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Physical Properties of Geopolymers Made from Mineral Waste

Gotfrids Noviks
Institute of Engineering Sciences
Rezekne Academy of Technologies,
Rezekne, Latvia
Gotfrids.Noviks@rta.lv

***Abstrac*t. Geopolymer is an alumino-silicon gel consisting of tetrahedral SiO 4 and AlO 4 sections, polycondensed in a spatial structure as a result of the reaction between aluminosilicates and an alkaline activator.The report is a part of the complex research plan for geopolymers, in which information is given about the experimental results in the preparation of geopolymers from natural and man-made mineral components characteristic of Latvia (clay, sand, wood ash, brick waste).**

The aim of the study was to find out the dependence of the geopolymer formation process on the composition of the reacting components at constant exposure factors. Sodium alkali solution and sodium silicate was used in the experiments. The raw materials used are red and gray clay, sand, wood ash.

The composition of the clay, ash and sand composition was changed with an interval of twenty percent. The obtained geopolymer samples were subjected to physical and technical tests. The compositions that are perspective in terms of properties in the studied modes of exposure have been determined.

Keywords: Geopolymer, mineral waste, alkaly activators, mechanical properties of minerals.

I. INTRODUCTION

Geopolymers according to J. Davidovits [1] are synthetic alkali aluminosilicates - or inorganic polymers , which are formed as a result of the reaction between aluminum and silicon-containing hard minerals and high-concentration alkalis (NaOH, KOH) or acids (H_3PO_4) [2] .The spatial structure of geopolymers consists of SiO_4^{4-} and AlO_4^{5-} tetrahedra, which are mutually combined with oxygen molecules. Thanks to such a structure, they acquire many positive mechanical properties - strength, water resistance, heat resistance..., as a result of which they have become a perspective material in construction and have potential successfully compete with cement [3]. The original geopolymers were made of metakaolin[4], but the researches carried out later, proved that a very wide range of different minerals can serve as raw materials for the geopolymer, including a whole series of man-made mineral waste. Studies have been conducted in which were proved that mineral waste such as fly ash of coal, blast furnace slug and sludge, silica fume, mining waste , ore enrichment tailings and others may be used in the production of geopolymers[5,6,7,8].

If also to take into account the fact that the production of geopolymers does not require firing at high temperatures, which is typical in the cement production process and thus drastically reduces the impact on the environment (including carbon dioxide emissions in the atmosphere) [9], it is understandable that there is a great interest in in exploring possibilities of the efficient production of this product. In perspective, geopolymer can replace the use of cement in various spheres.

Studies have been conducted for their use in road surfaces, water tanks, building construction elements, tile production, 3D printing, etc.[10,11,12].

However, the competitiveness of geopolymers with Portland cement has not yet been ensured. Its use is episodic but impressive and promising(Brisbane West Wellcamp Airport in Toowoomba,in Australia,the Global Change Institute at the University of Queensland)[13,14].

Circumstances that do not allow to expand the use of geopolymers are related, first of all, to raw materials. It can not rely only on metakaolin. It is necessary to use a wider range of raw materials. Emphasis is placed on the use of mineral waste, but their composition is diverse and it requires optimizing the parameters of the production process every time. The mechanisms of the polymerization process are explained in different ways, but nevertheless they are generalized to a wide range of

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minerals. [15,16] . There are problems with efflorescence also [17] .

That is why most researches are now conducted using the trial-and-error approach in their investigations. It is necessary to develop the relevant standards for the relevant compositions of raw materials.

Studies have shown that the best results are achieved when the raw materials are fine milled.[18] But the grinding of hard mineral materials is a very energy-intensive process - the specific energies can be as high as 60 kWh/t. [19], which immediately makes the final product more expensive.

The use of activators – alkali and silicates in the process also makes a big contribution to the increase in the price of the final product.The cost of activators often exceed 50%of total expenses [20].

In addition, sodium silicate is a material in high demand in other industrial sectors as well, and this limits the possibilities of using it in large-scale geopolymer production.

