Development of Geopolymer Concrete Supported by System Analytical Tools

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1 Introduction

In the field of building materials development environmental aspects become more and more important. Besides reducing energy consumption and CO_2-emission in cement production processes efforts are being made to use more secondary and waste materials. Another option is the development of alternative binders such as alkali-activated materials or geopolymers, respectively, and which are labelled as environmental friendly in literature.
Normally material development is driven by technical aspects, while economic and ecological assessments take place afterwards. In this project, Life Cycle Thinking is integrated into the development phase of materials right from the beginning, in order to identify technical, economic, and ecological benefits and drawbacks of developed geopolymers in comparison to traditional materials.

2 Geopolymer cement

Geopolymers are inorganic binders whose name was coined by Davidovits in the 1970s, related originally to the investigations on the reaction of metakaolins in alkaline media under formation of aluminosilicate polymers [1, 2]. The prefix “geo” was set to symbolize the constitutive relationship of the binders to geological materials, i.e. natural stone and/or minerals. Similar materials had already previously been investigated by Glukhovsky and, in the late 1950s, made known under the term “soil cements” [3].

Geopolymer cements are inorganic 2-component systems, consisting of
a *reactive solid* component that contains SiO_2 and Al_2O_3 in sufficient amount and in reactive form (e.g. ashes, active clays, pozzolana, slags etc.) and
an *alkaline activation solution* that contains (apart from water) individual alkali hydroxides, silicates, aluminates, carbonates and sulphates or combinations thereof.
When the solid and the activator components come into contact with each other, hardening results due to the formation of an aluminosilicate network

ranging from amorphous to partial crystalline aluminosilicate, which is water resistant.
A large number of possible primary and secondary raw materials as binding materials as well as a wide variety of material combinations and activator compositions can be used to produce a geopolymer binder. The performance of each single geopolymer is strongly correlated to its composition. What are the most influencing factors of geopolymer composition? Due to definition of a 2-component system both components will affect the performance and maybe the structure of hardened geopolymer.
Surprisingly geopolymers have not yet reached a wide application, even though many advantages compared to commercially available materials are reported in literature for instance high strength, temperature resistance, and resistance against acids. The performance of each single geopolymer is strongly correlated to its composition. Although geopolymers are always stated as ecological advantageous materials and therefore often cited [3]. Nevertheless proper investigations of life cycle assessment (LCA) or even streamlined LCA were not done so far.

3 Approach

The project presented trials to bend a bow from the raw material screening over a mixture design up to the binder optimization in terms of a defined application. The selection and evaluation of the raw materials is done by consideration of all three aspects: technical, ecological and economical ones. In the further development system analysis incorporating e.g. LCA and LCC lead to the generation of a performance profile of every single optimised mixtures in accordance to the special application field.
The project is subdivided into three consecutive work steps as shown in Figure 1 with:

the 1st step “Raw material screening”,
the 2nd step “Streamlined LCA” and
the 3rd step “Optimisation and detailed LCA”.

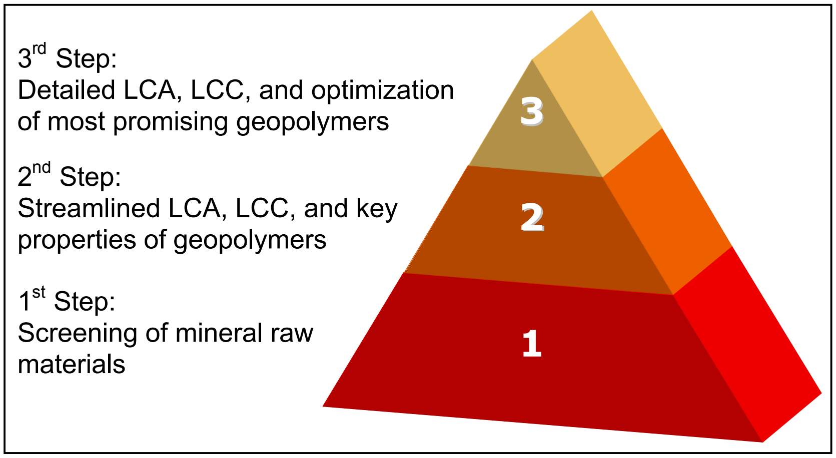

Figure 1 Work steps of the project

In this contribution, the authors focus on the first of the three steps, the evaluation of raw materials, which include the screening and classification of raw materials.

