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The Urban infra revolution project
Zoom-in n 01
Project led by the city of Lappeenranta

Zoom-in title:
Do we need innovations?
Zoom-in on geopolymers composites

Table of contents

1. What is a geopolymer?

According to scientific knowledge, geopolymers are a group of materials defining as inorganic aluminosilicate polymers with specific composition and properties. They are obtained in the reaction of polycondensation of ortosilicans (comprising Si and Al atoms in their structure) with activated NaOH or KOH. However, it can be more easily defined as a 'green' alternative to cement. The final products are similar to concreate (Figure 1.), but the material is much more environmental friendly. It is estimated that the production of geopolymers create 4-8 times less carbon dioxide than cement production. The process needs twice less energy than the manufacture of Portland cement. Additionally, low emissions of CO_2, SO_2 and NOx [1], [2].

Figure 1. The examples of the products made from geopolymers[2].

Additionally, these materials have very high mechanical properties and excellent resistance to chemically aggressive environments, especially resistance to a variety of acids and salts[3]. They were initially developed as a fire resistant alternative to organic polymers. They have good fire resistance (up to 1000°C) and no emission of toxic fumes when heated[4].

Nowadays, the geopolymers are mainly applied in construction industry and they are the most promising alternative for Portland cement technology. The main motivators for work on this materials are growing environmental awareness and importance of development of sustainable construction materials for decreasing environmental impact of construction industry. Especially, it is worth to notice that:

- Present Portland cement technology has a lot of disadvantages such as: energy- and non-renewable natural resource-intensity, intolerable volume of CO_2 emissions and questionable durability, among others.

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[1] Palomo A., Krivenko P., Garcia-Lodeiro I., Kavalerova E., Maltseva O., Fernández-Jiménez A., 2014, *A review on alkaline activation: new analytical perspectives*, Mater. Construcc., vol. 64, Iss. 315, pp. 22.

[2] Łach M., Korniejenko K., Hebdowska-Krupa M., Mikuła J., 2018, *The Effect of Additives on the Properties of Metakaolin and Fly Ash Based Geopolymers*, MATEC Web of Conferences, vol. 06005, pp. 8.

[3] Alomayri T., Shaikh F.U.A., Low I. M., 2013, *Thermal and mechanical properties of cotton fabric-reinforced geopolymer composites,* „Journal of Material Science", vol. 48, p. 6746-6752.

[4] Vickers L., van Riessen A., Rickard W.D.A., 2015, *Fire-Resistant Geopolymers. Role of Fibres and Fillers to Enhance Thermal Properties*, Springer, Singapore - Heidelberg - New York - Dordrecht - London, pp. 129.

- These materials have very high mechanical properties. In the same time, have fire resistance (up to 1200 °C) and no emission of toxic fumes when heated.
- Excellent resistance to chemically aggressive environments, especially resistance to a variety of acids and salts.
- Effectiveness of the manufacturing process - low temperature. Simplicity of application: low shrinkage and adherence to materials such as concrete, steel, glass, ceramics.

2. Who invented geopolymers?

The name ‘geopolymer’ was first used by the French scientist Professor Joseph Davidovits in 1970. However, the earliest attempts to use geopolymers was back in 1930, when H. Kühl published a research on the setting of slag mixed with dry potassium solutions. Next, L. Chassevent and R. Feret subsequently defined the need to study slag as a cement component. In 1940, A.O. Purdon published the results of the first large-scale laboratory study on cements made with slag and live lime in the absence of portland clinker. Later, in 1957, V. Glukhovsky was the first to research the possibility of preparing low-calcium or even calcium-free cementitious materials, which he initially called “soil cements”, using clays and alkaline metal solutions. Depending on the composition of the starting materials, Glukhovsky classified these products under two main systems: Me2O Me2O3-SiO2 H2O and Me2O MeO Me2O3 SiO2 H2O. These early approaches were followed by any number of formulations using a wide spectrum of materials, including blast furnace slag, clay, aluminosilicate rocks and ash[5].

