

## OBTAINING COMPOSITION OF GEOPOLYMERS (ALKALI ACTIVATED BINDERS) FROM LOCAL INDUSTRIAL WASTES

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### ABSTRACT

*The aim of the research is development of geopolymers – the new, knowledge-based, multi-functional materials with high performance, reduced environmental impact and adjustable to customer needs. Depending on selection of the raw material and processing conditions, geopolymers can exhibit a wide variety of properties and characteristics, including high compressive strength, low shrinkage, fast or slow setting, acid resistance, fire resistance and low thermal conductivity. Materials used in preparation of geopolymers are local industrial waste and by-products such as ashes obtained from burning grasses, glass powder recycled from lamp demercuration facility in Liepaja and calcined clay minerals. Raw materials were investigated and treated by using calcination and grinding methods to increase their activity. Mechanical and physical properties of obtained geopolymers were tested. A variety of results were observed. Depending on the used waste materials in geopolymer composition and curing conditions hardened geopolymer samples possessed either good compressive strength results and waterproof or marginally low compressive strength and weak waterproof.*

**Key words:** geopolymers, local industrial waste, construction material, compressive strength

### INTRODUCTION

Ordinary Portland cement is the most commonly used cementitious material nowadays. During production of one ton of cement 0.65-0.92 tons of CO<sub>2</sub> gasses are released in the atmosphere. This is a significant degree of pollution, which enhances greenhouse effect. To avoid further pollution and CO<sub>2</sub> emission, new cementitious materials are created (Davidovits, 2008; Juenger et al., 2010). Geopolymers are among the most efficient. Glukhovsky first introduced a general conceptual model for the alkali activation of the aluminosilicate materials in 1950s (Glukhovsky, 1959). However the term “geopolymer” was introduced by J. Davidovits (Davidovits, 1991) to describe mineral binders closely related to artificial zeolites. Development of geopolymers – a new generation of cementitious materials being an alternative to traditional cement and concretes through alkali activation of industrial waste is a relatively new area and research topic for the scientific community. The alkali activation of materials is a chemical process that ensures rapid transformation of some specific phases (partially or totally amorphous) into compact cemented frameworks. To obtain alkali-activated binder the source materials must be rich with alumina and silicate. Such elements are widely spread in different types of ashes, glass and clay minerals.

Development of geopolymer technology is in accordance with the requirements of sustainable development, because in this way significant

amounts of industrial waste materials are not only used as a secondary raw material, but are converted to a new product. Creation of a new material from different industrial by-products might result in reduced energy consumption, reduction of waste production, reduction of global CO<sub>2</sub> emissions, as well as in the reduction of exploitation of natural resources, which are commonly used for production of Portland cement. The production of geopolymers could reduce 80% of those CO<sub>2</sub> emissions, which are released during ordinary Portland cement production (Duxson et al., 2007; Gartner, 2004).

The aim of this work is to obtain geopolymer binder material with proper mechanical and physical properties from local industrial waste and by-products. In mix design either single by-product material like ashes or combination of waste materials are used in order to improve chemical composition and obtain higher mechanical properties. In this work six different geopolymer mortars have been created.

### MATERIALS AND METHODS

The materials used in geopolymer composition are mainly by-products and industrial wastes. The bottom ashes used in geopolymer compositions were taken from local heating plant furnaces. Wood bottom ashes and barley bottom ashes were tested as potential geopolymer compounding material. Ashes were ground in a planetary ball mill to obtain powder particle material, to ensure material homogeneity and enlarge specific surface area in

order to make material more reactive. Chemical compositions of ground bottom ashes were determined.

The other raw material used in investigations was taken from the local fluorescent lamps utilisation plant. Glass is rich with siliceous dioxide and it is an excellent source for amorphous siliceous in geopolymer composition. Glass from fluorescent lamps is not possible to recast in the traditional way due to unacceptable and toxic impurities. Landfill disposal of the glass waste is common solution until now. The utilisation of this type of glass as a raw material in geopolymer composition will make unequivocal positive impact to environment. Fluorescent lamp glass normally is roughly grounded in the plant during recycling process. Roughly grounded and additionally grounded glass was used in the investigations.

Another important component in geopolymers is alumina. Alumina is needed to form aluminosilicate, which is the compound that gives strength and other physical and mechanical properties to the obtained material.

