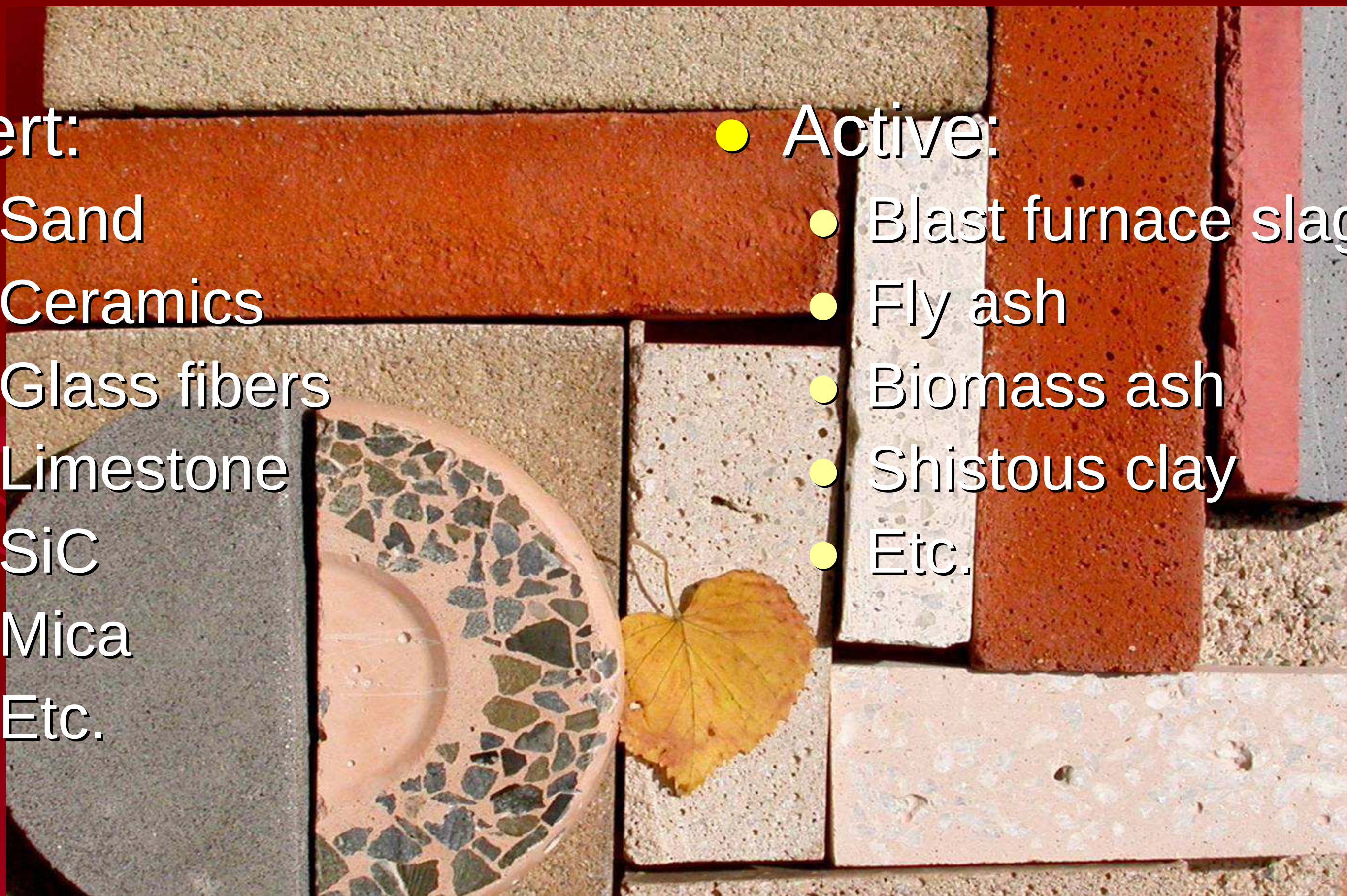
- Naturally long-term burning processes – thermal transformation
- Chemical analyses
- ^{27}Al MAS NMR in solid state:

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



Additives

➢ 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.

