Durability of cement and geopolymer composites

T Blaszczyński 1 and M Król 2

1 Poznan University of Technology, Piotrowo 5, 60-965 Poznań,
2 Koszalin University of Technology, Śniadeckich 2, 75-453 Koszalin,

E-mail: tomasz.blaszczynski@opal.info.pl

Abstract. Concrete structures are constantly moving in the direction of improving the durability. This main feature depends on many factors, which are the composition of concrete mix, the usage of additives and admixtures and the place, where material will work and carry the load. The introduction of new geopolymer binders for geopolymer structures adds a new aspect that is type of used activator. This substance with strongly alkaline reaction is divided because of the physical state, the alkaline degree and above all the chemical composition. Taking into account, that at present the geopolymer binders are made essentially from waste materials or by products from the combustion of coal or iron ore smelting, unambiguous determination of the effect of the activator on the properties of the geopolymer material requires a number of trials, researches and observation. This paper shows the influence of the most alkaline activators on the basic parameters of the durability of geopolymer binders. In this study there were used a highly alkaline hydroxides, water glasses and granules, which are waste materials in a variety of processes taking place in a chemical plants. As the substrate of geopolymer binders there were used fly ash which came from coal and high calcium ash from the burning of lignite.

1. Introduction
Concrete cement can boast of a number of unique properties. These include high temperature, resistance, excellent compressive strength, ease of forming different shapes and forms in architecture or can be combined with other materials such as steel and various types of composites. Concrete, however, has a number of properties which make that it is being considered as a material difficult to design, requiring complex care during repairing and whole construction lifetime. This is related directly with susceptibility to weather conditions or corrosive agents. Traditional, also called ordinary, Portland cement has at the moment new competitor which is growing in strength in terms of implementation possibility. It is geopolymer cement. Not present in Europe, as part of ready mix concrete, geopolymer cement, is distributed here as repair material. Both binders differ in the method of production, composition and method of activation. This results in new material with very similar properties. In each of the comparisons geopolymer cement falls much better. However, the factor which is not connected to mechanical or chemical properties of geopolymer concrete will be the biggest catalyst for the dissemination of this binder. Geopolymers compared to ordinary cements are from 3 to even 20 times more environmentally friendly. This environmental issue has already been described many times in the scientific literature. Many organisations created under the aegis of the national government conduct constant research aimed at verifying amount of carbon dioxide which is getting into the atmosphere (Figure. 1).
Thanks to them we are able to recognize the seriousness of the issue. Permanently rising CO₂ concentration corresponds with the increasing consumption of cement. According to the CDIAC (Carbon Dioxide Information Analysis Center) cement production has increased from 3 to 8% at the turn of the last decade (Figure 2, 3). This situation according to speculation on cement production is likely to increase even more in the coming years.

The solution to the problem of carbon dioxide emission which is sourced by cement industry is the development of new binders. According to the calculation carried out by independent research institutes [2-4] the opportunity to reduce greenhouse gas emissions produced during the manufacture of concrete is limited. It is recognized that the lower limit of CO₂ emissions in idealized conditions will not be lower than 0.7t per 1t of produced cement. In the case of geopolymer cement this value is estimated in the best case even below 0.2t per 1t of produced binder (Figure. 4).
Therefore, despite the fact that geopolymer concrete achieves better results in terms of strength and durability, the feature associated with its environmental performance will be a factor that will make the new binder will be much often present as material used in the new and upgraded buildings or structures.

Concrete cement always has been an excellent material for resistance to undesirable high temperatures. Protect vulnerable to high temperature steel reinforcement in composite structures or form a barrier that can withstand long fire. The article is an attempt to compare the two described cements exposed to temperatures likely to arise during the course of fire.

2. Research base
Since the prevalence of cement and concrete in the construction the fire is becoming less threat. However, this does not mean, that it should be marginalized because it is still a very serious problem. Study of materials due to high temperatures take place on the basis of actual and theoretical function
of temperature accorded to time of a fire. Currently, there are two basic curves characterizing this relationship [5]. These are:

- Traditional fire development curve (Figure 5a),
- Typical curve of a fire in modern construction (Figure 5b).

![Figure 5. Curves for traditional and typical fire expansion [5].](image)

Both the time-temperature functions describe the possible result of a fire. The first one describes the traditional model, which relates to circumstances with limited load of burned material. This situation may occur in buildings with a high degree of fire insulation where the spread of the fire is limited and does not allow the combusted material to raise the temperature and duration of the fire longer than the barriers are able to stop the action of heat. In the second case, which occurs much more frequently now, fire spread simulation includes access to a factor of combustion such as oxygen. This is because the nowadays structures are large tighter. There often does not occur traditional ventilation system.

At the height of the temperature that can be reached during the fire affect four basic factors [6]:

- The number and size of the burned load,
- Type and ventilation occurring in the building,
- Geometric shape and size of the facilities etched by fire,
- Fire Properties partitions used.