The properties and structure of the manufactured geopolymer also depend on the conditions under which the material is compacted and hardened.

Until now, it is not clear what geopolymer curing regimes are optimal - curing temperature and time, atmospheric humidity, etc., because different authors give different information about them.[21]

In our research, as the first task, we decided to investigate the possibilities of geopolymer formation under the same process conditions from charachateristic for Latvia raw materials - technogenic and natural mineral resources - wood ash, clay and sand taken in different proportions. In order to evaluate the principial possibilities of creating a geopolymer with lower energy consumption, the process conditions were those selected when the primary treatment of substances has been reduced to a minimum (there is no crushing,milling, only sieving, grain sizes 0.25, 0.1 mm, curing takes place at normal atmospheric temperature without heating.

II. MATERIALS AND METHODS.

In accordance with the stated goals of geopolymer research, mineral resources widely represented in Latvia were used as raw materials for the preparation of samples, such as natural ones - clay and sand, as well as a technogenic mineral waste - wood ash.

Clay was obtained from the largest Kuprava clay deposit in Latvia, Katlešu suite. The Kuprava clay reserves are significant - 16 million m^3, and the forecasted reserves exceed several billion m^3. At the same time, mining of this clay is currently not taking place. Therefore, it is useful to consider all possible options for the inclusion of this clay in the Latvian economy. One of them is to analyze the possibilities of using them in the production of geopolymers.

The clay of the Katlesi suite in the Kuprava deposit consists mainly of clay minerals illite and kaolin. The content of illite is predominant. The other minerals are quartz, dolomite, calcite and minerals of the feldspar [22](Fig. 1).

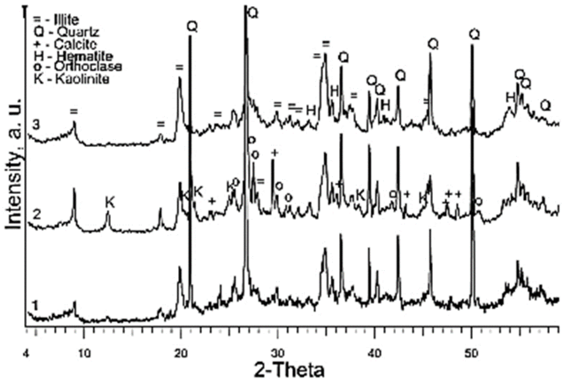

Fig.1. Kuprava clay deposit clay mineral composition X-ray diagram . 1- Kuprava district clay , 2- Mednieki deposit clay , 3- South section of quarry clay.

The chemical composition of Kuprava clay is characterized by a high content of silicon oxides SiO_2 (50-43%) and aluminum oxides Al_2O_3 (14-17%). The content of calcium oxide in clay is quite low and does not exceed 5% [22](table 1).

TABLE1 Chemical composition of Kuprava clay

Clay	*SiO_2*	*Al_2O_3*	*Fe_2O_3*	*K_2O*	*CaO*	*MgO*	*TiO_2*
White	46,8-50,0	14,6-16,4	5,1-5,6	3,6-5,6	2,2-3,0	2,2	NA
Brown	43,8-45,4	8,3-10,0	8,3-9,9	4,5-5,5	0,8-4,8	1,6-2,4	0,98

Sand is also one of the most common useful mineral resources in Latvia.[23]

Sand with a quartz content of 60-70% was used in the study. The fraction with a grain size < 0.25 mm was sieved for the preparation of geopolymer samples. Some samples were prepared of sands witn a grain size less than 0.1. In the studies related to the production of geopolymers, mostly coal ash and the finest part of it - fly-ash was used as one of the mineral waste components. This kind of ash is not decisive in Latvia, due to the very low share of the use of hard coal in the energy sector. The main amounts of ash are the bottom ash of furnaces formed as a result of burning wood and, to a lesser extent, other types of biomass. The wood ash amounts will increase gradually in nearest years due to using pellets and chipped firewood in the state energy production sector.