4 Raw material screening

Within the 1st step (raw material screening) of the project "System-analytical and life-cycle-analysis embedded development of geopolymer binders" at least 58 primary and secondary materials subdivided in to the five material groups such as clays, volcanic materials, ashes, slags and ceramic wastes, has been collected and tested [4-8].
In order to get a meaningful screening the right indicators were chosen for the later evaluation of the materials by intense discussion. The technical parameters were selected in dependence on the needs of the application; ecological and economical parameters were selected based on life cycle thinking. The following indicators were chosen for the three objective fields:

Technique
- mechanical strength (including reactivity, quantitative)
- resistance against acids (qualitative)
- temperature resistance (quantitative)
- setting time (quantitative)
- workability (qualitative)

Economy
- raw material costs (quantitative)
- costs of the thermal activation of raw materials (qualitative)
- costs of grinding raw materials (qualitative)
- follow-up costs caused by slow setting (qualitative)
- follow-up costs caused by high water sorption (qualitative)

Ecology/Health

- availability/consumption of mineral resources (quantitative)
- consumption of energy resources (qualitative)
- toxic load (qualitative)
- health and safety at the workplace (qualitative)

4.1 Results of technical parameter

Being aware the difficulties that occur presenting all of these results from all 58 materials some exemplary materials and their results were chosen for presentation and discussion.

Solubility tests in alkaline solution allow the direct determination of the reactive silicate and aluminate amount. The following test regimes has been used: 10 w.-% NaOH solution; solution/solid=1000; 60°C. Beside the information of the absolute soluble silicate and aluminate species (see table 1; row 2-4), the kinetic of dissolution can be determined and symbolizes the reaction kinetic of the alkaline activation in general.
The metakaolin MK-MS1 promotes a quick dissolution of silicate and aluminate in the same order of magnitude into the 10 w.-% NaOH solution. Ashes can be dissoluted even slower because of their lower surface area. The silicate content may reach similar levels compared to metakaolins (see table 1) but the aluminate content is mostly lower. Ceramic wastes (for instance sanitary elements and tiles) and volcanic rocks may show a relative high solubility of silicate but the dissolution rate is very low as well as the soluble aluminate content. The aluminates are mostly bounded in stable crystalline phases for instance feldspars.
The dissolution method is an excellent tool to characterize the reactivity of alumosilicate materials but fails if a remarkable amount of reactive calcium is present (in the material). Calcium and silicate will condense to calcium silicate hydrates and the whole amount of solved silicate can not be measured in the solution. Therefore no results of the dissolution can be presented in table 1 for the materials numbered with 17, 22 and 47.

To obtain binder properties the solid raw materials were mixed with 8 mol/l NaOH solution in a certain solution-to-solid ratio that gives the same consistency of the binder pastes. The necessary solution-to-solid ratio is an indicator of the workability of the raw material and shown as water/ binder ratio in Table 1. The binders were cast in 1x1x6 cm^3 moulds for 20 h at 40°C in principle unless the binders weren't hardened at that time. The demoulded samples were stored at 100 % r.h. and room temperature furthermore. Compressive strength measurements, density and porosity and special tests as acid and temperature resistance tests were investigated.

Table 1 Selected results of technical parameter; exemplary materials

		dissolved monomers in 10 % NaOH after 14 d [mmol/g]			Water/ binder ratio	compressive strength [N/mm²]		
		Si	Al	Si/Al		7 d	28 d	200 d
Ashes								
1	SFA-S1	6.6	3.4	2.0	0.34	1.9	3.9±1.0	9.9±2.6
3	SFA-O3	7.7	3.6	2.1	0.22	1.3	11.4±2.5	19.9±4.9
6	BFA-J1	4.0	1.5	2.7	0.33	1.3	14.2±1.5	13.6±3.6
7	BFA-T2	8.1	3.6	2.3	0.33	1.3	7.0±0.7	10.0±1.0
Slags								
17	MVS-SP3	-	-	-	0.23	28	35.6±4.2	63.2±2.3
19	SKG-S1	10.3	3.8	2.7	0.23	1.2	3.8±0.4	6.3±0.7
22	S-S2	-	-	-	0.30	24.6	29.8±4.8	31.3±4.5
Ceramic wastes								
26	ZA-L1	3.2	0.7	4.9	0.29	1.6	2.1±0.3	3.5±0.2
29	SKB-DM1w	7.5	1.6	4.9	0.27	0	0.9±0.3	3.4±1.1
30	SKB-DM1b	7.8	1.6	4.9	0.26	1.5	2.0±0.9	10.6±1.2
31	SFB-SM2	4.8	2.6	1.8	0.34	1.4	2.6±0.3	5.1±0.9
Clays								
40	MK-MS1	7.7	6.7	1.1	0.74	7.7	11.6±1.5	15.8±3.5
47	Ntst775+50D	-	-	-	0.43	5.0	13.2±1.5	19.2±1.8
Natural pozzolana								
48	TM-Ba1	4.2	1.5	2.8	0.39	2.8	4.1±0.8	8.7±0.6