Most common alumina containing material used in geopolymers is metakaolin. Since metakaolin is not the local raw material, calcined clay with low content of carbonates was used as alumina source in geopolymer composition. Calcined clay was obtained from producer of ceramic building materials JSC Lode or made in laboratory by treatment of clay in the furnace under 700°C for 3 hours.

In the experimental work activation solution (6M NaOH) was used.

### Chemical composition of raw materials

Preliminary investigation of chemical and mineralogical composition of geopolymer raw materials was carried out. Chemical analysis results

for ashes, waste glass and calcined clay are summarized in Table 1.

**Table 1**

Chemical composition of raw materials

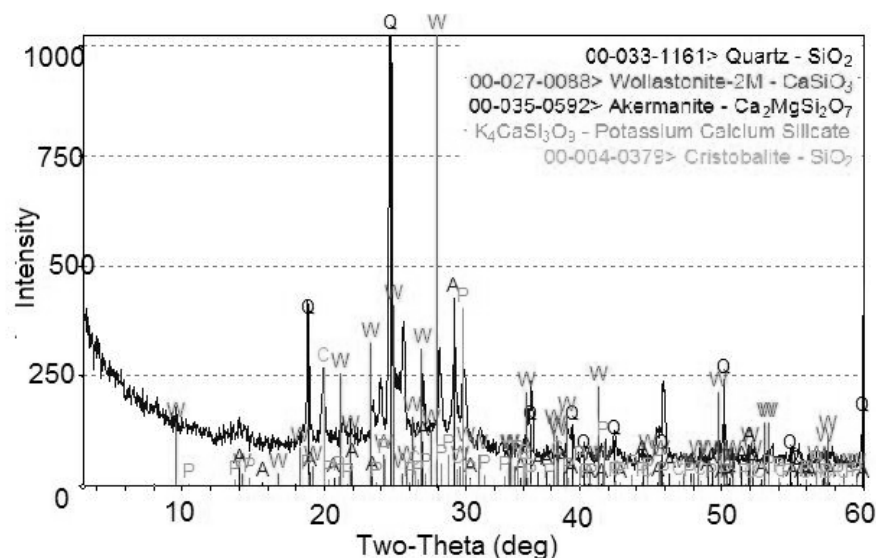
	Barley ash	Wood ash	Waste glass	Calcinated Clay
Loss of ignition	0.49	0.64	0.5	0.1
SiO <sub>2</sub>	66.07	59.92	74.25	68.41
CaO	6.06	19.89	2.09	0.91
MgO	1.68	2.32	0	1.41
Al <sub>2</sub> O <sub>3</sub>	5.38	4.3	1.65	14.01
Fe <sub>2</sub> O <sub>3</sub>	1.78	1.6	0.16	5.55
Na <sub>2</sub> O	0.24	0.37	3.82	0.29
K <sub>2</sub> O	7.14	3.59	0.93	3.48
B <sub>2</sub> O <sub>3</sub>	0	0	16.63	0

As it seen in the Table 1, materials used in geopolymer composition are rich with silica dioxide SiO<sub>2</sub> – from 59.92% to 74.25%. The other important element is Al<sub>2</sub>O<sub>3</sub>. Clay contains 14.01% of Al<sub>2</sub>O<sub>3</sub>, while ashes contain only 4.3-5.38% of Al<sub>2</sub>O<sub>3</sub>. Barley ashes contain the highest alkali content – 7.38% K<sub>2</sub>O+Na<sub>2</sub>O.

The geopolymerisation process involves the dissolution, migration and polymerization of Al and Si elements. The presence of cat ions (Na, K and Ca) in the composition is very important, because they provide balancing and catalytic properties (Luna et al., 2007)

The results of XRD analysis for wood ash are given in Figure 1.

As it is seen, wood ashes are very rich with crystalline quartz (SiO<sub>2</sub>). Also wollastonite (CaSiO<sub>3</sub>) and akermanite (Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>) are found as most common minerals. Small amount of potassium calcium silicate (K<sub>4</sub>CaSi<sub>3</sub>O<sub>3</sub>) as well as cristobalite (SiO<sub>2</sub>) were determined in the wood ash. Mineralogical composition of wood ashes corresponds to the results from chemical analysis.