Therefore, wood ash (a mixture of coniferous and deciduous trees) was used in our experiments. Ash density is determined to be 1.74-1.82 g/cm^3, porosity in the embankment is 68-72.5%, loss on ignition is 6.9-7.8%.The analysis of wood ash showed that their chemical composition varies within quite wide limits and is different from the composition of coal ash [24] (table 2). Wood ash has a much lower content of silicon and aluminum oxides compared to coal ash, but the content and the ratio of these components are determinants, as found in many studies [25,26,27,28] for the successful development of the geopolymerization process.

TABLE 2 Chemical composition of ash in terms of oxides

Oxide	*Wood ash content, wt %*	*Coal ash content, wt %*	*Sewage sludge ash, wt%*
SiO_2	20-60	40-70	27
Al_2O_3	0,1-12	14-35	14,4
Fe_2O_3	1,5-5,3	2-20	8,2
Fe_3O_4	-	2-14	-
MgO	0,3-5	1-10	3,2
Na_2O	0, 1-0,8	0,1-5	0,5
CaO	0,8-43	0,5-30	21

NaOH solution with a concentration of 12M and industrially produced sodium silicate with a density of 1.39g/cm^3 and a ratio of SiO_2:Na_2O=3:1 (SiO2- 28.1%, Na_2O- 9.6%) were used as process activators. Based on literature data [29] and our test measurements, the mixture of activators was taken as the closest to the optimum in the ratio Na_2SiO_3:NaOH=3:1. This relationship remained constant throughout the experiments.

In the previous test experiments, the ratio of solid components GS to the total amount of activators GA of the activator solution was also evaluated as the most optimal. For further experiments, this ratio was assumed as GS:GA = 3:1. Water from 2 to 8% of the total mass of the mixture was added only to some samples.

Mixtures of solid components were made in three groups of experiments : 1)only one component (sand, ash, clay); 2) a mixture of two components; 3) different proportions of all three components.

The process of making the samples was as follows.

At least one day in advance, the activator was prepared - a solution of a mixture of sodium silicate and sodium alkali. The solid components were weighed and thoroughly mixed in the appropriate proportions. An activator (Na_2SiO_3 +NaOH) was added to the mixture and the whole mass was intensively stirred for 5-7 minutes. In the next stage, the dissolved material was placed in plastic cylindrical forms (d=28mm, h=28mm), compacted with vibration and left to harden at ambient temperature for 5 days. After that, they were removed from the containers and left for further curing for 10 days. After this period, the samples were subjected to measurements. Their density was measured by hydrostatic weighing method according to standard ASTM D7263 – 21[30], moisture capacity and water resistance were determined by immersing them in water for 5 days according to standard methods[31]. Dry samples were subjected to strength determination according to standard test methods [32].

III. RESULTS AND DISCUSSION

The testing results of the obtained geopolymer samples are summarized in the table 3 and figure 2.

TABLE 3 Mechanical properties of produced geopolymer samples

Sample Nr	*Composition Sand:Clay: Ash (%)*	*Density,ρ, g/cm^3*	*Moisture capacity ,w,%, water resistance*	*Compressive strength,σ, MPa*
1	100:0:0	1.98	Disintegrate	0.10
2	60:40:0	2.30	Disintegrate	7,8
3	33:33:34	1.72	12,8	4.17
5	80:20:0	2.18	Disintegrate	
6	0:50:50	1.88	13.7	
7	50:0:50	2.00	Disintegrate	
8	20:50:30	1.99	Disintegrate	4.54
9	60:20:20	1.62	Disintegrate	
10	25:25:50	1.84	5,6	5.70
11	40:40:20	1.87	Disintegrate	1.70
12	40:30:30	1.84	Disintegrate	2.30
13	0:50:50	2.08	20.8	2.60
14	0:0:100	1.59	16.5	2,20
15	0:100:0	2.97	Disintegrate	7,15
17	75:10:15	1.80	Disintegrate	2.35
18	10:10:80	1.65	13.6	2.30
X	0:31:36+b1+b2	1.97	16.3	7.53