In 1981 J. Davidovits, published results obtained with blends of metakaolinite, limestone and dolomite, whose products he called geopolymers. That term has since been widely accepted for the group of materials associated with the [Me2O Me2O3 SiO2 H2O] system defined earlier by Glukhovsky. In 1986 P. Krivenko published the results of research on the principles governing the physical and mechanical properties of concretes prepared by alkali-activating slag. That same author, in conjunction with professors D. Roy and C. Shi, published the first book on alkaline activation in 2006. Glukhovsky proposed a general model to describe and explain the activation reactions in this type of materials, in which he identified three very distinct stages: (a) destruction-coagulation; (b) coagulation-condensation; and (c) condensation-crystallisation[6].

Nevertheless, the name ‘geopolymer’ was first used by Professor Joseph Davidovits; he emphasizeD the importance of specific internal construction this material as 3D network of mineral molecules linked with co-valent bonds (Figure 2.).

[5] Palomo A., Krivenko P., Garcia-Lodeiro I., Kavalerova E., Maltseva O., Fernández-Jiménez A., 2014, *A review on alkaline activation: new analytical perspectives*, Mater. Construcc., vol. 64, Iss. 315, pp. 22.
[6] Ibidem.

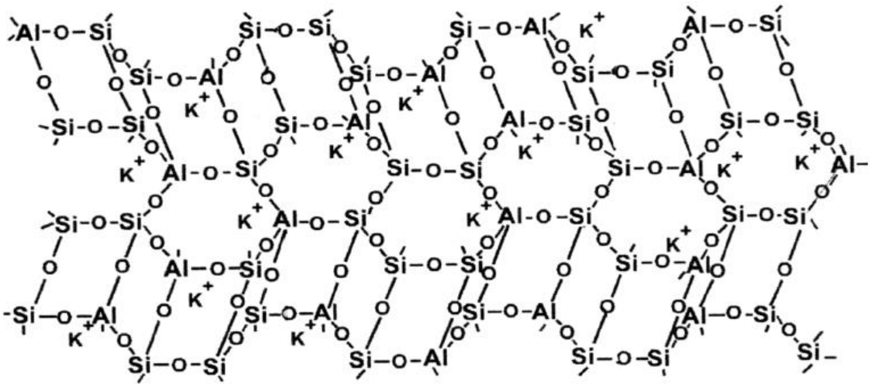

Figure 2. Model of geopolymer structure[7]

3. How we may produce them?

The process of synthesis of geopolymer required binding material and activator. The most popular binding materials are[8]**:**

- kaolinite (metakaolin)
- calcined clays,
- industrial waste and by-products (e.g. ashes, slag, waste glass, red mud, mine tailings (different eg. copper, vanadium), gauges etc.
- many other natural and artificial silicoaluminates (e.g. zeolite, pure Al2O3–2SiO2 powder,
- magnesium-containing minerals.

The most popular activators alkali reactant is soluble alkali metal based on sodium or potassium. They include alkali silicates, hydroxides, carbonates and other addition such as sodium aluminates or cement kiln dust. The most commonly used alkaline reactant solution is a mixture of hydroxides (NaOH or KOH) and silicates solution (Na2SiO3 or K2SiO3). Nowadays, the trials with acid based geopolymers are being developed. The general scheme for the production process is presented in Figure 3.

[7] Davidovits J., 1994, *Geopolimers: Man-Made Rock geosynthesis and the resulting development of very early strength cement*, Journal of Materials Education, vol. 16, p. 91 – 139.

[8] Yun-Ming L., Cheng-Yong H., Bakri M.M. Al, Hussin K., 2016, *Structure and properties of clay-based geopolymer cements: A review*, Progress in Materials Science, 83, p. 595-629.