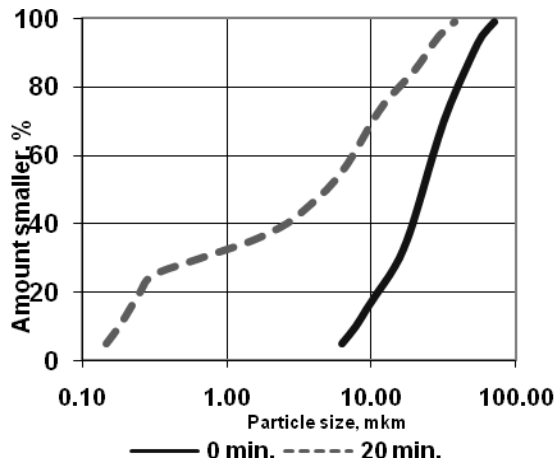


**Figure 1.** XRD analysis of wood ash.

### Grading analysis of raw materials

Particle size and particle size distribution of raw materials also was obtained. Materials used in geopolymer composition were finely ground in the planetary ball mill to improve the homogeneity and reactivity of them.

Barley ashes were ground for 4 minutes, but wood ashes were ground for 10 min. Particle size distribution of wood and barley ashes was smaller than 63µm.



**Figure 2.** Roughly ground waste glass and additionally ground waste glass particle size distribution curves.

Waste glass was already roughly ground during the recycling process. Part of glass was additionally ground for 20 min to enlarge fineness of glass particles and increase glass reactivity. The particle size distribution curves of the roughly ground waste glass and additionally ground waste glass are summarised in Figure 2.

Calcined clay particle size used in geopolymer composition was smaller than 0.315mm.

### Geopolymer composition

Different potential geopolymer compositions were created from alumina and silicate rich industrial waste materials and by-products. Proper chemical and mineralogical composition as well as particle size distribution is common requirements for raw materials used in the production of geopolymers.

The curing temperature of geopolymers is another important aspect. Geopolymerisation process is less active at the ambient temperature, but using higher curing temperature should accelerate it. In finally solid material can be marked with higher mechanical properties.

Six different geopolymer compositions were obtained and tested. Barley ash (BA) and wood ash (WA) were activated by adding 6M NaOH solution. Certain amount of NaOH solution was added to

ashes to achieve the optimal consistence of binder and to ensure proper moulding properties. The other two mixes were obtained from waste glass and calcined clay. The ratio of calcined clay and glass was kept constant at ratio 1:3. In the first mix the original roughly ground glass (ORG) was used, but in the second - additionally ground waste glass (AGW) was used. The last two mixes were combinations of both barley (BTG) or wood ashes (WTG) and calcined clay. Mix compositions are shown in Table 2.

**Table 2**

Geopolymer composition material ratios

Material	Material ratios in composition					
	WA	BA	OWG	AGW	BTG	WTG
Wood ash	1	-	-	-	-	1
Barley ash	-	1	-	-	3	-
Rough Ground Glass	-	-	1	-	-	-
Additionally ground glass	-	-	-	1	-	-
Teniside	-	-	3	3	1	3
Burned clay	-	-	-	-	-	-
6M NaOH	0.407	0.405	2.08	1.65	1.9	1.41

Mixed geopolymer binder mortar was cast in 40x40x160mm bar moulds and the curing conditions were kept constant at the two different temperature regimes: at ambient temperature of 20°C±2°C and 75°C for 24h to improve the process of geopolymerisation.

Physical and mechanical properties of hardened geopolymer mortar bars were tested. Mineralogical composition of specimens was determined by using X-ray diffraction spectroscopy, but scanning electron microscopy (SEM) was used to examine structure of obtained geopolymers.

### RESULTS

Samples, which were cured at elevated temperatures, were fully hardened after 24h at 75°C. Samples which were cured at ambient temperature after 24h were still soft and not solid. Samples were held in moulds for 72h to ensure mortar bar safe remoulding without damaging the sample.

It is important to note that some samples cured at elevated temperature showed high shrinkage (mix OWG) and minor cracks (WA). The reason of shrinking and cracking of specimens should be resulted by thermal shock or rapid reaction progress.

### Water absorption

Water absorption of geopolymer specimens hardened in the different temperatures was tested. Water absorption of geopolymer specimens is shown in Table 3.