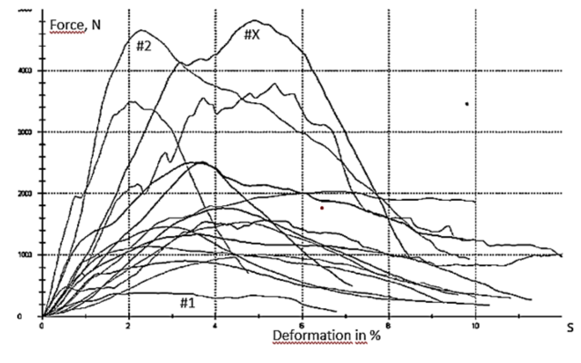

Fig.2. Stress-deformation curves for studyed samples.

The analysis of the produced geopolymer samples showed that the polymerization process strongly depends on the composition of the components.

Water resistance tests showed that many samples after 5 days curing did not obtain water resistance – they disintegrate in water partly or completely.

Compression tests after 20 days curing showed that strength of obtained samples did not achieve sufficient strength – in the most cases it was between 2- 4 MPa.

Thus, comparing single-component samples, it was found that samples made from wood ash are best subjected to polymerization.

Ash-based geopolymers are characterized by a mostly amorphous structure, which means a full-fledged polymerization process, they have water resistance - no changes in properties were observed after 10 days in water, the average moisture content is in the range of 15-16%, volumetric weight 1.55-1.6 g.cm $^{-3}$,conpressive strength 2 MPa and more (Fig.3,sample14)

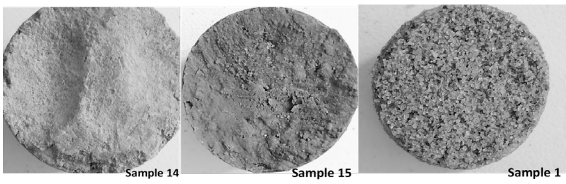

Fig.3. Single-component samples.

Samples made of 100% clay, judging by the structure, are only partially amorphized, water resistance is not sufficient - 10 days of exposure to water led to partial collapse - mass loss is more than 50% , but tests on compressive strength showed relatively higher values - more than 7MPa (Fig.3, sample15).

Samples made only from sand are the least susceptible to the polymerization process - the produced samples practically consist of quartz grains, the bonds between which are weak and as a result of exposure to water they disintegrate after only one day. Their density is 1.98 g.cm^{-3} , compressive strength very low – does not exceed 1 MPa. (Fig.3 ,sample1).

Two-component composition samples with a 1:1 ratio of components by mass (Fig.4) show that their degree of polymerization is also related to the presence of sand in the composition.

Geopolymer from sand and ash is crystalline in structure, density is 2g/cm $^{-3}$, disintegrates in water. (Fig.4, sample 7).

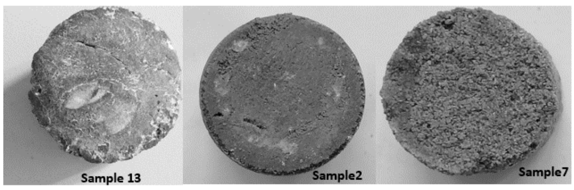

Fig.4 . Two- component samples.

Contrary, the samples whose raw material was clay and ash (fig.4, sample13) showed full polymerization, characterized by a homogeneous dense structure and water resistance. Moisture content from 14 to 20%wt depending on the geopolymer curing conditions. Density 1.9-2.1 g.cm-3,compressive strength – 2.6 MPa.

A composite of equal amounts of clay and sand (Fig.4, sample 2) shows that the structure is denser and more uniform, but the samples are not water resistant. An at the same time their compressive strength turned out to be larger if compared with other samples.(see table3).