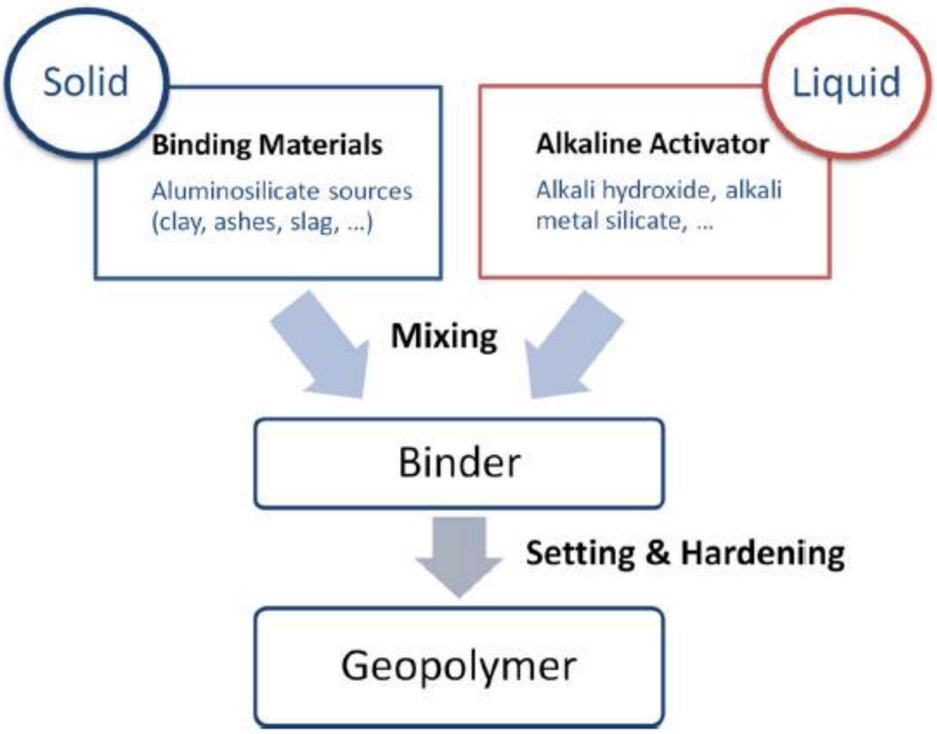

Figure 3. Scheme of geopolimerization process[9]

For the proper chemical reaction sutible proportion of ingredients are required. Geopolymers properties are dependend on diffrent indicators, the most common values, based on literature, are presented in the Table 1.

Table 1. Indicators between particular ingredients

Indicator	Values
SiO_2/Al_2O_3	3,5 – 4,5
Na_2O/SiO_2	0,095 – 0,12
H_2O/Na_2O	10 – 14
W/S (water/solid)	0,15 – 0,24
Water glass/r-r NaOH	0,4 – 2,5
Molar ratio r-r NaOH	6 - 16

The manufacturing of geopolymers usually required temperature of processing between 60 and 80°C. However the manufacturing in ambient temperature, such as 20°C, is also possible. In lower temperature, a longer time for receiving reasonable mechanical properties is required. In case of manufacturing in higher temperature the products are ready after 4h (because of high value of early stage mechanical properties) and then it is possible demoulding the final product. However, the standard time of curing for the materials is 28 days when their receive full values of mechanical properties.

[9] Ibidem

4. How do we want to do them in the project?

One of the expected result of the Urban Infra Revolution project is to design new materials for additive manufacturing, materials with tailored properties that are environmentally friendly and cost effective. The project will demonstrate the ability of new materials – geopolymers and processes to achieve finished components for construction industry with reduced life cycle costs. These composites should:

- close the loop of construction material;
- be applicable for extreme (arctic) weather conditions;
- be reinforced with bio-fibres;
- be based on local industry wastes.

The material for the project will be a composite based on geopolymer matrix with fibre reinforcement. In this case, the most promising matrix materials are side streams and recycled materials used as raw materials to avoid the use of virgin materials. In the project, there has been carefully investigated more than 20 raw materials (ashes, green liquor dregs, tailings, construction waste) and they are applied as a part of geopolymer composites (Figure 4). Some promising recipes have been developed. The materials based mainly on fly ashes form bio-mass combustion (fly ashes), including paper manufacturing and side streams from mining industry. The main problem was a high amount of calcium that happened very quick process of material bounding (even during mixing process).