Temperature level depend on time in the form of a curve determined at ISO 834. It presents a systematic reflection occurring fire temperature to its duration. This curve was developed in the 30s of the nineteenth century on the basis of information obtained from real fires occurring in homes and offices [7]. This curve in a very accurate way reflects the relationship described to conventional buildings. However it's been a long time from identifying the described curve. Since then, structures have evolved. Standards have changed the materials from which construction and other building elements have been performed too.

There has been used an electric furnace of high temperature for testing (Figure 6a). The analysis of temperature-time curve, the value of the temperature was set in the range of 100°C to 800°C in steps of 100 degrees. Time which samples spend in furnace was constant, and it was set up to 240min for each temperature range. Samples were prepared as classical cement beams of dimensions 4x4x16cm (Figure 6b, 6c). Their size was forced by the fact that they were repair materials, which the manufacturers have not recommended the use of layers thicker than 4cm.

Tests were conducted on four types of materials supplied by the leading manufacturers of this type of solution in the country. The first two use technology of geopolymer binder. The next two are based on the traditional Portland cement (Table 1). The exact composition of the mixtures for the sake of industrial secrecy could not be presented. Here were given only main data about binder types. It
describes type of used cement, given by the producers recommended water to mixture ratio, class of mortars according to European Code 1504 and size of used grain which was used.

![a/](image1)

![b/](image2)

![c/](image3)

**Figure 6.** View of used furnace (a) and research base (b – geopolymer samples, c – ordinary cement samples).

**Table 1.** Properties of research base used in the studies.

| Material symbol | Type of Binder                  | W/M ratio* | Mortar class (according to EN 1504) | Aggregate size [mm] |
|-----------------|---------------------------------|------------|-------------------------------------|---------------------|
| M1              | geopolymer                      | 0,18       | R4                                  | 0-0,5               |
| M2              | geopolymer clinker modified by polymer | 0,14       | R4                                  | 0-2,5               |
| M3              | geopolymer clinker modified by polymer | 0,16       | R4                                  | 0-4                 |
| M4              | geopolymer modified by polymer  | 0,16       | R4                                  | 0-2                 |

3. **Results**

The results of carried tests are the values of the compressive strength obtained depending on the temperature set in the furnace (Figure 7, 8). The samples after mixing were stored in air-dry conditions at a temperature of 20°C and a relative humidity of 50%. After that, they were placed in a furnace and subjected to heating. At the desired temperature the samples were placed in an oven for 240 min, which corresponds to the average duration of the fire, and remained to cool down. Then they were subjected to strength test.
Figure 7. Compressive strength of geopolymer mortars.

Figure 8. Compressive strength of Portland cement mortars.

Figure 9. Compressive strength of Portland cement concrete C30/37 [8].
As seen in the results of the studies, which were additionally compared with studies of classical cement concrete class C30/37 (Figure 9) [8], and composite designed for testing (Figure 10) [9] they are congruent to each other. Geopolymer materials recorded a decrease of strength equal to 45% at temperature of 800°C. This result was a much better than the one recorded by samples of mortar M3 and M4. Binder based on clinker cement for the same temperature of 800°C reached only 15% of initial strength. It is worth attention that in geopolymer bond there is nonlinear strength degree due to high temperatures growth. Our study showed a unique relationship of geopolymer binder, which resulted in the increase of compressive strength when the temperature did not growth under 200°C. This situation has been confirmed in many independent test results. Of course geopolymer binders are harvested mainly as waste material, which is why at the moment it is difficult to talk about systematizing research and the creation of design guidelines.

It turns out that not only heat resistance but also other properties such as corrosion resistance, strength increase or shrinkage binding mixture in comparison to Portland cements are much better [10]. According to presented high temperature tests, they were conducted other one on same materials (Table 1).

The study of material's resistance to the corrosive substances was conducted on beams cement in following dimensions: 4x4x16 cm. Corrosive agent used for tests was two aqueous solutions. The agents were sodium chloride’s (NaCl) and calcium chloride’s (CaCl₂) at a different concentration, first one of 6M mixture and second of 3M mixture (Table 2). Samples were cut in the middle of it width through all width. Cut has width of 1 mm and a depth of 10mm (Figure 11).
Such prepared beams were exposed to corrosive agents. The result show information about values of depth and width of cut after given time (Figure 12).

**Table 2.** Properties of aggressive agents used on prepared beams.

| Conditions                        | NaCl       | CaCl₂      |
|-----------------------------------|------------|------------|
| Moll mass [g/mol]                 | 58.44      | 110.99     |
| Agent moll mass [M]               | 12         | 8          |
| Temperature [°C]                  | 20         | 20         |
| Time of influence [weeks]         | 12         | 12         |

**Figure 12.** The graph describing crack dimension under the action of two various corrosive agents to the fourth different samples, a) crack width for NaCl, b) Crack depth for NaCl, c) crack width for CaCl₂, d) Crack depth for CaCl₂.
Action of corrosive agents to tested samples shows almost insensitivity of the geopolymer binders. Clinker concrete after a short time in this environment significantly changed its pH and had expansion in the range of the measurement base. Two source of alkaline with varying degrees of impact assessments have not contributed to the degradation of samples using geopolymer binder. Problem of concrete and cementious shrinkage is a well-known phenomenon. Binders based on geopolymer do not exhibit shrinkage as we can see in the case of mixtures with the classical Portland cements (Figure 13) [10-11]. Even geopolymer binders which achieve very rapid growth of early and primary strength are close to free from this condition.