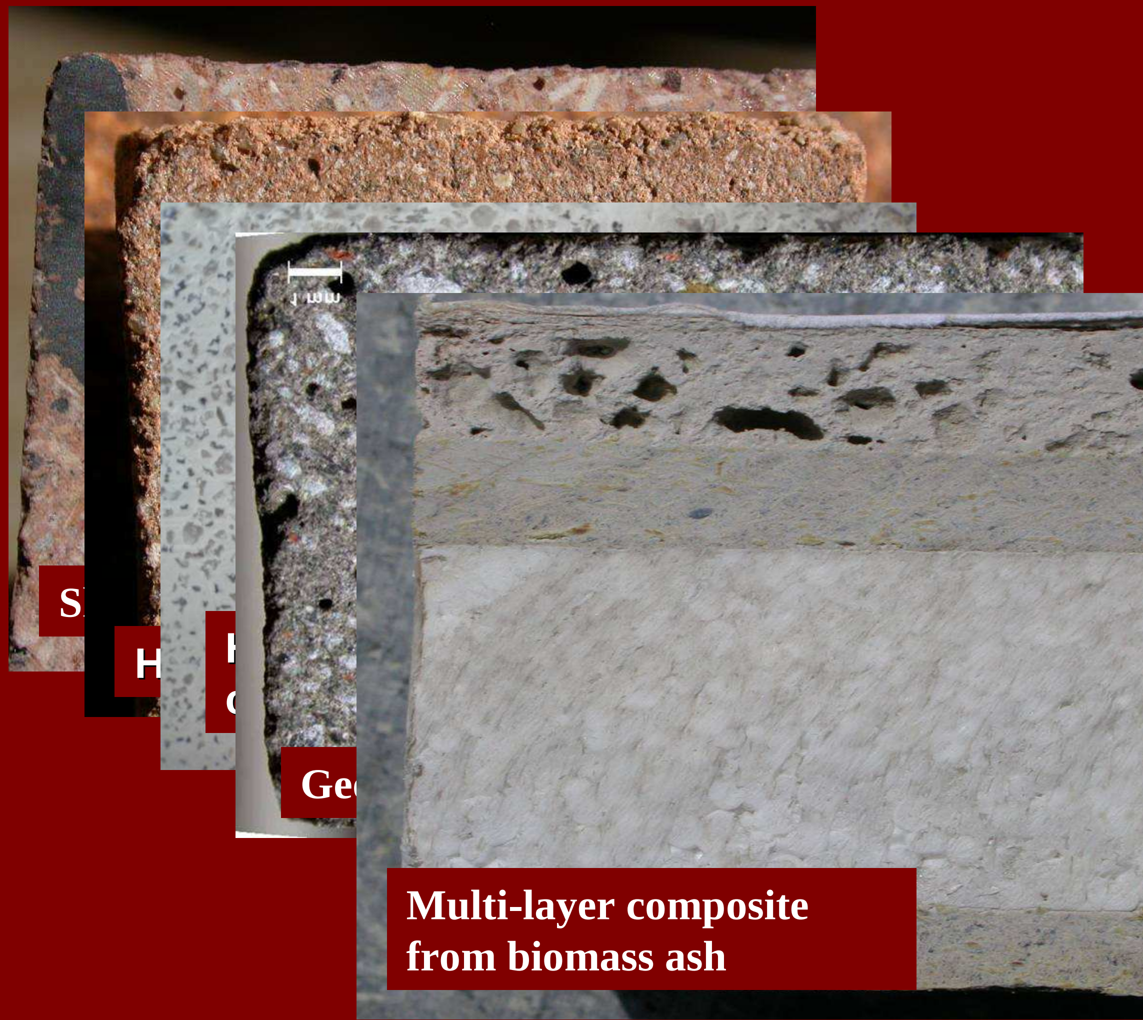
Inert additives

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

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 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