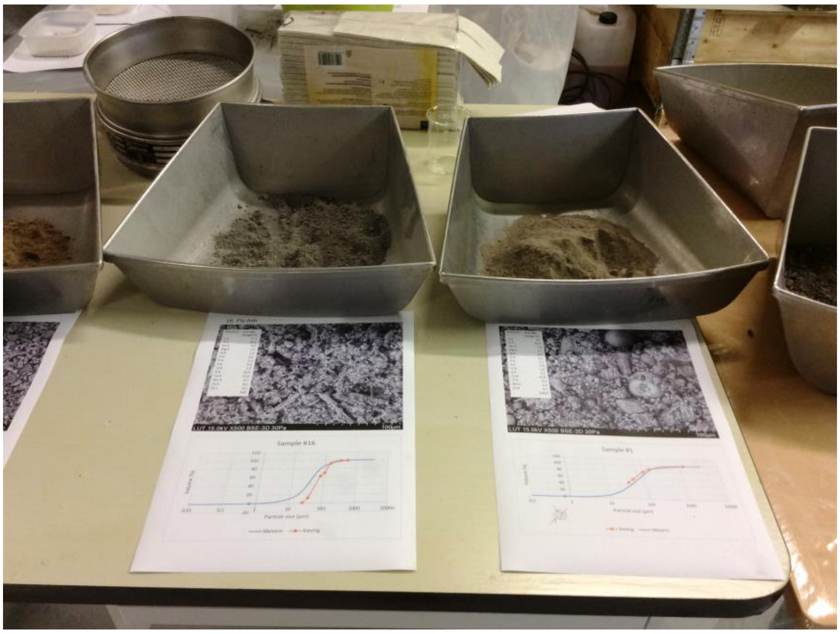

Figure 4. The raw materials investigated in the project.

Additionally, the project takes into consideration the challenge connected with bio-fibres addition for the reinforcement the composites. Currently, is the bio-composites are one of the most important research area. The improvement of the mechanical properties, by reinforcing the matrix through bio-fibres addition is beneficial form the environmental point of view[10]. The replacement of the synthetic

[10] Korniejenko K., Łach M., Hebdowska-Krupa M., Mikuła J., 2018, *The mechanical properties of flax and hemp fibres reinforced geopolymer composites*, IOP Conference Series: Materials Science and Engineering, vol 379, pp. 9.

fibres with their natural counterparts reduces significantly the environmental impact (closing important life cycles, including CO_2). The natural fibres have also other features such as: low cost of production, low density, they are renewable in short time, non-toxic, and easy to process[11]. It is also one of the most important innovative aspects in the project.

5. Why do we want to develop geopolymers?

The project is a response for market and society needs, especially in the area of development technologies for circular economy. The main challenge is not only the development of zero-waste technology of 3D printing, but also the use as a raw material of waste products, aiming at the production of prototype solutions for urban architecture. Cities in Europe are in reformation due to urbanization and climate change. Novel space usage, multifunctionality of the structures and material resistance in rapidly changing climate conditions are in demand. As the amount of construction increases in the cities, also the amount of cement originated CO_2 emission increases (being 5.2 billion ton in 2015). According to calculations it is nearly 10% of all human CO_2 emissions. The project aims to develop procedures, technologies and business models for practical application of side streams. The project will help convert unutilized side streams into sustainable, high-quality, low in CO_2 materials, with improved mechanical properties.

The need of developing new eco-friendly materials is a results for planned outcomes. The outcomes contribute directly to the ambitious goal on carbon free and waste free cities by reduced amount of unutilised waste from local industries and lower CO_2 emissions. The project aims are holistic solutions for developing climate change adaptation and mitigation that enhance the storage of carbon in process of raw material sourcing, manufacturing, transportation, installation and assembly. The project allows to introduce the circle economy through closing the loop with 3D printable, recyclable geopolymer composites made of side-streams. The project helps the Lappeenranta to significantly reduce CO_2 emissions. The main goal is 80% reduction of CO_2 emissions from 2007 level to the target for 2030 and completely eliminate waste is the target for 2050.

The project emphasizes on new products by a functionalized approach that will have strong societal and environmental impact. More important social and environmental benefits from the implementation of the project results will include in particular:

- Energy efficiency – lower energy consumption in comparison with cementitious materials, especially due to lower temperature of manufacturing.
- Reduction of carbon foot print - geopolymers during production emit much lower greenhouse gases compering to traditional construction materials such as Portland cement. It is estimated that the production of geopolymers produce 4–8 times less carbon dioxide than cement production, and in the same process the use of energy is limited (2–3 times).
- Waste reduction – manufacturing without waste.
- Circular economy – possibilities of using for manufacturing waste products as a raw materials such as fly ashes or clay bricks.

[11] Natali A., Manzi S., Bignozzi M.C., 2011, *Novel fiber-reinforced composite materials based on sustainable geopolymer matrix*, Procedia Engineering, vol. 21, p. 1124-1131.