The results of the strength development are shown in Table 1. The following facts can be remarked:

- Two materials with quite high strength, these are calcium containing slags (S-S2 and MVS-SP3) where one of it reaches almost the final strength whereas the MVS-Sp3 reaches only half of its final strength.
- Ashes have usually a quit low reaction rate due to the little surface.
- The ceramic waste material show in general a low reaction rate as already seen in solubility measurements.
- The strength of metakaolin containing samples (MK-MS1) were expected to be higher, but the high surface area lead to higher water/solid ratios and therefore to a higher porosity that causes lower strength.
- Calcium or dolomite containing clays (Ntst775+50D, clay mineral: illite) reached a comparatively high strength.

4.2 Selection of raw materials by the help of Multi Criteria Decision Analyses

Decision-making under the consideration of different objectives can be described as difficult. The situation becomes even more complex, if conflicts of objectives exist and/or the number of alternatives is high. Both is true in the presented development phase of geopolymers. The methods of Multi Criteria Decision Analyses (MCDA) are potentially helpful to support decision-making in complex decision situations. Besides compensatory methods, also a non-compensatory method called "dominance concept" has been applied to identify the most promising candidates for a specific application field.

The laboratory results, but also the results of the economic and ecological investigations are stored in a data-base. The different quantitative and qualitative indicator values are comparable and countable, as they are normalized to values between 0 and 1. Values close to 0 are less favourable, values close to 1 are highly favourable. For each indicator, a proper scale of transformation has to be determined, cf. [4, 9]. The results of the normalized technical indicators of selected materials are summarized in Table 2.

These data were used in a non-compensatory method to find out the most promising candidates for the chosen application field: "mass concrete wall element". The results are shown in Figure 2. The alternatives (raw materials) in the diagram, which are far away from the origin, represent better solutions (high values), the alternatives close to the origin are sub optimal. The pareto optimums (which is not dominate by the other alternatives) are highlighted as crosses (Figure 2). Pareto optimums are the materials MVS-SP3, SFA-M4, SFB-SM, BFA-T2, KA-P1, ZA-L1, S-S2.

Table 2 Normalized results of technical parameter; exemplary materials

		Strength 28 d	water demand	Kinetic of hardening	Temperature resistance	Acid resistance
Ashes						
1	SFA-S1	0.23	0.47	0.19	1	1
3	SFA-O3	0.36	0.73	0.07	1	1
6	BFA-J1	0.21	0.48	0.10	1	0.75
7	BFA-T2	0.25	0.47	0.13	1	1
Slags						
17	MVS-SP3	1.00	0.68	0.44	1	0.75
19	SKG-S1	0.07	0.68	0.19	0	1
22	S-S2	0.25	0.53	0.79	0	0.25
Ceramic wastes						
26	ZA-L1	0.07	0.55	0.47	0	1
29	SKB-DM1w	0.04	0.58	0.00	1	1
30	SKB-DM1b	0.11	0.62	0.15	1	1
31	SFB-SM2	0.10	0.46	0.28	1	1
Clays						
40	MK-MS1	0.37	0.21	0.49	1	0.25
47	Ntst775+50D	0.38	0.37	0.26	0	0.5
Natural pozzolana						
48	TM-Ba1	0.17	0.41	0.32	1	0.75

In the case of the non-compensatory method the solution space is afflicted with two problems [6]:

1.) A pareto optimum does not necessarily represents a promising raw material. For instance, one alternative is from an ecological perspective the best solution (highest value on the ecology axis), but from a technical and economic perspective quite bad (low values). The ecological advantages cannot compensate, in this case, the technical and economic disadvantages.
    To overcome this problem in general, for each objective minimum requirements has to be defined to shorten the solution space.
2.) Alternatives which are close to pareto optimum represents interesting and valuable candidates. In addition every indicator value is more or less tainted with uncertainties.
    To identify all valuable candidates, also under the consideration of the uncertainties, a 3-D nappe (“pareto front”) is used to separate the promising from the less promising alternatives. The materials on or above the nappe represents the valuable alternatives (cf. Figure 2).