Samples made from a mixture of all three components in different proportions showed that the presence of sand more than 25% by mass has a negative effect on the polymerization process, does not ensure water resistance of the geopolymer. However, the presence of ash in the mixture has a beneficial effect on the polymerization process, especially if its content is more than 40%.(Fig.5,samples10 ,18)

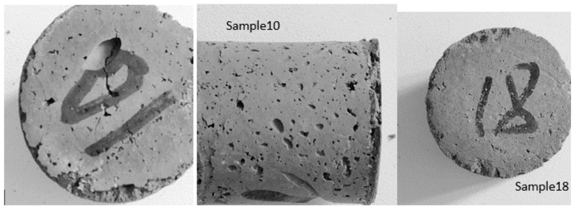

Fig.5. Three- component samples.

The samples obtained under these conditions are characterized by maximum water resistance, the moisture content is within 13-17%.

By summarizing all the experimental data, the optimal area of the composition of these three components (sand + ash + clay) can be determined in a triangle diagram with limits - the amount of sand does not exceed 30%, the amount of ash is greater than 40%, the clay content is up to 50%. (Fig.6). The results which correlate with our experiments were obtained in other works [6,7].

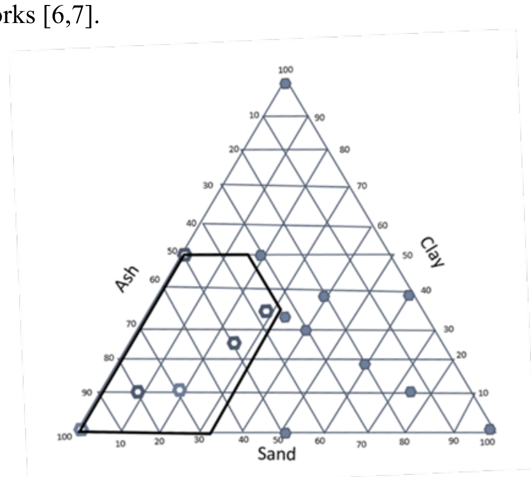

Fig.6. Triangle phase diagram: sand - clay - ash. The perspective area of the composite content is marked by the thick line.

Data from the literature [33]show that the water resistance at the normal curing temperature of the geopolymer mass is determined by the use of blast furnace slag as one of the components. In other cases, the increased curing temperature regime is required. Since in Latvia these slags are not available optimization of the composition and its curing conditions is required.

In addition to the examined series of geopolymer samples, consisting of three components - clay, ash and sand, samples were made that also included waste from the construction process - ground fragments of clay bricks and silicate bricks (Fig.7.sample X , Table3).

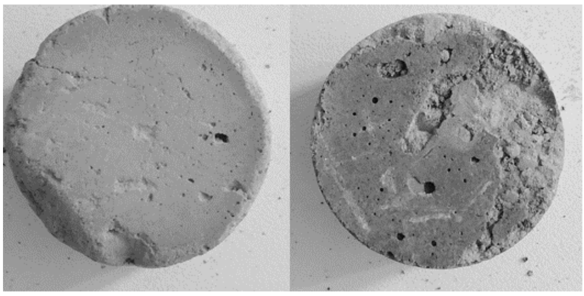

Fig.7. Sample X, prepared from clay, ash, sand and waste silicate and clay bricks.

These samples showed the highest strength and water resistance in this study. This indicates that supplementing the composition with recycled construction materials is a promising direction in the production of geopolymers and, therefore, in the inclusion of man-made waste in the economic cycle.

IV. CONCLUSIONS

The studies showed the principle possibility of obtaining geopolymers from man-made and natural mineral resources available in Latvia. Since the experiments were performed based on the minimum pretreatment of the raw materials, the desired strength of the geopolymer was not achieved, but the proportions of the composition of the geopolymer raw materials were determined, which are promising for further research. These proportions shown on the graph (Fig.6) is as follows: sand does not exceed 30%, the amount of ash is greater than 40%, the clay content is up to 50%.

Increasing the mechanical properties of geopolymers is possible:

- Expanding the composition of raw materials to include construction and demolition mineral waste;
- By increasing the reactivity of the components (chemical activity) by grinding them to particles of about 20-60 μm;
- Specifying the amount and concentration of activators corresponding to each composition of the composite;
- By carrying out the curing process at elevated temperature and humidity.

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