**Table 3**

Geopolymer water absorption

Composition	Water absorption, %	
	20°C	75°C
WA	13.2	12.7
BA	12.4	11.9
OWG	9.7	7.9
AGW	9.5	8.2
BTG	12.5	12.4
WTG	11.7	11.9

Specimens cured at temperature 75°C demonstrated lower water absorption compare with specimens cured at the ambient temperature. It is explained by geopolymerisation process, which is more active at elevated temperature.

The specimens made from waste glass and calcined clay (AGW and OWG), cured at elevated temperature, demonstrated lowest water absorption 8.2% and 7.9% respectively, but specimens with same composition, cured at ambient temperature showed water absorption 9.5% and 9.7%. Geopolymers containing ashes showed the highest water absorption ranging between 11.9-13.2%. Similar results showed specimens made from ashes and calcined clay (11.4-12.5%).

### Compression strength

Compression strength of hardened geopolymer samples was determined. Results of compression strength are given in Figure 3. As seen in the Figure 3, the curing temperature is the key determinant factor, which divides the samples into two large groups with diverse compressive strength. Samples cured at 75°C for 24h show from 6.46-

16.36 MPa, i.e., better compressive strength results than the samples cured at ambient temperatures. The elevated temperature provides reaction or geopolymerisation process and at higher temperatures geopolymers originates much faster.

The specimens cured at ambient temperature provided compression strength from 2.7-6.8MPa. The best results were demonstrated by the geopolymers with composition OWG and AWG (6.6 and 6.8 MPa), but geopolymers which are containing ashes showed on average a 50% less compressive strength results compared to the samples with glass and calcined clay.

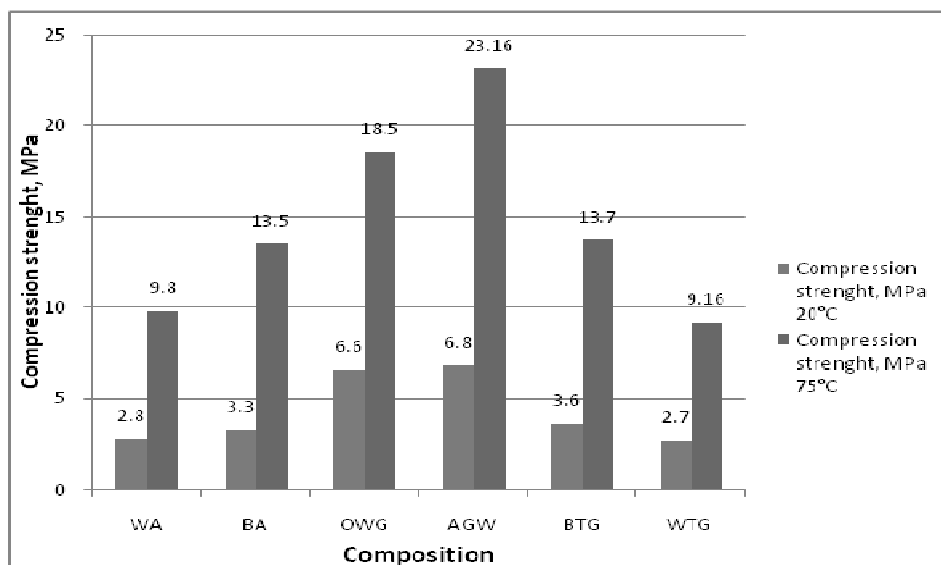
At the curing temperature of 75°C the compression strength for geopolymer mixes demonstrated larger variety of results. The best strength gain was demonstrated by the AWG mix which is 23.16MPa. Barley ash geopolymer composition strength grew to 13.5MPa and wood ash geopolymer strength – 9.8MPa.

Geopolymer containing ashes in the composition with calcined clay provided strength results similar to the specimen without clay minerals. In the mix with wood ashes the compression strength was 9.16MPa and the mix with barley ash - 13.7MPa.

### XRD analysis

Mortar bars were tested with X-ray laser diffraction spectroscopy to characterize geopolymer mineralogical composition.

Geopolymers are often described as ‘X-ray amorphous’ (Duxon et al., 2006). Although this material appears amorphous to XRD initially, evidence of crystalline phase can be observed. XRD results are given in Figure 4 and 5.