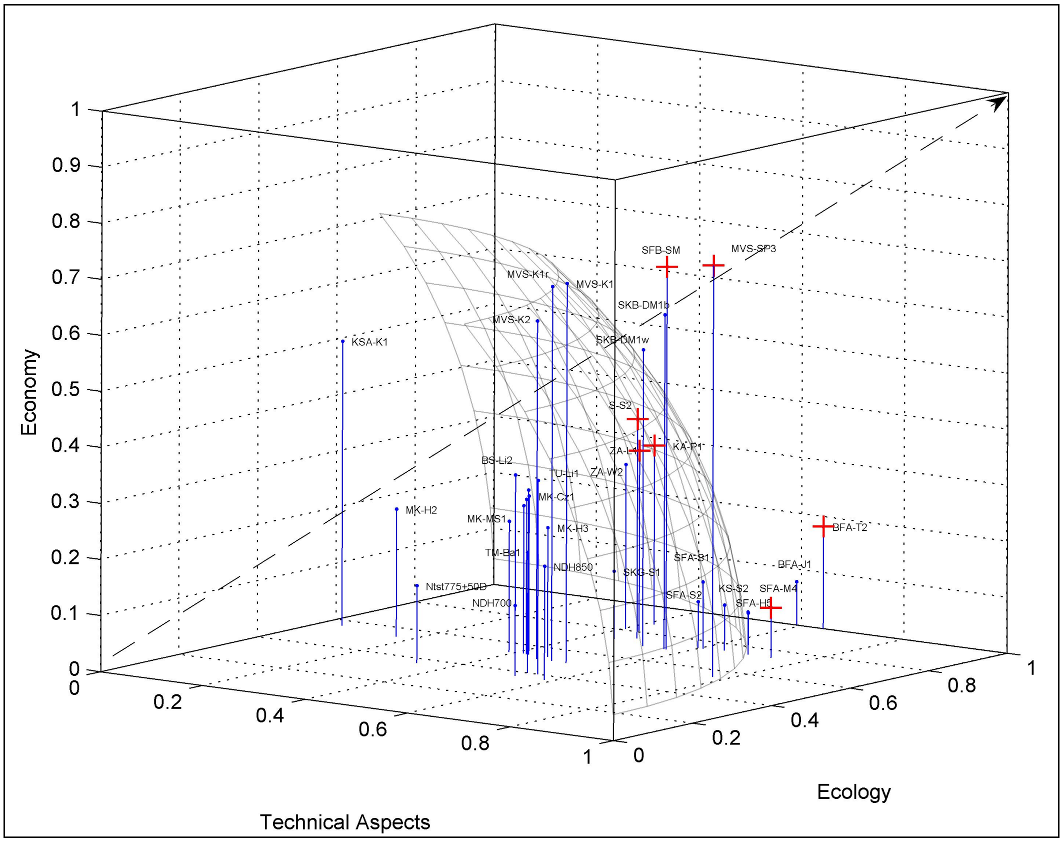

Figure 2 Identification of promising candidates. Crosses refer to pareto optimum, called dominant alternatives, nappe refers to pareto front [6].

By means of the described procedure the promising candidates can be determined. The results are compared with the results of the compensatory method described in [9]. Hence, after an expert discussion, the most promising raw materials are selected for the design phase of geopolymer mixtures for three different application fields.

5 Concrete design, preparation, investigations and results

Using the selected most promising raw material two different material-blends were chosen for the concrete design: (I) Slag S-S2 + Ash SFA-M4; (II) BFA-T2 + ZA-L1; but only results from the first blend will be presented herein. The mixture composition is seen in Table 3. Three mixture compositions of geopolymer concrete as well as one comparative mixture basing on ordinary portland cement is shown. All four mixes have the same ratio between binder paste volume and volume of the aggregates. The alkaline activator was prepared by mixing the 50 w.-% NaOH solution with water and sodium silicate solution (Na_2O:8.0 w.-%; SiO_2:26.4 w.-%). Casting and curing were orientated at usual standards for portland cement concrete.