This project strives for high quality, multifunctional, industrial scale urban construction in extreme weather areas. It wants to bring the production close to the building site, use local raw materials and close the material loop in order to diminish the CO_2 emissions of urban building and enhance zero waste arctic cities.

6. Where we may use geopolymers?

Thanks to the geopolymers properties such as chemical and thermal resistance and excellent mechanical properties increasing the use of their economic importance is growing. Currently, these materials are used mainly in construction industry for production of construction materials such as bricks, pavements, fire-resistant wood panels, sandwich panels and walls and energy efficient ceramic tile. They could be also used for the industry, as a material for various applications, especially in areas where the heat- and fire resistant are required and in particular, as a construction material used for power station, heat shields for space shuttle, as well as fire barriers. Another potential application is as a protective coating material (e.g. for various types of steel), especially against corrosion, for example moulds in aluminium foundries, an off-shore infrastructure (against salt water). Important area of implementation can be also emergency repair runways. Some successful trials has been made also with using geopolimers as a material for chemical immobilization — an environment-neutral matrix in which toxic waste, including radioactive substances, are stored for safe inactivation.

In comparison to traditional building materials (such as concrete), geopolymers have many advantages. They can operate under normal ambient conditions (which are environmentally friendly alternative), and in extreme conditions (in which traditional materials wear out quickly and cannot be used at all). An important factor in the growth of interest geopolymers as a new material is also a growing public awareness of the need to protect the environment. At the same time, these materials behave like or obtain better properties than conventional materials such as cements, especially[12]:

- High initial strength, wherein the standard Portland cement concretes exhibit a compressive strength of between 30 MPa - 60 MPa, and the strength of geopolymers reach up to 100 MPa.
- Reduced shrinkage and low thermal conductivity - high dimensional stability.
- Good fire resistance (up to 1000 ° C) and no emission of toxic fumes when heated.
- High level of resistance to a variety of acids and salts.
- Good resistance to abrasion, especially when mixed with teflon (PTFE) as a filler.
- Adherence to the new and old concrete, steel, glass, ceramics.
- A high capacity for mapping the surface patterns of amplified form.
- Corrosion resistance in geopolimers with steel addition (reinforcement) and a high degree of adhesion geopolimers to steel.
- Resistance to atmospheric conditions.
- Availability of raw materials and lower costs, with the possibility geopolimers material production from waste materials such as fly ash from thermal power plants and power plants.
- Reduced energy consumption in the manufacturing process (environment friendly).
- Possibility of hazardous waste immobilization by shutting them in geopolimers composites.

[12] Ibidem

7. Has anyone used them yet?

The some small application has been introduce in Europe. One of them in small scale is ”sensoric garden” in Cracow, Poland, where the elements of small architecture such as pots and sitting places were manufactured from geopolymers at Cracow University of Technology (Figure 5).

Figure 5. Some elements for sensoric garden in Cracow made from geopolymer concrete

The application in large scale is possible to find in Australia. The first public building with structural geopolymer concrete was built in 2013 in Australia[13]. Queensland’s University GCI building with 3 suspended floors made from structural geopolymer concrete (Figure 6 and 7).

Figure 6. Queensland’s University GCI building

[13] https://www.geopolymer.org/news/worlds-first-public-building-with-structural-geopolymer-concrete/

Figure 7. Queensland's University GCI building – cellings/floor (geopolymer cement based on fly ash)

The other application is the greenest airport in the world Toowoomba Wellcamp airport[14]. The main elements of the airport has been produced based on geopolymer concrete (Figure 8).

[14] https://www.wagner.com.au/main/our-projects/efc-geopolymer-pavements-in-wellcamp-airport

Figure 8. Toowoomba Wellcamp airport
Source : https://www.wagner.com.au/main/our-projects/efc-geopolymer-pavements-in-wellcamp-airport

In case of using geopolymers for additive manufacturing technology, still, there is not successful implementation in this area in industrial scale.

8. What are we planning to use in the project?

The project's main implementation are new innovative products and new industrial scale technology that enhance the local industry business and accelerate the employment possibilities in circular economy. Developed materials and technology improve the safety of construction areas and enhance construction industry sustainability and productivity. The Industrial symbiosis generated, adds bilateral value to project partners and local construction industry, creating improved opportunity to operate in South Karelia region, which in turns affects positively the vitality of respected urban areas. Aesthetic urban scenery upgrades the living convenience in the city, whereas multifunctional and technically improved urban structures strive for improving the citizen welfare in the city, by a holistic approach that enables, for example, better noise control, more versatile urban space usage and new possibilities for outdoor recreation and light traffic in extreme conditions. The exemplary application in this area are:

- Small architecture elements (Figure 9),
- Elements for skate parks (Figure 10),
- Sculptures / miniatures for historical place (Figure 11).