**Figure 3.** Compression strength results for geopolymer specimen cured at ambient temperature and 75°C.

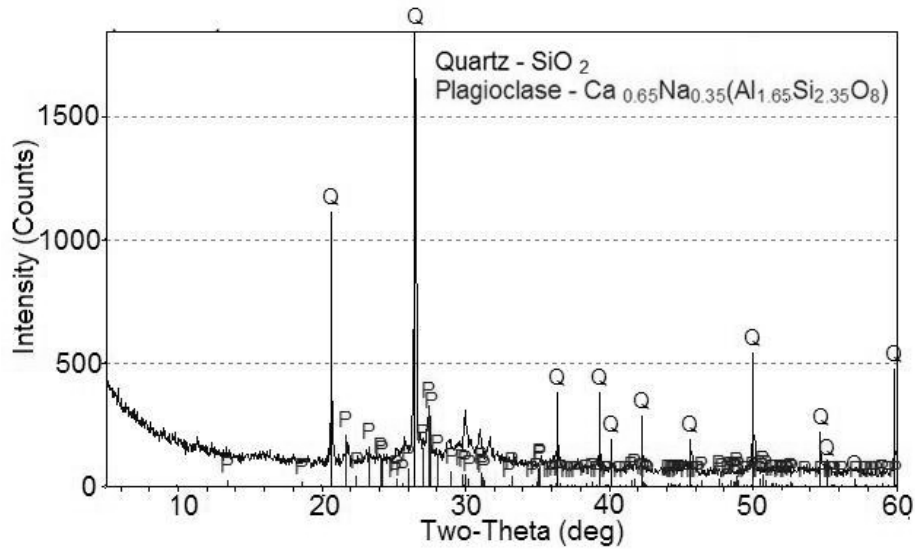


Figure 4. XRD diffractogram of hardened specimen contained wood ash (WA)

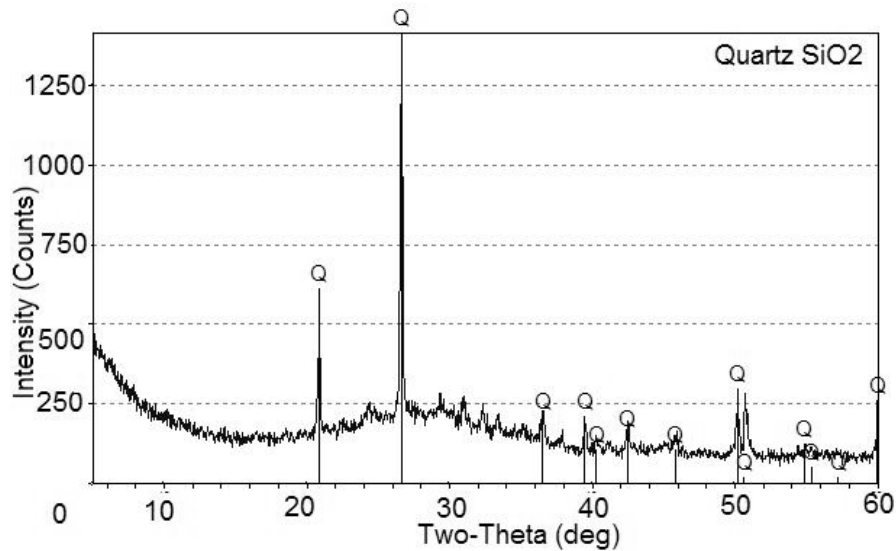


Figure 5. XRD diffractogram of hardened specimen contained additional ground glass waste (AGW)

Amorphous and crystalline quartz phases appear in all geopolymer mix compositions. Presence of plagioclase minerals was characteristic only to geopolymers containing wood ash. Quartz minerals are typical for geopolymers containing waste glass and calcined clay.

#### Scanning electron microscope analysis

Scanning electron microscope (SEM) analysis was performed in order to study the microstructure and to view the reacted and unreacted region of the geopolymer's samples. SEM analysis results of specimen with additional ground glass and calcined clay are given in Figure 6, but in the Figure 7 is shown microstructure of geopolymer specimen made from wood ash.