Table 3 Mixture composition

w.-%	**MI-1**	**MI-3**	**MI-5**		**OPC**
solid binder material					
S-S2	2.5	6.2	9.7	portland cement	14.2
SFA-M4	9.9	6.2	2.4		
activator					
sodium silicate solution	2.2	2.5	2.8		
NaOH solution	2.6	2.3	2.1		
water	3.6	3.9	4.3	water	7.1
aggregates					
0-2 mm	33.2	33.1	33.0	0-2 mm	32.9
2-8 mm	27.0	26.9	26.8	2-8 mm	26.8
8-16 mm	19.1	19.0	19.0	8-16 mm	19.0

5.1 Strength development

The following measurements were carried out at the samples of all four mixtures:

- density of fresh concrete
- slump tests on the fresh mortars according to DIN EN 1015-3
- strength development, density and porosity after 7, 28 and 90 days
- freeze-thaw /deicing salt resistance according to CF/CDF-test
- carbonation test
- reaction degree and phase composition

Because of ongoing investigations only preliminary results can be presented herein. Figure 3 shows the strength development of the four mixtures. As expected mixture MI-1 with highest content of fly ash reacts slower and gives lower strength compared to the ordinary portland cement concrete (OPC). Already the mixture MI-3 with 50 w.-% fly ash and 50 w.-% slag performs as good as the OPC sample. The more slag containing sample MI-5 reached the highest strength after 7 and 28 days.

Because of the type of raw material an increasing of strength up to 90 days will be expected especially for sample MI-1.

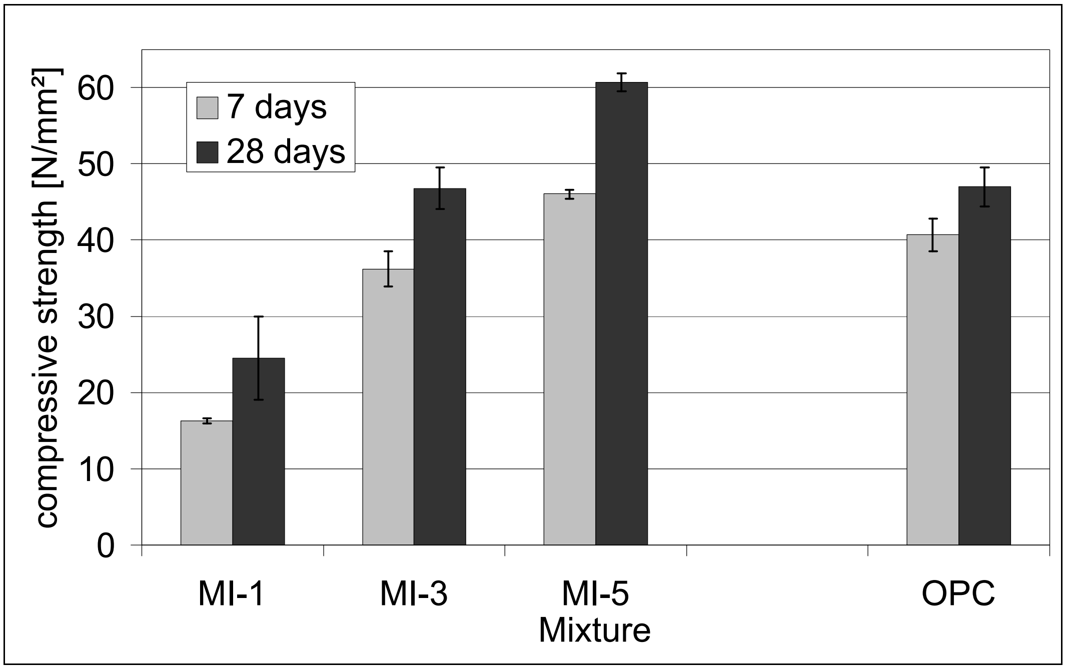

Figure 3 Strength development of the geopolymer concretes and the comparative concrete with ordinary portland cement (OPC)