Figure 9. Small architecture elements
Source: https://www.uia-initiative.eu/en/news-events/citizens-ideas-how-use-new-circulative-sidestream-based-construction-material

Figure 10. Elements for skateparks
Source: https://www.uia-initiative.eu/en/news-events/citizens-ideas-how-use-new-circulative-sidestream-based-construction-material

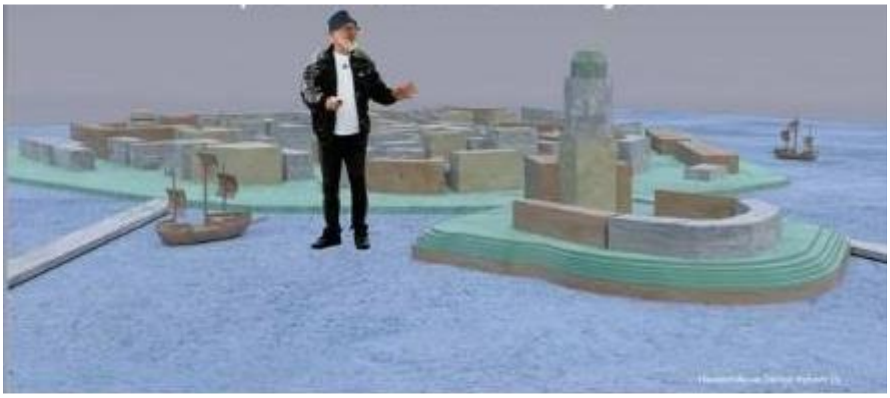

Figure 11. Sculptures / miniatures for historical place
Source: https://www.uia-initiative.eu/en/news-events/citizens-ideas-how-use-new-circulative-sidestream-based-construction-material

9. …so, why are not they popular?

The most important challenge in the application geopolymers in EU, as well as in the project are legislation rules. The solution represents new construction materials which existing product standardization and regulations cannot be directly applied. The main barrier is the lack of proper regulations and standards, especially in EU and The USA. The applications required additional material and product property testing and preparing appropriate product acceptance procedure. Revolutionary materials and construction designs may also face lack of trust from the regulated, conservative construction industry.

The other technical problem is small amount of research connected with durability, especially long term durability data. Because of that some additional research are required. The other limitation for wide use geopolymers is also a common problem with efflorescence caused by excess sodium oxide remaining unreacted in materials. Geopolymers are created by reaction between alkaline solutions and solid aluminiosilicates. The activation process required high pH. In some cases unreacted sodium oxide create white efflorescence on the surface – it is sodium carbonate heptahydrate $Na_2CO_3 \cdot 7H_2O$. It could be a large problem, because it decreases not only aesthetic value for the final products, but also mechanical properties of the material. However the proper design of manufacturing process could eliminate this barrier.

Another potential barrier is also using as a raw materials the wastes form industrial processes. The main technical problem is connected with changes of raw material in case of their production form wastes. It required the introduction of additional quality procedures in the process. Also, the idea of using side streams in central city constructions may awake concerns about health and safety and environmental safety in public. This presumable resistance is overcome by the dialogue with authorities and by creating transparent product acceptance procedure for those product including the physical and chemical properties of the material.

Conclusions

One of the expected result of the project is to design new materials for additive manufacturing, materials with tailored properties that are environmentally friendly and cost effective. The project will demonstrate the ability of new materials – geopolymers and processes to achieve finished components for construction industry with reduced life cycle costs. Finland is one of the leading countries in the world in micro- and nano-scale cellulose composites. This technology is transferred to serve inorganic material technology and building industry. The innovation itself is potentially the first manufacturing method demonstrating fully closed loop construction: on-site built, local waste based and fully recyclable construction materials. The designed materials should:

- close the loop of construction material;
- be applicable for extreme (arctic) weather conditions;
- be reinforced with bio-fibres;
- be based on local industry wastes is developed.