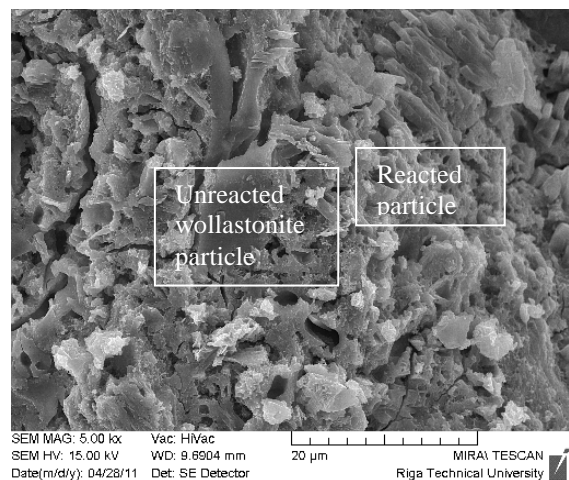
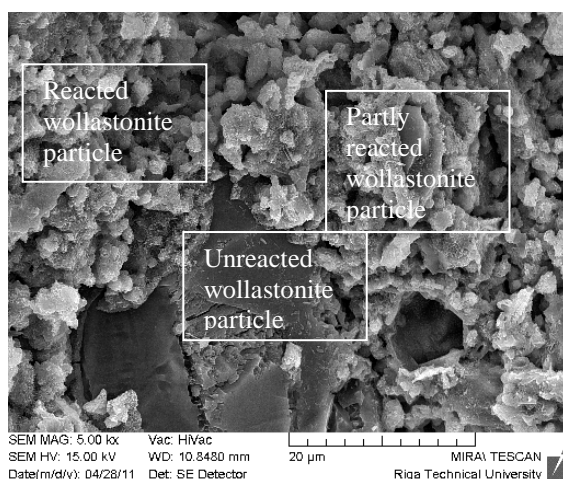


Figure 6. SEM image of hardened geopolymer contained additional ground glass (AGW).



**Figure 7.** SEM image of hardened geopolymer contained wood ash (WA).

Annotated SEM micrographs of geopolymer show a highly complex product morphology that consists of unreacted, partially reacted, and completely reacted materials. The geopolymer matrix also includes quartz crystals and mullite needles.

Unreacted wollastonite minerals can be observed in the both figures. Typical pore structure for a geopolymer is nonuniform with a wide size distribution (Figure 6 and 7). It is confirmed also by Waltrud (2008).

## DISCUSSION

Waste materials examined in this work proved to be an appropriate material for development of geopolymers. Industrial waste and by-products like different types of ashes obtained as bottom ash from thermal furnaces could be used in geopolymer composition as a secondary raw material when the bottom ashes are ground to fine particles.

Additional grinding of the glass made the material more reactive thus accelerating the reaction process and gaining additional strength.

Mixes with ashes and composition with ashes and calcined clay did not demonstrate as high result as the samples with glass and calcined clay composition. However an increase in strength is considerable from the temperature regime aspect.

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This work proved the importance of the temperature level. After 24h curing at ambient temperature geopolymer specimen were slightly hardened. Samples cured at 75°C for 24h were completely hardened and showed good compression strength results.

To reduce thermal shock during curing at elevated temperature, the temperature regime should be better studied in order to reduce geopolymers shrinkage and cracking.

A lot of research is still required to further investigate geopolymer binder properties and material characteristics. The economic aspect must be taken into account as well as mix design optimisation should be carried out.

Lack of appropriate standards and test procedures prevents geopolymer binders from wider application therefore in order to test new material samples mortar and concrete standards and methods should be developed.

Further investigations should include geopolymer-sand mortar tests at different curing temperature regimes and mix designs.

## CONCLUSIONS

Water absorption for obtained geopolymers varied from 7.9-13.2% where the lowest water absorption value was for heat cured OWG specimens.

Geopolymers cured at ambient temperature showed compressive strength in the range 2.7-6.8 MPa. This proves that ambient temperature does not provide the rapid geopolymerisation process.

Specimens cured at elevated temperature showed significant increase of the compression strength. It varied from 9.16 to 23.16MPa. The best compressive strength results were achieved by mixes containing rough ground (OWG) and additional ground glass (AGW): 18.5 MPa and 23.16 MPa.

According to XRD amorphous and crystalline quartz phases appear in all compositions of geopolymers.

SEM micrographs of geopolymers show a highly complex morphology of microstructure which consists of unreacted, partially reacted, and completely reacted materials.

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