![Figure 13. Shrinkage series division of investigated materials (M1 – M4) and simple concrete admixture without any supplements (M5).](image)

In the chart we can see a huge advantage of geopolymer cements whose total shrinkage is close to 20 times less than materials prepared with the technically advanced repair materials based on clinker cement binders. Comparing geopolymer mortar with classical concrete (M5) of C30/37 class we can see that total shrinkage is even 80 times lower.

During time a new binder will be more available thanks to regulations which will bring limits in the contaminating atmosphere by CO₂. Unfortunately, ecological sanctions are respected only by developed countries, where production of cement falls, and its amount is small share of global production. Most of global production is being held in countries which are not obligated to European laws and restriction. Furthermore in China and India carbon footprint measured by one citizen is lower than in North America or even Europe (Figure 14, 15). International communities which fight with climate change are facing difficulties of reaching agreement on the regulation of greenhouse gases emission. Biggest problem is measuring of relative contribution, which is given by First and Third World countries. Developing countries have contended that industrialized countries had caused the climate change problem, so now they should face the regulation of CO₂ and other greenhouse effect gases. Of course, the production of new green binder is not the only possibility of greening the construction industry. For the production of concrete we can use aggregates waste, where we can bring into production local deposits which can eliminate the carbon dioxide footprint associated with the transport [12]. It is important that we should have environment awareness.
When comparing resistance to high temperature geopolymer binders again proved to be superior to conventional materials based on Portland cement. This is not surprising, as in many other fields also manage much better. Probably often we hear question: „why modern binder is not widely available in the cement industry?“ In this case, we can answer a very similar question, i.e. „why we are still using fossil fuels to run our cars, heat our homes and produce electricity?“. The studies leave no doubt that the geopolymer cement dominates the Portland on each field. For the future implementation of new binders, legal regulation will be needed. Technical information of making geopolymer “the cement of the future” are essential for authorities and industry. Only then our action and decisions can go together with knowledge. This awareness should be passed to next generation. Only in this way we can work to preserve our environment in shape enabling healthy and safety existence [13].

References
[1] Carbon Dioxide Information Analysis Center Global Carbon Budget 2014, September 21, 2014.
[2] J.G.J. Olivier, G. Janssens-Maenhout, J.A.H.W. Peters, “Trends in global CO₂ emissions”, PBL Netherlands Environmental Assessment Agency 2012.
[3] B. C McLellan, R. P. Williams, J. Lay, A. Arie van Riessen, G. D. Corder, “Costs and carbon emissions for geopolymer pastes in comparison to ordinary portland cement”, Journal of Cleaner Production, pp. 1080-1090, 2011.

[4] Cembureau The European Cement Association, Activity Report 2013, Brussels 2014.

[5] P.J. Norwood, F. Ricci, “Ventilation limited fire: Keeping it rich and other tactics based off science”, www.fireengineering.com 2014.

[6] Z. Ma, P. Makelainen, “Parametric temperature-time curves of medium compartment fires for structural design”, Fire Safety Journal, Vol. 34 , pp. 361-375, 2000.

[7] J. Zehfuss, D. Hosser, “A parametric natural fire model for the structural fire design of multi-storey building”, Fire Safety Journal, Vol. 42, pp. 115-126, 2007.

[8] Z. Bednarek, R. Krzuwoblocka-Laurów, T. Drzymała, “Effect of high temperature on the structure phase composition and strength of concrete”, Zeszyty naukowe SGSP, No 38, pp. 5-25, 2009.

[9] J. Davidovits, M. Davidovics, “Geopolymer: ultra-high temperature tooling material for the manufacture of advanced composites”, Gepolymer Tooling Material, Saint Quentin, France pp.1939-1949, 1991.

[10] T. Blaszczyński, M. Król, “Durability of Green-Concretes”, Proceedings of 8th International Conference AMCM 2014, Wroclaw, Poland, pp. 530-540, 2014.

[11] T. Blaszczyński, M. Król, “Usage of green concrete technology in civil engineering”, Procedia Engineering, Vol. 122, pp. 296-301, 2015.

[12] W. Głodkowska, J. Laskowska-Bury, “Waste sands as a valuable aggregates to produce fibre-composites”, Annual Set - The Environment Protection, Vol. 17, pp. 901-918, 2015.

[13] I. Piecuch, T. Piecuch, “Environmental Education and Its Social Effects”, Annual Set - The Environment Protection, Vol. 15, pp. 1561-1568, 2013.