5.2 Production costs

The presented cost analysis focused only on the production phase and will be extended in the further project work on the whole life cycle. The data of raw material costs is based on a survey in 2005/2006 for the region Germany, Central Europe [7]. The raw material provider was asked for the net price for bigger quantities (big back, tanks, container), ex factory (without transport). Because the manufacturing process of geopolymer concrete and OPC concrete is comparable, the manufacturing costs are not included. Figure 4 shows the minimum and maximum production costs of geopolymers concretes (MI-1, MI-3, MI-5) and OPC concrete. The maximum costs of the different geopolymers concrete mixtures are only slightly higher than the maximum cost of OPC concrete. In comparison to the minimum costs of OPC concrete mixtures the minimum costs of the different geopolymer concrete mixtures are lower. The cost drivers (besides aggregates) of geopolymers mixtures are the activators (sodium silicate solution, NaOH solution), and solids (slag, fly ash), the cost drivers of OPC concrete is the cement content. It has to be stated, that either the geopolymers composition nor the OPC concrete mixtures are optimised. Thus, in the ongoing project the optimised geopolymer mixtures has also to be compared with concrete mixtures with CEM II or CEM III cements.

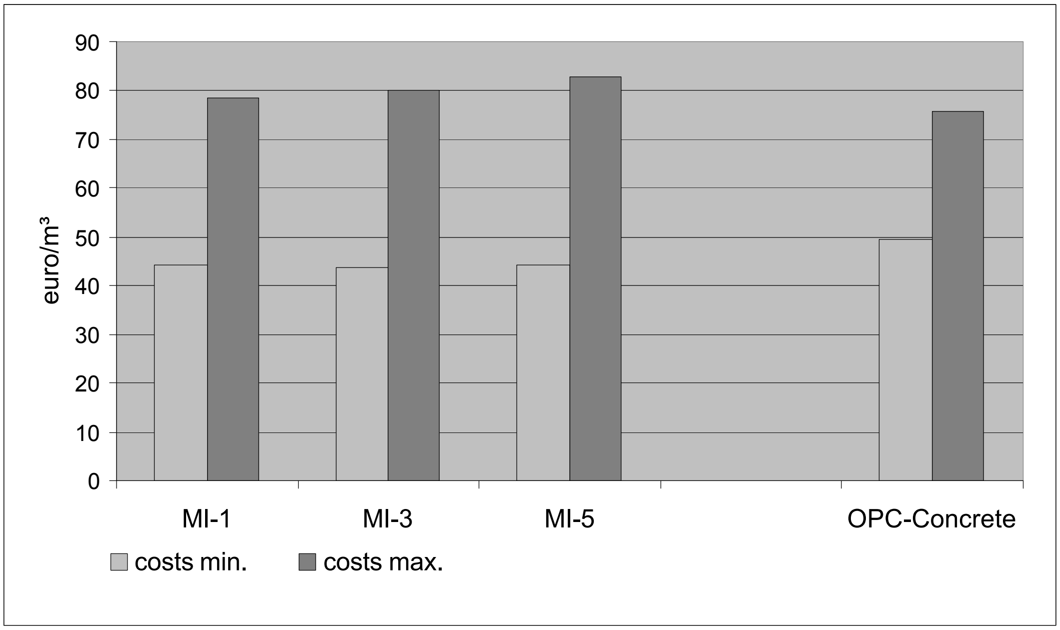

Figure 4 Minimum and maximum production costs of geopolymer concrete and OPC concrete

6 Conclusion

The sustainable development of materials with enhanced properties, but also with economic and ecologic advantages is one of the challenges of modern materials science. In practice, economic and ecological aspects are considered rarely, which is probably due to the low level of information available in the early phase of material development. Based on the example of the development of geopolymers, the authors presented a methodological approach to integrating technical, economic, and ecological aspects in the early stages of material development.

The presented preliminary technical, economic and ecological result shown significant differences between the raw material groups, but also within the raw material groups itself. This performance information built up the database, which is used within the Multi Criteria Decision Analyses (MCDA) to select the most promising raw materials for a specific application field.

For the mass application concrete production, three geopolymer mixtures ,with promising raw materials, are compared with the traditional OPC concrete. The presented preliminary results can be used for the further optimization step of the geopolymer concrete mixtures.

Acknowledgements

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